

YEAR XV

Issue 2 / 2021 ISSN PRINT 1313-0226
ISSN WEB 1314-507X

International journal
for science, technics and
innovations for the industry



MACHINES
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INTERNATIONAL SCIENTIFIC JOURNAL

ISSN PRINT 1313-0226, ISSN WEB 1314-507X, YEAR XV, ISSUE 2 / 2021

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Energy and exergy losses analysis of back-pressure steam turbine from CHP plant

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Abstract: In this paper is analyzed back-pressure steam turbine which operates in CHP (Combined Heat and Power) plant from the aspect of energy and exergy losses. Produced turbine power, used for electricity generator drive equals 62548.77 kW, while the turbine mechanical loss is 1934.50 kW. Exergy analysis of the turbine shows that cumulative exergy loss is composed of two losses - mechanical loss and steam exergy loss. Steam exergy loss is additional loss which takes into account the state of the ambient in which turbine operates (unlike energy analysis which is independent of the ambient state). Change in the ambient temperature resulted with a change in turbine exergy efficiency for less than 0.5 % on average, while the change in the turbine exergy loss (for the same temperature change) equals 266.21 kW on average.

KEYWORDS: BACK-PRESSURE STEAM TURBINE, ENERGY LOSS, EXERGY LOSS, CHP PLANT

1. Introduction

Steam turbines are nowadays the basic power producers which drive electricity generators and produce electric power [1, 2]. The majority of such steam turbines (for electricity generator drive) are condensation type, which mean that steam after expansion through the turbine has pressure lower than atmospheric pressure – such steam is delivered to a steam condenser (or more of them) [3, 4].

Some steam turbines which operate in steam power plants are also used for electricity generators drive, but are of back-pressure type (steam after expansion in the turbine has pressure above the atmospheric pressure and is used for heating of any heat consumer [5]). Such steam turbine is analyzed in this paper.

Based on measured steam operating parameters from the literature [6] it is performed energy and exergy analysis of back-pressure steam turbine. Energy analysis involved mechanical loss which occurs in the turbine cylinder. It is investigated energy and exergy flow streams throughout analyzed steam turbine and it is compared energy and exergy losses. Cumulative exergy loss of the analyzed turbine contains additional steam loss which cannot be obtained through energy analysis of the same turbine. The variation of the ambient temperature is also performed – to investigate turbine operating parameters, exergy loss and exergy efficiency at different ambient conditions.

2. Description of the analyzed back-pressure steam turbine from CHP plant

Back-pressure steam turbine which operates in CHP plant [6] is analyzed in this paper from the energy and exergy aspect. General operating scheme of the analyzed turbine is presented in Fig. 1.

Produced power from the analyzed steam turbine is used for electricity generator drive. In the energy analysis, mechanical loss which occurs into the turbine is taken into account. In this case, steam turbine drive electricity generator directly (without the gearbox usage). If the steam turbine drives any other power consumer through the gearbox, than the mechanical loss of the gearbox also must be taken into account when calculating power amount distributed to power consumer.

Complete energy and exergy analysis of back-pressure steam turbine is based on three turbine operating points presented in Fig 1. – the first operating point is turbine inlet, the second is steam extraction and last third operating point is turbine outlet. As the exergy analysis of any component in the steam power plant is dependable on the conditions of the ambient (the ambient temperature and pressure) [7, 8] this analysis also includes variation of the ambient temperature in order to obtain turbine exergy loss and exergy efficiency at different ambient conditions.

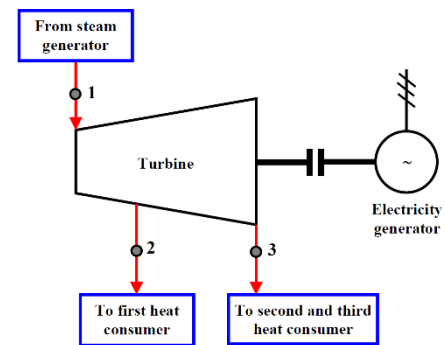


Fig. 1. Scheme and operating points of the analyzed back-pressure steam turbine from CHP plant

3. Equations for energy and exergy analysis

3.1. General equations

For any analyzed control volume or a system in which mass flow rate leakage does not occur is valid a following mass flow rate balance [9]:

$$\sum \dot{m}_{IN} = \sum \dot{m}_{OUT}, \quad (1)$$

where: IN = inlet (input), OUT = outlet (output), $\dot{m}$ = fluid mass flow rate (kg/s). The first law of thermodynamics gives a definition of energy analysis [10], which is completely independent of the ambient conditions in which analyzed control volume or a system operates [11]. Basic energy balance for a control volume or a system in steady state while disregarding potential and kinetic energy, according to [12, 13] is:

$$\sum \dot{m}_{IN} \cdot h_{IN} + \dot{Q} = \sum \dot{m}_{OUT} \cdot h_{OUT} + P, \quad (2)$$

where: h = fluid specific enthalpy (kJ/kg), $\dot{Q}$ = heat transfer (kW), P = produced power (kW). Energy power of any fluid flow (n), according to [14] is defined as:

$$\dot{E}_{EN,n} = \dot{m}_n \cdot h_n, \quad (3)$$

where: $\dot{E}_{EN,n}$ = energy power of fluid flow (kW), n = index for observed operating point (fluid flow). Unlike energy analysis, exergy analysis of control volume or a system is defined by the second law of thermodynamics [15]. Exergy analysis is based on the ambient conditions in which control volume or a system operates [16]. The main exergy balance equation, according to [17, 18] can be written as:

$$\sum \dot{m}_{IN} \cdot \varepsilon_{IN} + \dot{X}_{heat} = \sum \dot{m}_{OUT} \cdot \varepsilon_{OUT} + P + \dot{E}_{EX,D}, \quad (4)$$

where: $\dot{E}_{EX,D}$ = exergy destruction = exergy loss (kW). In Eq. 4, $\dot{X}_{heat}$ is the exergy transfer by heat (kW) at the temperature T (K) which is defined, according to [19, 20] as:

$$\dot{X}_{\text{heat}} = \sum (1 - \frac{T_0}{T}) \cdot \dot{Q}, \quad (5)$$

where: 0 = index of the ambient condition. The last undefined parameter from Eq. 4 is specific exergy of the fluid stream (ε), which definition can be found in [21]:

$$\varepsilon = (h - h_0) - T_0 \cdot (s - s_0), \quad (6)$$

where: s = fluid specific entropy (kJ/kg·K). Similar to energy power of fluid flow, exergy power of any fluid flow (n) can be defined by following equation [22]:

$$\dot{E}_{\text{EX},n} = \dot{m}_n \cdot \varepsilon_n, \quad (7)$$

where: $\dot{E}_{\text{EX},n}$ = exergy power of fluid flow (kW). For any control volume or a system, general definition of exergy efficiency (η_{EX}), according to [23] is:

$$\eta_{\text{EX}} = \frac{\text{Exergy output}}{\text{Exergy input}}. \quad (8)$$

3.2. Energy and exergy analysis of back-pressure steam turbine from CHP plant

All the equations for the energy and exergy analysis of back-pressure steam turbine from CHP plant in this section will be based on turbine operating points from Fig. 1.

3.2.1. Energy analysis

Turbine power, without taking into account the mechanical loss, is calculated from steam expansion throughout the turbine as:

$$P_T = \dot{m}_1 \cdot (h_1 - h_2) + (\dot{m}_1 - \dot{m}_2) \cdot (h_2 - h_3), \quad (9)$$

where: P_T = turbine power without mechanical loss (kW). Turbine real power, with taking into account the mechanical loss is:

$$P_{\text{RE}} = [\dot{m}_1 \cdot (h_1 - h_2) + (\dot{m}_1 - \dot{m}_2) \cdot (h_2 - h_3)] \cdot \eta_{\text{MECH}} = P_T \cdot \eta_{\text{MECH}}, \quad (10)$$

where: P_{RE} = turbine real developed power with mechanical loss (kW), η_{MECH} = turbine mechanical efficiency (%). In the analysis is assumed that mechanical efficiency of the observed back-pressure steam turbine is equal to 97 %. From Eq. 9 and Eq. 10, analyzed turbine mechanical loss is:

$$P_{\text{MECH}} = P_T - P_{\text{RE}} = P_T - P_T \cdot \eta_{\text{MECH}} = P_T \cdot (1 - \eta_{\text{MECH}}), \quad (11)$$

where: P_{MECH} = turbine mechanical loss (kW). Energy power of fluid (steam) flow in each operating point of the analyzed turbine (Fig. 1) is calculated by using Eq. 3.

3.2.2. Exergy analysis

Cumulative exergy loss (cumulative exergy destruction) of the analyzed turbine is:

$$\dot{E}_{\text{EX},D,CUM} = \dot{E}_{\text{EX},1} - \dot{E}_{\text{EX},2} - \dot{E}_{\text{EX},3} - P_{\text{RE}} = \dot{E}_{\text{EX},1} - \dot{E}_{\text{EX},2} - \dot{E}_{\text{EX},3} - P_T + P_{\text{MECH}}, \quad (12)$$

where: $\dot{E}_{\text{EX},D,CUM}$ = turbine cumulative exergy loss (kW). Cumulative exergy loss of the turbine ($\dot{E}_{\text{EX},D,CUM}$) can be divided on two different losses - the first is a steam exergy loss ($\dot{E}_{\text{EX},D,steam}$) and the second is mechanical loss (P_{MECH}) defined by Eq. 11. Therefore, steam exergy loss is:

$$\dot{E}_{\text{EX},D,steam} = \dot{E}_{\text{EX},1} - \dot{E}_{\text{EX},2} - \dot{E}_{\text{EX},3} - P_T, \quad (13)$$

where: $\dot{E}_{\text{EX},D,steam}$ = steam exergy loss (kW). Analyzed back-pressure steam turbine exergy efficiency is:

$$\eta_{\text{EX}} = \frac{P_{\text{RE}}}{\dot{E}_{\text{EX},1} - \dot{E}_{\text{EX},2} - \dot{E}_{\text{EX},3}} = \frac{P_T \cdot \eta_{\text{MECH}}}{\dot{E}_{\text{EX},1} - \dot{E}_{\text{EX},2} - \dot{E}_{\text{EX},3}}. \quad (14)$$

Exergy power of fluid (steam) flow in each operating point of the analyzed turbine (Fig. 1) is calculated by using Eq. 7.

4. Steam operating parameters of the analyzed back-pressure turbine

Steam operating parameters (pressure, temperature and mass flow rate) in each operating point of the analyzed back-pressure turbine (Fig. 1) were found in [6] and presented in Table 1. In all operating points steam is superheated.

Table 1. Steam operating parameters in each operating point of analyzed back-pressure turbine [6]

Operating point*	Pressure (bar)	Temperature (°C)	Mass flow rate (kg/s)
1	84.0	500.0	103.7
2	11.0	232.5	15.6
3	3.5	147.0	88.1

* Operating points refer to Fig. 1.

To perform complete energy and exergy analysis along with calculation of losses, steam operating parameters from Table 1 is used for calculation of specific enthalpy, specific entropy and specific exergy again in each operating point of the observed turbine. Those operating parameters were calculated by using NIST-REFPROP 9.0 software [24] and presented in Table 2.

Table 2. Steam specific enthalpy, specific entropy and specific exergy in each operating point of analyzed turbine

Operating point*	Specific enthalpy (kJ/kg)	Specific entropy (kJ/kg·K)	Specific exergy (kJ/kg)
1	3394.7	6.70	1401.80
2	2899.8	6.80	876.91
3	2750.4	6.99	672.54

* Operating points refer to Fig. 1.

Steam specific exergies in Table 2 are calculated for the base ambient state which is in this paper selected as: the ambient pressure = 1 bar, the ambient temperature = 25 °C = 298 K.

5. The results of performed analysis and discussion

5.1. Back-pressure steam turbine energy and exergy losses at the base ambient state

In Fig. 2 are presented energy flow streams throughout the analyzed steam turbine (steam energy streams at turbine inlet, outlet and at turbine extraction). While neglecting steam mass flow rates lost on the turbine front and rear gland seals, cumulative produced power of the analyzed turbine (power without taking into account the mechanical loss) is equal to the steam energy flow stream at the turbine inlet lowered for steam energy flow streams at turbine outlet and at turbine extraction.

A power which will be used for any power consumer drive (in this case electricity generator drive) is lower (in comparison with power without taking into account the mechanical loss) for mechanical loss into the analyzed turbine. The calculation of this power is ensured with Eq. 10 (power with taking into account the mechanical loss). According to steam operating parameters of the analyzed back-pressure turbine (Table 1 and Table 2), mechanical loss is equal to 1934.50 kW, while power for the electricity generator drive will be equal to 62548.77 kW, Fig. 2. It should be noted that if the power consumer is driven by the analyzed turbine indirectly (by using gearbox) mechanical power delivered to such power consumer should be additionally lowered for mechanical loss in the gearbox.

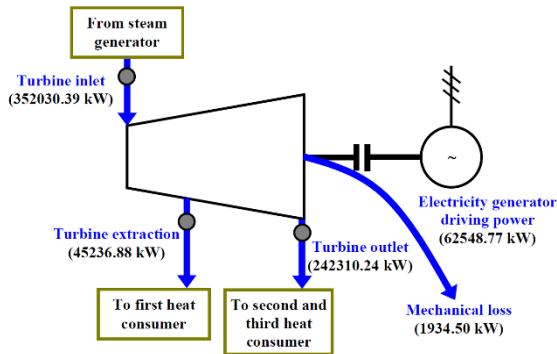


Fig. 2. Energy flow streams of the analyzed back-pressure steam turbine

Exergy flow streams and exergy loss throughout the analyzed back-pressure turbine at the base ambient state are presented in Fig. 3. First of all, it should be noted that steam exergy streams (at turbine inlet, outlet and at turbine extraction) are much lower when compared to the same steam energy streams (Fig. 2).

Analyzed turbine power produced, mechanical loss and power used for electricity generator drive are the same as in energy analysis (Fig. 2). As the exergy analysis takes into account the conditions of the ambient in which turbine operates, a cumulative turbine exergy loss which amount 9887.32 kW can be divided in two parts – the first is mechanical loss and the second is a steam exergy loss which is for the analyzed turbine equal to 7952.82 kW, Fig. 3. Like in energy analysis, in the turbine exergy analysis are also neglected steam mass flow rates lost through front and rear gland seals.

The analyzed back-pressure steam turbine is a good example that exergy analysis (in comparison with energy analysis) involves additional loss related to the ambient conditions.

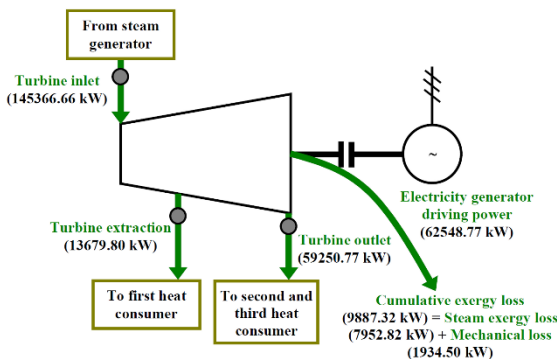


Fig. 3. Exergy flow streams of the analyzed back-pressure steam turbine (the base ambient state)

5.2. Back-pressure steam turbine exergy loss during the ambient temperature change

The analyzed back-pressure steam turbine has three operating points – the first is turbine inlet, the second is turbine extraction and the third is turbine outlet, Fig. 1. Exergy flow streams (steam exergy streams) in each turbine operating point, during the change in the ambient temperature are presented in Fig. 4. From Fig. 4 can clearly be seen that the change in ambient temperature significantly influenced steam exergy streams of the analyzed turbine – increase in the ambient temperature decreases each steam exergy stream in all operating points.

The ambient temperature in which analyzed turbine operates is varied from 5 °C to 55 °C. In such ambient temperature range, steam exergy stream at the turbine inlet decreases the most during the ambient temperature increase, for 32499.58 kW (from 158806.18 kW at the ambient temperature of 5 °C to 126306.6 kW at the ambient temperature of 55 °C), while the lowest decrease in the steam exergy stream during the ambient temperature increase can be observed for steam extraction (Operating point 2), Fig. 4.

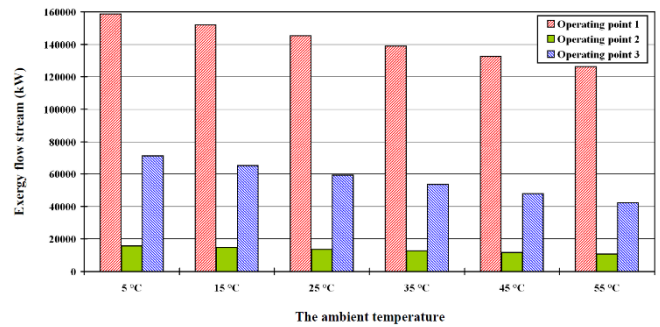


Fig. 4. Exergy flow streams (steam exergy streams) in each operating point of the analyzed back-pressure turbine during the ambient temperature change (according to Fig. 1)

Decrease in all analyzed turbine steam exergy streams during the increase in the ambient temperature resulted with an increase in turbine cumulative exergy loss (from 9362.71 kW at the ambient temperature of 5 °C to 10693.75 kW at the ambient temperature of 55 °C), Fig. 5. It should be noted that in cumulative turbine exergy loss, mechanical loss remains the same at all observed ambient temperatures, while steam exergy loss notably increases during the increase in the ambient temperature.

An increase in the ambient temperature simultaneously increases analyzed turbine cumulative exergy loss and decreases turbine exergy efficiency, from 86.98 % at 5 °C to 85.40 % at 55 °C. It can be concluded that an increase in the ambient temperature for 10 °C reduces analyzed back-pressure turbine exergy efficiency for less than 0.5 % on average, so the analyzed turbine exergy efficiency is not significantly influenced by the ambient temperature change. However, the ambient temperature change notably influenced analyzed turbine cumulative exergy loss which increase for 266.21 kW on average for every increase in the ambient temperature in step of 10 °C.

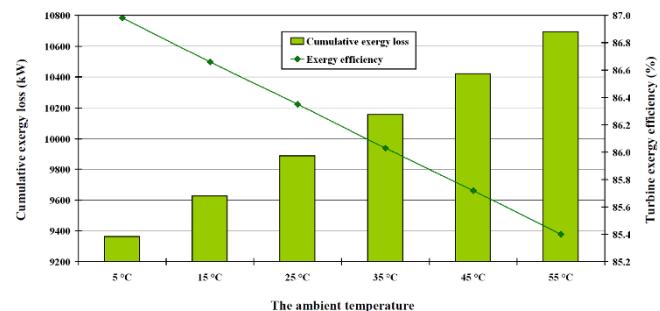


Fig. 5. Cumulative exergy loss and exergy efficiency of analyzed steam turbine during the ambient temperature change

Further research and possible optimization of the observed steam turbine will be performed by the application of many artificial intelligence methods and processes already developed and implemented by our research team [25-30].

6. Conclusions

In this paper is presented exergy and exergy losses analysis of back-pressure steam turbine from a CHP plant. Energy analysis takes into account only mechanical loss (energy flows lost through front and rear gland seals are neglected). Exergy analysis is performed for the selected base ambient state and then the ambient temperature is varied in order to obtain the change in turbine exergy efficiency and loss. The major conclusions of this analysis are:

- Analyzed back-pressure steam turbine, for the known steam operating parameters and mechanical efficiency equal to 97 %, has mechanical loss equal to 1934.50 kW and produced 62548.77 kW of power used for electricity generator drive. Energy analysis of this (and any other steam turbine) is always the same - it did not depend on the ambient conditions in which turbine operates.

- Exergy analysis shows that cumulative exergy loss of the analyzed turbine is composed of the sum of two losses - mechanical loss and steam exergy loss. Therefore, exergy analysis takes into account additional loss related to the state of the ambient in which steam turbine operates.

- An increase in the ambient temperature resulted with a decrease in all steam exergy streams of the analyzed turbine. The most notable change in steam exergy streams during the ambient temperature change is observed for the steam stream at the turbine inlet.

- An increase in the ambient temperature reduces turbine exergy efficiency (and vice versa) but the change is small. Notable change during the ambient temperature change is observed in the turbine exergy loss. An increase in the ambient temperature for 10 °C resulted with an average decrease of analyzed turbine exergy efficiency for less than 0.5 % and simultaneously with an average increase of turbine exergy loss for 266.21 kW.

7. Acknowledgment

This research has been supported by the Croatian Science Foundation under the project IP-2018-01-3739, CEEPUS network CIII-HR-0108, European Regional Development Fund under the grant KK.01.1.1.01.0009 (DATA-CROSS), project CEKOM under the grant KK.01.2.2.03.0004, CEI project "COVIDAI" (305.6019-20), University of Rijeka scientific grant uniri-tehnic-18-275-1447 and University of Rijeka scientific grant uniri-tehnic-18-18-1146.

8. References

- [1] Wilding, P. R., Murray, N. R., & Memmott, M. J. (2020). *The use of multi-objective optimization to improve the design process of nuclear power plant systems*. Annals of Nuclear Energy, 137, 107079. (doi:10.1016/j.anucene.2019.107079)
- [2] Lorencin, I., Andelić, N., Mrzljak, V., & Car, Z. (2019). *Genetic Algorithm Approach to Design of Multi-Layer Perceptron for Combined Cycle Power Plant Electrical Power Output Estimation*. Energies, 12(22), 4352. (doi:10.3390/en12224352)
- [3] Pattanayak, L., Padhi, B. N., & Kodamasingh, B. (2019). *Thermal performance assessment of steam surface condenser*. Case Studies in Thermal Engineering, 14, 100484. (doi:10.1016/j.csite.2019.100484)
- [4] Škopac, L., Medica-Viola, V., & Mrzljak, V. (2020). *Selection Maps of Explicit Colebrook Approximations according to Calculation Time and Precision*. Heat Transfer Engineering, 1-15. (doi:10.1080/01457632.2020.1744248)
- [5] Kostyuk, A., & Frolov, V. (Eds.). (1988). *Steam and gas turbines*. Mir Pub..
- [6] Holmberg, H., Tuomaala, M., Haikonen, T., & Ahtila, P. (2012). *Allocation of fuel costs and CO₂-emissions to heat and power in an industrial CHP plant: Case integrated pulp and paper mill*. Appl. En., 93, 614-623. (doi: 10.1016/j.apenergy.2011.11.040)
- [7] Zueco, J., López-Asensio, D., Fernández, F. J., & López-González, L. M. (2020). *Exergy analysis of a steam-turbine power plant using thermocombustion*. Appl. Therm. Eng., 180, 115812. (doi: 10.1016/j.applthermaleng.2020.115812)
- [8] Baressi Šegota, S., Lorencin, I., Andelić, N., Mrzljak, V., & Car, Z. (2020). *Improvement of Marine Steam Turbine Conventional Exergy Analysis by Neural Network Application*. Journal of Marine Sci. and Eng., 8(11), 884. (doi:10.3390/jmse8110884)
- [9] Lorencin, I., Andelić, N., Mrzljak, V., & Car, Z. (2019). *Exergy analysis of marine steam turbine labyrinth (gland) seals*. Pomorstvo, 33(1), 76-83. (doi:10.31217/p.33.1.8)
- [10] Kanoğlu, M., Çengel, Y. A. & Dincer, I. (2012). *Efficiency Evaluation of Energy Systems*. Springer. (doi:10.1007/978-1-4614-2242-6)
- [11] Medica-Viola, V., Baressi Šegota, S., Mrzljak, V., & Štifanić, D. (2020). *Comparison of conventional and heat balance based energy analyses of steam turbine*. Pomorstvo, 34(1), 74-85. (doi:10.31217/p.34.1.9)
- [12] Ahmadi, G. R., & Toghrade, D. (2016). *Energy and exergy analysis of Montazeri steam power plant in Iran*. Renewable and Sust. Energy Rev., 56, 454-463. (doi:10.1016/j.rser.2015.11.074)
- [13] Mrzljak, V., & Poljak, I. (2019). *Energy Analysis of Main Propulsion Steam Turbine from Conventional LNG Carrier at Three Different Loads*. NAŠE MORE, 66(1), 10-18. (doi:10.17818/NM/2019/1.2)
- [14] Aljundi, I. H. (2009). *Energy and exergy analysis of a steam power plant in Jordan*. Applied Thermal Eng., 29(2-3), 324-328. (doi:10.1016/j.applthermaleng.2008.02.029)
- [15] Szargut, J. (2005). *Exergy method: technical and ecological applications* (Vol. 18). WIT press.
- [16] Medica-Viola, V., Mrzljak, V., Andelić, N., & Jelić, M. (2020). *Analysis of Low-Power Steam Turbine With One Extraction for Marine Applications*. NAŠE MORE, 67(2), 87-95. (doi:10.17818/NM/2020/2.1)
- [17] Baldi, F., Ahlgren, F., Nguyen, T. V., Thern, M., & Andersson, K. (2018). *Energy and exergy analysis of a cruise ship*. Energies, 11(10), 2508. (doi:10.3390/en1102508)
- [18] Mrzljak, V., Blecich, P., Andelić, N., & Lorencin, I. (2019). *Energy and Exergy Analyses of Forced Draft Fan for Marine Steam Propulsion System during Load Change*. Journal of Marine Sci. and Eng., 7(11), 381. (doi:10.3390/jmse7110381)
- [19] Koroglu, T., & Sogut, O. S. (2018). *Conventional and advanced exergy analyses of a marine steam power plant*. Energy, 163, 392-403. (doi:10.1016/j.energy.2018.08.119)
- [20] Mrzljak, V., Poljak, I., & Prpić-Oršić, J. (2019). *Exergy analysis of the main propulsion steam turbine from marine propulsion plant*. Brodogradnja, 70(1), 59-77. (doi:10.21278/brod70105)
- [21] Tan, H., Shan, S., Nie, Y., & Zhao, Q. (2018). *A new boil-off gas re-liquefaction system for LNG carriers based on dual mixed refrigerant cycle*. Cryogenics, 92, 84-92. (doi:10.1016/j.cryogenics.2018.04.009)
- [22] Mrzljak, V., Senčić, T., & Žarković, B. (2018). *Turbogenerator steam turbine variation in developed power: Analysis of exergy efficiency and exergy destruction change*. Modelling and Simulation in Engineering, 2018. (doi:10.1155/2018/2945325)
- [23] Mrzljak, V., Poljak, I., & Medica-Viola, V. (2017). *Dual fuel consumption and efficiency of marine steam generators for the propulsion of LNG carrier*. Applied Thermal Engineering, 119, 331-346. (doi:10.1016/j.applthermaleng.2017.03.078)
- [24] Lemmon, E. W., Huber, M. L., & McLinden, M. O. (2010). NIST Standard Reference Database 23, *Reference Fluid Thermodynamic and Transport Properties (REFPROP)*, version 9.0, National Institute of Standards and Technology. R1234yf. fld file dated December, 22, 2010.
- [25] Baressi Šegota, S., Lorencin, I., Ohkura, K., & Car, Z. (2019). *On the Traveling Salesman Problem in Nautical Environments: an Evolutionary Computing Approach to Optimization of Tourist Route Paths in Medulin, Croatia*. Pomorski zbornik, 57(1), 71-87. (doi:10.18048/2019.57.05)
- [26] Lorencin, I., Andelić, N., Mrzljak, V., & Car, Z. (2019). *Marine Objects Recognition Using Convolutional Neural Networks*. NAŠE MORE, 66(3), 112-119. (doi:10.17818/NM/2019/3.3)
- [27] Car, Z., Baressi Šegota, S., Andelić, N., Lorencin, I., & Mrzljak, V. (2020). *Modeling the Spread of COVID-19 Infection Using a Multilayer Perceptron*. Computational and Mathematical Methods in Medicine, 2020. (doi:10.1155/2020/5714714)
- [28] Lorencin, I., Andelić, N., Mrzljak, V., & Car, Z. (2019). *Multilayer Perceptron approach to Condition-Based Maintenance of Marine CODLAG Propulsion System Components*. Pomorstvo, 33(2), 181-190. (doi:10.31217/p.33.2.8)
- [29] Baressi Šegota, S., Lorencin, I., Musulin, J., Štifanić, D., & Car, Z. (2020). *Frigate Speed Estimation Using CODLAG Propulsion System Parameters and Multilayer Perceptron*. NAŠE MORE, 67(2), 117-125. (doi:10.17818/NM/2020/2.4)
- [30] Lorencin, I., Andelić, N., Šegota, S. B., Musulin, J., Štifanić, D., Mrzljak, V., ... & Car, Z. *Edge Detector-Based Hybrid Artificial Neural Network Models for Urinary Bladder Cancer Diagnosis*. In Enabling AI Applications in Data Science (pp. 225-245). Springer, Cham.

Development and analysis of normative technique for designing the small sea port facilities

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Abstract: At present, with rapid growth in maritime transport, the issue of improving the quality and reducing the time of design of marine terminals, ports and related facilities comes to the forefront. To this end, it is necessary to perform design works which are of integrated nature and are distinguished by high level of automation. The problem can be solved by creating a highly efficient automated system of design based on modern methods of engineering analysis and modeling.

KEY WORDS: SMALL MARITIME PORT, LANDING-STAGE, YACHT CLUB, PORT HANDLING.

1. Introduction

Along with rapid growth in maritime transport, the issue of improving the quality and reducing the time of design of marine terminals, ports and related facilities comes to the forefront.

The process of creating port or terminal, as well as of any transport infrastructure facility proceeds through several stages, from business idea to the analysis of commercial results of operation. This process involves creation of the design and working documentation, as well as the construction, putting into operation and operation of a facility. Besides, the process of creation of a facility involves several parties, including: customer, investor, designer, operator, supervisory authorities, consumers and so on.

The main element of the port technological structure is a shipping complex, which is a complex of engineering means (buildings, installations, equipment, transport and engineering communication) required for port activities. implies cargo receipt, loading, unloading and comprehensive maintenance of maritime transport ships. Port operation also envisages receipt and delivery of cargo by rail, road, river, pipeline and other types of transport.

That is, the main task of the technological processes of port is to make the optimal decision, which includes safe handling of ships, rapid loading and unloading and comprehensive maintenance. At the same time, it is necessary to enhance the capacity of cargo turnover, development, environmental safety and economic feasibility of the decisions taken.

2. Preconditions and means for resolving the problem

The design process with regulated norms can be divided into several stages. At the initial stage, two or more competitive versions of the technological process and the shipping complex master plan are discussed. At the same time, the technical data of production should not be below the standard level.

In the next stage, the effective investments are calculated on the basis of quantitative and qualitative indicators obtained in the development of the relevant part of the project. As a separate section of the project there is considered such organization of major and auxiliary works when occupational health and fire safety requirements are completely observed.

At the initial stage of the calculation of the construction of port, there is considered the intensity of the loading and unloading operations, which is determined by the duration of works, production breakdown time and is calculated by the formula:

$$P_{\text{daily}} = \frac{1}{\sum_{i=1}^n \frac{A_i(t_{\text{cti}} - t_{\text{sti}})}{24D_i}} \cdot \frac{T}{\text{day} - \text{and} - \text{night}}, \quad (1)$$

where

n – number of ships under study;

D_i – estimated cargo turnover of i -type ship, T;

A_i – estimated share of i -type ship in the estimated cargo turnover;

t_{cti} – time spent on loading (unloading) operations, hr;

t_{sti} – standing time of ship at a port, hr.

The weighted share of i -type ship in total cargo turnover (Q) is a value ($A_i \cdot Q$), from which the total maintenance time of a given type of ships is calculated by the formula:

$$T_i = \frac{A_i \cdot Q}{P_i},$$

where the value P_i is a daily intensity of ship operation and is calculated by the formula:

$$P_i = 24D_i / (t + t)$$

If you divide total cargo turnover (Q) by the time of its handling $T = \sum T_i$, we get the formula $T = \sum T_i$ in the reduced form, or what is the same with the composition of ships having the given initial values, their share in the estimated cargo turnover and by processing technological parameters, we can get the average value - daily cargo production.

The annual capacity in tonnes can be calculated by the formula:

$$P_{\text{an}} = \frac{30P_{\text{daily}} \cdot K_{\text{met}} \cdot K_{\text{del}} \cdot N_m}{K_m}, \quad (2)$$

where

N_m – number of months of navigation;

K_{met} – meteorological conditions factor;

K_{del} – ship delay factor;

K_m – irregularity monthly coefficient.

By analyzing the formula 2, we get the following sequence of the used estimated values:

1. If the daily productivity calculated by the formula 1 we multiply by 30, we get the maximum (monthly) intensity of cargo turnover - $30P_{\text{daily}}$.

2. If the obtained value ($30P_{\text{daily}}$) we multiply by the irregularity monthly coefficient (K_m), we get the average monthly cargo turnover $30P_{\text{daily}} / K_m$.

3. The value $30P_{\text{daily}} \cdot K_{\text{met}} / K_m$ is the average monthly cargo turnover with account for metrological conditions.

4. The value $30P_{\text{daily}} \cdot K_{\text{met}} \cdot K_{\text{del}} / K_m$ is the average monthly cargo turnover with account for metrological conditions and delay (without breakdown).

5. The value $30P_{\text{daily}} \cdot K_{\text{met}} \cdot K_{\text{del}} \cdot K_m / K_m$ is the annual with account for metrological conditions and delay.

That is, the annual capacity of port is the volume of cargo turnover that it can provide for a given use factor. Obviously, this volume is lower than the capacity of ports.

