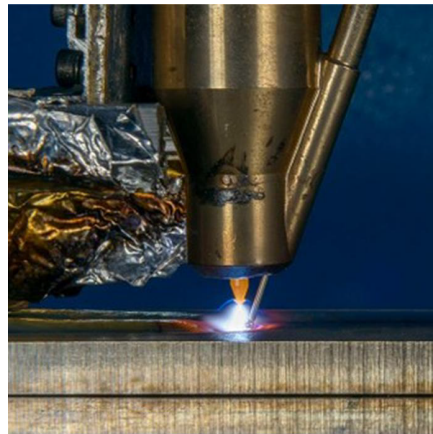


International journal
for science, technics and
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MACHINES
TECHNOLOGIES
MATERIALS

YEAR XVIII Issue **1** / 2024 ISSN PRINT 1313-0226
ISSN WEB 1314-507X



Published by
Scientific technical
Union of Mechanical Engineering



MACHINES. TECHNOLOGIES. MATERIALS

INTERNATIONAL SCIENTIFIC JOURNAL

ISSN PRINT 1313-0226, ISSN WEB 1314-507X, YEAR XVIII, ISSUE 1 / 2024

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Exergy analysis of a complex three-cylinder steam turbine at various loads

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Abstract: Exergy analysis results for the Whole observed steam Turbine and each of her cylinders at three loads are presented in this paper. Observation of all cylinders shows that LPC (Low Pressure Cylinder) is the dominant mechanical power producer at the highest observed load, while at partial loads the dominant mechanical power producer is IPC (Intermediate Pressure Cylinder). At Load 100% Whole Turbine produces mechanical power equal to 341.11 MW. IPC is the cylinder with the lowest exergy destruction and the highest exergy efficiency (higher than 95%) at all observed loads. The exergy