Let us consider the essential and critical explanation, such as the irregularity of cargo traffic and explain how it interrelated with the major calculated parameters. In general, the ratio of the maximum value of cargo traffic to the average value is called the

irregularity ratio of cargo traffic. For example, for monthly cargo traffic $K_m = Q_m / Q_{m.av.}$, from which the maximum monthly turnover is

$$Q_m = K_m \cdot Q_{m.av.} = K_m \cdot Q_{an} / 12 \quad (3)$$

In the technological design, it is important to determine the loading (occupancy) ratio of port. It is recommended to specify the number of harbors according to the formula

$$N = \frac{Q_m}{30P_{daily} \cdot K_m \cdot K_{met}}$$

where Q_m – the estimated monthly cargo turnover in a port, t/per month ;

P_{daily} – the intensity of loading and unloading operations, t/daily;

K_{met} – the utilization ratio of working hours of port with account for breakdowns caused by meteorological conditions;

K_m – monthly irregularity ratio.

If we provide the simplest transformations of the formula, we'll get:

$$N = \frac{Q_m}{30P_{daily} \cdot K_m \cdot K_{an}} = \frac{Q_m \cdot N_m}{P_{an}} = \frac{Q_{an}}{P_{an}} \quad (4)$$

That is, the essence of the obtained formula is that we must divide the total required annual cargo turnover of port or terminal by the estimated theoretical cargo turnover of a single harbor that gives us the required number of harbors. In addition, the value obtained should be rounded up to the nearest whole number. At this time, the effect of this rounding up is on the initial value of the harbor use ratio is not considered. If in calculating the given value of use factor $K_{use} = 0,5 \div 0,6$, the number of harbors is 1.3, then rounding up to the nearest calculation number will give us 2, although this will reduce the use factor K_{use} to 0.35. That is, there will be ship demurrage. The rounding up to 1 results in an increase in the use factor K_{use} up to 0.9, which is higher than the recommended value.

For the sake of clarification, let us consider the following example: assume that, the basic navigation period is 300 days, for the sake of simplicity, there is no monthly irregularity. At the same time, cargo turnover is carried out by two types of ships - the estimated capacity of one is 100,000 tons and 10,000 tons is the estimated capacity of the other. At the same time, their quantitative ratio is 3:1 and the maintenance time is 6 days and 1 day, respectively. In this case we can calculate the rate of working on a ship:

$$P_{daily} = \frac{1}{0,75 \cdot \frac{6}{100000} + 0,25 \cdot \frac{1}{10000}} = 14290 \text{ t}$$

It is widely accepted that the use factor for ships carrying general cargo is $K_{use} = 0,6$, the navigation capacity is:

$$P_{zn} = 300 \cdot 0,6 \cdot 14290 = 2571430 \text{ t}$$

If the volume of ships is 30 and 100 ships respectively, then the cargo turnover is:

$$30 \cdot 100\,000 = 3\,000\,000 \text{ t/annually, and}$$

$$100 \cdot 10\,000 = 1\,000\,000 \text{ t/annually, and}$$

That is, the total cargo turnover is 4 000 000 t/annually, and the calculated number of harbors is:

$$N_{harb} = 4\,000\,000 / 2\,571\,430 = 1,55$$

If in this case we round the number of harbors up to 2, then the time budget will be 600 days. It should be noted that the maintenance time of ships with a capacity of 100,000 tons is 180 days, while for ships with a capacity of 10000 tons, the maintenance time is 100 days. That is, for a total of 280 days, from which $K_{use} = 280/600 = 0,47$, while the initial value was 0.6.

That is, it is clear that the construction of two full-scale harbors that will enable us to handle large ships is not feasible. Therefore, it is feasible to construct one harbor to berth ships, which will provide its loading capacity with a use factor $K_{use} = 180/300 = 0,6$. Another harbor will be used simultaneously for other ships with a load factor of $K_{use} = 100/300 = 0,33$.

Practically, during the 300-day navigation period, in the case of 30 large ships, for each one there are 10 days, and the maintenance time is 6 days. In the case of 100 small ships, for each one there are 3 days on average, including 1 day for maintenance. This distribution pattern is shown in Figure 1.

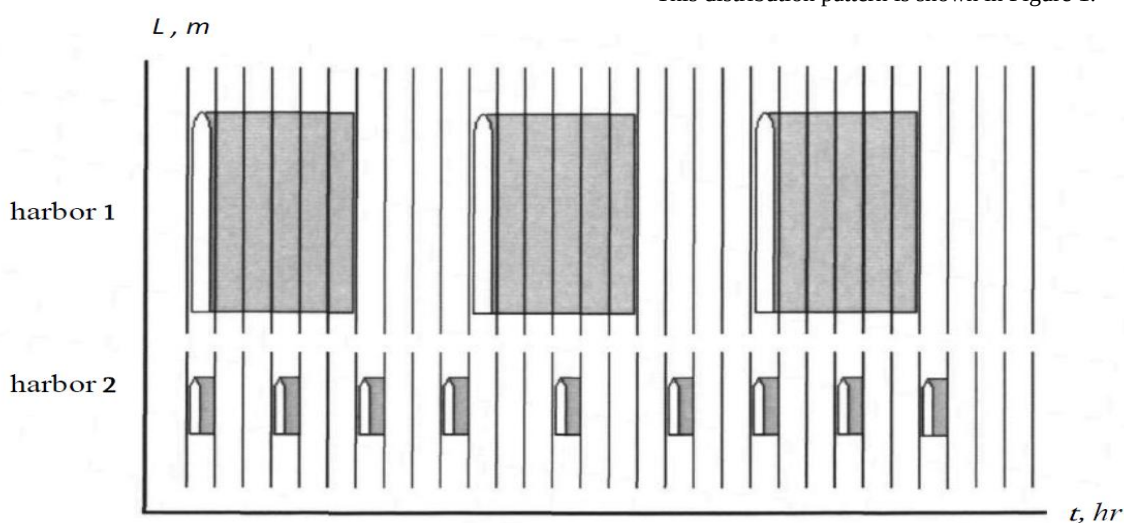


Fig. 1. Handling of ships by two harbors

It should also be noted that if all ships are handled by one harbor, then the use factor is $K_{use} = 290/300 = 0,96$, and this maintenance pattern is shown in Figure 2.

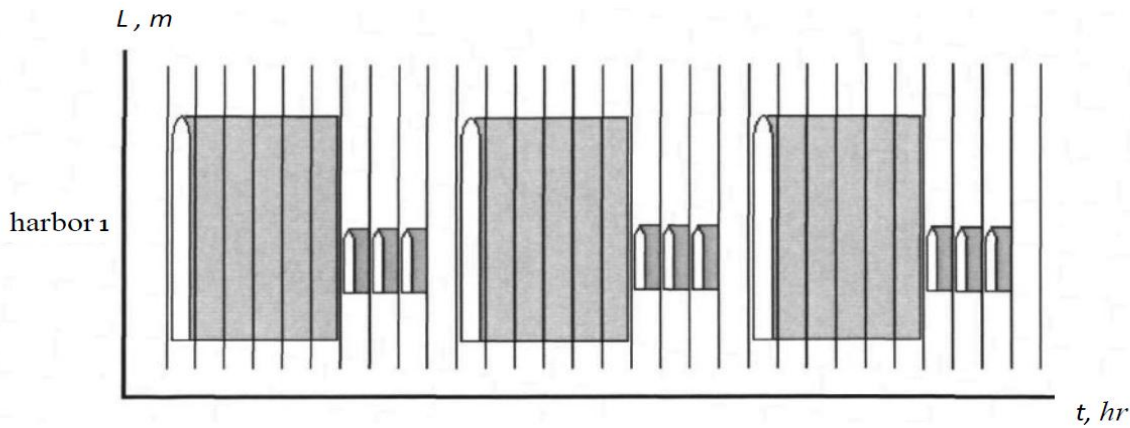


Fig. 2. Handling of ships by one harbor

If the small ships are handled during a large period of time, they will not affect the maintenance time of the large ships (that is, when the large ships enter, the small ones are in standby mode). In addition, with a high productivity of harbor, which is rated to the large ships, the maintenance time for the small ships can be reduced, or several small ships can be handled simultaneously.

3. Conclusion

In the technological design, it is important to determine the utilization ratio of working hours in ports, with account for meteorological conditions. The numerical value of this ratio (K_{met}) is important for determining the values, such as the annual required capacity of port and the number of harbors. The ratio essentially takes account for the effect of precipitation, wind and ambient temperature the operating conditions. By multiplying this ratio by the annual navigation time budget, the designer reduces the port's operating time budget. In fact, due to the impact of unfavorable meteorological conditions, there occur delayed entries of ships to a port in the fleet. In this period, additional equipment shutdowns, and in some cases the ship is moved from the shore to the inshore mooring.

The purpose of future work is to design the construction of small harbors for the small-capacity ships on the Black Sea coast, particularly on the Batumi-Poti section, based on the technique, with a view to delivering transport and logistics services.

4. References Spasskii I. automation of technological design of port terminals based on simulation. Dissertation theses. St. Petersburg, 2012.

2. Bying Kwon Lee, Bong Joo Jung, Kap Hwan Kim, Soon Oh Park, Jeong Hoon Sco, A simulation study for designing a rail terminal in a container port. Winter Simulation Conference, USA, Monterey, Kalifornia, December 3-6, 2006.

Thermodynamic analysis of a 17.5 MW geothermal power plant operating with binary Organic Rankine Cycle

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Abstract: This article presents the thermodynamic analysis of a 17.5 MW gross electric geothermal power plant based on binary cycle technology with isobutane. The geothermal power plant comprises two separate closed loops: the geothermal fluid flows in one loop and the Organic Rankine Cycle (ORC) fluid flows in the second loop. The geothermal fluid is extracted from a depth of 2500-3000 m with a temperature of 170 °C and a pressure of 25 bar. Two production wells supply geothermal fluid (brine and steam) with a high fraction of non-condensable gases (NCG). A separator extracts NCG from the geothermal fluid. Isobutane is preheated and evaporated before entering the ORC turbine with a temperature of 133 °C and a pressure of 28 bar, where expands to the condenser pressure of 4 bar. Electricity is generated by a 17.5 MW axial ORC turbine and additionally by a 1.5 MW NCG turbine. The analysis revealed that the configuration without NCG turbine achieves a net efficiency of 12.73% and a net electric power of 13.68 MW while the configuration with NCG turbine achieves a net efficiency of 14.04% and a net electric power of 15.16 MW but with much higher CO₂ emissions into the atmosphere.

Keywords: GEOTHERMAL POWER PLANT, ORGANIC RANKINE CYCLE, ISOBUTANE, NON-CONDENSABLE GASES

1. Introduction

Geothermal energy is a sustainable and renewable source of energy used for electricity generation and for supplying heating energy to various industries. The world total installed geothermal power capacity has seen a steadily increase over the last decade: 10.9 GW in 2010, 12.3 GW in 2015 and 16.0 GW in 2020 [1]. The world total installed capacity is expected to come around 20.0 GW in 2020. By installed geothermal power capacity, the leading countries are: USA (3700 MW), Indonesia (2289 MW), Philippines (1918 MW), Turkey (1549 MW), Kenya (1193 MW), New Zealand (1064 MW), Mexico (1006 MW), Italy (916 MW), Iceland (755 MW), Japan (550 MW), Costa Rica (262 MW), El Salvador (204 MW), Nicaragua (159 MW). The world total electricity generation from geothermal sources is estimated at 95 TWh in 2020. For comparison, the world total wind power capacity of 622.7 GW generated 1429.6 TWh of electricity in 2019 and the world total solar power capacity of 586.4 GW generated 724.1 GWh of electricity in 2019 [2]. The annual growth rate of geothermal power (4%) is significant, although nowhere near the growth rates of wind power (17%) and solar power (42%) in recent years [2]. However, geothermal power offers an exciting possibility for sustainable electricity generation at acceptable costs and low emissions of greenhouse gases emissions. The total installed costs per unit of installed capacity in geothermal power is on average 3916 US\$/kW, with the range between 2000 and 6000 US\$/kW, depending on the specific project and technology [3]. In 2019, the weighted average levelized cost of electricity (LCOE) generation from geothermal power plants was 73 US\$/MWh. For comparison, the average LCOE of the other renewable energies were: hydro (47 US\$/MWh), onshore wind (53 US\$/MWh), biomass (6 US\$/MWh), solar PV (68 US\$/MWh), offshore wind (115 US\$/MWh) and solar CSP (182 US\$/MWh) [3]. The CO₂ emissions from geothermal power units are estimated in the range between 20 and 57 kg/MWh_{el}, which is comparable to other renewable energy sources. The carbon footprint from solar PV power is in the range between 29 and 80 kg/MWh_{el} while that from wind power is between 8 and 20 kg/MWh_{el}. Large hydropower and nuclear power generate electricity at specific emissions of 3-7 kg/MWh_{el} and 8-45 kg/MWh_{el}, respectively. On the other hand, conventional fossil fuel power plants have much higher CO₂ emissions, in the range of 422-548 kg/MWh_{el} for natural gas, 722-907 kg/MWh_{el} for fuel oil and 877-1130 kg/MWh_{el} for coal [4].

The geothermal power technologies with largest shares in the total global installed capacity are 1) flash steam: 58%, 2) dry steam: 26% and 3) binary cycle: 15%. 1) Flash steam units use high-pressure and high temperature (>180 °C) hot water. Hot water boils into steam as it flows through the pipes of the production well. The remaining hot water is flashed into steam inside low-pressure separator tanks. Flash steam expands in the turbine, and the useful

work drives the electric generator. Leftover liquid water from the separator and condensed steam are returned into the geothermal reservoir by injection wells. 2) Dry steam units use exclusively dry geothermal steam having temperatures in the excess of 150 °C. Hot water may be present in the geothermal reservoir but only dry steam is drawn in the production wells. After the production wells, no heat exchangers or separators are necessary and the dry steam is directly expanded in the turbine. The turbine rotates and drives the electric generator. After the expansion, the exhaust steam is turned into liquid water by the condenser. Waste heat is dumped into the atmosphere through the use of cooling towers while condensed water is returned into the geothermal reservoir by injection wells. 3) Binary cycle units can operate with geothermal temperatures as low as 60 °C by using double loop configuration. Organic Rankine cycles (ORC) and Kalina cycles can be used in for geothermal binary technology. The geothermal fluid, flowing inside the primary loop supplies the thermal energy for preheating and evaporation of the working fluid. In the secondary loop, the working fluid absorbs the geothermal heat and powers the turbine to generate electricity. The working fluid selection depends on the available geothermal temperature and cycle configuration [5-7]. Working fluids can be classified into: 1) hydrocarbons (HC), 2) chlorofluorocarbons (CFC) 3) hydrochlorofluorocarbons (HCFC), 4) hydrofluorocarbons (HFC), 5) hydrofluoroethers (HFE) and 6) mixtures such as ammonia-water for the use in Kalina cycles [8-9].

Nowadays, geothermal energy is drawing increasing interest from research and industrial entities. Ehyaei et al. [10] carried out ORC optimization based on a genetic algorithm. For a geothermal source with a mass flow rate of 15 kg/s and temperature of 150 °C, they found that the optimal thermal efficiency is 14.1% at a capacity of 0.433 MW. Algieri [11] investigated the energy performances of a small-scale ORC for high temperature geothermal sources (230 °C), using subcritical and transcritical isobutane, isopentane and R245ca as the working fluids. Transcritical configurations guarantee highest performance while, among the observed working fluids, isopentane achieves the highest thermal efficiency (17.7%). Morroni and Algieri [12] analyzed the energy and economic performance of a combined geothermal-natural gas CHP system, with an installed electric and thermal capacity of 101.4 kW_{el} and 249.5 kW_{th}, respectively. The combined CHP system achieves an electric efficiency of 13.4%, an energy utilization factor of 19.3% and supplies 95% of the electrical demand and 90% of the thermal demand of a commercial building. Prasetyo et al. [13] carried out experimental analysis of an ORC performance with R123 for a low-temperature geothermal source (120 °C). The ORC unit employs superheated R123 in scroll-type expander and achieves thermal efficiencies in the range between 7.2% and 8.6%. Typically, the ORC thermal efficiency is influenced by the type of working fluid, the cycle configuration and the geothermal temperature. Generally, thermal efficiencies in the range between 10% and 14% can be

achieved for geothermal temperatures between 100° and 220 °C. The present study complements the literature by studying the various factors affecting the energy performance of a 17.5 MW geothermal power plant using medium-temperature geothermal sources (170 °C) and isobutane as the working fluid.

2. The geothermal power plant model

The first geothermal power plant in Croatia was commissioned in early 2019 at the Velika Ciglena site. The Velika Ciglena power plant uses a single-pressure ORC configuration with isobutane as the working fluid. The geothermal power plant has a gross electric capacity of 16.5 MW and a net electric capacity 13.5 MW. Total investment costs were €44 million, corresponding to specific costs of 3260 €/kW (4000 US\$/kW). The generated electricity is 82 GWh per year, at average capacity factor of 70% (6100 full load hours). The ORC turbine is a five-stage axial turbine with design power of 17.5 MW. The Velika Ciglena geothermal field is characterized by porous carbonate rocks, with a geothermal gradient of 62 °C/km and brine temperatures of up to 175 °C. The process flow diagram of the geothermal power plant Velika Ciglena is given in figure 1.

Two production wells extract the geothermal brine and steam from a depth of 2500-3000 m. The geothermal fluid mass flow rate is 800 t/h, with 95% hot water and 5% steam [14], at well-head temperature and pressure of 165 °C and 26 bar, state ⑨. Non-condensable gases (NCG) are separated from the geothermal fluid in the separator. Heat exchange between the geothermal fluid and the ORC fluid occurs in the evaporator and the preheater. The geothermal fluid is cooled from ⑩ to ⑪ in the evaporator and from ⑪ to ⑫ in the preheater. Two injection wells return the geothermal fluid into the geothermal reservoir. The geothermal fluid temperature at the injection wells is 70 °C, state ⑫, which prevents scale and fouling in pipes while allowing for appropriate thermal regeneration in the geothermal reservoir. In the ORC fluid loop, isobutane expands in the turbine from state ① to ②. Isobutane is a dry working fluid and turbine expansion ② ends in the superheated region. This is because isobutane exhibits positive slope in the saturation vapor curve, meaning that by decreasing the saturation temperature the specific entropy also decreases ($dT/ds > 0$). For comparison, water vapor is a wet working fluid, having negative slope on the saturation vapor curve, where the specific entropy increases if the saturation temperature decreases ($dT/ds < 0$). Isobutane expands in the superheated region with temperature above the saturation temperature in the condenser. The energy content of the superheated vapor, which would otherwise be simply discharged in the condenser, can be used to preheat the ORC liquid condensate. In the heat recuperator, the superheated ORC vapor cools from ② to ③ before entering the condenser where is desuperheated, ③ → ④, and condensed, ④ → ⑤. After the

condenser, the liquid condensate is pumped by the ORC feed pump, ⑤ → ⑥, and preheated in the heat recuperator, ⑥ → ⑦. By preheating the liquid condensate, the heat recuperator reduces the heating duty of the preheater, positively affecting the cycle overall thermal efficiency. The ORC liquid condensate is heated up to the boiling point in the preheater, ⑦ → ⑧, evaporated and superheated in the evaporator, ⑧ → ①, up to the pressure and temperature at the turbine inlet. The condenser is water cooled and the waste is discharged into the atmosphere by forced-draft cooling towers.

At the Velika Ciglena site, the geothermal fluid contains a high content of dissolved non-condensable gases (NCGs) and minerals. Dissolved minerals (24 kg/m³) consists mainly of chlorine (13 kg/m³) and sodium (9 kg/m³) with trace amounts of carbonates, sulphates, magnesium, lithium, mercury and radon (4.85 Bq/l). Carbon dioxide (CO₂) represents 99.5% of the NCGs, with a specific content of 55 kg/m³ per unit of geothermal fluid volume [15]. Further, NCGs contain smaller fractions of nitrogen, methane ammonia and hydrogen sulfide (H₂S). The H₂S concentration is 59 ppm. In dry steam and flash steam geothermal power plants, the presence of NCGs may decrease the power output from the turbine. This is caused by NCGs buildup in the condenser, which leads to increased turbine backpressure and decreased power. Further losses are caused by the auxiliary power duty of vacuum pumps, steam-jet ejectors or turbo-compressors for the removal of NCGs from the condenser [16]. In binary cycles, the NCGs could accumulate inside the preheater and evaporator, reducing the heat transfer rate from the geothermal fluid to the ORC fluid.

As remedy, modern geothermal power plants use upstream separators (reboilers), installed after the production well, where NCGs are separated from the geothermal fluid and afterwards discharged into the atmosphere or compressed and reinjected into the geothermal reservoir [17]. From environmental standpoint, NCGs reinjection is certainly the better solution as CO₂ and H₂S are stored into the geothermal reservoir. NCG discharge increases the power plant net electricity by eliminating the compression power duty, but at the downside of CO₂ and H₂S emissions into the atmosphere. At geothermal sites with high NCG contents, discharge into the atmosphere is a questionable practice, which does not adhere to low carbon power generation principles. In the Velika Ciglena geothermal power plant, the NCG collected from the separator first a NCG turbine, rated at 1.5 MW power, for additional electricity generation and after that is discharged into the atmosphere. In the present study, the NCG is modelled as 100% CO₂, with a mass flow rate of 10.45 kg/s, corresponding to 85% removal rate in the separator. The remaining 15% of CO₂ is dissolved in the geothermal fluid as it crosses the evaporator and preheater sections. In the NCG turbine, CO₂ is expanded to atmospheric pressure, state change ⑬ → ⑭. The NCG turbine is also seen in the Lartera geothermal power plant in Italy [18].

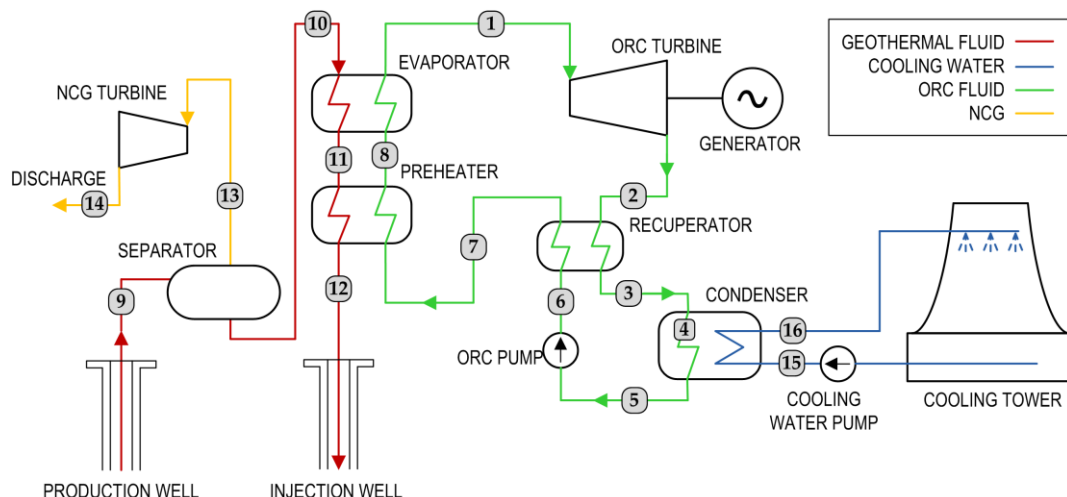


Fig. 1. The process diagram of the binary cycle geothermal power plant Velika Ciglena

In the analyzed configuration, shown in figure 2, the geothermal fluid delivers the following heat flow rates to the evaporator and the preheater heat transfer surfaces

$$\text{evaporator: } \dot{Q}_{EV} = \dot{m}_{GTF}(h_{10} - h_{11}) \quad (1)$$

$$\text{preheater: } \dot{Q}_{PR} = \dot{m}_{GTF}(h_{11} - h_{12}) \quad (2)$$

The actual heat transfer rates absorbed by the ORC fluid are reduced by heat transfer losses, η_{EV} and η_{PR} . The corresponding heat balance equations for the evaporator and the preheater are

$$\text{evaporator: } \dot{m}_{ORC}(h_1 - h_8) = \dot{m}_{GTF}(h_{10} - h_{11})\eta_{EV} \quad (3)$$

$$\text{preheater: } \dot{m}_{ORC}(h_8 - h_7) = \dot{m}_{GTF}(h_{11} - h_{12})\eta_{PH} \quad (4)$$

The evaporator and preheater heat loss is assumed 10%, returning heat transfer efficiencies of $\eta_{EV} = 0.90$ and $\eta_{PR} = 0.90$. Equations (3) and (4) are solved taking into account two minimum temperature conditions. The first is the reinjection temperature of the geothermal fluid, set to $T_{12min} = 70$ °C. The second is the minimum pinch-point temperature difference between the geothermal fluid and the ORC fluid occurring at the evaporator cold end, $\Delta T_{ppmin} = 10$ °C. Note that the pinch-point temperature difference must be increased if the solution yields an injection temperature under 70 °C. The heat balance equation for the heat recuperator is

$$\text{recuperator: } \dot{m}_{ORC}(h_2 - h_3)\eta_{RE} = \dot{m}_{ORC}(h_7 - h_6) \quad (5)$$

The heat transfer efficiency of the heat recuperator is $\eta_{RE} = 0.95$, corresponding to 5% heat losses. The temperature difference between the heat recuperator outlet and the condenser saturation temperature is 10 °C. The condenser heat balance is

$$\text{condenser: } \dot{m}_{ORC}(h_3 - h_5) = \dot{m}_{CW}(h_{16} - h_{15}) \quad (6)$$

It is assumed that the cooling water temperature increases by 8 °C across the condenser. The cooling water temperatures are calculated taking that the cooling tower efficiency is 75% at the ambient temperature of 20 °C and relative humidity of 50%. The ORC fluid saturation temperature is determined taking that the pinch-point temperature difference in the condenser is 5 °C. The geothermal power plant generates electricity from the ORC turbine and additionally from the NCG turbine. The power of the ORC turbine and NCG turbine are calculated assuming adiabatic expansion

$$\text{ORC turbine: } \dot{W}_{T,ORC} = \dot{m}_{ORC}(h_1 - h_{2s})\eta_{T,ORC} \quad (7)$$

$$\text{NCG turbine: } \dot{W}_{T,NCG} = \dot{m}_{NCG}(h_{13} - h_{14s})\eta_{T,NCG} \quad (8)$$

The isentropic efficiency of the ORC and NCG turbine is assumed at $\eta_{ORC} = 0.88$ and $\eta_{NCG} = 0.82$, respectively. The power duties of the ORC feed pump and of the cooling water pump are

$$\text{ORC pump: } \dot{W}_{P,ORC} = \frac{\dot{m}_{ORC}(h_{6s} - h_5)}{\eta_{P,ORC}} \quad (9)$$

$$\text{cooling water pump: } \dot{W}_{P,CW} = \frac{\dot{m}_{CW} g H}{\eta_{P,CW}} \quad (10)$$

The isentropic efficiency of the two pumps are $\eta_{P,ORC} = 0.80$ and $\eta_{P,CW} = 0.80$ while the head in the cooling system is set at $H = 20$ m. The gross electrical power is the sum of the power generated from the ORC turbine and the NCG turbine, reduced by the mechanical and electrical losses in the electricity generator

$$\text{gross power: } \dot{W}_{gross} = (\dot{W}_{T,ORC} + \dot{W}_{T,NCG})\eta_m \eta_g \quad (11)$$

The mechanical and electrical efficiencies of the electric generator are $\eta_m = 0.98$ and $\eta_{el} = 0.98$. The net electrical power of the geothermal power plant is obtained subtracting the gross power by the pumping duties and the auxiliary power consumption of other systems (cooling tower fans, downhole pumps)

$$\text{net power: } \dot{W}_{net} = \dot{W}_{gross} - (\dot{W}_{P,ORC} + \dot{W}_{P,CW} + \dot{W}_{aux}) \quad (12)$$

The auxiliary power consumption is assumed 5% of the gross power, that is $\dot{W}_{aux} = 0.05 \dot{W}_{gross}$. The thermal efficiency of the binary cycle, based on First Law analysis, can be determined from

$$\text{thermal efficiency: } \eta_{th} = \frac{\dot{W}_{net}}{\dot{Q}_{EV} + \dot{Q}_{PH}} \quad (13)$$

Table 1. gives the list of input parameters and assumption in the geothermal binary ORC power plant.

Table 1: Input parameters for the binary ORC analysis

Parameter	Value
Geothermal well-head temperature	165 °C
Geothermal well-head pressure	26 bar
Geothermal fluid mass flow rate	222 kg/s
Heating pinch-point temperature difference	10 °C
Minimum geothermal reinjection temperature	70 °C
Evaporator and preheater heat transfer efficiency	90%
Recuperator heat transfer efficiency	95%
Recuperator / condenser temperature difference	10 °C
ORC working fluid	isobutane
ORC turbine isentropic efficiency	88%
ORC feed pump efficiency	80%
ORC fluid pressure drop in preheater / evaporator	1 bar (each)
Electric generator efficiency, %	98%
Mechanical efficiency	98%
NCG mass flow rate	10.45 kg/s
NCG turbine isentropic efficiency	82%
Cooling tower efficiency	75%
Cooling water pump efficiency	80%
Cooling water temperature difference	8 °C
Cooling pinch-point temperature difference	5 °C
Ambient air temperature	20 °C
Ambient air relative humidity	50%
Auxiliary power consumption (% of gross power)	5%

3. Results and discussion

The performance of the geothermal power plant is a function of the type of working fluid, the fluid temperature and pressure at the turbine inlet as well as on the condenser pressure. These last two are influenced by the parameters of the available geothermal fluid and the ambient conditions. The geothermal power plant Velika Ciglena uses isobutane as the selected working fluid since it matches best the geothermal fluid temperature profiles in the preheater and the evaporator. Isobutane is operated in a subcritical cycle with superheat vapor at the turbine inlet. Subcritical cycles with saturated vapor and transcritical cycles are also possible for geothermal binary power plants. Figure 2. shows the temperature entropy chart of the subcritical ORC with superheated isobutane as the working fluid. The superheat vapor temperature and pressure are 133 °C and 28 bar, which presents a good tradeoff between generated power and cycle efficiency. The achieved gross thermal efficiency is 16.77% and the gross electric power is 18.11 MW, including 1.48 MW from the NCG turbine. The difference between gross and net electric power is due to the auxiliary power consumers: 1.45 MW in the ORC feed pump, 0.59 MW in the cooling system pump and 0.91 MW in other consumers. The resulting net electric power is 15.16 MW and the net thermal efficiency of the geothermal power plant is 14.04%. By recovering the NCG energy content, the geothermal power plant net efficiency is increased by 10.3%. Without the NCG turbine, the net efficiency of the binary cycle would be 12.73% and the net electric power 13.68 MW. However, this net electricity increase comes at the cost of increased CO₂ emissions into the atmosphere. The NCG turbine discharges a total of 37.6 t/h of CO₂ into the atmosphere, which converts into a specific CO₂ emission of 2482 kg/MWh. For comparison, the Lartera geothermal power plant in Italy discharges 70 t/h of NCG (83% wt. CO₂), which returns a CO₂ emission per unit of generated electricity of around 2000 kg/MWh [18]. Specific CO₂ emissions from geothermal sites with high fractions of carbonaceous rocks can exceed CO₂ emissions from coal-fired power plant [17], which range between 700 and 1000 kg/MWh [19].

The binary cycle efficiency is positively affected by the heat recuperator transferring heat from the superheated turbine discharge to the liquid condensate. Without a heat recuperator and a NCG turbine, the net thermal efficiency and the net electric power would be further reduced to 11.38% and 12.24 MW. If the superheated

Rankine cycle is replaced by a saturated Rankine cycle, the net efficiency and electric power are reduced. Although the critical pressure of isobutane is 36.3 bar, saturated cycles with evaporation pressures above 22.9 bar are avoided in order to prevent vapor condensation in the turbine. Specifically, in the temperature-entropy chart, the turbine expansion curve could intersect the saturated vapor line for any starting point above the maximum entropy point ($p_{\text{sat}} = 22.9$ bar, $T_{\text{sat}} = 107.8$ °C) on the saturated vapor line, which would reduce the turbine efficiency and accelerate blade erosion. The saturated Rankine cycle with isobutane yields a net efficiency of 11.81% and as net electric power of 12.76 MW, figure 3.

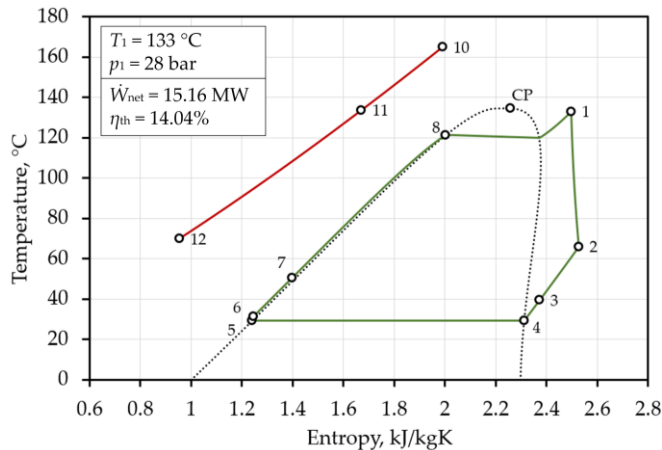


Fig. 2. Temperature-entropy chart for the superheated ORC with isobutane

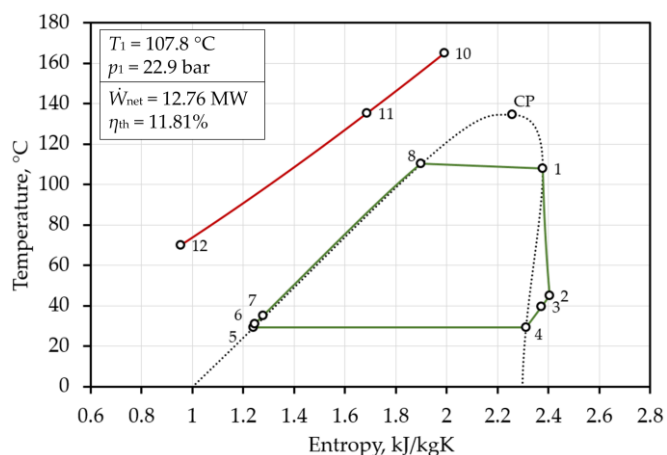


Fig. 3. Temperature-entropy chart for the saturated ORC with isobutane

4. Conclusions

Geothermal power generation is expected to keep growing in the next years. The total global installed capacity is expected to surpass 19 GW by 2025. Nowadays, the exploitation of geothermal energy is principally focused on medium-temperature sites with binary ORC technologies. In Croatia, new geothermal power plants are planned. Recently, a 20 MW binary cycle power plant is considered at the Legrad site (northern Croatia), with an expected annual electricity generation of 165 GWh/year. The geothermal power potential in Croatia is estimated at 100 MW by 2030, and possibly up to 300 MW by 2050. From the present perspective these numbers are attainable as geothermal power is currently generously subsidized within the Croatian feed-in tariff system for renewable energy. At the moment, the feed-in tariff for geothermal electricity is 254 US\$/MWh which, against an average LCOE of 73 US\$/MWh, makes geothermal power a very attractive renewable energy solution with short return of investment periods.

5. References

1. G.W. Huttner, Geothermal power generation in the world 2015-2020 update report, Proceedings World Geothermal Congress 2020, Reykjavik, Iceland, April 26 – May 2, 2020.
2. BP Statistical Review of World Energy 2020, 69th edition, London, UK, 2020. <https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html>
3. IRENA: Renewable Power Generation Costs in 2019, International Renewable Energy Agency, Abu Dhabi, UAE.
4. W. Moomaw, P. Burgherr, G. Heath, M. Lenzen, J. Nyboer, A. Verbruggen, Annex II in IPCC: Special Report on Renewable Energy Sources and Climate Change Mitigation, 2011.
5. N. Javanshir, S. Mahmoudi, M.A. Rosen, Thermodynamic and Exergoeconomic Analyses of a Novel Combined Cycle Comprised of Vapor-Compression Refrigeration and Organic Rankine Cycles, Sustainability (2019), 11, 3374.
6. F.A. Latrash, B. Agnew, M.A. Al-Weshahi, N.M. Eshoul, Optimal Selection of Using Fluids (HFC, HCFC, HFC) for an Organic Rankine Cycle Utilizing a Low Temperature Geothermal Energy Source, 5th International Conference on Environment Science and Engineering, Vol. 83 (2015).
7. K. Darvish, M.A. Ehyaei, F. Atabi, M.A. Rosen, Selection of Optimum Working Fluid for Organic Rankine Cycles by Exergy and Exergy-Economic Analyses, Sustainability (2015), 7, 15362-15383.
8. M. Akbari, S. Mahmoudi, M. Yari, M.A. Rosen, Energy and Exergy Analyses of a New Combined Cycle for Producing Electricity and Desalinated Water Using Geothermal Energy, Sustainability (2014) 6, 1796-1820.
9. N. Javanshir, S. Mahmoudi, M.A. Kordlar, M.A. Rosen, Energy and Cost Analysis and Optimization of a Geothermal-Based Cogeneration Cycle Using an Ammonia-Water Solution: Thermodynamic and Thermo-economic Viewpoints, Sustainability (2020), 12(2), 484.
10. M.A. Ehyaei, A. Ahmadi, M.A. Rosen, A. Davarpanah, Thermodynamic Optimization of a Geothermal Power Plant with a Genetic Algorithm in Two Stages. Processes (2020), 8, 1277.
11. Angelo Algieri, Energy Exploitation of High-Temperature Geothermal Sources in Volcanic Areas - a Possible ORC Application in Phlegraean Fields, Energies (2018), 11, 618.
12. P. Morrone, A. Algieri, Integrated Geothermal Energy Systems for Small-Scale Combined Heat and Power Production: Energy and Economic Investigation. Applied Science (2020), 10, 6639.
13. T. Prasetyo, M.D. Surindra, W. Caesarendra, T. Taufik, A. Glowacz, M. Irfan, W. Glowacz, Influence of Superheated Vapour in Organic Rankine Cycles with Working Fluid R123 Utilizing Low-Temperature Geothermal Resources. Symmetry (2020), 12, 1463.
14. M. Guercio, J. Bonafin, The Velika Ciglena geothermal binary power plant, Proceedings of the 6th African Rift Geothermal Conference, 2-4 November 2016, Addis Ababa, Ethiopia.
15. M. Bošnjaković, M. Stojkov, M. Jurjević, Environmental impact of geothermal power plants, Technical Gazette (2019), 26 (5), 1515-1522.
16. R. DiPippo: Geothermal Power Plants: Principles, Applications, Case Studies and Environmental Impact, 4th Edition, Butterworth-Heinemann, Waltham, MA, USA, 2016.
17. J. Bonafin, C. Pietra, A. Bonzanini, P. Bombarda: CO₂ emissions from geothermal power plants: evaluation of technical solutions for CO₂ reinjection, European Geothermal Congress 2019, 11-14 June 2019, Den Haag, The Netherlands.
18. A. Baldacci, R. Dupont, C. Piemonte: Electricity generation from NCG (non-condensable gases) expansion in Lateral geothermal plant, Latium, Italy, Bulletin d'Hydrogeologie (1999), 17, 415-423.
19. B. Tramošljika, P. Blecich, I. Bonefačić, V. Glažar: Advanced ultra-supercritical coal-fired power plant with post-combustion carbon capture: analysis of electricity penalty and CO₂ emission reduction, Sustainability (2021), 13(2), 801.

The use of encapsulated sodium ferrate in wastewater treatment in the production of animal feed

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Abstract: The article presents the results of studies devoted to the use of ferrate in wastewater treatment in the production of animal feed. A method of wastewater treatment from various substances is proposed using the example of phenol. The possibility of obtaining of encapsulated sodium ferrate based on hexane, ethylcellulose and paraffin was revealed; its stability in air and in an alkaline solution was established. It has been proven that the reuse of industrial wastewater is a determining direction in preserving the health of animals and birds and the ecological cleanliness of the environment in general.

Keywords: WASTE WATER PURIFICATION METHOD, CAPSULATED SODIUM FERRATE BASED ON HEXANE, ALKALINE SOLUTIONS, ELECTROCHEMICAL GENERATION OF FERRATE IONS

1. Introduction

With the rapid growth of the world's population and the rapid development of industry, the problem of drinking water (i.e., free from pollutants and sludge) has arisen. The main sources of water supply are the central source or water intake from rivers and wells, where the main wastewater discharge is carried out by local industrial enterprises.

Industrial wastewater is contaminated with products of processing raw materials, as well as various impurities of substances used in technological processes. The production of finished feed produces wastewater with a high organic content. They pose a significant risk if they enter water bodies without pretreatment, since they may contain: particles of organic materials (e.g. grain, proteins, food); medical supplements; detergents; solvents and oils used in the operation of equipment; oils, fats and molasses from mixed foods. The discharge of wastewater into water bodies leads to their pollution, which, even if the requirements for maximum permissible concentrations are met, causes irreversible changes in the water body [1]. Water from water bodies is used not only for the life of the local population, but also for the needs of feed production, including for conditioning grain with steam during the granulation process; adding water to the mixture to increase the moisture content of the feed to the level required for granulation; preparation of a starter culture for processing a feed mixture, etc.

Since the water used for the preparation of feed must be suitable in terms of its qualities, the problem of water purification is urgent.

Wastewater generated during washing, surface water runoff and steam condensation in feed production, as well as in technological operations of other industrial enterprises, is a complex mixture of insoluble mineral and organic contaminants, true and colloidal solutions. Such mixtures may even include fibers, particles of lubricants, dyes, synthetic surfactants, finishing agents, reagents, and other insoluble impurities. Wastewater has a pH value in the range of 6 ... 12 and may differ in pronounced coloration. Unevenly flowing effluents from production are not discharged directly into city-wide treatment facilities, but are preliminarily purified [2].

For the complete treatment of wastewater from enterprises, biological methods are used. However, biological wastewater treatment in most cases is hampered by their high hydration alkalinity and lack of biogenic elements. Therefore, biological treatment, as a rule, should be preceded by preliminary mechanical or chemical treatment of effluents.

Currently, electro-chemical wastewater treatment is gaining popularity, but it, like reagent treatment, does not completely remove surfactants [3]. A high degree of wastewater treatment from surfactants and other contaminants is achieved using the ion exchange and hyperfiltration method, i.e. filtration of waste water under pressure through semi-permeable membranes. In this case, the treated wastewater is returned to production, which leads to water savings.

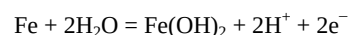
2. Results and discussion

The analysis of scientific, technical and patent literature showed that the number of publications devoted to the use of ferrates for water purification is increasing every year. Many foreign companies are interested in ferrate technology. Foreign practice shows that the purification of industrial effluents requires the involvement of expensive technologies and equipment, which leads to additional significant investments. However, enterprises in Kazakhstan do not have sufficient funds to equip production with new environmentally friendly equipment [4].

In the scientific literature, the issues of effective wastewater treatment are devoted to the anodic dissolution of iron silicides in an alkaline electrolyte [5].

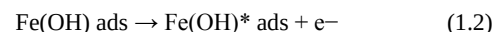
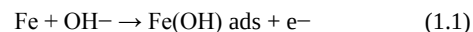
Analysis of the features of anodic dissolution of iron in alkaline electrolytes in the work of Shein A.B., Rakityanskaya I.L., Lomaeva S.F. [6] shows that the anodic process at the potentials of the initial section of the polarization curve cannot be identified only with the dissolution of the metal in the active state. The maximum current i depends on the potential sweep rate, and there is no maximum at all on the stationary curve.

The possibility of $\text{Fe}(\text{OH})_2$ formation also follows from an analysis of the E-pH diagram for the Fe-H₂O system. In the initial part of the polarization curve, one can expect the simultaneous oxidation of iron by reactions:



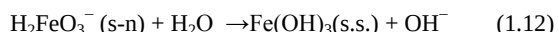
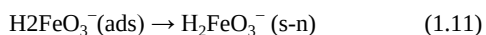
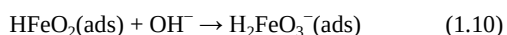
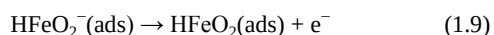
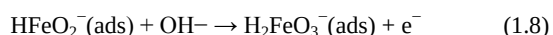
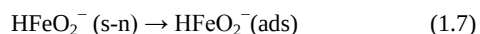
$\text{Fe}(\text{OH})_2$ hydroxide forms a passivating film and partially dissolves in the electrolyte with the formation of γ - FeOOH and $\text{Fe}(\text{OH})_4^-$. Subsequently, in the section where the current is independent of the potential on the surface of the iron electrode, according to the studies by Shein A.B. [7], there are 3 oxide phases: a passivating film γ - FeOOH , loose Fe_3O_4 and a film γ - Fe_2O_3 , covering magnetite.

According to the results of the work of Freire L. [8], the anodic process of iron dissolution proceeds according to the following scheme:



Iron goes into solution according to equation (1.3) in alkaline solutions, the concentration of which is $\leq 5\text{N}$. In more concentrated and hot solutions, the FeO_2^{2-} ion is formed. The course of the process according to equation (1.4) leads to the passivation of the metal. The speed of the first anodic process is limited by the stage.

The second anodic process occurs at more positive potentials in the following stages:

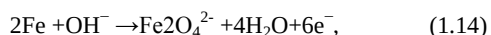


These processes are carried out with low overvoltage. The rate of the process is limited by the diffusion of iron ions in concentrated solutions (> 2N), and in more dilute solutions, perhaps, one should take into account the slow diffusion through solid oxides.

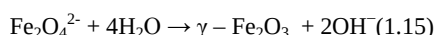
During the course of the second anodic process, spontaneous processes of dehydration and crystallization of $\text{Fe}(\text{OH})_3$ still take place, as a result of which the potential of the electrode shifts to the negative side and the process also begins, without significant overvoltage.



In a number of works by Freire L. it is shown that such an anodic process is also possible [8]:

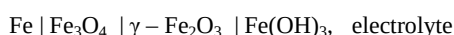


which runs at 20°C and alkali concentrations up to 4N. During this process, a black precipitate forms on the electrode, which is γ - Fe_2O_3 :



An active iron electrode in alkaline solutions can be passivated relative to the above processes due to the formation of FeOOH , δ - FeOOH and γ - Fe_2O_3 . Passivation of an iron electrode in alkaline solutions occurs if trivalent oxides or oxide hydrates are formed on the surface.

Recently, the following structure of the passivating layer on iron in neutral and alkaline Massot L. solutions has been proposed. [nine]:



However, the formula $\text{Fe}(\text{OH})_3$ is often considered unfounded. In alkaline media, hydrated FeOOH is offered instead of $\text{Fe}(\text{OH})_3$.

It should be noted that the composition of individual layers may be non-stoichiometric and there is no sharp transition between them. The first peak of active dissolution on the CVA curve of the Fe electrode practically degenerates already in the 2nd cycle, which indicates a deep passivation of the electrode. With a decrease in the anodic polarization on the CVA curve in the 1st cycle, peaks are observed (at more negative values of the potential than the peaks in the section of the forward stroke curve). The latter indicates the possibility of reduction of the formed oxide films.

A clearly pronounced anodic peak is also observed on the CV curve of FeSi , which disappears already in the second cycle. The peak potential is close to that for Fe; however, the current density of this peak is 3.3 A/m², that is, it is much lower than that for Fe ($i_a = 14$ A/m²). As the anodic polarization of FeSi decreases, a weak cathodic peak appears in the CV curve.

An even greater decrease in the anodic peak currents occurs for higher silicides with a decrease in the content of Fe atoms (FeSi_2 and $\text{FeSi}_2\text{-Si}$) in them.

So, in the case of FeSi_2 , the value of i_a , max is ~ 0.3 A/m², and for $\text{FeSi}_2\text{-Si}$, i_a , max = 0.45 A/m². A certain increase in i_a , max for $\text{FeSi}_2\text{-Si}$ compared to FeSi_2 can be associated with an increase in the

heterogeneity of the eutectic alloy surface and an intensification of the anodic process along the phase boundaries.

To clarify the role of silicon in the process of anodic dissolution of iron silicides, anodic CV curves were taken on pure silicon in 0.1-5.0 N NaOH. It is known that, in contrast to acidic electrolytes, where silicon is stably passivated due to the formation of a stable passive film consisting of SiO_2 , in alkaline media it is quite well soluble by the reaction:



Silicon has a high affinity for oxygen. Its surface in air is always covered with an oxide film, the thickness of which reaches 30Å under normal conditions. The study of the mechanism of coupled electrochemical reactions in potassium hydroxide solutions in the work of Nikolić-Bujanović, L., Čekerevac, M., Vojinović-Miloradov, M., Jokić, A. Simićić, M. [10] showed that for p- and n-types of silicon, the rate of self-dissolution is practically the same, that is, the process does not depend on the type of conductivity of silicon. At the anodic sites, the silicon dissolution reaction occurs with the formation of SiO_2 , and at the cathode sites, the process of hydrogen evolution occurs.

The results presented in this work make it possible to make an assumption about the mechanism of anodic dissolution of iron silicides in an alkaline electrolyte.

Thus, the above experimental data show that the mechanisms of anodic dissolution of iron silicides in acidic and alkaline electrolytes are different. In acidic electrolytes, as it was established earlier, selective dissolution of iron from the sublattice in silicide occurs, while silicon remains on the electrode surface and, being oxidized, forms a silicon dioxide (SiO_2) film. Since SiO_2 is characterized by high stability in acidic fluoride-free environments, iron silicides are also slightly soluble in acidic electrolytes.

In alkaline electrolytes, despite the increased activity of silicon (its increased solubility), the rate of the anodic process is determined by the formation of protective films of iron oxides and hydroxides, which passivate the surface and make iron silicides sufficiently stable in alkalis. One should not forget about the high strength of the Fe - Si bond, which also determines the resistance of silicides.

The results of electrochemical studies carried out on iron and iron silicides reveal the general regularities of their anodic behavior in alkaline media. These include: the presence of an anodic dissolution peak, which is most pronounced in the first cycle, an increase in the peak current and a shift in the peak potential to a more positive side with an increase in the potential sweep rate, a decrease in anode currents with a decrease in the pH of an alkaline electrolyte. These regularities do not appear for the Si-electrode, the dissolution rate of which increases in more concentrated alkaline solutions.

In Kazakhstan, there is enough secondary iron-containing raw materials, including scrap metal, from which anodes for the production of ferrates can be made at low cost. In addition to the mention in the scientific literature on the use of electrodes made of pressed steel chips [11] and galvanized wire in order to increase the true surface of the anode, to date, detailed studies on the use of VS in the technology of obtaining ferrates by electrochemical method have not been carried out. Obviously, such studies are relevant, since a variety of waste, in addition to iron, can contain other metals, for example, zinc, tin, etc., widely used for anticorrosion protection, which, in parallel with Fe, can participate in chemical and electrochemical transformations and have a certain effect on basic electrode processes.

A promising method of water purification is the use of ferrates (VI) of alkali metals, which have a multifunctional effect. Ferrates (VI) are one of the most powerful known oxidants (in an acidic medium the potential of FeO_4^{2-} an ion is higher than the potential of ozone) and is capable of decomposing many toxic chemicals to low-toxic products (oxidizing effect), as well as causing the death of microorganisms (disinfecting effect). The product of the decomposition of the ferrates themselves in solution is iron hydroxide, that is, a low-toxic product. In addition, iron hydroxide is

released in the form of colloidal aggregates with a very developed surface, which effectively adsorb heavy metal ions, suspension particles and organic residues, providing additional water purification by coagulation of pollutants (coagulating action).

One of the most promising, but at the same time poorly studied, is the electrochemical method for producing alkali metal ferrates.

3. Conclusion

The conducted literature review showed that the problem of water purification by electrochemically generated ferrate ions is complex, and a number of problems must be solved for a successful choice of purification conditions [12]. First, the material of the soluble anode must be selected. The composition of the anode, namely, the content of silicon and carbon in it, pays great attention to the current efficiency of ferrate ions. It is necessary to select the conditions under which the reaction of oxygen evolution during the anodic polarization of the electrode would proceed at a minimum rate in order to avoid a significant decrease in the current efficiency of ferrate ions.

Large problems in the electrochemical generation of ferrate ions are caused by the anode passivation in an alkaline medium. In 10-20 minutes after the start of electrolysis, the yield of ferrate ions drops sharply due to the formation of a passivating film on the anode surface. In this case, the dissolution of the steel anode deteriorates sharply, and almost all the current goes to the side reaction of oxygen evolution. The development of measures that reduce the degree of anode passivation during electrolysis in an alkaline electrolyte is not an easy task. It can be solved by careful selection of the electrode material, as well as its preliminary polarization (pre-polarization).

Ferrates (VI) are one of the most powerful known oxidizing agents of alkali metals (in an acidic medium, the potential of FeO_4^{2-} ion is higher than the potential of ozone), and is the largest among the currently used compounds and is capable of decomposing many toxic chemicals to low-toxic products (oxidizing effect), and also cause the death of microorganisms (disinfecting effect). The product of the decomposition of the ferrates themselves in solution is iron hydroxide, that is, it is possible to obtain a low-toxic product. In addition, iron hydroxide is released in the form of colloidal aggregates with a very developed surface, which effectively adsorb heavy metal ions, suspension particles and organic residues, provide additional water purification by coagulation of pollutants (coagulating action). Sources of drinking water supply disinfected with sodium ferrate by the example of phenol are non-toxic.

Ferrates (VI) of alkali metals can replace widely used oxidizing agents (pyrolusite, bleach), the use of which leads to secondary contamination of solutions with manganese and chlorine compounds. The use of ferrates will eliminate secondary contamination of the treated solutions.

In connection with the above, the development of a wastewater treatment technology, as a result of obtaining encapsulated sodium ferrate based on hexane, ethylcellulose and paraffin, will be of great importance not only for feed production, but also for all industrial enterprises. Treatment of reused industrial wastewater will reduce its discharge into water bodies, improve its sanitary condition, and also contribute to the natural circulation of water in nature.

4. Used literature

- 1 Egorov Yu.A., Nikolsky V.S., Suzdaleva A.A. Environmental monitoring in the regions of the Republic of Kazakhstan // Engineering ecology. - 2011. - No. 1. - P.10-15.
- 2 Kadnikova, Olga; Altynbayeva, Gulnara; Aidarkhanov, Arman; and others. Potential analysis of implementation of developed technology for processing of sewing and knitting fabrics: International Scientific/ Environmental and Climate Technologies. Riga, LATVIA Energy Procedia. – 2017. – T. 128.: P. 411-417.
- 3 Golitsyn A.N. Fundamentals of Industrial Ecology. - M., 2002. - 45 p.
- 4 Kadnikova, O., Altynbayeva, G., Kuzmin, S., Toretayev, M., Khabdullina, Z. Ecological Feasibility of Applying Technology in Recycling Garment and Knitwear Production / Environmental and Climate Technologies, 2019, 23(2), p. 291–309
- 5 Environmental information technologies: Textbook / Ed. Grinina A.S. - Kaluga: State Unitary Enterprise "Oblizdat", 2009. - 177 p.
- 6 Shein A. B., Rakityanskaya I. L., Lomaeva S. F. Anodic dissolution of iron silicides in alkaline electrolyte // Protection of Metals. – 2007. – T. 43. – №. 1. – P. 54-58.
- 7 Shein A. B. Effect of the metal component on anodic dissolvability of iron, cobalt, and nickel silicides // Protection of Metals. – 2001. – T. 37. – №. 3. – P. 281-284.
- 8 Freire L. et al. Electrochemical and analytical investigation of passive films formed on stainless steels in alkaline media // Cement and Concrete Composites. – 2012. – T. 34. – №. 9. – P. 1075-1081.
- 9 Massot L. et al. Silicon recovery from silicon-iron alloys by electrorefining in molten fluorides // Electrochimica Acta. – 2013. – T. 96. – P. 97-102.
- 10 Nikolić-Bujanović, L., Čekerevac, M., Vojinović-Miloradov, M., Jokić, A. Simić, M., A comparative study of iron-containing anodes and their influence on electrochemical synthesis of ferrate (VI) // Journal of Industrial and Engineering Chemistry. – 2012. – T. 18. – №. 6. – P. 1931-1936.
- 11 Rekus I.G., Shorina O.S. Fundamentals of ecology of rational nature management. Tutorial. - M.: Publishing house of MGUP, 2001. –146 p.
- 12 Kadnikova, O., Altynbayeva, G., Kuzmin, S., Aidarkhanov, A., Shaldykova, B. Recycling of production waste as a way to improve environmental conditions/ Energy Procedia, 2018, 147, p. 402–408

Polypropylene-Polycarbonate composites with graphene oxide nanosheets: synthesis and characterization

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Abstract: Herein the effect of graphene oxide nanosheets (GOSs) on the thermo-mechanical stabilities of polypropylene (PP)/polycarbonate (PC), polymer blend nanocomposites (PNCs) fabricated via melt compounding has been explored. The comparison of properties of pure blend with PNCs, pointed out whether the mixing sequences have any effect on thermo-mechanical stabilities of PNCs. The PP/PC/GO nanocomposite exhibited an excellent increment in tensile strength and melting temperature as compared to the neat blend. In contrast, the PC/GO/PP nanocomposite, prepared by mixing the GOSs with PC first and then PC/GO with PP, has lower thermo-mechanical stability than PP/PC/GO. Interestingly, PP/GO/PC nanocomposite prepared by mixing the GOSs with PP first and then PP/GO with PC, showed the highest improvement in thermo-mechanical stability as compared to pure blend, PP/PC/GO, and PC/GO/PP. We attribute this trend of stabilities for PNCs due to the different extent of GOSs distributions within the polymer matrix. For PP/PC/GO, the GOSs were effectively dispersed in the PP phase due to low viscosity. In the case of PC/GO/PP, only small amount of GOSs was localized in PP and most of GOSs remain in PC phase. However, in case of PP/GO/PC, almost all GOSs were dispersed homogeneously in both phases resulting in a distinct increment of thermo-mechanical stabilities.

Keywords: GRAPHENE OXIDE NANOSHEETS, MIXING SEQUENCE, MELT COMPOUNDING AND THERMO-MECHANICAL PROPERTIES

1. Introduction

Polymers play very crucial role in every part of our lives and it is very difficult to imagine present advancements without polymeric products. Polymer composites, because of their outstanding properties, like super toughness, lightweight, high elasticity, low cost, transparency and easy processing make them an excellent class of materials for the modern innovations [1-2]. The demand for polymeric materials is increasing steadily, mainly due to its extensive applications in healthcare, entertainment, clothing, food, communication and transportation industries [3]. Polycarbonate (PC) is an efficient and most commonly used amorphous engineering thermoplastic polymer. It is transparent and shows outstanding toughness up to the temperature of 140 °C [4]. The excellent toughness and tensile strength of PC is due to the existence of molecular dissipation (a sub glass transition temperature). However, it exhibits high notch sensitivity, high melts viscosity, hygroscopy and is prone to cracking with time. To avoid aforementioned shortcomings of PC, several modification have been reported [4, 5]. Among the various modifications, blending is an efficient technique in the polymer processing industries not only for the creation of new materials but also for hands-on recycling [6-7]. The melt compounding of PC with suitable polymers such as PMMA, Polyethylene, PP, and Nylons have been explored for the challenging applications as discussed in review papers [8-11]. PP is also engineering thermoplastic and commonly used for textiles, packaging stationery, automotive components and for laboratory equipment. However, most of the reported work to improve the toughness of PP/PC blend with fillers are acquired at the cost of tensile strength and thermal resistance [12]. Therefore, numerous strategies have been applied to avoid phase separation and weak interfacial adhesion due to the aggregation of fillers selectively in one of two polymer matrices [13, 14]. Often used facile routes to improve the quality of PP-PC blend was reviewed by Tchoudakov *et al.* where different approaches have been explored to create a network like covalent bonding at the interfaces of blending partners [14, 15]. Hanim *et al.* reported adsorption of nanofiller on the surface of PP chains and then melt compounding of PP-nanofiller with butadiene styrene to achieve desired thermo-mechanical stability [16]. Šupová *et al.* and few other workers recently have reviewed the effect of functionalization, size, and quantity of most frequently used fillers on polymer blend nanocomposites to improve physical properties of PP based polymer composites [17]. Hsieh *et al.* and Balazs *et al.*, reported homogeneous dispersion of layered silicate nanoclay in PC to increase stiffness, heat resistance and Young's modulus, which makes a persuasive case for exploring PC nanocomposites, predominantly if toughness is wanted to be preserved. Thus, ample

of works have been performed to achieve desired properties of PP/PC blend [18, 19].

In this work, we demonstrate the use of GOSs as a nano compatibilizer as well as a reinforcement to achieve better thermo-mechanical properties of PP/PC blend. The GOSs are single layered sp³ (predominantly) and few sp² hybridized carbon sheets [20]. They are decorated with –OH and –COOH groups at the edges while epoxy and ketonic groups are on its surface [20]. Several methods have been coined for the synthesis of GOSs and discussed in details elsewhere [21-22]. However, GOSs can be easily obtained from graphite powder as reported by Marcano *et al.* [22]. During the last two decades GOSs have been widely studied in the context of several challenging applications, such as energy storage, separation of heavy ions from water, drug delivery and also as nanofiller for polymer blends [20, 23]. Many workers have proved that the thermo-mechanical characteristics, chemical inertness, gas barrier and electrical properties of the polymer composites can be enhanced by the incorporation of a minute amount GOSs [20]. Herein we report the role of mixing sequence on selective migration of GOSs into PP/PC blend that can offer an opportunity for the production of large-scale, high-quality blend nanocomposites. Rheological, mechanical and thermal properties of the as prepared PNCs are examined and discussed regarding their phase morphology and the selective distribution of GOSs in polymer matrices.

2. Experimental

2.1 Materials

Commercially available pure isotactic PP (grade LG SR20NS) was supplied by Bayer Materials Science, Thailand. Polycarbonate (grade LG 2S) was also obtained from same source. We have not determined the molecular weight of these polymers because of its proper solubility in a particular solvent. For the synthesis of GOSs, we have used graphite powder, 98% H₂SO₄, 88% H₃PO₄, KMnO₄ and 30% H₂O₂ from Sigma Aldrich (India).

2.2 Preparation of GOSs and Polymer blend nanocomposites

Prior to compounding, GOSs, PP, and PC were well dried in a vacuum oven at 50 °C for about 72 hours to remove moisture. The idea of mixing sequence was employed to produce three PNCs filled with GOSs and the neat blend. These PNCs and the neat blend were prepared by melt blending compounding using twin screw extruder at the working temperature 230 °C and 15 rpm and the mixing was performed for 15 minutes. Neat blend and PNCs was assembled in a definite shape using compression molding, at ~230°C and 12 MPa pressure for the mechanical property analysis, consequently the samples were cooled to room temperature. The composition and the

code of each polymeric sample are shown in the Table 1. We have used GOSs as synthesized and reported in our previous work [21].

Table 1. Composition and corresponding codes of the studied samples

S.N	Composition and mixing order	Sample Code	Processing Conditions
1	PP (70%) + PC (30%)	PPPC	Temp. 230°C, rmp. 15
2	PP (69.5%) + PC (29.5%) + GO (1%)	PP/PC/GO	Same
3	PP (69.5%) + GO (1%) + PC (29.5%)	PP/GO/PC	Same
4	PC (29.5%) + GO (1%) + PP (69.5%)	PC/GO/PP	Same

3. Characterization

Differential scanning calorimetry (DSC) analysis of neat blend and PNCs was performed in nitrogen gas environment with a DSC instrument (Model: NETZCH DSC 200 PC instrument). The standardizations of heat flow and temperature were based on a run in which pure indium was heated through its melting point. The neat blend PNCs having a mass of about 30 mg were used for the study up to 200 °C at the heating rate 10 °C/min. The tensile test of the neat blend and PNCs were carried out on a dumb-bell shaped samples using a UTM instrument (Model No. Hounsfield HS 10 KS) operated at room temperature. The values of mechanical parameters reported in the present work are the average of the result for the test run on five samples. Dynamic mechanical analysis (DMA) was accomplished with a DMA analyzer (model No. 2980) for pure blend and PNCs. The test sample dimensions were approximately 50.0 x 13.0 x 3.5 mm. Liquid N₂ was used to attain the low temperatures and was also used to precisely control temperatures during the experiment. For TEM (JEM -2100 HRTEM, Make-JEOL, Japan) analysis, neat blend and PNCs were cut properly respective to their length axis using a ultramicrotome under cryogenic conditions with a thickness of around 70-100 nm for analysis. The cuts were taken from a middle and edge positions of the samples and then suitable sections were selected for the analysis. The instrument for analysis was operated at 100-120 kV and the micrographs were collected using an energy filter in zero loss mode for an optimal contrast of the GOSs.

4. Result and Discussion

4.1 ATR (Attenuated total internal reflectance) FTIR spectroscopy

The ATR-FTIR spectrum of pure blend and PNCs showed several bands (Fig. 1.) confirming structural entities which are present in the PP, PC and GOSs. The major spectral features correspond to the IR absorption in the pure blend and PNCs are listed in Table 2 [23, 24]. The neat blend showed all characteristic peaks of PC and PP as previously reported by Renaut and co-workers [25]. The incorporation of GOSs leads to a notable change in the band positions and the intensities for PNCs in comparison to the neat blend as shown in the magnified IR spectra. It is well established that PP and PC form an incompatible blend due to the large viscosity lag and unfavourable interactions between the same [24-25]. In the fabricated PNCs, PC has excess polar components and, therefore, it may easily interact with GOSs. We have also analysed

the C=O stretching region of PC to access the possible interaction between PC and GOSs. As shown in Fig. 1, the C=O stretching frequency of PC is centred at around 1737 cm⁻¹ and shifts to higher wavenumber with the incorporation of GOSs. This shift can be attributed to the hydrogen bonding between oxygen functional moieties of GOSs and C=O of PC. This shift suggests the presence of GOSs in the PC phase which is due to the better interaction of GOSs with PC phase as compared to PP. However, hydrogen bonding between PC and GOSs could decrease the stretching frequency of C=O of PC but an increase in the wavenumber can be explained in terms of stacking of PC chains on GOSs [26]. The stacking of PC on the GOSs may be attributed to π - π interaction between the similar carbon skeleton of PC and GOSs. It is well known that any restriction on the vibration of bonds require higher energy to exert the vibrational deformation. Therefore, an increase in the wavenumber can be observed for the C=O of PC in the case of PNCs. Due to the better interaction between GO and PC, polymer chains of PC get wrapped over the GOSs driven by the hydrogen bonding and π - π stacking between graphitic sheets and aromatic backbone of PC. This wrapping of polymer chains restricts the vibration of C=O and hence increased the wavenumber probably through thermal energy migration dynamics mechanism as discussed by Li *et al.* [27]. A similar shift was also observed when GOSs was added to the PC phase first then with PP matrix which is an indication of presence of GOSs in PC phase. Interestingly, when GOSs was added first to PP matrix followed by PC, then the peak shift was also observed but the band was broadened as compared to PC/GO/PP sample (magnified FTIR graph). It might be due to the incomplete migration of GOSs from PP phase to the PC phase. Moreover, when GOSs was mixed first in PP followed by PC, then due to the better nonbonding interactions between PC and GOSs, the GOSs started migration from the PP to PC matrix. This migration might not be completed during the mixing duration and hence some C=O of PC remained unaffected without any interaction with GOSs and possessed its characteristic peak at 1737 cm⁻¹ due to which the peak broadened. So, FTIR analysis explains why the mixing sequences of GOSs can affect the dispersibility of blending partners and influence the incompatibility. If this selective dispersion occurred during melt blending then it must affects its thermal stability. Hence, the thermal stabilities of PNCs were analysed with DSC in the next section.

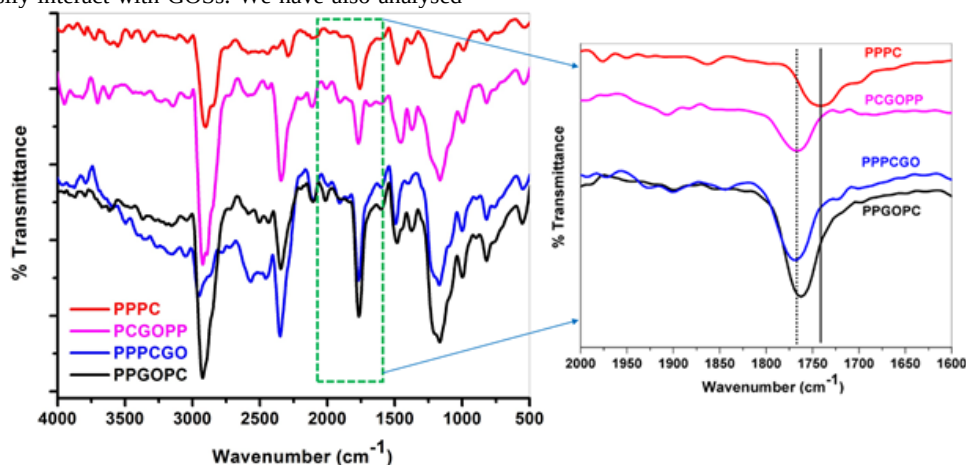


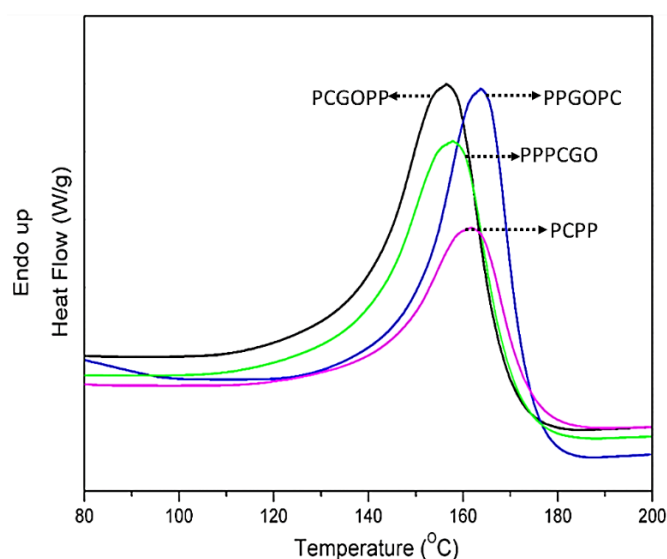
Fig. 1 ATR-FTIR spectra of as prepared neat blend and PNCs. Magnified section of FTIR graph showing impact of GOSs incorporation into PP/PC blend.

Table 2. FTIR peaks corresponding to the functional groups present in the studied samples

Wave number (cm ⁻¹)	Functional group
996, 971	-CH ₃ rocking vibration of PP&PC and
1045	-C-O-C and C-O groups from PC
1170	-CH ₃ symmetric deformation vibration of PP
1268	Epoxide linkage of GO
1374	-CH ₃ bending vibration of PP&PC
1455	-CH ₂ bending vibration of PP&PC
1605	-C=C stretching from aromatic
1732	-C=O stretching of PC
2748	-C-O stretch carboxylic acid of GO
2918, 2863, 2833	-C-H stretching vibration of PP&PC
3200-3400	-OH group of GO

4.2 DSC Analysis

DSC analysis of polymeric samples was carried out and the respective graphs are shown in **Fig. 2**. It is established that glass transition temperature of PC, melting temperature of PP and melting temperature of neat PP/PC is around ~140-145 °C, ~158-160°C and ~158 °C, respectively [14,28]. The melting temperatures of each sample can be derived from the derivative DSC curve. In the present work each of studied samples shows a broad peak corresponding to the melting temperature and melting temperature of the as-prepared pure blend as reported elsewhere by Laoutid et al. [14]. The reason for the appearance of melting peak rather than glass transition temperature for the PP/PC based composites is outlined in [14]. A significant increment in melting temperature for the as-fabricated PNCs can be observed due to the incorporation of GOSs as nanofiller. This feature may be attributed to the function of GOSs as a nucleating agent as well as a nano compatibilizer during the crystallization process of PNCs. As expected, the melting temperature of PP/GO/PC system is significantly higher than that of other PNCs fabricated on the basis of mixing sequence. The greater thermal stability of PP/GO/PC is in accord with previous work [14] and depends on homogeneous dispersion of GOSs in the blend components as discussed in ATR-FTIR section. Remarkably, melting temperature of PP/PC/GO is of ~4° C higher than PC/GO/PP. This indicates that most of the PP chains were not covered by GOSs due to their aggregation in the PC phase and therefore a free movement of PP chains leads to an easy chain loosening process. This observation offered us another very strong evidence that the mixing sequence of GOSs played a crucial role in uniform distribution GOSs in both polymer matrices of PNCs.

**Fig. 2** DSC plot of fabricated PNCs and neat blend showing its melting point

4.3 TEM Analysis

The TEM images of the pure blend and PNCs are presented in **Fig.3a-d**. The TEM images of the neat blend (**Fig.3a**) clearly show phase separation and droplets of PC domains. The droplets of PC are quite prominent and depict incompatible behavior of neat blend. This result is in agreement with our previous investigations [29]. The phase of the neat blend is indicated by the red circles in TEM micrographs of PP/PC (**Fig.3a**). The incorporation of 1% of GOSs provides a notable improvement in compatibility between PP & PC due to the nanosizing effect and nucleation effect of GOSs and it can be seen in the TEM micrographs of PNCs in **Fig. 3b-d**. However, the contribution of mixing sequence of GOSs on the same cannot be denied. The TEM micrograph of PC/GO/PP (**Fig.3b**) shows a huge agglomeration of GOSs mainly in PC domains as explained in FESEM section in our previous work [29]. For the sake of clarity we have highlighted aggregation of GOSs at interfaces in the **Fig. 3b**. Such selective dispersion of GOSs mainly in the PC phase is due to the lucid interaction between PC and GOSs as discussed in the FTIR section. The PP/PC/GO showed better surface morphology and proper dispersion of GOSs in PC and PP in comparison to the PC/GO/PP (**Fig. 3c**). However, in this case the accumulation of GOSs can be observed at the interfaces of PP and PC instead of a homogenous distribution. This aggregation of GOSs at interfaces is highlighted in TEM image of PC/GO/PP (**Fig. 3c**). The TEM micrograph of PP/GO/PP (**Fig. 3d**) shows a very uniform dispersion of GOSs in the PP and PC. For PP/GO/PC, when GOSs was mixed with PP first then with PP, the chains were adsorbed properly on the graphene oxide nanosheets and consequently strong hydrogen bonding and intense π - π interaction between GOSs and PC resulted in excellent thermo-mechanical stability as compare to other fabricated systems.

4.4 DMA Analysis

The tan delta value is a good measure of the leather-like midpoint between the rubbery and glassy region for the polymeric materials and therefore it is an important parameter to evaluate the thermo-mechanical stability of polymeric materials [34]. A typical tan delta curve of the neat blend and PNCs is shown in the **Fig.4**. Herein, tan delta curves do not show any sharp and intense T_g peaks, because the neat blend and PNCs chains are not arranged in ordered crystals and are just strewn around in random fashion, even though they are in the solid state [35]. Thus, the shape and height of the tan delta peak changes spontaneously with a degree of amorphous content present in the PNCs. A broad peak between 60-160 °C in tan delta curves can be seen for the neat blend and PNCs. This tan delta peak is a signature for the presence of major amorphous portions in the studied samples. This is why the studied samples could not have any high-pitched glass transition temperature and melting temperature peaks. The neat blend showing a broad tan delta peak at around 66 °C depicts the high degree of incompatibility between PP and PC, which promoted micro-crack formation at the interface as well as non-uniform stress transfer due to unfavorable morphology (as shown in TEM images of the neat blend). However, a noteworthy shift in tan delta peak can be seen for the PNCs due to the incorporation of GOSs (**Fig. 4**) indicating

an increase in the thermo-mechanical stabilities of PNCs. The tan delta peak for PP/GO/PC was noted at the highest temperature among all the PNCs owing to homogeneous dispersion of GOSs in both phases of PNCs. On other hand either due to the aggregation of

GOSs or due to its selective dispersion of GOSs in PC phase, both PP/PC/GO and PC/GO/PP shows reduced thermo-mechanical properties as comparisons to PP/GO/PC.

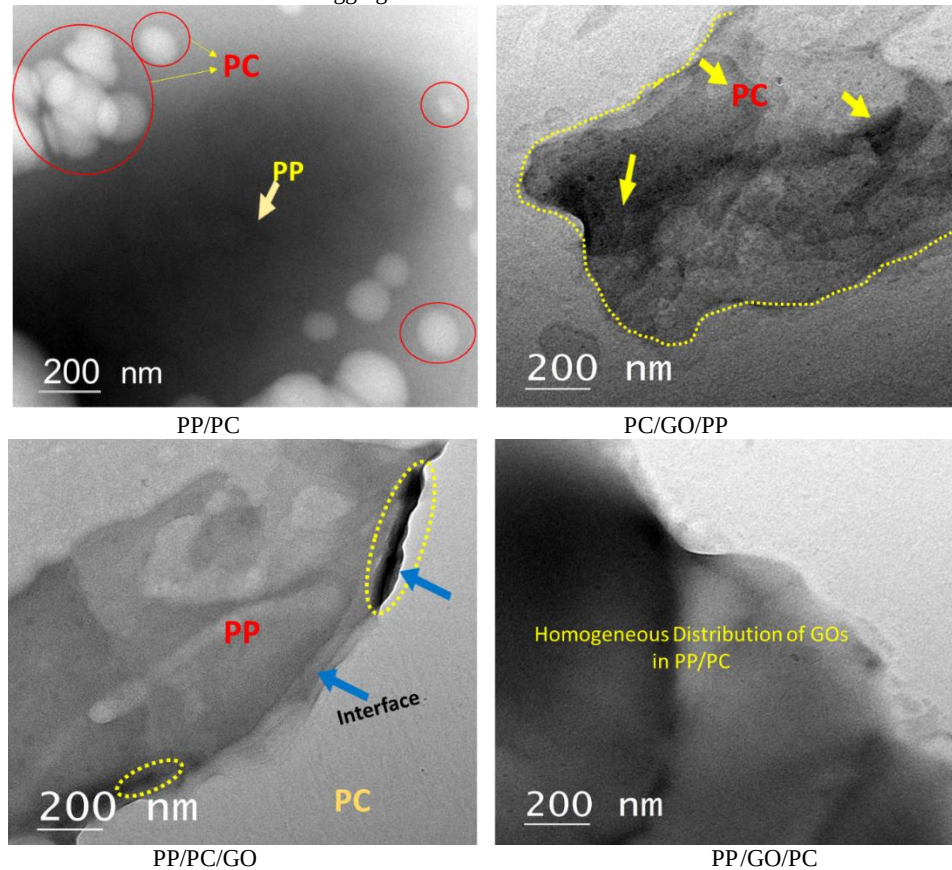


Fig. 3 TEM images of neat blend (a: PP/PC) and PNCs (b: PC/GO/PP, c: PP/PC/GO and d: PP/GO/PC) showing the dispersion of GOs in polymer matrices

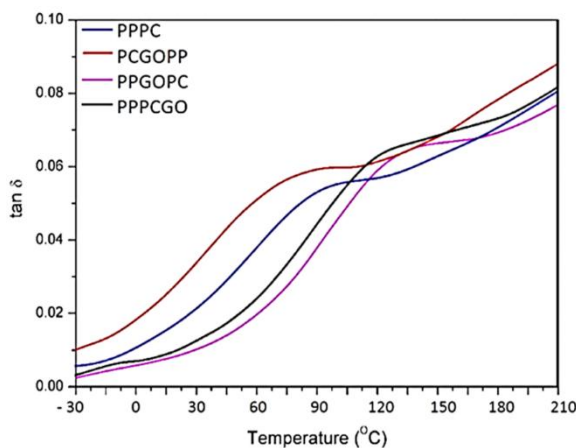


Fig. 4 Tan delta graph showing thermal properties of PNCs and neat blend

4.5 Rheological Analysis

The rheological properties of the neat blend and PNCs were investigated to understand the microstructural change occurring due to the incorporation of GOSs in light of the mixing sequence methodology. **Fig.5** displays the typical melt viscosity Vs shear rate graph for the PNCs and the neat blend. One can observe that the introduction of GOSs to the neat blend induced an apparent change in the melt viscosity and it can also be noticed that mixing sequence of GOSs plays an important role to define the viscoelastic properties of PNCs. The largely increased viscosity is obtained at low frequencies when GOSs were first added to PP, then PP/GO to PC (i.e. in the case of PP/GO/PC). This is in a good agreement with the thermal and morphological investigations as discussed in the previous sections. The high viscosity of PP/GO/PC is due to

nucleating effect and homogeneous distribution of GOSs in PP/PC matrix which reduced the mobility of melts (polymeric components) possibly due to the cross-linking effect of GOSs as discussed in the FTIR section. However, it is worth to note that at the relatively higher shear rate, the difference in melt viscosity for PC/GO/PP and PP/PC becomes much smaller in comparison to PP/GO/PC and PP/PC/GO. This signifies that under the condition of high shear rate PC/GO/PP due aggregation of GOSs and neat blend due to the high degree of interfacial slippage between the blend components leads to phase separation. In other words, we can say that the only incorporation of GOSs to neat blend does not apparently affect the viscoelastic behavior of PNCs but it also depends on mixing sequence of GOSs.

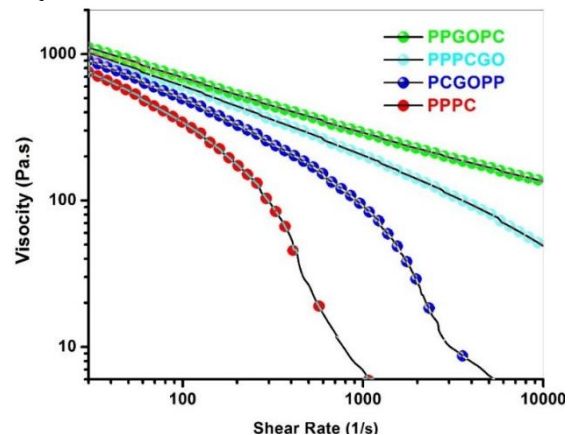


Fig. 5 Typical rheology graph of PNCs and neat blend showing viscoelastic properties

4.6 Mechanical Properties

The effect of GOSs on the mechanical competency of the neat blend and PNCs were tested using an UTM instrument. **Fig.6** shows the graph of Young's Modulus (**Fig.6a**) and the tensile modulus (**Fig.6b**) for the studied samples. The mechanical property of PNCs was greatly improved due to the incorporation of GOSs. The GOSs serve as not only the compatibilizers but also as the reinforcing negotiators due to their excellent mechanical properties. The mechanical properties of GOSs-compatible PNCs are substantially increased and this finding suggests that GOSs are desirable over the conventional nanofillers. This difference can be described in terms of homogeneous dispersion, nanosizing effect, and nonbonding interactions of GOSs with PC. The reason behind the homogeneous dispersion of GOSs and suitable crosslinking between filler and matrix in the case of PP/GO/PC was discussed in the FTIR section which created a situation for uniform stress transfer through GOSs present at the interface of PP and PC. Thus, the presence of GOSs at the interface of PP and PC can act as stress transferring medium and consequently high tensile modulus in the case of PP/GO/PC (**Fig. 6a**). On other hand, in case of PP/PC/GO and PC/GO/PP the tensile strength is lower as compared to PP/GO/PC due to the difference in the mixing sequence (**Fig. 6a**). This decrement in tensile modulus might be attributed to the low ability of stress transfer owing to the aggregation of GOSs in single

phase and result in a weak interfacial bonding. Hence, the proficiency of stress transfer was reduced by the weak interfacial bonding between filler and matrix. Similarly, no significant interfacial bonding was found in case of the neat blend. Therefore, a very little stress transfers between PP-PC and lowest tensile strength was observed. This reasoning was pointed out by many other researchers as discussed elsewhere [36]. **Fig.6a** illustrates the Young's modulus of the neat blend and PNCs. All PNCs showed increasing trend on Young's modulus because the GOSs were quite rigid than the PP and PC. Therefore, the stiffness of all nanocomposites increased with the incorporation of GOSs as expected and similar achievement has been reported by many researchers. This increase in Young's modulus was also well supported by the increased thermal stability of PP/PC due to the addition of GOSs. Thus it seems that the presence of GOSs endorsed transcrystallization due to the nucleation effect of GOSs. As a result, the crystalline region in PNCs is increased, and it might increase the Young modulus of PNCs. The Young modulus of PP/GO/PC was significantly higher other PNCs as expected. The exceptional increase in tensile modulus of PP/GO/PC was due to the homogeneous interfacial bonding between the PP, GO and the PC as discussed in FTIR and TEM sections.

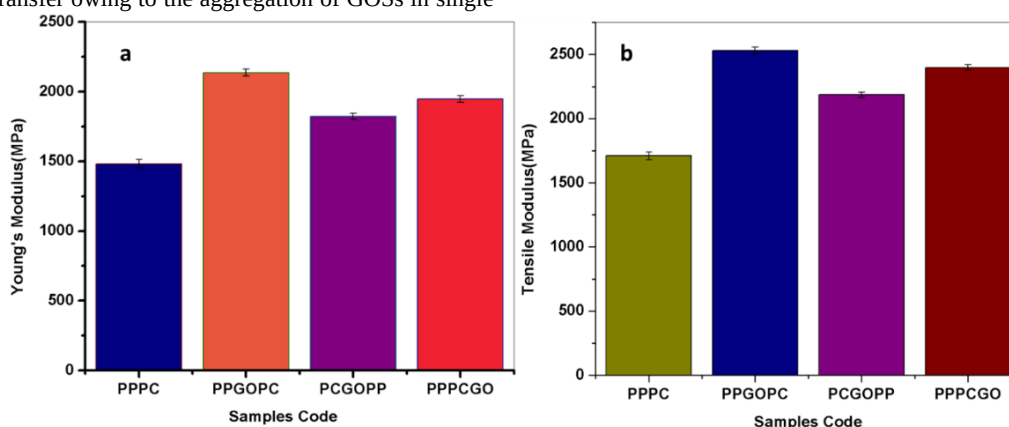


Fig. 6 Effect of mixing sequence and GOSs loading on (a) Young's modulus and (b) tensile strength of PP/PC based PNCs produced via melt compounding.

5. Conclusion

In this work the effect of graphene oxide nanosheets (GOSs) and their mixing sequence on thermo- mechanical stabilities of PP/PC blend and nanocomposites was studied. The best dispersion of GOSs was obtained for PP/GO/PC (among the other prepared blends e.g. PP/PC/GO, PC/GO/PP and PP/PC) after using melt compounding under the controlled temperature and pressure. It was found that the uniform distribution of GOSs resulted in excellent mechanical strength and thermal stability for PP/GO/PC comparing to poorly dispersed GOSs in cases of PP/PC/GO and PC/GO/PP. However, the significant increments in both mechanical and thermal properties were observed in contrast to the neat blend. The increases in the tensile strength values are ~50% and ~28% for the nanocomposites with 1% wt. of highly and poorly dispersed GOSs in comparison to the neat blend, respectively. Moreover, the homogeneously dispersed GOSs are much more operative in improving the melting temperature and the tensile modules of nanocomposites than the poorly dispersed GOSs and the neat blend. The TEM and rheological investigation showed that the mixing sequence are the key elements of the toughening effect in the PP/PC-based nanocomposites. It was also found that the aggregation of GOSs in polymer matrices results in a tremendous decrease in thermo-mechanical properties of nanocomposites.

Acknowledgement

Prof. G.C. Nayak (Dept. of Applied Chemistry, IIT Dhanbad, India) is greatly acknowledged for his suggestion and support during the experimental work. SKT would like to thank the Polish National

Agency for Academic Exchange for the NAWA research grant (PPN/ULM/2019/1/00008/DEC/2).

References

1. Parameswaranpillai, J., Thomas, S. and Grohens, Y., 2014. Polymer blends: state of the art, new challenges, and opportunities. *Characterization of Polymer Blends: Miscibility, Morphology and Interfaces*, 1-6.
2. Robeson, L.M., 1984. Applications of polymer blends: emphasis on recent advances. *Polym. Eng. Sci.* 24(8), 587-597.
3. Yu, L., Dean, K. and Li, L., 2006. Polymer blends and composites from renewable resources. *Prog. Polym. Sci.* 31(6), 576-602.
4. Adam, G.A., Cross, A. and Haward, R.N., 1975. The effect of thermal pretreatment on the mechanical properties of polycarbonate. *J. Mater. Sci.* 10(9), 1582-1590.
5. Shenoy, A.V., Saini, D.R. and Nadkarni, V.M., 1983. Rheograms for engineering thermoplastics from melt flow index. *Rheologica Acta*, 22(2), 209-222.
6. Parker, D., Sue, H.J., Huang, J. and Yee, A.F., 1990. Toughening mechanisms in core-shell rubber modified polycarbonate. *Polym.* 31(12), 2267-2277.
7. Zhihui, Y., Xiaomin, Z., Yajie, Z. and Jinghua, Y., 1997. Morphological, thermal, and mechanical properties of polypropylene/polycarbonate blend. *J. Appl. Polym. Sci.* 63(13), pp.1857-1863.

8. Chand, N. and Vashishtha, S.R., 2000. Development, structure and strength properties of PP/PMMA/FA blends. *Bull. Mater. Sci.* 23(2), 103-107.
9. Zhihui, Y., Yajie, Z., Xiaomin, Z. and Jinghua, Y., 1998. Effects of the compatibilizer PP-g-GMA on morphology and mechanical properties of PP/PC blends. *Polym.* 39(3), 547-551.
10. Gupta, A.K. and Srinivasan, K.R., 1993. Melt rheology and morphology of PP/SEBS/PC ternary blend. *J. Appl. Polym. Sci.* 47(1), 167-184.
11. Mueller, C.D., Nazarenko, S., Ebeling, T., Schuman, T.L., Hiltner, A. and Baer, E., 1997. Novel structures by microlayer coextrusion—talc-filled PP, PC/SAN, and HDPE/LLDPE. *Polym. Eng. Sci.* 37(2), 355-362.
12. Shubhra, Q.T., Alam, A.K.M.M. and Quaiyyum, M.A., 2013. Mechanical properties of polypropylene composites: A review. *J. Thermoplast. Compos. Mater.* 26(3), 362-391.
13. Sumita, M., Sakata, K., Asai, S., Miyasaka, K. and Nakagawa, H., 1991. Dispersion of fillers and the electrical conductivity of polymer blends filled with carbon black. *Polym. Bull.* 25(2), 265-271.
14. Laoutid, F., Estrada, E., Michell, R.M., Bonnaud, L., Müller, A.J. and Dubois, P., 2013. The influence of nanosilica on the nucleation, crystallization and tensile properties of PP-PC and PP-PA blends. *Polym.* 54(15), 3982-3993.
15. Tchoudakov, R., Breuer, O., Narkis, M. and Siegmann, A., 1996. Conductive polymer blends with low carbon black loading: polypropylene/polyamide. *Polym. Eng. Sci.* 36(10), 1336-1346.
16. Hanim, H., Zarina, R., Ahmad, M.Y.F., Mohd, Z.A. and Hassan, A., 2008. The effect of calcium carbonate nanofiller on the mechanical properties and crystallisation behaviour of polypropylene. *Malay. Polym. J.* 3(12), pp.38-49. *Science, Part B*, 53(7), 1193-1204.
17. Šupová, M., Martynková, G.S. and Barabaszová, K., 2011. Effect of nanofillers dispersion in polymer matrices: a review. *Sci. Adv. Mater.* 3(1), 1-25.
18. Balazs, A.C., Emrick, T. and Russell, T.P., 2006. Nanoparticle polymer composites: where two small worlds meet. *Science*, 314(5802), 1107-1110.
19. Hsieh, A.J., Moy, P., Beyer, F.L., Madison, P., Napadensky, E., Ren, J. and Krishnamoorti, R., 2004. Mechanical response and rheological properties of polycarbonate layered-silicate nanocomposites. *J. Polym. Eng. Sci.* 44(5), 825-837.
20. Tiwari, S.K., Kumar, V., Huczko, A., Oraon, R., Adhikari, A.D. and Nayak, G.C., 2016. Magical allotropes of carbon: prospects and applications. *Critical Reviews in Solid State and Materials Sciences*, 41(4), pp.257-317.
21. Tiwari, S.K., Huczko, A., Oraon, R., De Adhikari, A. and Nayak, G.C., 2016. A time efficient reduction strategy for bulk production of reduced graphene oxide using selenium powder as a reducing agent. *J. Mater. Sci.* 51(13), 6156-6165.
22. Marcano, D.C., Kosynkin, D.V., Berlin, J.M., Sinitskii, A., Sun, Z., Slesarev, A., Alemany, L.B., Lu, W. and Tour, J.M., 2010. Improved synthesis of graphene oxide. *ACS nano*, 4(8), 4806-4814.
23. Santhoskumar, A.U., Palanivelu, K., Sharma, S.K. and Nayak, S.K., 2010. Comparison of biological activity transition metal 12 hydroxy oleate on photodegradation of plastics. *J. Bioremed. & Biodegrad* 1(2).
24. Dybal, J., Schmidt, P., Baldrian, J. and Kratochvil, J., 1998. Ordered structures in polycarbonate studied by infrared and Raman spectroscopy, wide-angle X-ray scattering, and differential scanning calorimetry. *Macromol.* 31(19), 6611-6619.
25. Renaut, N., Duquesne, S., Zanardi, S., Bardollet, P., Steil, C. and Delobel, R., 2005. Fire retardancy, thermomechanical and thermal properties of PP/PC blends. *J. Macromol. Sci Part A: Pure & App. Chem.* 42(8), 977-991.
26. Shen, B., Zhai, W., Tao, M., Lu, D. and Zheng, W., 2013. Chemical functionalization of graphene oxide toward the tailoring of the interface in polymer composites. *Compos. Sci. Technol.* 77, 87-94.
27. Li J, Qian H., Chen H, Zhao Z, Yuan K., Chen G, Miranda A, Guo X., Chen Y, Zheng N, Wong MS. Two distinctive energy migration pathways of monolayer molecules on metal nanoparticle surfaces. *Nat. commun.* 2016. 7, doi: 10.1038/ncomms10749
28. Fatou, J.G., 1971. Melting temperature and enthalpy of isotactic polypropylene. *Eur. Polym. J.* 7(8), 1057-1064.
29. Tiwari, S.K., Oraon, R., De Adhikari, A. and Nayak, G.C., 2017. A thermomechanical study on selective dispersion and different loading of graphene oxide in polypropylene/polycarbonate blends. *Journal of Applied Polymer Science*, 134(28), p.45062.
30. Xu, J., Wang, L. and Zhu, Y., 2012. Decontamination of bisphenol A from aqueous solution by graphene adsorption. *Langmuir*, 28(22), 8418-8425.
31. Han, S.J., Lee, H.I., Jeong, H.M., Kim, B.K., Raghu, A.V. and Reddy, K.R., 2014. Graphene modified lipophilically by stearic acid and its composite with low density polyethylene. *J. Macromol.* 23(45)345-352
32. Yun, Y.S., Bae, Y.H., Kim, D.H., Lee, J.Y., Chin, I.J. and Jin, H.J., 2011. Reinforcing effects of adding alkylated graphene oxide to polypropylene. *Carbon* 49(11), 3553-3559.
33. Lin, Y., Jin, J. and Song, M., 2011. Preparation and characterisation of covalent polymer functionalized graphene oxide. *J. Mater. Chem.* 21(10), 3455-3461.
34. Jayanarayanan, K., Thomas, S. and Joseph, K., 2009. Dynamic mechanical analysis of in situ microfibrillar composites based on PP and PET. *Polym.-Plast. Techn. Eng.* 48(4), 455-463.
35. Dai, S. and Ye, L., 2008. Effect of novel compatibilizers on the properties and morphology of PP/PC blends. *Polym. Adv. Technol.* 19(8), 1069-1076.
36. Crosby, A.J. and Lee, J.Y., 2007. Polymer nanocomposites: the “nano” effect on mechanical properties. *Polym. Rev.* 47(2), 217-229.

High-temperature layered composite with a metal matrix, reinforced with single-crystal sapphire fibers

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Abstract: Heat-resistant composites with a layered niobium-based matrix reinforced with single-crystal sapphire fibers have been obtained. The fibers were grown from the melt by the modified Stepanov method. The composites were prepared by solid-phase technology by diffusion welding of multilayer packages of foils of the Nb–0.1% C and aluminum alloy, interlaid with sapphire fibers in layers of a suspension mixture of Nb powder. The production of fibers, their structure and strength testing procedure are described. The formation of multilayer packets, the structure and results of bending strength tests of composites are presented.

KEYWORDS: COMPOSITE, LAYERED-FIBROUS STRUCTURE, METAL MATRIX, NIOBIUM, MOLYBDENUM, SAPPHIRE FIBERS, STEPANOV'S METHOD, HEAT RESISTANCE, ULTIMATE STRENGTH, FRACTURE SURFACE.

1. Introduction

The development and research of composites with refractory metal matrices is a promising direction, first of all, because it opens up opportunities to increase the operating temperatures of structural elements used in modern engines, including gas turbine ones. This implies an increase in the efficiency of power plants by increasing their efficiency, saving fuel and reducing the burden on the environment. The metal matrix makes the developed composite materials related to metal alloys. It can absorb their advantages, proven by many years of practice, associated, first of all, with the high fracture toughness of many alloys, inaccessible to intermetallic and ceramic materials.

But the possibilities of traditional alloys are practically exhausted today. This is determined either by the limitation of the operating temperature ceiling due to the proximity of the melting temperatures of alloys, for example, based on nickel, leading to low creep resistance [1, 2], or low crack resistance of heavily alloyed alloys, for example, based on niobium [3], or difficulties production and use of refractory structural materials based on, for example, molybdenum due to high density [4], as well as problems associated with gas corrosion [5]. The last two factors apply especially to the materials for the rotor blades of gas turbine engines.

Optimally "designed" composite structures based on a sufficiently plastic matrix reinforced with high-strength (albeit brittle) oxide fibers can provide not only acceptable fracture toughness, but also high strength in a wide temperature range and the required creep resistance at high temperatures. The growing requirements for increasing the ceiling of the working temperatures of structural materials inevitably lead to the need to include traditionally unused compounds (oxides, intermetallic compounds) as essential structural components in their composition. With potentially high stiffness, strength and creep resistance, these joints are brittle in many cases. This poses the challenge of developing non-fragile structures containing fragile components. On the whole, the achievement of a balance in a certain sense of the conflicting requirements of strength, crack resistance and creep resistance is an important problem in the development of this type of materials [2].

The flow of publications on high-temperature materials is practically limitless. But we will note only a few characteristic and related publications related to fibrous and layered composites. It was shown in [6] that the reinforcement of a well-known nickel alloy with eutectic fibers from aluminum oxides and rare earth elements made it possible to obtain the alloy creep resistance of 150 MPa at 1150°C and 1% deformation in 100 hours. An example of a layered composite based on niobium and titanium with an operating temperature of up to 1200°C for use in moderately loaded structural elements is presented in [7]. We also note recent works [8–10] aimed at obtaining composites for temperatures up to 1400°C with oxide and silicide fibers and a molybdenum matrix.

But we are not aware of any publications on high-temperature laminated composites reinforced with oxide fibers using solid-phase technology for their production. In this sense, the presented work is new. In it, for the first time, composites with a multilayer matrix based on niobium or niobium, molybdenum and aluminum are

strengthened by reinforcing the matrices with high-strength single-crystal sapphire fibers obtained by the Stepanov method.

The experimental data presented in this work open up, in fact, a new direction in the development and research of composites of this kind, which combine high-strength oxide fibers and a crack-resistant, potentially creep-resistant layered composite matrix containing high-temperature alloys, solid solutions, and intermetallic compounds in a hierarchically organized structure. The presented materials are the results and development of the work carried out by the authors on the development and study of high-temperature layered and layered-fibrous composites [11–14].

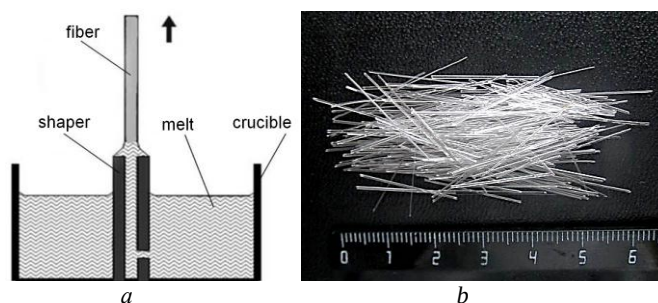
The composites developed in this work not only realize the advantages of high-strength reinforcing oxide fibers and crack-resistant layered composite matrices with strong intermetallic and plastic metal solid solutions contained in them, but also the advantages of specially organized boundaries between structural components that inhibit crack propagation [15]. They allow themselves to still achieve higher characteristics due to the synergistic effect of optimally organized structures [16], which can significantly exceed the characteristics estimated by the "rule of mixtures".

A method for producing fibers, their structure and test procedure for strength, structure, and results of testing fiber-reinforced composites for bending strength are presented. In addition, the presence of relatively light oxide fibers and intermetallic layers in these structures reduce the density of the materials compared to the base metals on the basis of which the materials are made. This increases the specific mechanical characteristics of composites in general, which is very important for many applications.

2. Production and testing of single crystal sapphire fibers

Sapphire fibers 150–300 μm in diameter were grown from the melt by the modified Stepanov / EFG (Edge-defined Film-fed Growth) method [17] (Fig. 1, a).

The fibers were formed from a melt of aluminum oxide Al_2O_3 filling a molybdenum crucible with a shaper containing a capillary channel. The melt rose to the top and was then pulled into the cold zone by a single crystal sapphire seed. The pulling speed was 200–300 mm/h. The resulting fibers were up to one and a half meters long.



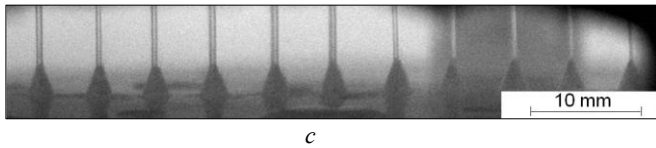


Fig. 1. Scheme of obtaining sapphire fibers from a melt, the arrow shows the direction of fiber pulling (a), a bundle of fibers prepared for reinforcing composite prototypes (b) and a scheme of group fiber growth (c)

A group growing method was used (Fig. 1, c), which made it possible to significantly increase the productivity of fiber production. This method is beneficial to the real use of fibers not only as a reinforcing component in structural composite materials, but also in other areas of their application. A bundle of fibers prepared for reinforcing experimental composites 35 mm wide is shown in Fig. 1, b.

The strength of the fibers was determined by the method [18], which consisted in winding individual fibers, previously fixed on an adhesive tape, around rigid cylinders (Fig. 2, a), which consistently differed in diameters from maximum to minimum. In the process of winding, the fibers were broken (Fig. 2, b).

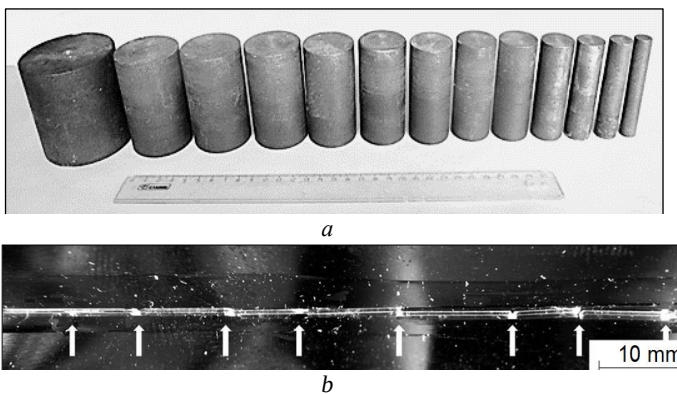


Fig. 2. Cylinders used when testing fibers for bending (a) and fiber after testing (b): arrows indicate the points of fracture

At each diameter, the maximum fracture strain arising in the fiber was determined $\varepsilon = d/D$ (d is the fiber diameter, D is the cylinder diameter) and the average distance between fractures. As a result, a dependence of the breaking deformation of the fiber ε on its length was obtained (Fig. 3, a: each character corresponds to one fiber). Taking into account the brittle fracture with a linear nature of the deformation behavior of the material, multiplying the values of ε by Young's modulus E , taken for sapphire, equal to 400 GPa, we obtain the dependence of the fiber strength on its length.

The test results showed a rather high strength of the fibers, which was facilitated by their developed fracture surface (Fig. 3, b). Such fracture surfaces of fibers located in the structure of metal composites are capable of initiating micro fracture clouds in the adjacent matrix in the zone of their breakage. This increases the fracture toughness of the composite structure as a whole.

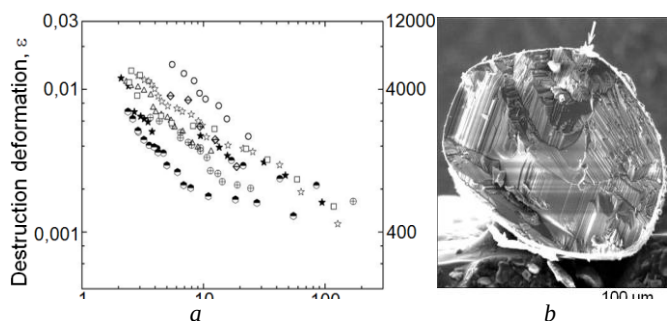


Fig. 3. Results of bending tests of fibers: dependence of ultimate deformation at break and strength of fibers on their length (a) and fracture surface of one of the tested fibers, the arrow shows the direction of load application during tests (b)

Stepanov's method used to obtain fibers was improved by a system for stabilizing the diameter of grown fibers [19] (Fig. 4, a), developed at our institute. With the help of it, the vibrations of the fibers that appeared in the ascending gas flow of the thermal zone of the installation for growing crystals were removed.

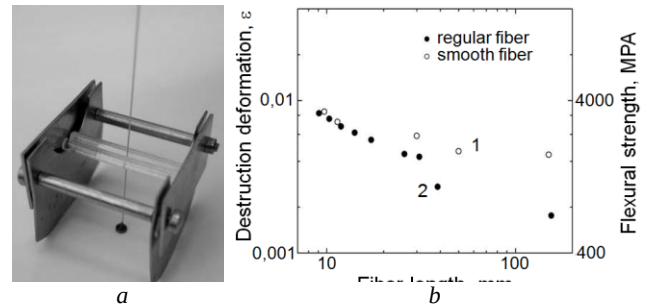


Fig. 4. Device for stabilizing the position of the fiber during their growth (a) and the dependence of the ultimate deformation and bending strength of the fiber grown with stabilizing device 1 and without device 2 (b) on the fiber length

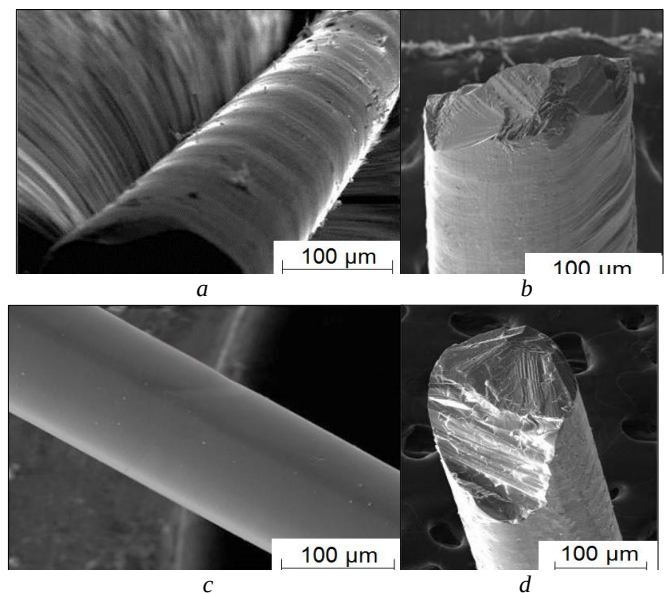


Fig. 5. Surfaces (a and c) and sections of fiber breaks after tests (b and d) grown in the usual way (a and b) and with a device for stabilization (c and d)

Mechanical tests showed that fibers grown with a stabilizing device had a higher strength, starting from a length of 20 mm and more (Fig. 4, b). Stabilization of fiber growth removed the roughness of their surface, which significantly increased its optical transmission. In addition, a smooth fiber almost always had an oblique fracture, which significantly exceeded the area of the fracture of rough fibers, which passed across the fiber (Fig. 5, b and d).

3. Obtaining, structure and results of strength tests of composites reinforced with sapphire fibers

The basic elements of the layered composite with a niobium matrix were a U-shaped element made of Nb-0.1%C alloy foil 0.25 mm thick and a U-shaped element 1 (see Fig. 6) made of Al-foil 10 μ m thick, containing one row of sapphire fibers in a finely dispersed Nb-powder of technical purity.

The production of aluminum U-cells 1 was carried out in this way. The counted number of sapphire fibers was laid out with a given pitch and parallel to each other on one of the inner Al surfaces along the width of the U-element and fixed with glue. Then the layer of fibers was "poured" with a suspension coating on polyvinyl-butyral made of commercially pure niobium powder, which dries at room temperature. It was better if the coating thickness was slightly greater than the fiber diameter. This layer

was covered from above with the other half of the Al element (see Fig. 6).

In fig. 6 shows an assembly diagram of the main elements of a composite with an Nb matrix.

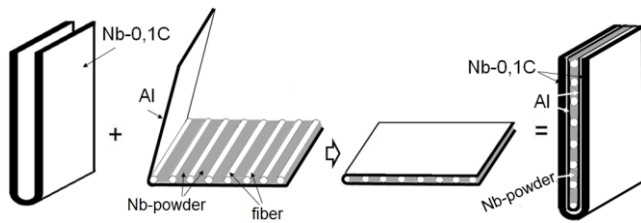


Fig. 6. Manufacturing of initial U-elements (1 and 2) for a multilayer package based on niobium: U-element made of Nb–0.1%C alloy foil; 1 – U-element made of Al-foil with sapphire fibers and Nb-powder; 2 – U-element from Nb–0.1% C + U-element 1

It was expected that the layer of "commercially pure Nb-powder" will largely determine the strength, stiffness and creep resistance of the entire composite.

The total number of Al-foil U-elements in the composite is 9 pcs., five of them are enclosed inside the U-shaped foil of the Nb–0.1% C alloy, forming element 2 (see Fig. 6). Four other elements 1 are placed between elements 2 at the final assembly of the package.

Thus, the initial package for obtaining a layered composite based on an Nb–0.1% C alloy reinforced with sapphire fibers was assembled from elements 1 and 2 in the amount of four and five pieces, respectively (Fig. 7, a). The length and width of both elements, and then the dimensions of the package, were ~60 and ~30 mm, respectively. The length of the fibers used varied from 25 to 28 mm, the average diameter was 0.3 mm. Note that the fibers were laid along the element width, which coincided with the direction of rolling of the Nb–C alloy foils.

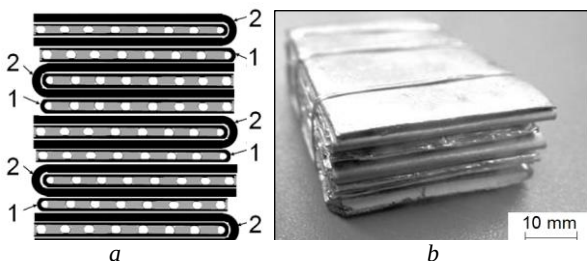


Fig. 7. Schematic drawing of a longitudinal section of a multilayer package assembly (a) and a really formed package with segments of TEG tapes on surfaces (b): 1 – U-elements from Al-foil with Nb-powder and sapphire fibers, 2 – U-elements from alloy Nb–0.1% C with U-elements 1 inside

Of interest was also the total length of consumed sapphire fibers in 9 layers with 65 segments in each layer, if their average length was 26.5 mm. Then the total number of used segments is 585, and the total length of the entire sapphire fiber spent on assembling the multilayer package was 15.7 m.

We also note the following. The purpose of the Al-foils in the package is wider than being a container for sapphire fibers. The melting point of aluminum, equal to 660°C, promotes the initial bonding of the components of the welded package, which have significantly higher melting points. As for the contacting Al/Nb pair in the composite, the result of their interpenetration was the formation of intermetallic compounds NbAl₃ (already at 550–600°C) and much higher-temperature Nb₂Al and Nb₃Al, stable up to 1800°C and higher, and, therefore, capable to some extent determine the strength, crack resistance, elastic modulus, and creep resistance of the matrix, and, therefore, the entire composite.

In fig. 7, b shows an experimental package composed of elements 1 and 2 in the amount of 4 and 5 pieces, respectively. Both

outer surfaces of the package are covered with two ribbons of thermally expanded graphite (TEG) 0.3 mm thick.

In this form, the package was subjected to solid-phase sintering under pressure P in a diffusion welding installation equipped with a high-strength graphite heater in a vacuum of ~10^{–4} Hg. Art. by mode: 1400°C at 12 MPa for 30 min (Fig. 8). The package 1 was located between the movable and stationary punches 3. Between them and the package were laid two pieces of TEG tape, which prevented the package from possible welding to the surface of the punches. Heating to the melting point of aluminum was carried out in a slow (~ 1.5 h) mode so that aluminum, before reaching its melting point, could form an intermetallic compound NbAl₃ with niobium with a high (1680°C) melting point.

After diffusion welding (DW) at 1400°C, the thickness of the package was ~3 mm (Fig. 9). A reflection of the package design is the macrostructure of the cross-section of the laminated composite after welding (Fig. 10), which is an alternation of layers of a light background made of Nb–C alloy and layers of sintered Nb powder with sapphire fibers. The volume fraction of sapphire fibers in the composite was 18%.

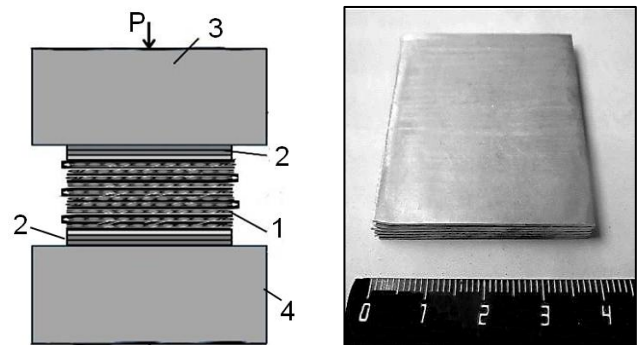


Fig. 8. Location of the multilayer package in the diffusion welding installation: 1 – package; 2 – gasket of two TEG strips; 3, 4 – upper and lower punches, P – pressure

Fig. 9. Package after diffusion welding

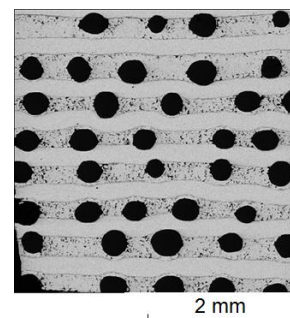


Fig. 10. Macrostructure of a layered composite based on niobium after DW

After solid-phase sintering, the package was subjected to heat treatment (HT) in a vacuum resistance furnace according to the mode: 1750°C, 2 h at 0.16 MPa + 1950°C, 2 h at 0.28 MPa. A slight pressure was created due to the fact that the package was "under the yoke" of the Mo-load. The microstructure of the composite in the state "after HT" is shown in Fig. 11.

The structure and phase composition of the composites were studied using Tescan VEGA-II XMU and CamScan MV230 digital scanning electron microscopes (VEGA TS 5130MM). Microscopes are equipped with detectors of secondary and reflected electrons and energy-dispersive X-ray microanalyzers. Microscopes are equipped with detectors of secondary and reflected electrons and energy-dispersive X-ray microanalyzers. The probe size is 5–7 μm.

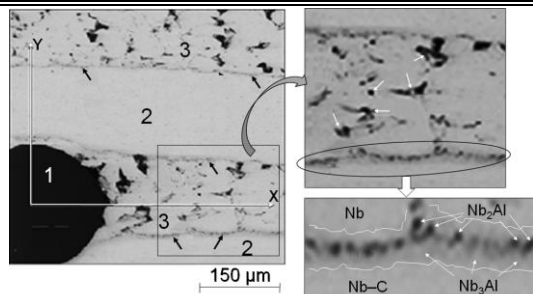


Fig. 11. Microstructure of the longitudinal (along the length) section of the composite based on niobium after DW + HT: 1 – sapphire fiber; 2 – a layer of foil made of an Nb-0.1%C alloy; 3 – a layer of Nb powder.

It can be stated that the layered structure of the composite had a lapidary character and consisted of layers 2 that inherited the foils of the Nb-C alloy and layers 3 that inherited the powder coating and, therefore, contained many pores ranging in size from <1 to 20–25 μm. In the microstructure fragment outside the main microstructure, the pores are shown by short arrows and are surrounded by a light halo.

The boundaries between sapphire fibers 1 and both matrix layers 2 and 3 appear to be clear, especially if they fall on the Nb-C alloy foil. The complete non-interaction of sapphire with the matrix layer of sintered Nb powder is evidenced by the concentration dependences of Nb and Al along the X axis (Fig. 12, a), plotted from the data of local X-ray spectral (XS) analysis.

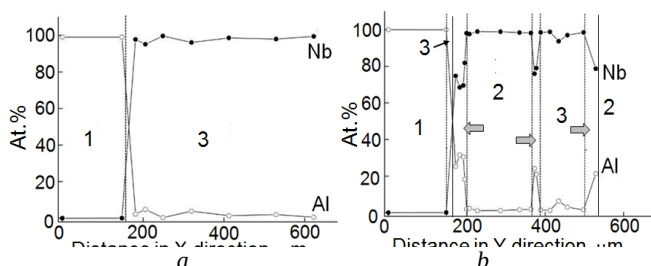


Fig. 12. Concentration dependences of Nb (●) and Al (○) according to local RS analysis along the X (a) and Y (b) axes: 1 – sapphire fiber; 2 and 3 – layers inheriting foils of Nb-C alloy and Nb-powder, respectively; horizontal markers show layers of Nb₂Al and Nb₃Al

The boundaries between the foils made of the Nb-C alloy and the powder component of the niobium composite were of interest for the study. In a multilayer bag, they were separated by an Al foil. After DW and HT, thin interlayers with a thickness of no more than 1.5 μm were formed in the multilayer composite in place of the Al foils, which did not have clear boundaries, but differed from the neighboring layers by a light gray contrast. In the main figure, they are marked with black arrows. A part of one of the interlayers is taken out as a separate fragment down to the right of the figure (see Fig. 11), so that the phase structure of the interlayers also appears. Diffuse inclusions with a contrast from dark gray to black were clearly defined on a light gray background.

Now, after such, in general, simple technical operations with an electron microscopic image, we will be guided by the data of local PC analysis. The concentration dependences in Fig. 12, b showed that these interlayers contain from 20 to 30 at. % Al and the rest is niobium. In the Nb-Al phase diagram, such concentrations correspond to the 2-phase region of the intermetallic compounds Nb₃Al and Nb₂Al, which are responsible for the colors of gray and dark contrasts, respectively.

Note that, in contrast to the X direction, the first layer in the Y direction after the sapphire is a thin layer of powder niobium 3 (see Figs. 11 and 12, b).

It can be predicted that further holding at high temperatures will form a thin layer of the Nb₃Al intermetallic compound.

4. Results of the first bending strength tests of composites

After diffusion welding and heat treatment, the composites were in the form of plates ~40 и 50–60 mm and a thickness of 2–2.5 mm (see Fig. 9). Samples for mechanical testing were cut along the width of the bags, that is, along the reinforcing sapphire fibers.

The first 3-point flexural strength tests were carried out at room temperature. The load was applied perpendicular to the layers of the composite. In fig. 13 shows the dependences of the deflection on the load for composites, respectively: after 30-minute diffusion welding under pressure at 1400°C (a) and after welding and two heat treatments at 1750 and 1950°C for 2 h (b).

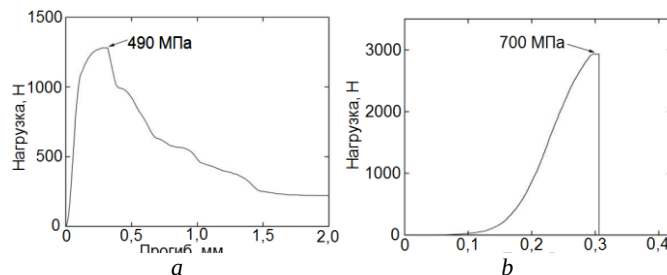


Fig. 13. Load-deflection curves of a composite made of layers of Nb-0.1% C alloy and layers of sapphire fibers in Nb-powder after DW (a) and after DW and HT (b)

Heat treatment at high temperatures, carried out after welding, significantly increased the ultimate strength of the composite, from 490 to 700 MPa. However, judging by the deformation curve, the material became significantly more brittle. The first thing that can explain such a degeneration of the material is the presence of aluminum in the composite and the formation of its intermetallic compounds with niobium.

Brittle compounds of aluminum with niobium Nb₂Al and Nb₃Al, formed during diffusion welding of the package at 1400°C, were also present in the samples after heat treatment at higher temperatures. Note that after HT at 1750°C and higher, only one intermetallic compound Nb₃Al should remain. But after HT at 1950°C, the intermetallic precipitates of Nb₃Al formed at lower temperatures could coagulate into larger ones, which would lead to the embrittlement of the entire composite. However, with such a sequence of transformations, a higher ultimate strength after DW + HT remains unexplained. It often happens that the coarsening of precipitates does not increase the strength of the material.

A slightly different development of the transformations seems more probable. After welding at 1400°C, a certain amount of intermetallic compounds was formed, which still does not negatively affect the fracture toughness of the material, but is also unable to provide the composite with a decent level of strength. The material after DW is plastic.

The next heat treatment of the composite at significantly higher temperatures caused the intensive formation of the intermetallic compound Nb₃Al. As a result, the strength increased greatly, but the bending specimens showed a brittle state of the test material.

The deformation curves were used to determine the effective surface energy g of both composite materials, as the work of external forces applied to the sample, referred to the doubled area of its cross section [9]. In practice, it is determined by calculating the area under the experimental load-deflection curve. For the sample after DW (see Fig. 13, a), the value $g = 9.2 \times 10^3$, after DW + HT (see Fig. 13, b) – 8.8×10^3 J/m². The results are confirmed by microscopic observation data. After diffusion welding, the samples had a developed fracture surface (Fig. 14, a) with extended delamination. Subsequent heat treatment gave the structure proper intercomponent connectivity and completely eliminated delamination between the niobium-carbon alloy and sintered Nb powder (Fig. 14, b). However, the cohesive structure itself has less resistance to crack propagation. Therefore, both the sample deflection and the effective surface energy became smaller.

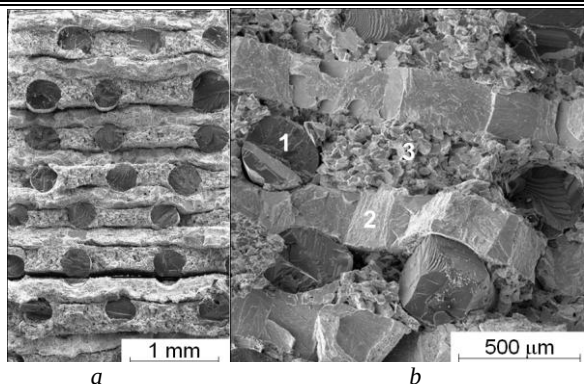


Fig. 14. Fracture surfaces of composites with a matrix based on Nb: after DW (a) and after DW + HT (b): 1 – fiber, 2 – Nb–0.1C foil layer, 3 – Nb-powder layer

The longitudinal structure of the composite (Fig. 15) was characterized by a regular arrangement of dense layers of cast alloy Nb–0.1C, porous layers of sintered Nb-powder and four sapphire fibers statistically found in the plane of the section. On top of the outer layer of the composite, you can see a thin layer of the heat-resistant coating we are developing.

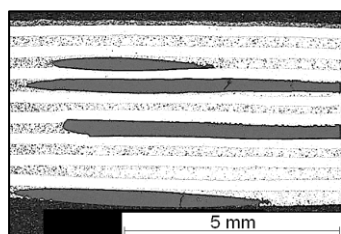


Fig. 15. Longitudinal sections of a composite after DW

In fig. 16 demonstrates the non-brittle nature of destruction of the laminated structure of the composite containing brittle fibers.

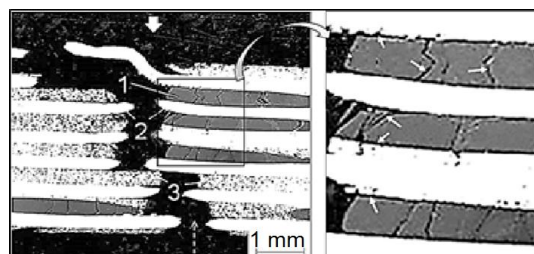


Fig. 16. Longitudinal sections of a composite after DW and after tests for strength: the arrow above shows the direction of load application; the dotted line is the direction of propagation of macrocracks: 1 – fiber, 2 – Nb–0.1C foil layer, 3 – layer of Nb-powder

Fragmentation of fibers 1 and delamination along the fiber-matrix boundaries (see arrows), plastic deformation with the formation of necks of the Nb–0.1C alloy 2, and nonplastic fracture of layer 3 with an inhomogeneous structure of Nb powder along grain boundaries are clearly visible. Microcracks in the fiber are retarded at the fiber-matrix boundaries. The fracture surface (see Fig. 14, a), formed after the passage of the macrocrack, confirms the described nature of the fractures.

The noted types of fractures, which are not in the plane of propagation of a macrocrack, increase the energy of inelastic scattering upon fracture of the composite and thereby increase the crack resistance of the material.

5. Summary and conclusions

1. Single crystal sapphire fibers obtained by the modified Stepanov method were used to reinforce a layered Nb-based composite developed for use at temperatures of 1300–1500°C. An

original procedure for testing fibers for bending is described. At a length of 10 mm, they had a strength exceeding 1000 MPa.

2. Developed and implemented in multilayer packages a hierarchically organized layered fibrous structure using foils of the Nb–0.1%C alloy, aluminum, Nb powder and sapphire fibers. The assembled package was subjected to diffusion pressure welding and subsequent heat treatment to obtain a composite with a layered-fiber structure reinforced with sapphire fibers.

3. The microstructure of the composites has been investigated. Strength bending tests have been carried out so far only at room temperature. The experimental load-deflection dependences made it possible to determine the effective surface energy of destruction of composites and to establish the correlation of mechanical characteristics with the structures of the composite after diffusion welding at 1400°C and after welding, followed by heat treatment at higher temperatures. The strength at room temperature exceeded 700 MPa, the effective surface energy was $12 \times 10^3 \text{ J/m}^2$.

4. The topography of the fracture surfaces of the composite specimens testified to the operation of various mechanisms of microfracture under loading of the material. Together, they provided the necessary fracture toughness to the composite containing brittle components.

5. The work and the results obtained are still more of a pilot nature, but will be the basis for further development and optimization of fiber composite structures, modes of their production using also other materials.

Acknowledgments

The work was carried out within the of the Russian Academy of Sciences with partial funding from the Russian Foundation for Basic Research (project 20-03-00296).

Literature

1. Properties, production and application of refractory compounds. Ed. Kosolapogo T.Ya. M.: Metallurgy, 1986, – 928 p.
2. Schneibel J.H. Intermetallics, 2003, No 11, pp. 625–632.
3. Sharif A.A., Misra A., Mitchell T.E. Scripta Materialia, 2005, No 52, pp. 399–402.
4. Jain P., Kumar K.S. Acta Materialia, 2010, v. 58, No 6, pp. 2124–2142.
5. A short guide to chemistry. Goronovsky I.T., Nazarenko Yu.P., Nekryach E.F. Kiev: Naukova Dumka, 1987, – 929 p.
6. Cook J., Gordon J.E. Proceedings of the Royal Society, 1964, v. 282, No 8, pp. 508.
7. Anischenkov V.M., Mileiko S.T. DAN SSSR, 1978, v. 241, No. 5, p. 1068.
8. Mileiko S.T. // Composite Science and Technology, 2001, v. 61, pp.1649–1652.
9. Ruditsin M.N., Artemov P.Ya., Lyuboshits M.I. A reference book on the strength of materials. Minsk: High. Sc., 1970. – 628 p.
10. Mileiko S.T. Comp. Sci. and Tech. // 2002, v. 62, p. 195–204.
11. Mileiko S.T., Kiiko V.M. // Mechanics of Composite Materials, 2004, vol. 40, p. 523–534.
12. Mechanics of a deformable solid. Yu.N. Rabotnov. Moscow: Nauka, 1979. –744 p.
13. Karpov M.I., Vnukov V.I., Stroganova T.S. et al. // Izvestia RAN. Physical series. 2019, vol. 83, no. 10, p. 1353–1361.
14. Svetlov I.L., Karpov M.I., Stroganova T.S., Zaitsev D.V., Artemenko Yu.V. Def. and destr. of mater., 2019, No. 11, p. 2–6.
15. Cook J., Gordon J.E. // Proceedings of the Royal Society A, 1964. – V. 282, Iss. 8. – P. 508–520.
16. Mileiko S.T. // Composites and nanostructures, 2015. – V. 7. No. 7. – P. 191–205.
17. Kurlov V.N., Stryukov D.O., Shikunova I.A. // Journal of Physics: Conference Series 673, 2016. – Art. 012017.
18. Kiiko V.M., Mileiko S.T. // Compos. Sci. Technol, 1999. – V. 59, Iss. 13. – P. 1977–1981.
19. Kurlov V.N., Shikunova I.A., Stryukov D.O. // RF Patent No. 2552436, Bulletin No. 16, 10.06.2015.

Preparation and characterization of $\text{BaTi}_{0.89}\text{Sn}_{0.11}\text{O}_3$ and $\text{Ba}_{0.89}\text{Sn}_{0.11}\text{TiO}_3$

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Abstract: In recent years, interest in the application and use of materials for supercapacitors for electric vehicles has grown significantly. The advantage of capacitor ceramics over other dielectric materials for producing supercapacitors is its environmental friendliness and high economic efficiency. This paper presents the results of a study of capacitor ceramics doped with Sn at different locations of the modifier (tin) in BaSnTiO_3 and BaTiSnO_3 crystal lattice. The influence of modifiers in low-temperature sol-gel synthesis was studied. The samples were annealed at 1000°C . The resulting phases were identified by X-ray phase analysis. Microscopic analysis was also performed.

Key words: SOL-GEL, CONDENSER CERAMICS, BaTiO₃

1. Introduction

At present, in the worldwide production of supercapacitors, porous carbon is most often used for both electrodes and a special electrolyte. The second well known method includes using of so-called carbon nanotubes. The possibility of a large area of the electrodes and a small distance between them is achieved and as a result acceptable dimensions for the supercapacitor [1].

Studies of compounds based on BaTiO₃ as a dielectric material have shown that it is possible to create a supercapacitor, both for the needs of electronics and for electric vehicles, where it is an important component device needed not to drive but to improve the dynamic driving qualities of the electric car and for absolutely trouble - free start in hybrid small and heavy cars [1-2].

BaTiO₃ is an electroceramics possessing good dielectric properties and does not emit harmful emissions into the environment. [3] The cubic phase of barium titanate shows a very high relative dielectric permittivity (1500-6000°C) (at room temperature) [4]. Meanwhile, tetragonal polymorphic forms possess ferroelectric, piezoelectric and thermoelectric properties. The most widely used application of barium titanate includes multilayer capacitors in electronic circuits, electro-optical devices, thermistors, piezoelectric drive, non-linear resistors, thermal switches, etc. [5-7].

Alkaline earth tin oxide compounds such as (MSnO_3) , where $\text{M}=\text{Ca}, \text{Sr}, \text{Ba})$ are a series of materials that are widely used in industry in the manufacture of capacitors. Ostrik and colleagues report the results of measurements [6] at high temperatures, which clarify the presence of defects in the crystal lattice of the material, which in some cases favor the production of materials, such as sensors, transducers and others. [7-9]. Despite this technological significance, any information on the processing and evolution of the microstructure of these materials and their impact on electrical characteristics is missing in the literature. [10] Suggestions for $\text{BaTiO}_3\text{-BaSnO}_3$ solid solution interaction have been made. [11] Barium titanate obtained by appropriate doping with Sn is known to have a very high dielectric constant ϵ , which can reach values up to 5.104. This high value of ϵ is considered suitable for energy storage devices used as portable and wear-resistant electronics. [12] The high value of the dielectric constant of Sn doped BaTiO_3 materials is attributed to their nano and distorted structures. [13] There are insufficient literature data on electrical measurements of materials with similar structures.

2. Experimental part

Ba(Ac)₂ Alfa Aesar and Ti(Obu)₄ 99% Alfa Aesar are the main precursors used for the synthesis of BaTi_{0.89}Sn_{0.11}O₃ and Ba_{0.89}Sn_{0.11}TiO₃. Sn(OOCCH₃)₂ and Sn(OOCCH₃)₄ were used as modifiers. The solutions of above mentioned compounds are mixed in suitable stoichiometric ratios, and are homogenized on a Techno Kartel T22 magnetic stirrer for 30 minutes - the required time for each of the solutions.

2.1. Synthesis of $\text{BaTi}_{0.89}\text{Sn}_{0.11}\text{O}_3$

Barium acetate is dissolved in water and acetic acid CH_3COOH is added to the resulting solution - to make the acetate solution more resistant to moisture. The molar ratio of $\text{H}_2\text{O}:\text{CH}_3\text{COOH}$ is 1:2 (Chernea 2006 [14]). Titanium butoxide is dissolved in a mixture of absolute alcohol and acetic acid, which acts as a catalyst and stabilizer of the synthesized titanium sol. Tin acetate - $\text{Sn}(\text{CH}_3\text{COO})_4$ after dissolution in absolute alcohol is added to barium acetate. Clear, stable solution is formed and is added to the sol of $\text{Ti}(\text{OBu})_4$. A new stable yellow sol is obtained. After heating to 60°C , the sol gels and dried afterwards at 100°C . The resulting dried gel – xerogel - is annealed at 1000°C for 10 hours.

2.2. Synthesis of Ba_{0.89}Sn_{0.11}TiO₃

The preparation of $\text{Ba}_{0.89}\text{Sn}_{0.11}\text{TiO}_3$ is similar to the synthesis of $\text{BaTi}_{0.89}\text{Sn}_{0.11}\text{O}_3$, but differs in that the starting compound of the tin is $\text{Sn}(\text{CH}_3\text{COO})_2$, Sn^{2+} is used, and for $\text{BaTi}_{0.89}\text{Sn}_{0.11}\text{O}_3$ $\text{Sn}(\text{CH}_3\text{COO})_4 - \text{Sn}^{4+}$ is used. In the process of synthesis it is noticeable that with $\text{Sn}(\text{CH}_3\text{COO})_2$ a suspension is obtained in a solution of absolute alcohol, while $\text{Sn}(\text{CH}_3\text{COO})_4$ dissolves very well in the absolute alcohol.

Characterization of the obtained samples is performed with Bruker 8 d advance \ automatic - X-ray diffractometer with CuK α radiation (Ni filter) and a Lynx Eve solid detector.

3. Results and Discussion

The performed X-ray phase analysis presented in Fig. 1 and Fig. 2 shows the patterns of diffraction of powders of tin-doped BaTiO₃ and products of a chemical reaction carried out at a temperature (1000°C). The data were taken with CuK α radiation ($\lambda=0.56$ Å) - Bragg angles 2 θ up to 120 degrees, ie. vectors with approximately 2 θ Å⁻¹ phases BaTi_{0.89}Sn_{0.11}O₃ and Ba_{0.89}TiSn_{0.11}O₃. The width of the peaks determine the size of the crystallites, which range from 89 up to 103 nm.

According to the X-ray phase analysis of the sample $\text{BaTi}_{0.89}\text{Sn}_{0.11}\text{O}_3$ only pure cubic BaTiO_3 phase with crystallite size of 103 nm is registered (fig.1), while concerning $\text{Ba}_{0.89}\text{TiSn}_{0.11}\text{O}_3$ a cubic BaTiO_3 is the main phase concomitant with small amount of SnO_2 , as well as of traces of Ti_2O_{13} and TiO_2 (rutile) (Fig. 2)

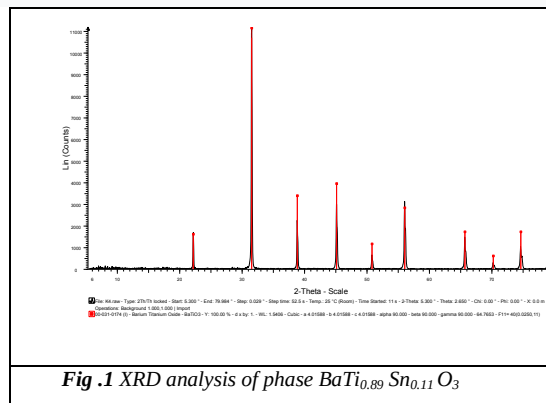


Fig .1 XRD analysis of phase $\text{BaTi}_{0.89}\text{Sn}_{0.11}\text{O}_3$

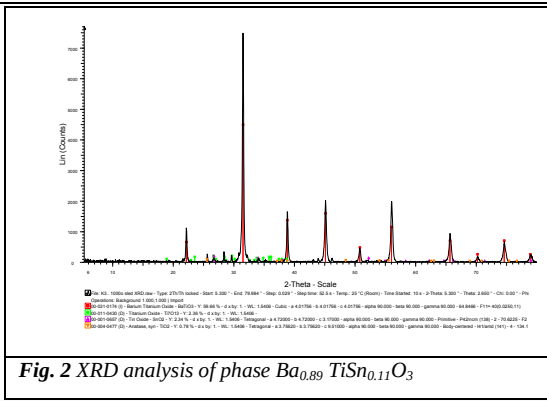


Fig. 2 XRD analysis of phase $Ba_{0.89}TiSn_{0.11}O_3$

The difference in the two diffractograms is due to mode of Sn substitution in the crystal lattice of the two compounds ($BaTi_{0.89}Sn_{0.11}O_3$ and $Ba_{0.89}TiSn_{0.11}O_3$), the temperature treatment and the time of soaking. The better result of $BaTi_{0.89}Sn_{0.11}O_3$ is obvious, because in this case tin replaces titanium in the crystal lattice and shows more reliable properties according to data from the literature for further future development, namely the preparation of a target for magnetron sputtering. After high-frequency magnetron sputtering, layers were deposited on stainless steel substrates and with a mirror surface with thicknesses of the seeded layers in the range of 40, 50, 100, 200, 500, 800, 1000 nm. The layers showing the best results are shown in Table 1. The studies are supported by microprobe analysis Fig.3.

Sample	Thickness (nm)	Standard deviation (nm)
4 hours	1400	120
2 hours	610	60
1 hour	230	25

Table. 1. Experimental results of the measured layer thicknesses

In the photomicrograph, the three thicknesses of the layers are clearly distinguished. The places with the best indicators in nanometers are marked, respectively 1400 nm, 610 nm and 230 nm.

The thin layers deposited by magnetron sputtering were examined with an Amplival microscope. The micrographs of the individual layers were taken with a Carl Zeiss digital camera, Jenoptic CT3. Microscope magnifications with 6.3 X, 12.5X and 25X lenses were used in combination with a 12.5X eyepiece.

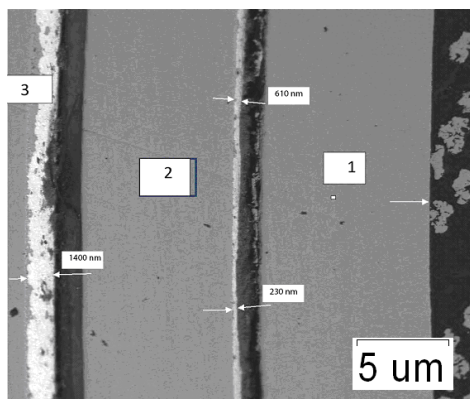


Fig.3. Microscopic analysis of layer thicknesses marker 5nm

4. Conclusions

In conclusion, it can be summarized that when Sn doped $BaTiO_3$ in the case when tin replaces titanium, a pure cubic phase of $BaTiO_3$ is obtained (concerning compound $BaTi_{0.89}Sn_{0.11}O_3$), while

when barium is replaced with tin, in addition to cubic $BaTiO_3$, small amounts of other phases: SnO_2 , TiO_2 . (for compound $Ba_{0.89}TiSn_{0.11}O_3$). The size of the crystallites - in the range up to 103 nm- is determined from the performed XRD analysis. After high-frequency magnetron sputtering of a target on an stainless steel substrate, the layer thicknesses were determined, with the best result being the 1400 nm layer. The present study also aims at additional analyzes to confirm the necessary conditions for further research.

Acknowledgement

The authors wish to thank the National Science Fund at the Bulgarian Ministry of Education and Science for financing their research project, (Contract No. KII-06-H 37/26) from 18.12.2019.

References

1. A. Mundy, G. L. Plette, Journ. of Energy Storage7,"Reduced-order physics-based modeling and experimental parameter identification for non-Faradaic electrical double-layer capacitor", (2016) 167-180.
2. A. Mazard, M. Hashim, S. Baptist, A. Badar, A. Haq, "Phase evolution and microstructural development in sol-gel derived $MSnO_3$ (M=Ca, Sr and Ba)", Journ. of Mat. Sci.,35 (2000), 5475-5483.
3. E. P. Kashchieva, V. D. Ivanova, B. T. Jivov and Y. B. Dimitriev, „Nanostructured borate glass ceramics containing $PbMoO_4$ ", Physics and Chemistry of Glasses, **41** (6), 2000, pp. 355-357.
4. Qingsong Zhang, Tahir Cagin, William A. Goddard III, "The ferroelectric and cubic phases in $BaTiO_3$ ferroelectrics are also antiferroelectric",PNAS October 3, 2006 103 (40) 14695-14700
5. E. P. Kashchieva, V. D. Ivanova, B. T. Jivov, P. K. Petkov and Y. B. Dimitriev, „Structure-property correlation in lead-borate composites with participation of $PbMoO_4$ ", In: Proceedings of the 13th Conference on Glass and Ceramics, 1999, Varna, Bulgaria, Vol. 1, Eds B. Samuneva et al., (Publishing House „Science Invest" Sofia, 1999), pp. 159-164.
6. R. Ostric, M. Fleisher and H. Meixner, J. Am.Cerm. Soc. **80** (1997), 2153.
7. P. T. Mousley, A. M. Stoneham and D. E. Williams, "Techniques and Mechanisms iin Gas Sensing", edited by P. T. Moseley, J.O.W. Norris and D. E. Williams, (Adam Hilder, Bristol,1991,ch.4).
8. P. Nanny, M. Viviani, V. Buscaglia, "Synthesis of dielectric ceramic Materials", Chapter 9, Handbook of Low and High Dielectric Materials and Their Applications, (1999)429-450.
9. O. Parkash, K. D. Mandal, C. C. Christopher, M. S. Sastray and D. Kumar, J. Mater. Sci. Lett. **13** (1994), 1616.
10. J. Cerda, J. arbiol, R. Diaz, G. Dezanneau, J. R. Morante, "Synthesis of perovskite-type $BaSnO_3$ particles obtained by a new simple wet chemical route based on a sol-gel process", Mater. Lett. **56** (2002) 131-136.
11. Bachvarova-Nedelcheva, R. Iordanova, K. L. Kostov, V. Ganev, St. Yordanov, Y. Dimitriev, "Synthesis and structural characterization of a glass in the $Ag_2O-SeO_2-MoO_3$ system", Journal of Non-Crystalline Solids, **481**, 2018, pp. 138-147.
12. J. Gao, Y.Wang, Y.Liu, X.Hu, X.Ke, L.Zhong, Y.He, X.Ren," Enhancing dielectric permittivity for energy- storage devices through tricritical phenomenon ", Scientific reports 7:40916/ DOI:10.1038/srep40916.
13. T. Shi, L.Hie,L. Gu and J. Zhu Why Sn doping significantly enhances the dielectric properties of $Ba(Ti_{1-x}Sn_xO_3)$, Scientific Reports5 : 8606 (2015) DOI: 10.1038/srep08606
14. M. Cernea, O.Monnereau, Ph.Llewellyn, L.Tortett, C.Callasi, "Sol-gel synthesis and characterization of Ce doped $BaTiO_3$ " Journal European Ceramic Society, **26** (2006) 3241-3246.

Investigation of solders surface tension in temperature range from melting point up to 673K

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Abstract Solders are fusible metal alloys, used in industry to create permanent bond between metal surfaces. In order to achieve this, solders need to be heated above their melting point and used in liquid phase. Low melting temperature is essential from technological point of view, as well as for soldered components safety. Typical solders have Lead (Pb) as a base component, having melting temperature of 600.6 K. Adding up to 60% of Tin (Sn) to the alloy, reduces melting temperature down to 456-461 K in average. Since 2006, RoHS regulation enforce industrial use of Lead-Free solders, typically having much higher melting temperature. However, Pb:Sn solders with up to 40% Sn still have their industrial applications, usually used for soldering Cu and Zn coated pipes while the 60% Sn containing solders are used for soldering of electrical cables.

The achieving of these goals requires knowledge of liquid phase surface tension. Because of the difficulties, related to such measurement, the available data in literature are limited. The current report presents an equipment for measurement of the surface tension, based on the Wilhelmy plate method as well as the applied measurement procedure. The Wilhelmy method has relatively good stability. The contact angle also can be considered zero for the examined samples therefore correction coefficients are not required for the measurement. The results from measurement of Pb:Sn in ratio 40:60 and also in ratio 60:40 show that the oxidation in excess of Pb lowers the surface tension while for the case with excess of Sn, the oxidation lead to increase of the surface tension if compare with the surface tension obtained for the same solders but under non-oxidizing conditions. This could be attributed to formation in excess of PbO and SnO on the liquid surface of the corresponding solder.

Keywords: TIN, LEAD, SOLDER, SURFACE TENSION, NUCLEAR REACTOR, OXIDIZING

1. Introduction

Solders are fusible metal alloys, used in industry to create permanent bond between metal surfaces. In order to achieve this, solders need to be heated above their melting point and used in liquid phase. Low melting temperature is essential from technological point of view, as well as for soldered components safety, because this way is achieved significant temperature difference from the critical temperature of the soldered components

Reports for the surface tension of liquid Pb:Sn mixture exists for more than a century, since the beginning of their application as a solder. The work by Bircumshaw, [1], Whites [2] and Kucharski et al., [3] provide detailed study on the surface tensions. The studies were further extended on wettability, by Gasior et al [4]. A summary of the available data as well as their independent verification is provided in [5, 6] under non-oxidation conditions. The phase diagram of Pb:Sn system is established for long time [7], but because of the importance of the topic, the studies on solidification and liquation still continue and the newer studies are ongoing, [8, 9] Obviously the accurate knowledge of phase diagram represents importance for surface tension measurement.

Typical solders have Lead (Pb) as a base component, having melting temperature of 600.6 K. Adding up to 60% of Tin (Sn) to the alloy, reduces melting temperature down to 456-461 K in average. Since 2006, RoHS regulation enforce industrial use of Lead-free solders, typically having much higher melting temperature. However, Pb:Sn solders with up to 40% Sn still have their industrial applications, usually used for soldering Cu and Zn coated pipes while the 60% Sn containing solders are used for soldering of electrical cables.

More recent application of Pb contained liquid alloys became important with the development of nuclear technology. The most popular of these alloys is Pb:Bi eutectic mixture because of the low melting temperature [10]. However, the potential of Pb:Sn alloys is known and they are currently under consideration [11].

2. Theoretical background

Surface tension of liquid soldering alloys plays important role in the process of soldering. It also has significant impact on the thermal properties of the soldering process, including the cooling stability. The lower surface tension facilitates the soldering process

and improves the property, called solderability. The appropriate surface tension ranges within 400-700 mN/m, [12]. In different proportion of their constituents, these alloys have found significant applications in the industry and the determination of their surface tension is important and challenging task. Thus, our interest is focused on investigation of the binary Pb:Sn alloys, used in low temperature soldering process.

Recent studies, reported in Ref. [5], provided an empirical correlation between the constituent proportions, that allows us to calculate the surface tension:

$$\sigma_{i,j} = \sigma_{Pb}X_{Pb} + \sigma_{Sn}X_{Sn} + (826.8 - 0.5526T)X_{Pb}^2 + (-420.4 + 0.3270T)X_{Pb}^3 \quad (1)$$

Where $\sigma_{Pb} = 497.5 - 0.1096 \times T$ is the surface tension of pure Pb and $\sigma_{Sn} = 5582.8 - 0.0834 \times T$ is correspondingly surface tension of pure Sn. The values X_{Pb} and X_{Sn} indicated the corresponding mass fractions. The temperature is provided as independent variable in Kelvins.

The equation, provided by Butler, derived based on equilibria between the bulk phase and surface monolayer becomes for Pb:Sn system [13] as follows:

$$\sigma_{m,i,j} = \sigma_{Pb} + \frac{RT}{A_{Pb}} \ln \frac{1 - X_{Sn}^S}{1 - X_{Sn}^B} + \frac{1}{A_{Pb}} [G_{Pb}^S(T, X_{Sn}^S) - G_{Pb}^B(T, X_{Sn}^B)] \quad (1a)$$

or

$$\sigma_{m,i,j} = \sigma_{Sn} + \frac{RT}{A_{Sn}} \ln \frac{X_{Sn}^S}{X_{Sn}^B} + \frac{1}{A_{Sn}} [G_{Sn}^S(T, X_{Sn}^S) - G_{Sn}^B(T, X_{Sn}^B)] \quad (1b)$$

Where R is the gas constant [J/(mol.K)]; T is the temperature in Kelvins; σ_{Pb} and σ_{Sn} are the corresponding surface tensions of pure Pb and Sn; A_{Pb} and A_{Sn} are the correspondingly for Pb and Sn the partial molar surface area of a monolayer of Pb or Sn. It can be obtained from $A_i = LN^{1/3}V_i^3$. Here N is the Avogadro's number, V_i is the molar volume of the corresponding component. The parameter L is assumed to be 1.091 for liquid metals with close packed structure. The parameters X_{Sn}^S and X_{Sn}^B are correspondingly the molar fractions of the component, Sn at the liquid surface and

the bulk. The partial Gibbs energy excess is correspondingly G_k^S and G_k^B for the surface and the bulk for the component $k = \{Sn, Pb\}$. The excess of Gibbs energy relation between the surface and the bulk, is provided by the following relation: $G_{Sn}^S(T, X_{Sn}^S) = \varepsilon G_{Sn}^B(T, X_{Sn}^B)$. The parameter ε is the ratio of coordination number of the surface to that of the bulk phase. It is assumed 0.83 for the liquid metals [13].

The surface tension, analyzed by the proposed technique, in the current paper, is obtained under non-equilibrium conditions. Therefore, the corresponding theory must be applied in order to improve the predictions. Reference [14], provides the following relation:

$$\sigma_{ij} = \sigma_{m,ij} - [S^A + C(\beta)](\tau - \tau_m) + \frac{4}{3}\beta\sigma_V K \left[\frac{1}{\sqrt{\tau}} + \frac{1}{\sqrt{\tau_m}} \right] \quad (2)$$

Where $S_i^A = \frac{2}{3}\frac{\beta\sigma_V K}{\tau^{2/3}} + C(\beta)$, $C(\beta)$ is an unknown function, $K = \frac{\tau_0 \exp A}{\sqrt{2\pi R A}}$ with constant of integration A, τ is the average time the atom spends on surface, τ_0 period of vibration for a surface atom; M is the molecular weight; R is the gas constant. The parameter $\beta = \frac{\theta - \theta_e}{\theta_e}$ represents surface adsorption, based on Langmuir model. The parameter θ is the fraction of the occupied sites, while the equilibrium fraction is $\theta_e = \frac{Z\tau N s}{1 + Z\tau N s}$; s is the occupied are per site, $-1 \leq \beta \leq 0$. The evaporation rate is: $Z = \frac{P_V}{\sqrt{2\pi M R T}}$ and vapor pressure: $P_V = \exp\left(A - \frac{\sigma_V}{RT}\right)$. At equilibrium $C(\beta)$ and β become zero and the equation is reduced to surface tension at constant equilibrium entropy.

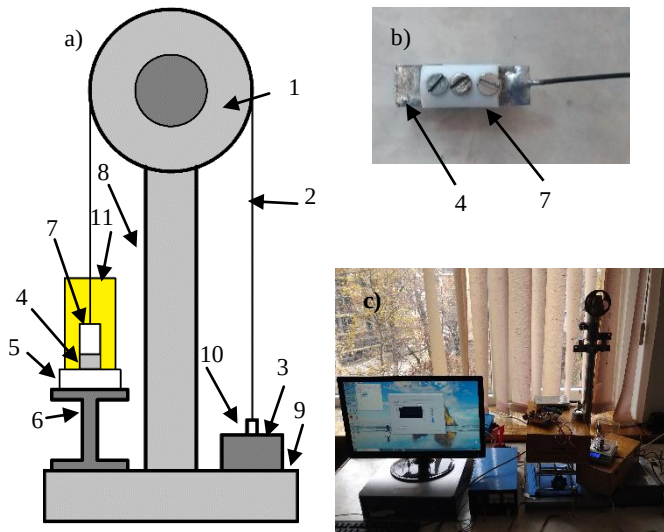


Fig. 1 Experimental setup: a) schematic presentation of the measuring unit: 1-pulley, 2-non-expanding string, 3-balance scale, 4-Wilhelmy plate, 5-oven, 6- Z-axis movable table, 7-Wilhelmy plate holder, 8, 9-support of the system, 10-weight, 11- isolating container; b) picture of Wilhelmy plate with the holder; c) picture of the entire setup including the controllers and the computer.

3. Experimental setup

The experimental setup was designed it in order to use the Wilhelmy plate method [15], a method that has relatively good stability. If the plate is properly prepared, the contact angle between the plate and the surface menisci is zero and therefore correction coefficients are not required for the measurement [15].

Schematic of the experimental setup is shown in Fig. 1a. We use an antivibration table 9, with pillar, 8, and a pulley, 1, on the top. Heating bed 5, is placed a top of a Z-axis movable supporting table 6. The tray is thermally isolated from the environment by a holder made of PTFE. We use HA2-60A or KERN 240-KB-3N balance scale, 3, that measure the calibration weight 10, with the mas of 50 g. The weight is connected by non-elastic cable 2, which

is a combination of stainless-steel chain and a flexible wire made by material with low heat transfer coefficient. The measurements of surface tension are performed by a traditional Wilhelmy plate with 10 mm length of the contact line. The plate, 4, is made of nickel with thickness of 300 μm . The plate is then attached to a holder 7, made by PTFE, that insulate the plate from the wire, keeping it temperature constant. In order to achieve zero degree contact angle, before each measurement, the plate was cleaned and coated by a layer of solder (Fig. 5b). The other side of the holder is connected by stainless steel wire with diameter $\varnothing 100 \mu\text{m}$ of length 100 mm, joined with the cable 2. The measuring unit is isolated by a glass container 11. This particular design, allows us, to separate thermally the plate, from the other part of the setup and keep the plate and the liquid metal, at the same temperature, with a minimal surface temperature gradient. In Fig. 1c is shown a picture of the experimental setup.

4. Materials and methods

Currently, the designed experimental setup is used for analysis the surface tension of three soldering alloys. The melting temperature ranges are presented in Table 1. The selected alloys in our study, are the following: Pb:Sn in ratio 40:60 is near to the eutectic point (Sn: 61.9 %). The other alloy has Pb:Sn content ratio 60:40. In addition, the surface tension of pure Sn melt is also considered to measurement. According to the specification, here Sn is 99.9%.

Table 1: Summary of the sample compositions [16].

Case		Melt. Temp., K Solidus	Melt. Temp., K Liquidus	Temp. K, Uses
A	Pb:Sn 40:60	456(183°C)	461(188°C)	(248°C)
B	Pb:Sn 60:40	456(183°C)	508(235°C)	(295°C)
C	Sn	505(232°C)	505(232°C)	(292°C)

Our intension is to investigate the surface tension of melt at relatively low temperatures, above the alloys melting ranges, under atmospheric pressure. At these conditions, the surface oxidation is not very intense, comparatively to the higher temperatures. In addition, at the selected temperature range, no significant structural transformations are expected. According to the available information, Sn oxidation is a threshold process that is initiated above the oxygen pressure of $(3.0-6.2) \times 10^{-10}$ bars, [17], (the partial pressure of oxygen in Earth atmosphere is ~ 0.2 bars). The oxidation of Sn exhibits a strong temperature dependence, [18]. A stable oxide layer of SnO is formed for less than 10 min above 673K (400°C), while below this point the process of oxidation is slower and it takes up to 60 min to reach a stable layer [18]. With increasing of the temperature, there coexists SnO and SnO₂, until temperature of 923 K(650°C) is reached, where all SnO is converted to SnO₂ [19]

The oxidation of Pb is well studied. The process of PbO formation in a melt is a nucleation process. Below 753K (490 °C), the oxides of Pb exist in tetragonal form [20]. The created PbO crystals can aggregate and to form larger crystals [21].

The measurement procedure involves the following steps: Initially the sample is heated up to 573 K(300 C) with dipped measuring plate to heat sufficiently the entire system. After that the temperature is reduced to the desired value. The liquid surface is brushed off the formed oxides by a silicone brush before every single measurement. The measurements begin after the system isolation with the glass container. The process of measurement starts from the lowest desired temperature and continues in direction toward the temperature increasing. Each measurement under stabilized conditions is repeated at least three times after brushing off the surface. In order to estimate the degree of non-equilibrium, at the beginning of our investigation, we measured the temperature of air near the liquid surface. We found a stable temperature gradient of about 10 K.

The solidification of the analyzed specimens, after completion of our set of measurements, is recorded by HDMI digital camera-microscope with 3MP image sensor, resolution 102×1080, 1080P with video recording speed 30fps. Its magnification range, by the design, is 10x-220x.

5. Results and discussion

We performed measurement of the three alloys with declared compositions in paragraph 4. The observed results, presented in Fig. 2, are quite interesting: Two cases provide very stable systematic results: Pb:Sn in composition 40:60 and 60:40 (case A&B, Table 1). The surface kinetics of Sn oxidation of the pure Sn liquid substance did not allow proper measurements of surface tension with the current configuration of our setup (case C, Table 1).

The results from our measurements showed that the surface tension of Pb:Sn in ratio 40:60 is increased to values predicted by Eq. (1) for pure Sn (compared to the data without oxidation, Fig. 1), possibly because of formation of SnO. With increasing of the temperature, the surface tension gradient is low. This result is possibly because the oxidized Sn already dominates at the surface.

In the case with Pb:Sn ratio of 60:40, a formation PbO possibly dominates at the surface, because at temperatures below 240°C, Pb partially separates. During the solidification, Pb is in excess (case B, Table 1). On the surface it possibly reacts with atmospheric oxygen and because of nucleation, formation of growing aggregates can take place. In this case the surface tension is lowered to the measured surface tension of pure Pb. A higher gradient with the increasing of temperature is exhibit (comparing to the surface tension at non-oxidizing conditions).

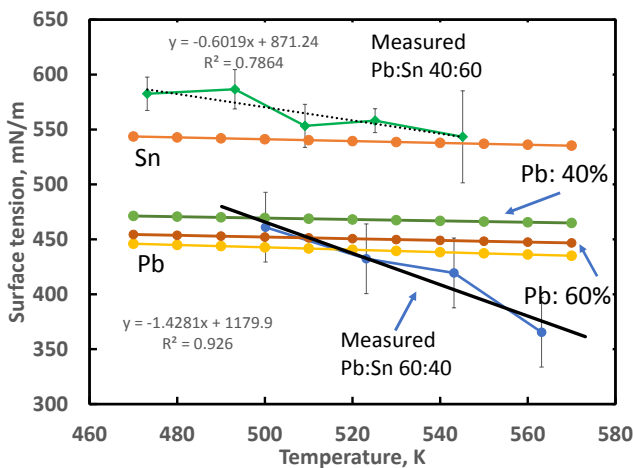


Fig. 2 Surface tension of Pb:Sn.

The performed experimental work allows to be analyzed the non-equilibrium contribution to surface tension that comes from the liquid surface oxidation. Based on the data, provided in Fig. 2 and combination of Eq. (2ab) with Eq. (3), we can write [22]:

$$\Delta\sigma_{i,j} = \sigma_{i,j} - \sigma_{m,i,j} \quad (4)$$

Where $\sigma_{i,j}$ is the obtained theoretically surface tension from Eq. (1) and $\sigma_{m,i,j}$ is the measured value. Based on this we estimate empirically the difference for Pb:Sn in ratio 40:60:

$$\Delta\sigma_{40:60} = 0.5249T - 380.68 \quad (5a)$$

Correspondingly, for ratio Pb:Sn 60:40 is obtained:

$$\Delta\sigma_{60:40} = 0.0134T + 10.567 \quad (5b)$$

In Eq. (5a) is shown that the adding surface energy rate because of oxidation and non-equilibrium thermal conditions is much higher in comparison to data in Eq. (5b). From the equations above is seen that the mixture near the eutectic point (of Pb:Sn in 40:60) stabilizes the surface tension as the added surface energy rate with increasing of the temperature is very low. However, the measurements of pure

Sn (Table 1, C) surface tension indicated that the first several minutes of Sn exposure on air, oxidation very actively takes place. This is indicated visually by the changing of the color of surface to yellow. Then, the formed oxide layer further stabilizes the surface properties of the liquid melt and suppresses the further oxidizing of Pb:Sn in ratio 40:60, contrary to the case 60:40, where is observed stronger gradient of the surface tension decrease with the increasing of the temperatures.

In order to understand better the processes, we recorded images of the solidification process and presented them below. This is helpful in providing a simple explanation of the obtained results. The pictures in Figs 3-5 represent the solid alloys shortly after the solidification of the investigated alloys, at the end of surface tension measurement. The cooling was performed by turning off the heating element and waiting the cooling of the samples to the ambient temperatures, 293 K, (natural speed). We selected this approach to cool the samples after several tests with controlled reduction of the speed of cooling below the natural but no differences were observed at the records of the surface solidification.

Figure 3 shows a picture of 60 % Sn and 40 % Pb sample surface shortly after its solidification. The formed structure consists from two constituent distinct phases: dark phase and crystalized structure [23] [24]. The dark occupied relatively large zones consist possibly from oxidized Pb, which remains on the surface. This conclusion is based on the fact that after solidification of Sn (Fig. 5) such dark phase formation is not observed.

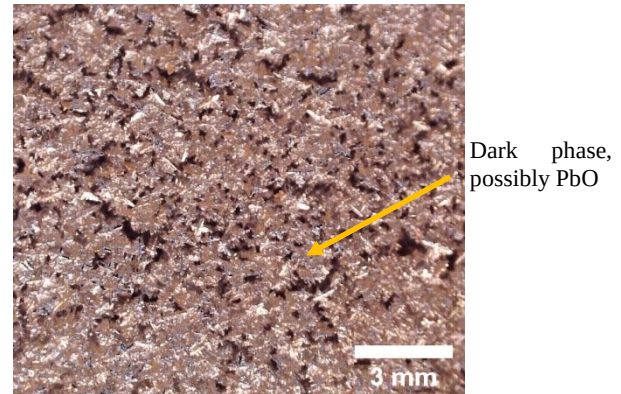


Fig. 3 Solidified melt Pb:Sn in ratio40:60 (POK60).

Figure 4 represents the surface of cooled and solidified sample of 40% Sn and 60% Pb near the melting point. It consists from two solid phases. However, the mixture is formed in a very small scale, and the phases are not distinguished on the picture. In our opinion, oxidized Pb is dominating over the surface.

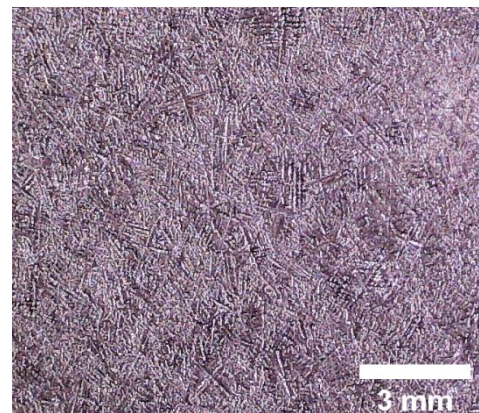


Fig. 4 Solidified melt Pb:Sn in ratio 60:40 ((POK40).

A picture of the solidified Sn is presented in Fig. 5. The structure looks very much lamellar. The surface color of the structure is nearly yellow at the solidification, which certainly indicates that a thin layer of SnO is covering the surface upon the oxidation.

For several minutes after exposure on air, just above the melting point, the surface obtains this specific yellow color. At the temperatures above 573 K, the color is changed to blue. This surface color changing is attributed to the transformation of SnO to SnO₂ at higher temperatures.

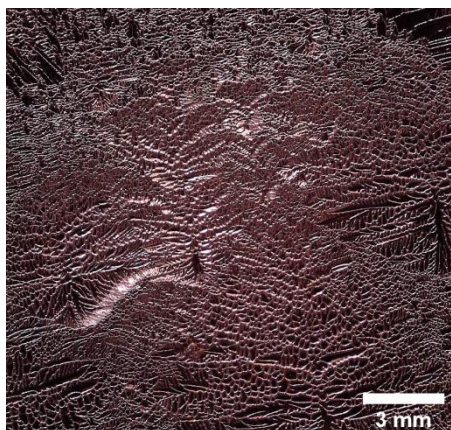


Fig. 5 Solidified Sn melt.

6. Conclusions

Based on the performed studies of the surface tension, we conclude that the proposed method of Wilhelmy plate is suitable for measurement of liquid metal surfaces even under non-equilibrium conditions. It is sensitive enough to be revealed the oxidation surface properties. We detected strong surface kinetics in Pb oxidation and the presence of oxidized Sn on the surface have the opposite stabilization effect.

The presence of PbO on the surface is acting toward reduction of surface tension in comparison with non-oxidized melt, while Sn oxides modify the surface tension in opposite direction, in comparison to the non-oxidized alloys. The significant Pb oxidation decrease the surface tension to become nearly the same as the surface tension of the pure Pb. The surface tension of the mixture Pb:Sn 40:60 became nearly at the same range as the pure Sn (See Fig. 2). The stabilization effects of oxidized Sn on the surface tension should be investigated in future.

7. References

1. L. L. Bircumshaw, Phil. Mag, **17**, 110, 181-191, (1934).
1. D. W. G. White, Metall. Trans. B, **2**, 3067–3071, (1971).
2. M. Kucharski M, Arch. HUTN., **2**, 22, 181-194, (1977).
3. K. Nogi, K. Oishi and K. Ogino, Mat. Trans., JIM, **20**, 2, 137-145, (1989).
4. W. Gasior, Z. Moser and J. Pstrus, J Phase Equilibria, **25**, 1, 20-25, (2001).
5. I. Kaban, S. Mhiaoui, W. Hoyer and J.-G. Gasser, J. Phys.: Condens. Matter, **17**, 7867–7873, (2005).
6. E. A. Brandes and G. B. Brook, *Smithells Metal Reference*, 7-th ed., Oxford: Butterworth–Heinmann, (1998).
7. Y. Xi, L.-J. Liu and Z.-H. Chen, Kovove Mater., **43**, 432-439, (2005).
8. Y. Kirshon, S. B. Shalom, M. Emuna, Y. Greenberg, J. Lee, G. Makov and E. Yahel, MDPI materials, **12**, 3999, (2019).
9. E. P. Loewen and A. T. Tokuhiko, J. of Nucl. Sci. and Technol, **40**, 8, 614–627, (2003).
10. J. R. Weeks, Nucl. Eng. Des., **15**, 363-72, (1971).
11. W. G. Gale and T. C. Totemeier, Eds., *Soldering and Bracing, in Smithells Metals Reference Book*, 8-th ed., Academic Press, 34-1-34-22, (2004),
12. J. A. V. Butler, Proc. Math. Phys. Eng. Sci., 348-375, (1932).
13. C. Maze and G. Burnet, Surf. Sci., **7**, 411-418, (1977).
14. W. Contributors, *Wilhelmy plate*, Wikipedia, The Free Encyclopedia, 19 December 2020. [Online]. Available:

- https://en.wikipedia.org/w/index.php?title=Wilhelmy_plate&ol did=989575010. (Accessed 2 February 2021).
15. An Avnet Company , <https://www.farnell.com>, 2019. [Online]. Available: <http://www.farnell.com/datasheets/315929.pdf>. (Accessed 23 Jan. 2021).
 16. A. Grigoriev, O. Shpurko, C. Steimer, P. S. Pershan, B. Ocko, M. Deutsch, L. Binhua, M. Meron, T. Graber and J. Gebhardt, Surf. Sci., **575**, 3, 225-232, (2005).
 17. E. Barreira, L. Pedrini, M. Boratto and L. Scalvi, Intl. J. of Modern Phys. B, **34**, 2050184-13p, (2020).
 18. J. Geurfs, S. Rau, W. Richter and F. J. Schmitt, Thin Solid Films, **121**, 3, 217-225, (1984).
 19. T. E. Weyand , *The oxidation kinetics of liquid lead and lead alloys*, University of Missouri--Rolla, (1970).
 20. K. Gladinez, K. Rosseel, J. Lim., A. Marino, G. Heynderickx and A. Aerts, Phys. Chem. Chem. Phys., **19**, 27593-27602, (2017).
 21. Y.-B. K. Kang, Calphad, **50**, 23-31, (2015).
 22. C. Basaran and R. Chandaroy, Appl. Math. Model., **22**, 601-627, (1998).
 23. P. T. Vianco, S. N. Burchett, M. K. Neilsen, D. A. Rejent and D. R. Frear, J. Elec. Mater., **28**, 1290-1298, (1999).

Post welding residual stress in P91 alloy steel

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Abstract: The chromium-molybdenum steel pipe P91 is widely used in the power plants construction, because they can withstand higher temperatures and operating pressures, in order to increase operating efficiency and output. This material has a complex microstructure which is extremely vulnerable to convert into Austenite form near the temperature for heat treatment. During the welding procedure should be very carefully, because otherwise the residual stress installed post welding will reach high values. A series of experimental studies was carried out, which has shown the development in the magnitude of transverse and longitudinal residual stresses and the values in both directions were determined. For but welded joints the residual stresses in the three direction were measured and the results are reported here. For measuring was used the hole drilling method through "measuring balls" or electrical strain gauge. Except the experiments the finite element method was used to determinate the value and the distribution of the residual stresses. The experimental and FEM results were compared between them and no discrepancy was found.

KEYWORDS: RESIDUAL STRESS, TRANSVERSE STRESS, LONGITUDINAL STRESS, TRANSVERSE WITHDRAWAL, STRESS DISTRIBUTION.

1. Introduction

The non-strictly metallurgical effects (deformations and tensions), produced by the execution of the welds, have been progressively analyzed and characterized since the 1940s, both on the basis of experimental tests and with the aid of mathematical models.

To date, it is important to know the mechanisms that govern their genesis in order to better manage manufacturing activities according to project expectations [1].

The properties of Grade 91 wholly depend on its chemical composition and microstructure. Welding P91 generally requires preheating the joint, maintaining interpass temperatures, hydrogen bakes, and postwelding heat treatment (PWHT).

The preheat temperature and interpass temperature was kept in the range of 200-250°C. The welding method used was GTAV with filler material ER90S-B9. In the figure 1, is shown the complete welding procedure.

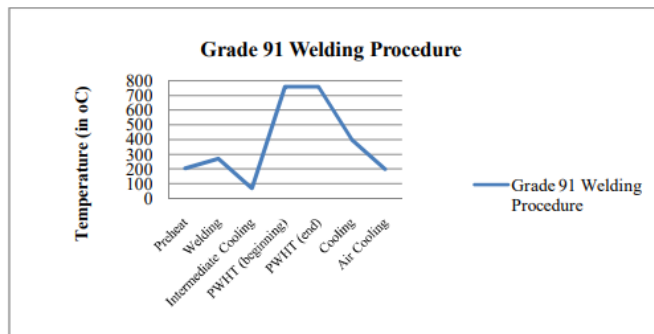


Figure 1. Welding procedure of a seamless pipe p91.

The figure 2 is shown the welding procedure for P91 pipe in site, during the preheating process.

Grade 91 Alloy Steel is a complex material to work upon. The most important and difficult task is to maintain its unique microstructure. Grade 91 is an upgrade to the regular Grade 22 alloy steel. In comparison with grade 22 alloy steel, following observations are made [2]:

- Reduction in wall thickness by two third; reduction in weight by 60%.
- Increase in allowable strength in 500 - 600°C range by 150%.
- Increase in oxidation limit by 40°C, enabling lower corrosion allowance.
- Increase in thermal fatigue life by a factor of 10-12.



Figure 2. Preheating procedure of a seamless pipe p91.

2. Experimental results for transverse withdrawal

The values that the transverse withdrawal can assume in the construction practice depend very much on the degree of constraint of the pieces, on the weight of the connected elements or they can also come from the use of assembly devices, specially designed to place the pieces in position and prevent deformations during and after welding. Establishing with precision the degree of constraint and then predicting the possible withdrawal on the basis of it, is often very difficult [3]. The values assumed by the withdrawal in the welded joints were determined by various experiments. For transverse withdrawal we will report some results taken from the experiments.

The diagram in figure 3, shows the variation of transverse withdrawal of butt-welded specimens with GTAV, as a function of the welding section and of the various thicknesses. It can be seen how the transverse withdrawal increases with the section of the weld, but much less rapidly, for greater thickness to be welded, it tends, however, to stabilize towards maximum values between 3 - 4 mm.

The diagram in figure 4, confirms the significant influence of the welding section, resulting from different shapes of the groove on the transverse withdrawal value. In the tests carried out with arc welding on a pipe with 14 mm of thickness, the X preparation determines a smaller withdrawal than the V one, and for each preparation the withdrawal is greater for more open angle of the bevel and for shorter distance between the edges.

Regarding the influence of executive factors on transversal withdrawal, it was found that this tends to increase with the number of passes [4]. In this regard, here below is shown the table 1, which includes the results of the experiments carried out. These results are for but welded specimens with thickness 14 mm, the V groove with angle of 90° and the distance between edges was 3 mm.

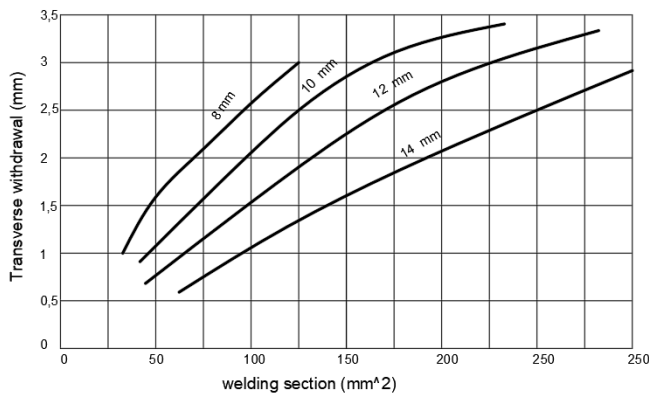


Figure 3. Transverse withdrawal of butt-welded specimens, as a function of the welding section and of the thicknesses.

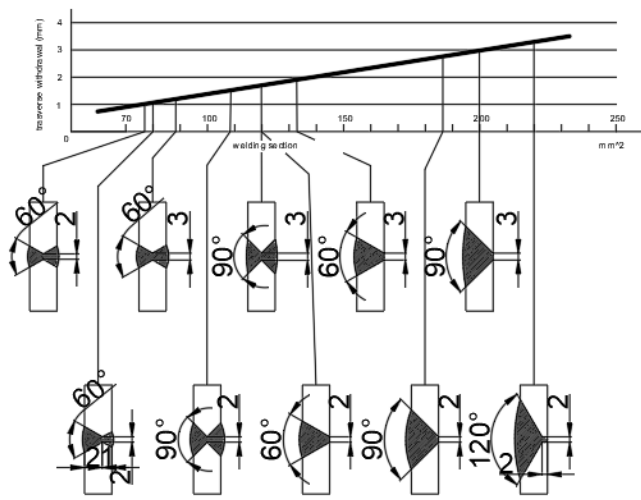


Figure 4. Transverse withdrawal of butt-welded specimens, as a function of the welding section.

Number of passes	Transverse withdrawal (mm)
6	3.15
8	3.45
10	4.10
12	4.35
15	4.55

Table 1. Transverse withdrawal of butt-welded specimens, as a function of the welding section.

The way each pass is performed also has some influence on the transversal withdrawal. In the case of arc welding, according to experiences made by Guyot, wide pass welding (with significant transversal movement of the electrode) produces a slightly greater transversal withdrawal than that with narrow passes side by side. Similarly, "step back" welding would produce a slightly less transversal withdrawal than continuous welding [5].

3. Transverse and longitudinal stresses in butt weld joints

The non-strictly metallurgical effects (deformations and tensions), produced by the execution of the welds, have been progressively analyzed and characterized since the 1940s, both on the basis of experimental tests and with the aid of mathematical models. Bierett and Granning made a series of theoretical-experimental studies that showed the development in the magnitude of residual

stresses in welding, both transverse and longitudinal in the butt welded joints and determined the values in both directions [6].

A lot of experiments were carried for different wall thickness. In the case of welding free samples without external constraints and therefore free to withdraw was found that for manual arc welding the distribution of stresses σ_L and σ_T is of the type indicated in the figures 5.

In a generic cross section x-x, figure 5, the trend of the longitudinal residual stresses indicated by the curve, shows that those stresses are in traction in the welded joint in the immediately adjacent area, and compression in the external areas.

The experiments have also shown that the distribution of longitudinal stresses is the same for all transversal sections, as indicated by the curve (blue color). From this it can be deduced that along a longitudinal plane y-y parallel to the axis of the joint and at a distance d from the axis itself, the σ_L remain constant and have a y value depending on the aforementioned distance d.

Figure 6 shows the distribution of transversal stresses (rotated 90° in their plane); from it, can be seen that these tensions, along the generic cross section, are always of the same direction (curves a and a'), and more precisely they are traction in the central part of the welded piece, while they become compression in the external areas. This is shown more evident in the curve b, which represents the distribution of the σ_T along a generic longitudinal section y-y.

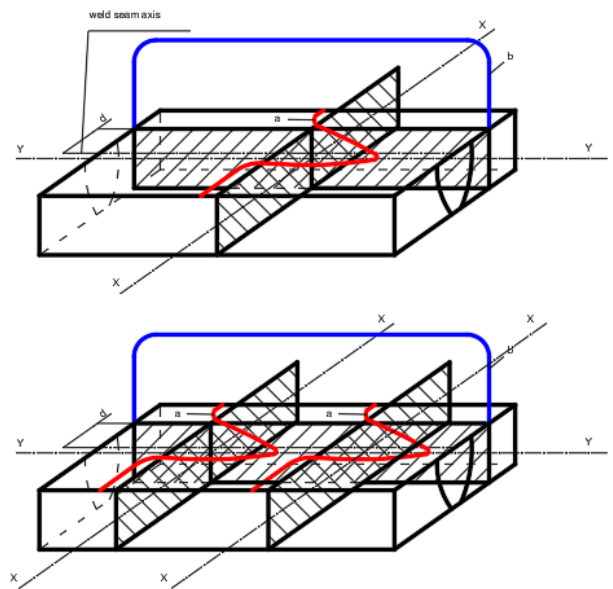


Figure 5. The distribution of the longitudinal stresses in the butt welding joint.

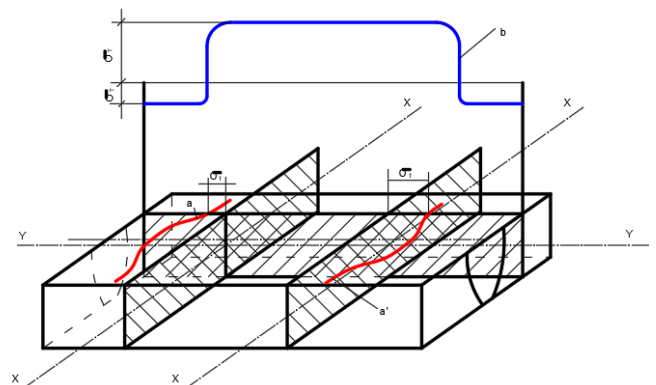


Figure 6. The distribution of transverse stresses in the butt welding joint for.

The distribution of residual stresses in a circumferential joint between pipes depends on the diameter and wall thickness of the pipe, the preparation and the welding sequence.

Strain gauge measurements were carried out on pipes with a diameter of 760 mm and a thickness of 11 mm, obtaining the transverse and longitudinal stress distribution as shown in Figure 7. The welding method used was GTAV with filler material ER90S-B9 [7].

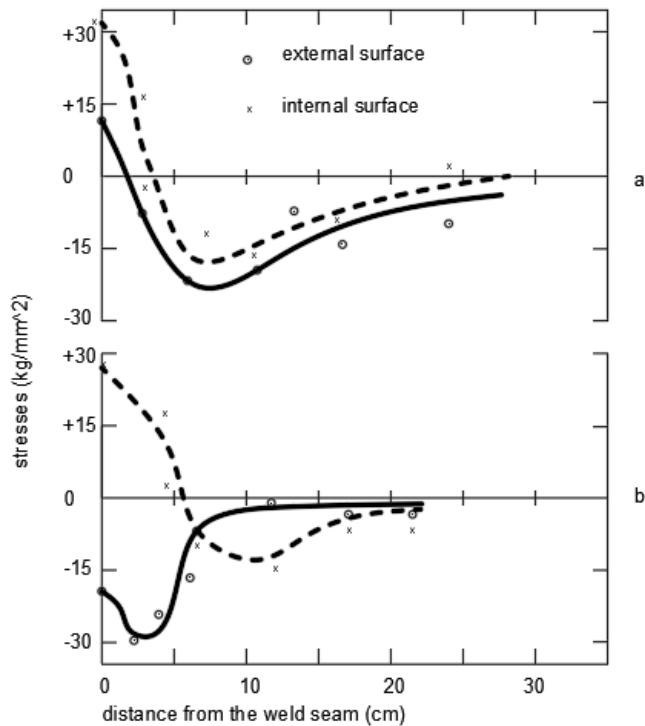


Figure 7. Longitudinal and transverse residual stress distribution

The trend of residual stresses was studied in the case of the pipes with a diameter of 250 mm and a thickness of 10 mm, with manual arc welding in the fixed position with horizontal axis. The results obtained are shown in the figure 8.

It appears clear that the higher states of stress, both for longitudinal residual stresses and for transverse stresses, occur on the internal surface and are in traction. An explanation of this could be given considering the different thermal gradients which during cooling affect the internal and external surfaces. Actually it has been experimentally verified that after the deposition of the last pass, during cooling, due to the greater heat exchange towards the outside, the internal wall was found in a temperature of about 80°C higher than the external wall, starting from temperatures (about 850°C - 900°C), below of which the differences in yield value are significant.

During the experiments were also analyzed the distribution of residual stresses along the thickness direction. In the case of welded pipes with a thickness greater than 10 mm, the residual stresses in the perpendicular direction can also become significant.

The figure 9 shows the distribution of residual stresses along the thickness direction in a butt joint, for chromium-molybdenum steel pipe P91, with X preparation, thickness 14 mm, diameter DN 1000 mm. The welding was executed with GTAV, alternately on both sides of the groove, in order to minimize distortion of the joint.

From the figure 9, it is noted that the longitudinal and transverse stresses are of traction in areas close to the sample surfaces. The transverse compression stresses, at the heart of the weld, are produced during the execution of the final filling passes of the groove.

In the figure 9.c is shown the distribution of the perpendicular residual stresses which vanishes at the two surfaces. Although this

distribution is compressive in the case shown here, other researchers consider that there may be states of tensile stress even within the welded thickness, particularly for high thicknesses.

Moreover the experiments a study was carried out with finite element theory based on a joint model as shown in the figure 10. This model represent the joint between two pipes [8].

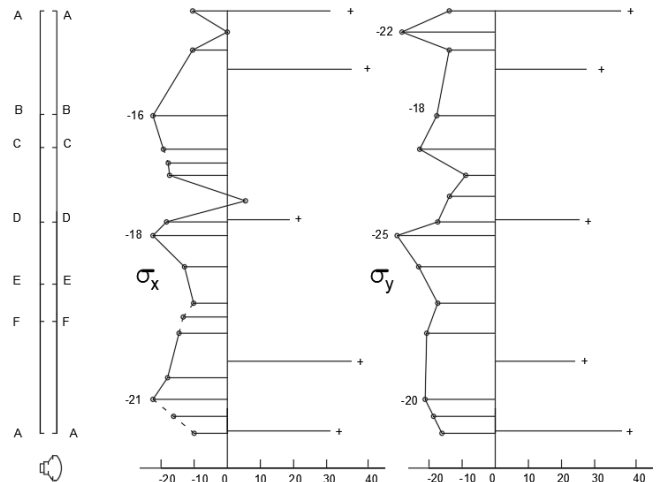


Figure 8. The trend of residual stresses.

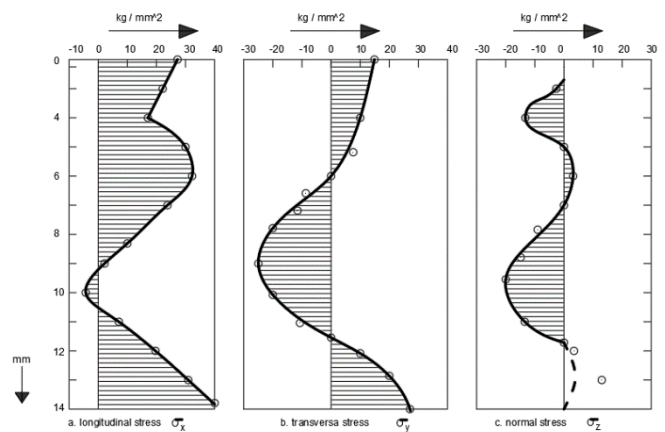


Figure 9. The distribution of the residual stress along the thickness direction in the butt welding joint.

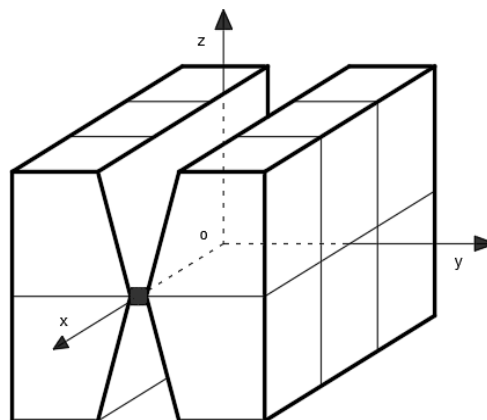


Figure 10. The model used for the FEM study.

The welding passes were deposited alternately on opposite sides of the groove in order to prevent angular distortion. It is a 9 Cr – 1 Mo steel and was welded with submerged arc procedure (50 kJ / cm) with similar filler material, and with a preheating of about 250°C. In the figure 11a and 11b are shown the residual longitudinal stresses in correspondence to various filling levels of the groove (inter pass temperature 250°C) respectively on the surface of the sample (in the direction normal to the axis of the bead) and in the direction of the thickness. These distributions were obtained with three-dimensional elastic-plastic finite element analysis.

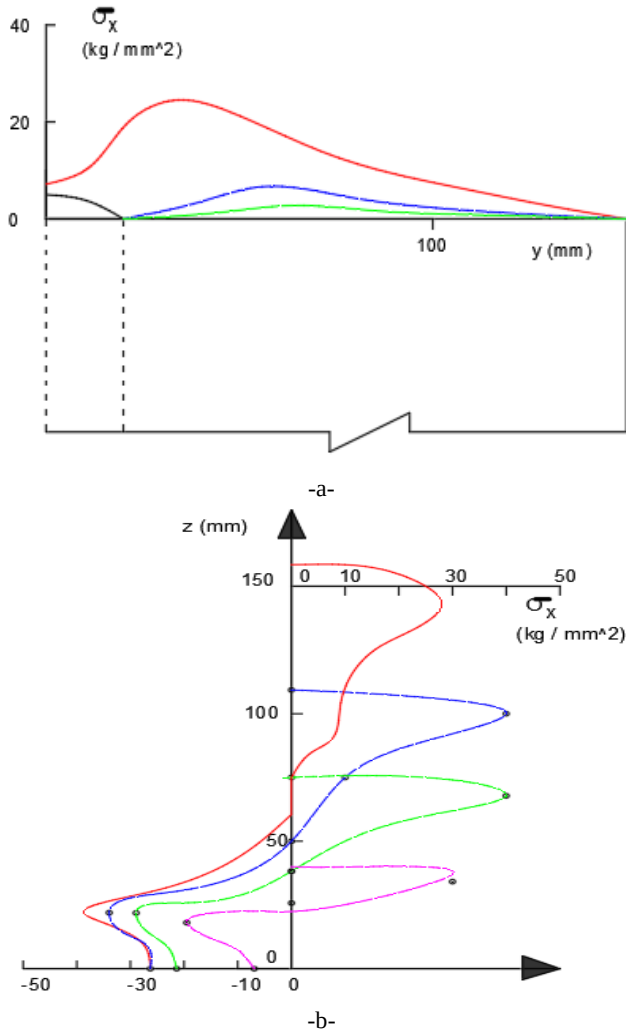


Figure 11a and 11b. Trend of residual longitudinal stresses as a function of different filling levels.

At the end of the welding, the distribution of the longitudinal residual stresses on the surface of the sample is shown in the figure 12a; it can be noted that the maximum value is displaced by about 20 mm with respect to the edge of the last pass. The figure 12b shows the distribution of the longitudinal residual stresses in the direction of the thickness at the axis of the bead and at two different distances from it. As shown in the figure 12, while at the external surface of the weld the residual longitudinal stresses are positive and of small entity, the highest value of these occurs at a certain depth, corresponding to some layers of passes.

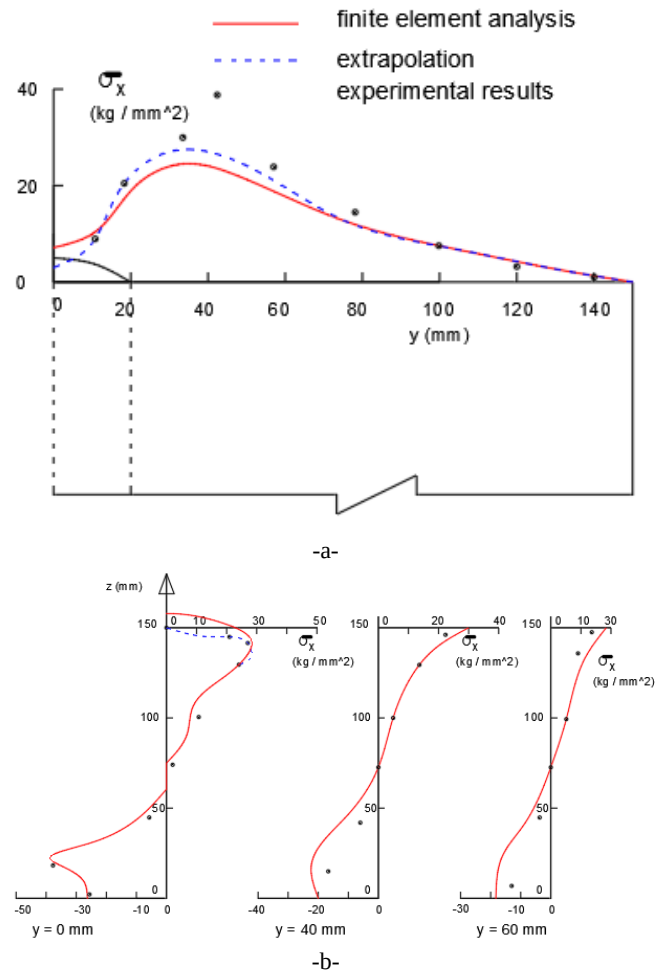


Figure 12a and 12b. Comparative distribution of stresses (experimental value vs values with FEM)

4. Method of measurement of residual stresses

4.1 The hole drilling method (basic method)

This is a method for the measurement of tri-axial stress states, based on experiments conducted by Mathar. The principle involves the execution of the holes in the thickness and the measurement of deformations in the radial direction, as shown in the figure 13, through "measuring balls" or electrical strain gauges straddling the hole itself [9].

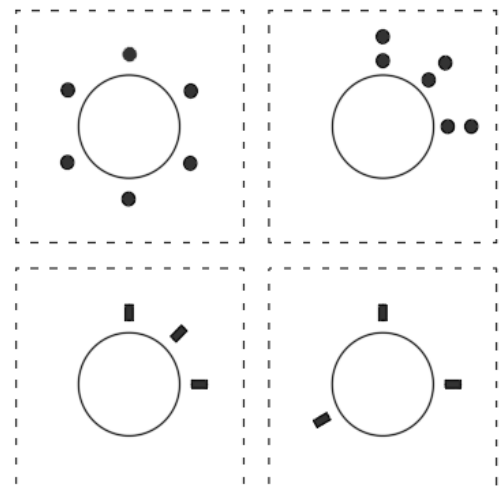


Figure 13. Application of "measuring balls" or strain gauges to measure radial deformations.

The method has been standardized by ASTM E 837-85.

Measured the deformations in the X and Y direction, it is possible to find the stresses σ_x and σ_y through the theory of elasticity applied to an infinitely thin plane, in which a circular hole is made, subject to a state of uniaxial tension. By substituting the data (diameter of the hole $d_0 = 12$ mm, measurement base $d = 16$ mm, $\nu = 0.3$) the stresses can be expressed as a function of the deformations Δx and Δy :

$$\sigma_x = E \left[0.99 * 2 \left(\frac{\Delta x}{d} \right) + 0.38 * 2 \left(\frac{\Delta y}{d} \right) \right]$$

$$\sigma_y = E \left[0.99 * 2 \left(\frac{\Delta y}{d} \right) + 0.38 * 2 \left(\frac{\Delta x}{d} \right) \right]$$

In order to express the radial deformation ε_r as a function of the stresses σ_x and σ_y , it is possible to introduce the parameters A and B, functions of the elastic characteristics of the material and of the geometry of the measurement system.

$$\varepsilon_r = (A + B \cos 2\beta) \sigma_x + (A - B \cos 2\beta) \sigma_y$$

Where:

$$A = - \frac{(1-\nu)}{2E \left(\frac{d_0}{d} \right)^2}$$

$$B = - \frac{(1+\nu)}{2E \left[\frac{4}{(1+\nu) \left(\frac{d_0}{d} \right)^2} - 3 \left(\frac{d_0}{d} \right)^4 \right]}$$

In the case of a state of biaxial residual stress of unknown direction, measurements made in at least three different directions are necessary (the relationships reported above do not take this general case into account). For this purpose, the method provides in its general version the use of strain gauge rosettes, as shown in figure 14, with the purpose of determining, in addition to the deformations, also the angle β between the direction of the main stress σ_1 and the direction of measurement σ_x .

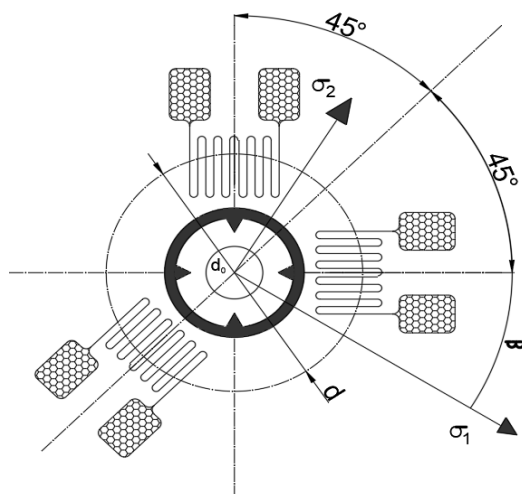


Figure 14. Application of "measuring balls" or strain gauges to measure radial deformations.

The angle β can be analytically expressed through the relationship:

$$\tan(2\beta) = \frac{(\varepsilon_{00} - 2\varepsilon_{45} + \varepsilon_{90})}{(\varepsilon_{00} - \varepsilon_{90})}$$

In general, the accuracy of the measurements depends, for this method, on the positioning of the measuring elements with respect to the hole. In the case of "measuring balls", they can be positioned at 1 mm from the edge, in that of strain gauges, at values between 2.5 and 3.4 of the d/d_0 ratio.

The diameter of the hole depends on the dimensions of the measuring elements (for example, the diameter d_0 equal to 1.5 - 3.0 mm and measurement bases equal to 1.5 mm are quite common).

It should be remembered that the method is based on models of elastic types, therefore the presence of stress states close to the yield point and/or the possibility of plastic-type deformations can false the results, providing absolutely unreliable results.

5. Results and discussion

In the distribution of transverse stresses it is noted that:

- Transverse stresses hardly exceed 100 N/mm² when welding with free withdrawal. With specimen embedded parallel to the welded joint, this value can be double.
- The maximum transverse stresses occur in a strip straddling the joint axis. They are positive (tension) in the central area and negative (compression) at a certain distance from the axis.
- The larger heating produces maximum values of transversal tension, a little less than those generated by a more restricted heating, in the case of free specimens. In the case of embedded test pieces, the opposite occurs, i.e. manual arc welding tends to cause transverse stresses lower than those of other mechanized processes. This is in harmony with the fact that the transverse withdrawal tends to increase with the width of the heated area, and therefore it is logical that the stress which represents the equivalent of the prevented deformation also tends to increase with it.
- The remote parts of the joint are generally compressed transversely. This distribution of transversal stresses is an advantage, because it can make the extremity defects (craters, disparity of shape, incompleteness, etc.) less dangerous. These kind of defects are much more frequent in the extremity than in the central areas.

In the distribution of the longitudinal stresses it is noted that:

- Longitudinal stresses, given that welding always takes place in conditions of strong self-constraint, tend to very high values and they easily can reach the elastic limit of the material and can consequently cause plastic deformations of the welded area.
- Manual arc welding produces maximum stresses higher than those caused by processes characterized by greater heat input. Often in both cases, but more frequently in the case of the manual arc, the elastic limit is exceeded.
- The welding area is tensed, while the lateral ones are compressed for the internal surface and it is all in compression for external surface of the pipe.
- The constraints which block the pieces parallel to the axis of the welding have no practical influence on the trend and on the value of the longitudinal tensions.

6. Conclusion

Grade 91 Alloy Steel is a complex material to be welded. The most important and difficult task is to maintain its unique microstructure. If the welding procedure is not done as per the specified guidelines given in the codes, the material properties can be ruined permanently. The conditions of failure and the methods to prevent them must be followed in order to ensure safe and successful hot working on the material without disturbing its microstructure. If the PWHT is carefully performed the material is relaxed and the residual stress are not relevant.

7. References

- [1] Francois M, Sprauel J.M, Dehan C.F, James M.R, Convert F, Lu J, Lebrun J.L, Ji N and Hendricks R.W, "Handbook of measurement of residual stresses", Liburn, Ga, Society For Experimental Mechanics, 1996, pp 71 -13.
- [2] Henry Jeffrey F, "Growing experience with P91/T91 forcing essential code changes", Alstom Power Inc and ASME Task group, Industry Alert, Combined Cycle Journal, 2005.
- [3] D. Camilleri, T Comleci and T.G.F Gray, "Journal of strain analysis for Engineering design", 2005, pp 161-176.
- [4] "Tensioni e deformazioni in saldatura", Istituto Italiano della Saldatura.
- [5] Mochizuki, M., Hayashi, M., Hattori T. "Residual stress distribution depending on welding sequence in multi-pass welded joints with Xshaped groove", International Journal of Pressure Vessels and Piping, 2000, pp 98-103.
- [6] Withers P.J and Bhadeshia H.K, "Residual stress, Nature, origins and measurements", 2001, pp 70-96.
- [7] ASME Section IIC, "Specifications for Welding rods, Electrodes and Filler Metals", 2004
- [8] Schajer, G.S, "Application of finite element calculations to residual stress measurements", ASME J. Eng Matr. Techno, 103(2), 1981.
- [9] Rendler N.I and I.Vigness, "Hole - drilling strain – gauge method of measuring residual stresses", 1996, Proc SESA XXIII, No 2, pp 577-586.

Assessment of toxic gas emissions from flammable building thermal insulation materials upon fire conditions

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Abstract: Smoke generated during a fire is a serious danger to people as a result of reduced air visibility, high temperature, toxicity and reduced oxygen content. In regard to victims, the inhalation of a mixture of toxic gases, which are formed as products of combustion, plays a key role. In the conditions of modern construction, and in order to improve energy efficiency in the buildings' construction, various insulating materials are used. Along with the advantages of good insulation, there are also dangers from the behavior of insulating materials in an event of fire. The purpose of the present study is to assess the hazards and to study the composition of the gas mixture released during the combustion of various thermal insulating materials: glass wool, stone wool; expanded polystyrene; extruded polystyrene.

Keywords: INSULATING MATERIALS, RISK IN CASE OF FIRE, CONSTRUCTION SAFETY

1. Introduction

The problem of sustainable building construction is a hot topic in the contemporary construction industry. This is a well-established practice in industrial developed countries with strong regulatory bases. Moreover, the problem addresses the so-called *green future* where safety, low-toxic materials and renewable material should applied in house constructions. The construction industry based on the green ideology avoids excessive use of material energy and raw materials, and refers to utilization of products or environmentally friendly or recyclable elements produced by green technologies. This approach allows buildings with comfortable living conditions to be created as well as low cost and safe maintenance there off. In Bulgaria, this approach is implemented slowly step-by-step by the construction industry mainly from the point of view related to long time investments in environmentally friendly and low energy consuming multi-family residential buildings. In this context, the idea is supported by a special program devoted to energy efficiency of multi-family buildings addressing desire levels of thermal comforts and living conditions.

The main task of the sustainable construction industry is the reduction of building effects on the environment during the entire life cycle combined with optimal economic efficiency and engineering quality at the design stage. Actually, this involves the best known practices in the design, practical implantations of new projects and effective reconstructions of old buildings [10]. The *green construction industry* approach promises acceptable living conditions upon continuously decreasing amounts of material resources, increasing effects of climatic changes as well as the demand of safety approach to the environments.

One of the principle criterion in the assessment of building energy efficiency is the quality of external thermal insulation. [11]. The quality of the thermal barrier depends on the applied materials which actually reduce the energy loses through building walls [8]. The insulation materials widely encountered in the building thermal insulations are mainly Rockwool, glass wool, expanded (EPS) or extruded (XPS) polystyrene.

The green construction industry encompasses a wide spectrum of techniques and technologies with the final goal envisaging the reduced effect of the new building on the environment and the quality of human life and health.

2. Applications of thermal insulations in the construction industry

The task to attain more comfortable living conditions with the help of the modern constructions technologies is reasonable in the modern era where the quality of the human life and health are primary goals [6]. The creation of comfortable thermal conditions by application of suitable insulation strongly depends on the adequate selection of materials used [1]. The insulation layers

deposited on the external building wall yields several benefits, among them:

- Reduces the energy required to achieve the desired thermal comfort in both the summer and winter conditions.
- Reduces the possibility to formation of surface layers of condensed water and consequent increase in the moisture of the walls ;
- The suitable color of the insulating panels allows building facades to be more acceptable from aesthetic point of view as well as the exploitation life of the complete thermal insulation to be extended as much as possible.

Moreover, the extremal thermal insulation allows the thermal bridges mainly appearing at the joints of wall building elements to be cancelled, which actually reduces the thermal losses from the building to the environment. It is worthy to mention here that when internal thermal insulation is applied such effects cannot be attained [15, 19]. The insulation of internal side of the wall allows higher moisture content of the air to be maintained which results in appearance of fungi. In addition, the external thermal insulation does not reduce the size of the rooms.

3. Characteristics of principle insulation materials

The principle characteristics defining the applicability of the insulating materials are: good thermal insulating properties, acceptable sound insulation, resistance upon direct fire, impermeable for moisture, passive ventilation, low mechanic deformation upon fire conditions, mechanical stability and resistance upon compression [15-18]. The main characteristic allowing adequate choice of suitable insulating material are: adequate size of the panels, density, heat conductivity, moisture and vapor permeability, the class of flammability, aging reissuance, etc. [17, 18].

Table 1. Advantages and disadvantages of the Rockwool

Advantages	Disadvantages
Good thermal insulation properties;	Reduced insulation properties with increase in the moisture content;
No destruction due to biological destruction (wet rot);	Production technology with high energy demand and high production cost;
Easy to be treated;	There are some organic components;
Permeable for water vapors (breathing walls);	There are emissions of fibers dangerous for the human health;
Inflammable. Resistant to fungi and insects;	Dangerous when are used as internal thermal insulations due to

There are enough raw deposits; Allow to be stored in depots of recyclable materials. With characteristics which do not vary upon hot climates.	possible release of short fibers.
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Table 2. Advantages and disadvantage of insulations based on EPS and XPS

	Advantages	Disadvantages
EPS insulation	- Good, acceptable thermal insulation properties; • Easy mechanical operations; • Low cost materials; • Resistance to moisture ingress; • There are no biological destructions (wet rot); • No risks to the human health exist since there are micro elements released in the environmental air.	• High energy demand in the manufacturing; • Dangerous and toxic emission in the manufacturing; • Dense smoke release with unburnt materials upon fire; • Limited material resources for manufacturing; • Unstable upon UV radiation; • Low diffusivity of moisture; • Ability thermal bridges to be created due to shrinking of EPS plates and voids formations.
XPS insulation	• High resistance upon compression; • There is no risk for the human health; • Resistible to moisture ingress; • Resistible to property changes due to aging; • There is no biological destruction (wet rot).	• High energy demand for manufacturing and consequent mechanical treatment; • Toxic gas release during the manufacturing; • Dense smoke and toxic gas release upon fire conditions; • Unstable upon UV radiation.

In the same time the benefits of thermal insulations of buildings should be considered parallel to their fire behaviors (fig.1). The practice provides facts showing that these materials can cause severe damages, mainly related to the fire extinction methods used. [11-13]. The danger upon fire related to a given material depends on a variety of properties which manifest themselves only when the material is burning. [9]. Some of these properties:

- *Flammability (ability to ignite);*
- *Rate of fire flame speeding;*
- *Smoke release ;*
- *Molten drop release ;*
- *Burning particles release;*
- *Amount of heat release Топлинна енергия;*
- *Toxic gas release.*

Resistance upon fire: This is a feature of construction materials and building constructions related to their ability to maintain unchangeable properties upon high thermal load in fire. The limit of the **fire resistance** of a certain material is defined as the time required the material to maintain its initial mechanical stability and the stability of the mechanical construction where it is involved as well as its thermal insulating [16, 19, 21].

Flammability (classification upon direct fire action): The flammability is characterized by the material behavior upon fire [19, 21]. The principle criterion allowing assessment of the material contribution to the fire spreading is the class when there is a direct access of open fire to the material. [1, 14].

Smoke: The smoke is a multiphase system containing toxic gases, unburnt particles, unburnt carbon, smoldering particles and liquid (water) droplets. The larger particles make the smoke visible with various colors but mainly black or gray [17, 19, 22, 23].



Fig. 1. Fire in a residential building in Sofia, housing estate Mladost 3, covered with thermal insulated panels

Smoke generation: The material classification depends on the intensity of smoke generation: **class s1** is with significantly reduced smoke release; **class s2** with moderate reduced and **class s3** when there are no restricting conditions with respect to the amount of smoke released upon fire [16, 19, 22, 23].

Formation of burning droplets: The formation of burning liquid droplets is mainly related to formation of melting components in the material since they can created hot spots or to be entrained the air flow thus creating new spots for fire ignition when flammable material are met. From this point of view the material classification is: **class d0** when there is no formation of burning particles are droplets; **class d1** when burning particles and droplets are rereleased but with short time extinctions; class d2 when there are no restrictions with respect to the amount burning particles and droplets released by fire exist [1, 16,19].

Toxicity of the burning gases: The smoke with all its characteristics is one of the reasons causing death to humans upon fire. The analysis reveals that high mortalities are result of toxic gases from the burning materials since the main cause of death is by poisoning [2].

4. Experimental

4.1. Materials tested

The study considered the following thermal materials for the fire tests performed (see Figs. 2-5):

- Rockwool (Fig.3)
- Glass wool (Fig.2)
- Polystyrene (or Polystyrol), XPS (Fig.4)
- Expanded polystyrene (EPS) (Fig.5)

4.2. Experimental set-ups

The experiments were performed in set-ups scaled as 1:40 (corresponding to 8 floors housing estate) made from 4 types of insulating materials. After the ignition, the sample surfaces where monitored by a thermovision camera. This allowed detecting the lowest temperature as well the rapidly changing one (theses data are not reported here.



Fig.2. Sample covered by glass wool



Fig. 3. Sample covered by rock wool



Fig. 4. Sample covered by EPS



Fig. 5. Sample covered by XPS

4.3. Combustion gas monitoring

The combustion gases released by the insulation materials tested were monitored for CO, CO₂, NO₂, SO₂, H₂ and O₂ by help of two multi-channel gas analyzers: ALTAIR 5X and Altair 4XR COMB/O₂/CO/NO₂ shown in Fig.6.



Fig.6. ALTAIR gas analyzers used in the tests

5. Results

5.1. Glass wool tests

It is well that the glass wall has a high thermal resistance and is inflammable. The experimental results reveal practically inflammability and smoke release with principle content of CO, SO₂, NO₂, H₂, CO₂ and O₂. The concentration of CO₂ is the higher in the combustion gases, followed by O₂ and CO. These data are shiowen in Fig.7 and Fig.8.

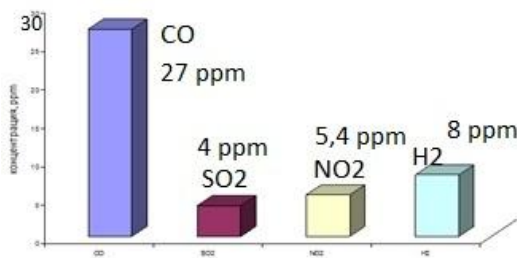


Fig.7. Concentration of CO, SO₂, NO₂ and H₂ in combustion gases of glass wool (in ppm)

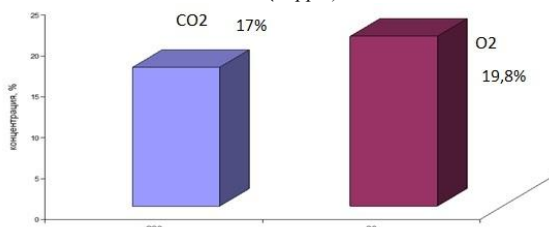


Fig.8. Concentration of CO₂ and O₂ (in percents) in combustion gases of glass wool

5.2. Rockwool tests

The general characteristic of the rock wool is that it is inflammable and does not allow fire spreading across the insulated

walls without toxic gas release [17, 19, 21]. The tests performed confirm the inflammability feature but it contradicted that it prevents the fire spread without toxic gas release. The data recorded by the gas analyzers are shown in Fig.9 and Fig. 10.

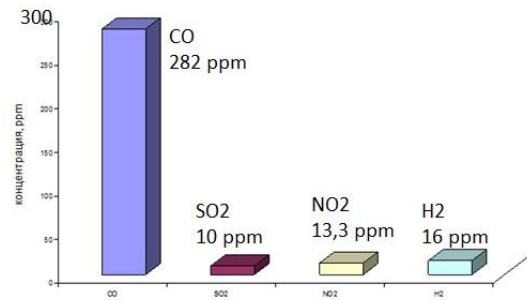


Fig. 9. Concentration (ppm) of CO, SO₂, NO₂ and H₂ release by rockwool samples

The results obtained are a little bit surprising taking into account the common information about the rockwool content: vulcanic rocks and native CaCO₃. After the removal of floor of the tested set-up irt was detected enormous smoke release. The gas detector recordered concentration of caarbon oxided 282 ppm. The xternal surface of the set-up remained unchanged except the point where the ignition ws initiated. However, the internal parts of the set-up was partially burnt (see Fig.11). The working hypothesis explained these facts by the rockwool permeability with respect to water vapors. To some extent, the low amount of oxygen in the closed volume of the set-up allows in the inernal temperature tio increase thus resulting in enormous gas emissions

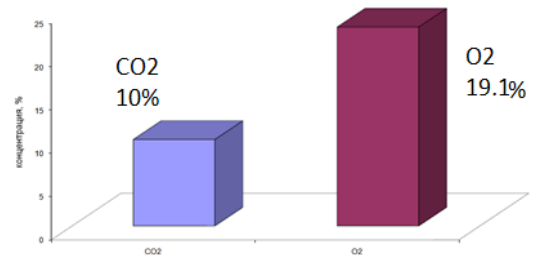


Fig.10. Concentration (%) of CO₂ and O₂ released by rockwool.



Fig.11. The area at the rockwool surface around the ignition spot (left) and the internal set-up area (right)

5.3. EPS tests

EPS is a flammable polymer and consequently the set-up covered by it was easily ignited. The concentrations of the combustions gases are shown in Fig.12. The highest gas concentrations were detected about CO, CO₂ and O₂. Duiring the set-up burning there was a enormous release of solid particles as soot. The concentration (in %) of CO₂ and O₂ in the combustion gases of EPS are 22% and 17% correspondingly.

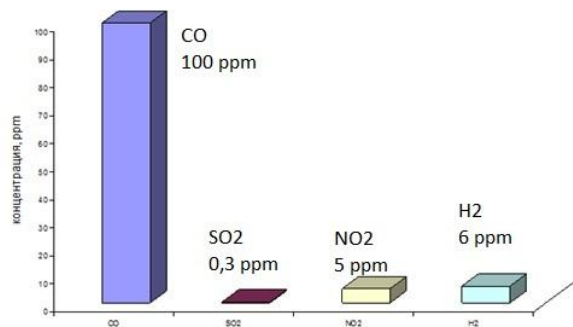


Fig.12. Concentration (ppm) of CO, SO₂, NO₂ and H₂ in the combustion gas of EPS

5.4. XPS tests

The extruded polystyrene is based on the same polymer as the expanded counterpart but with different technology of manufacturing. The experiment performed reveal easy XPS (easier with respect to or EPS) but followed by a rapid burning and much more dense smoke release (gases and solids). The visibility around the set-up was low due to existence of soot and high volatile compounds. The gas detector recorded high concentrations of CO, CO₂ and NO₂ (Fig. 13). The concentrations (%) of CO₂ and O₂ in the combustion gases of EPS was 23% and 16,6 %, accordingly.

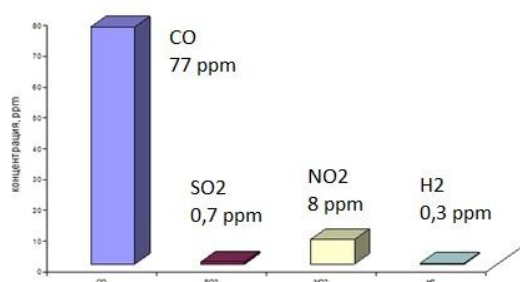


Fig. 13. Concentration (ppm) of CO, SO₂, NO₂ and H₂ in the combustion gases of XPS

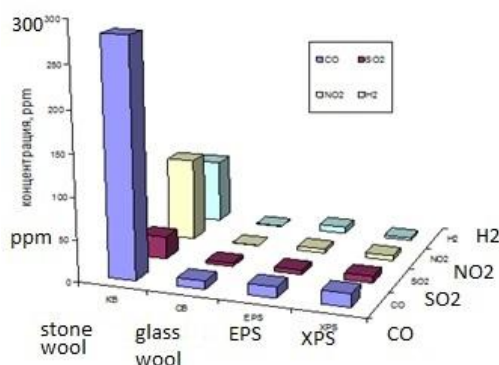


Fig.14. Comparison of the concentrations (ppm) of CO, SO₂, NO₂ and H₂ in the combustion gases of rockwool, galss wool, EPS and XPS.

6. Brief comments

The experiments carried out and the results obtained (Fig. 14) reveal that the practically inflammable thermal insulation materials as the rockwool and glass wool actually release toxic gases during the combustion process. The data indicate that there is a need of more deep investigation of the observed phenomena in order to understand the origins of the release combustion products.

The use of the information obtained for further identification of probable fire accidents could help the assessment of the components of the situations and the corresponding risk managements. In this context, it is important to assess the risk magnitude and its accessible level related to prescribed norms in regulatory documents [7, 8]. The risk assessment uses various quantitative and qualitative methods continuously in time by detecting the potentially dangerous events.

The approach suitable to analyze the risk consists of some steps, among them:

- Identification of available thermal insulating materials and areas of the housing estate external surfaces (facades) allowing easily development of fires.
- Identification of the sources of ignition;
- Assessments of the probabilities fires to be developed with selected thermal insulating materials;
- Determination and assessment of the adequacy of the fire protection measure carried out;
- Solution about preventing fire actions or managements of the particular situations in order to minimize the risks of ignitions and fire developments [7, 8].

7. Conclusions

In the last decades both the economics and society focus the attention on the sustainable development in the future centuries. The increase in the living conditions and house comfort go parallel with improvement the occupational safety issues. In Bulgaria there are about 80 000 multi-house estates with about 700 000 apartments inhabited by approximately 2 000 000 citizens which demand urgent renovations and augmentation of the thermal insulation conditions directly related to life comfort. The civil engineers, constructors and architects as well all domestic administration should re-arrange both the practice and regulatory documents in order innovative technologies to be applied. Irrespective of the type of material utilized for the external thermal insulation of the facades all technical parameter required by the domestic and European standards should be obeyed. In this context, the toxicity of the insulation of the material of the insulation panels is of primary important in order to reduce the risk upon accidental fire. The literature analysis reveals that the thermal insulation materials, discussed in this communication have been investigated in conditions where direct flame contact upon fire has been applied. Moreover there are data reporting the compositions of the combustion gases. In this context the experimental data reported indicate that the rockwool, irrespective of its mineral composition, the combustion gases contain the highest amounts of CO, NO₂, SO₂ and oxygen. The good understanding of the fire behavior of Fig. 13. Concentration (ppm) of CO, SO₂, NO₂ and H₂ in the combustion gases of XPS.

Acknowledgement

The financial support of Scientific Program, funded by the University of Mining and Geology "St. Ivan Rilski", Contract MTF/175/2020 Sofia is highly acknowledged.

The experiments were performed in the laboratory „F PLUS“.

8. References

1. Order I3-1971/29.10.2009 about the construction 3a rules and norms assuring fire safety (in Bulgarian)
2. Tv. Tsenov, Building materials upon fire conditions (2015), (in Bulgarian)
3. S. Dimitrov, Fire resistance of construction materials. Real behavior, methods and factors (presentation in Bulgarian)
4. T. Popov, M. Mavrova-Gerginova, Yu. Valchanova, Zh. Zhelev, Hadbook for risk assessment and required contents of the expert reports about the risky objects, Sofia, (2008) (in Bulgarian)
5. Zh. Balgaranova, A. Petkov, (Балгаранова Ж, Петков) A. Instruction manual for risk assessment in large accidents, Univ. Chem.Technol. Metall., Sofia, (2005) (in Bulgarian).

6. I. Todorov et al. Fire resistance and fire protection in the construction industry, Sofia (1998) (in Bulgarian)
7. S. Parvanov, S. Arabadzhieva, Hazards identification, risk assessment and preventive measures at specific sites, Scientific conference with international participation STEMEDU-2020, Veliko Tarnovo, (2020)
8. S. Parvanov, S. Arabadzhieva. On the significance of mathematical methods for assessing the risk of major industrial accidents, Mathematics and education in mathematics, 2019 Proceedings of the Forty-eighth Spring Conference of the Union of Bulgarian Mathematicians Borovetz, April 1–5, (2019)
9. Z. Dinchev, N. Kostadinova, E. Vlasheva: Adjustment of mining ventilation software for civil objects, *Journal of mining and geological sciences*, Vol. 60, Part II, Mining, Technology and Mineral Processing, (2017)
10. T. Hristova, The need to introduce $tg\delta$ as a criterion for assessing the quality of insulation material for high-operating temperature pipelines – (Необходимостта от въвеждане на $tg\delta$ като критерий за оценка на качеството на изолационните материали за топлопроводи), *Bulgarian Journal for Engineering Design BJED*, issue 30, October, (2016), pages 43-50, ISSN 1313-7530
11. M. Michailov, A. Krilchev, B. Vladkova, B. Dimova, Forschung eines neues Mittels zur Profilaktik und Löschen von endogenen Bränden, *Zeitschrift Bergbau*, 3/2011, Germany, ISSN 0342-5681, pp.114-118, (2011)
12. A. Krilchev, Risk management in endogenic fires of bulk materials in storage facilities, University of Mining and Geology “St. Ivan Rilski”, Sofia, (2013)
13. A. Krilchev, 90 microwave smoke test, in: 7th conference on civil safety, University of Mining and Geology “St. Ivan Rilski”, Sofia, (2014)
14. A. Hofmann, S. Kaudelka, S. Hauswaldt: Fire safety of FAÇADES with polystyrene foam insulation in: Conference: Interflam 2016 At: London, Royal Holloway College Volume: 2, July, (2016)
15. D. Spasov, B.K. Rozanov, Actual problems in the testing procedures defining the limits of fire resistances of building elements, *NPNIPAB*, issue 15, (2000)
16. D. Spasov, D. Doikov, Foamed polyurethane and its fire behavior, *NPNIPAB NTU*, issue 16, (2004)
17. D. Spasov, Tests and classifications of the products in the construction industry in accordance with the European regulatory norms, In: Expert workshop on fire safety in construction industry, (2010)
18. D. Spasov, B.K. Rozanov, A method for flammability testing of elements in the construction industries, Scientific and technical collection by Scientifically applied institute of fire safety and protection of the population, (1999)
19. D. Spasov, E. Hlerbarova, Fire reaction of materials, tests, classifications and regulatory base. *SOS 112*, issue 5, (2010)
20. D. Spasov, E. Hlerbarova, The basis of the assessment of the products in the construction industry and related documents assuring the required fire protection measures and characteristics, *SOS 112*, 8, (2010)
21. D. Spasov, E. Hlerbarova, Direct application of the fire behavior classification related to construction industry products, *Safety and Occupational medicine*, 5, (2011)
22. D. Spasov, D. Doikov, K. Ninova, Studies on the toxicity of combustion gases upon fires and methods for analyzes, Scientific and technical collection by Scientifically applied institute of fire safety and protection of the population, (2006)
23. D. Spasov, D. Doikov, K. Ninova, Studies on the smoke formation in fire behavior of polymers and liquid organic materials, Scientifically applied institute of fire safety and rescue, Scientific and technical collection 20, (2008)

Magnetism in 2D van der Waals halide VI_3

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Abstract: Magnetic van der Waals (vdW) materials composed of two-dimensional (2D) layers bonded to one another through weak interactions exhibit promising potentials for high-tech magnetic, magneto-electric, and magneto-optic applications in nanostructures. Due to their intrinsic magnetocrystalline anisotropy, several vdW magnets could be thinned down to nanoscale thickness, while still maintaining magnetism. Prominent examples of such materials are transition metal trihalides, in particular CrI_3 , a first atomically thin ferromagnet, realized in 2017.

Recently, VI_3 has been found to belong among 2D ferromagnets at temperatures below 50K. It is a semiconductor undergoing a subtle structural phase transition at 78K. Furthermore, its magnetic anisotropy exhibits rather unusual features. We have studied its properties by first principles calculations and reproduced the unusual magnetic anisotropy. Its properties have been linked to lattice distortions present at some of its low temperature phases.

Keywords: NANOMATERIALS, 2D MAGNETISM, VAN DER WAALS SYSTEMS, FIRST PRINCIPLES CALCULATIONS

1. Introduction

Van der Waals (vdW) crystals are fascinating materials with physical properties tuneable by varying the material thickness. Such lattice arrangement is predestined to exhibit complex magnetic structures with strongly anisotropic behaviour [1]. The early works in this field have mainly focused on creating of magnetism in nonmagnetic 2D materials through various approaches, including defect implementation, surface functionalization, and doping control. In contrast, in vdW halides of the compositions MX_2 and MX_3 where M is a transition metal cation and X is a halogen anion, magnetism is naturally incorporated by choosing a transition metal with a partially filled d-shell [2]. Up to only 3 years ago the possibility to create a monolayer 2D ferromagnet with nanoscale thickness was doubted, until first such case was discovered in a vdW halide CrI_3 [3]. The key to this success was its intrinsic magnetocrystalline anisotropy. The fundamental benefit is the richness of the transition metal halides family in which low dimensional magnetism can be examined and systematically investigated theoretically.

The possible appearance of ferromagnetism in 2D materials as well as their rich electrical and optical properties create opportunities not only for applications but for fundamental science discoveries like low-temperature quantum phenomena [4]. Current vdW materials exhibit various exotic physical properties, such as enhanced direct-gap semiconductors in monolayer MoS_2 , Ising superconductivity in ion-gated superconductivity MoS_2 and atomic layer NbSe_2 , robust in-plane ferroelectricity in atomic-thick SnTe , and complex magnetic interactions [5]. Mermin-Wagner theorem shows that the long-range 2D magnetic order is strongly suppressed above zero temperature for the isotropic Heisenberg model because the fluctuation is so strong that it destroys the spontaneous symmetry breaking immediately. But when magnetic anisotropy is included, the 2D ferromagnetism can be stabilized. It has just recently been realized in monolayer $\text{Cr}_2\text{Ge}_2\text{Te}_6$ [5] and CrI_3 [3].

Let us note that in the case of CrI_3 the t_{2g} triplet is fully occupied and orbital momentum is quenched. Therefore it is interesting to replace Cr by V having one electron less. Bulk VI_3 single crystals have been prepared recently. Information about the crystal structure at low temperatures has been contradictory in the beginning. The observed structures included trigonal $R\bar{3}$ [6] (similarly to CrI_3), $C2/c$ [7], while other works reported inconclusive data [8]. After a significant experimental work it was concluded that the system orders in the trigonal $R\bar{3}$ structure above the temperature T_s * [9]. At this temperature the system undergoes a monoclinic distortion. However, parameters of the monoclinic phase differ only slightly from the $R\bar{3}$ phase and they are therefore difficult to distinguish. Another structure transition takes place at 32 K [9], this time into a triclinic variant whose parameters are not known yet.

By applying hydrostatic pressure, the ferromagnetic transition moves to higher temperatures up to 99 K at 7.3 GPa. In contrast, the low-temperature bulk magnetization is significantly reduced by applying pressure (by more than 50% at 2.5 GPa) suggesting a possible pressure-induced reduction of vanadium magnetic moment [10].

Existing theoretical works predict magnetic anisotropy with a strong uniaxial component corresponding to the out-of-plane easy magnetization axis for VI_3 [11], similarly to the case of CrI_3 [12]. These studies have however assumed always the more simple $R\bar{3}$ structure. Current experiments predict perpendicular-to-plane easy axis (c axis) in works where only perpendicular and in-plane magnetizations were considered [7]. Studies of full angular dependence have shown a more unusual picture of MAE [13,14] with easy axis tilted about 40 deg from the c axis. In order to explain this discrepancy between experiment and theory we have examined whether the predicted easy axis direction is affected by the monoclinic distortion described above.

2. Results

Deeper understanding of the measured results is possible due to first principles calculation methods. Therefore the problem has been studied by the density functional theory (DFT) calculations employing the local spin-density approximation (LSDA), based on the full-potential linear augmented plane wave (FP-LAPW) method, as implemented in the band structure program ELK [15]. Spin-orbit coupling has been included in the calculation. The full Brillouin zone has been sampled by about 8000 k-points. For magnetic anisotropy calculations an increased accuracy of expansion into spherical harmonics has been used with $l_{\text{max}}=14$. Initial calculations were performed for the $R\bar{3}$ structure.

Since there were already indications that the material is a Mott insulator, we have also studied the effect of electron-electron correlations included in terms of the Hubbard correction term U acting on 3d electrons of V. In Figs. 1-2 we present densities of states for the cases with $U = 0$ and $U = 3.8$ eV, respectively. Notably the presence of U leads to opening of a gap between the conduction and valence band with a magnitude about 0.6 eV. Similar behavior can be seen in band structures (Figs. 3-4). Note the two rather flat separated bands above the Fermi level (Fig. 4), which correspond to minority spin e_g states. Since our aim was to study the effect of distortion, the modified structure has been included approximately in a repeated calculation. This does not lead to a significant change of the DOS visible by eye.

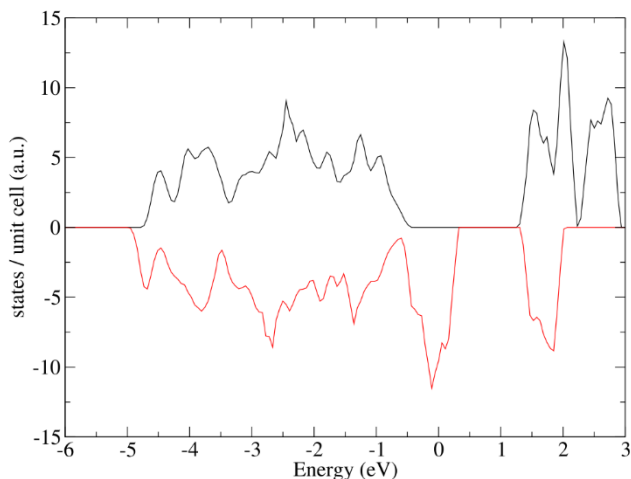


Fig. 1 VI_3 density of states calculated with $U=0$ eV.

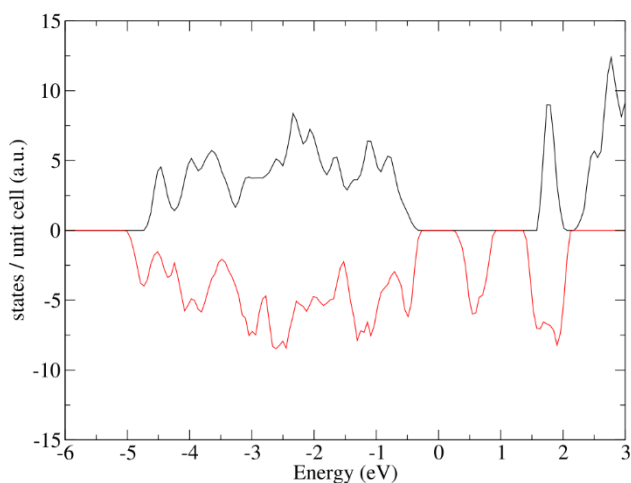


Fig. 2 VI_3 density of states calculated with $U=3.8$ eV.

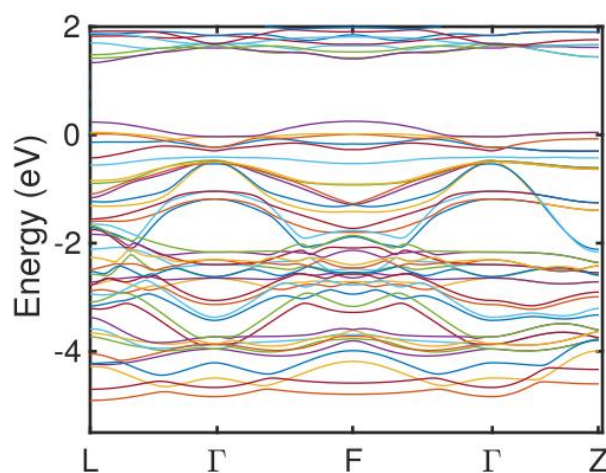


Fig. 3 VI_3 electronic band structure calculated with $U=0$ eV along the high-symmetry paths of the corresponding Brillouin zones.

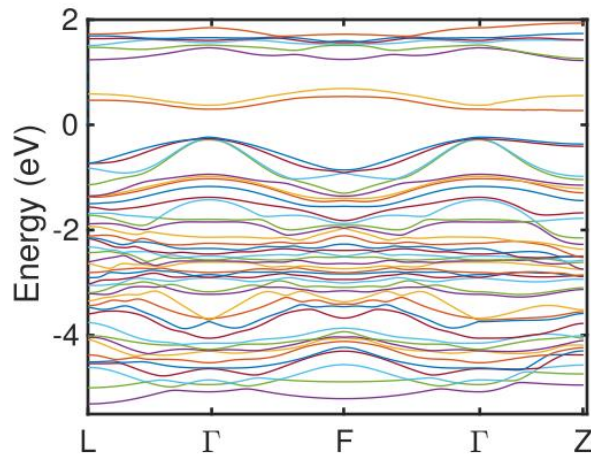


Fig. 4 VI_3 electronic band structure calculated with $U=3.8$ eV along the high-symmetry paths of the corresponding Brillouin zones.

In order to study magnetic anisotropy we calculated total energies of the structure for different tilting angles Θ from the c axis. These steps were performed for both the $R\bar{3}$ structure and the distorted monoclinic structure. The energy as a function of the tilting energy is shown in Fig. 5 and is affected strongly by the distortion. Magnetic anisotropy energy for the distorted structure exhibits a deviation for angles between 30 and 40 deg, where a new minimum is established, in agreement with experimental findings.

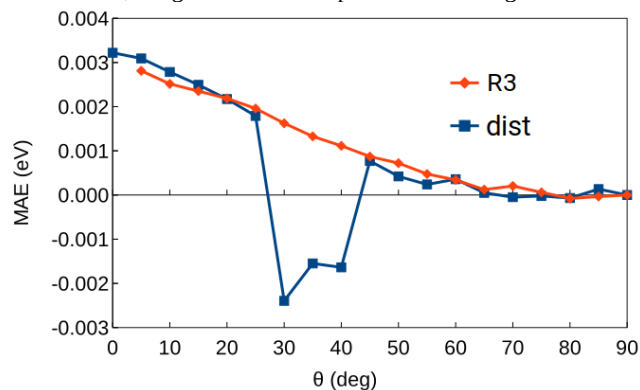


Fig.5 Magnetic anisotropy energy as a function of the tilting angle Θ (defined w.r.t the c axis) shown both for the unperturbed $R\bar{3}$ structure (red diamonds) and the distorted structure (blue squares).

In summary, our calculation methods have shown that the easy axis of VI_3 is indeed tilted by about 40 deg from the c axis as long as the monoclinic distortion of the lattice is taken into account.

This work is part of the research program GACR 19-16389J which is financed by the Czech Science Foundation.

3. References

- [1] M. A. McGuire, Crystals **7**, 121 (2017).
- [2] W. Zhang, et al., InfoMat **1**, 479 (2019).
- [3] B. Huang, et al., Nature **546**, 270 (2017).
- [4] G. T. Lin, et al., Appl. Phys. Lett. **112**, 072405 (2018).
- [5] C. Gong, et al., Nature **546**, 265 (2017).
- [6] S. Tian, et al., JACS **141**, 5326–5333 (2019).
- [7] S. Son, et al., Phys. Rev. B **99**, 041402(R) (2019).
- [8] T. Kong, et al., Adv. Mater. **31**, 1808074 (2019).
- [9] P. Doležal, et al., Phys. Rev. Mat. **3**, 121401(R) (2019)
- [10] J. Valenta et al., Phys. Rev. B **103**, 054424 (2021) [11] K. Yang, et al., Phys. Rev. B **101**, 100402 (2020).
- [12] J. L. Lado and J. F. Rossier, 2D Mater. **4**, 035002 (2017).
- [13] J. Yan, et al., Phys. Rev. B **100**, 094402 (2019).
- [14] A. Koriki et al., under review in PRB
- [15] <http://elk.sourceforge.net/>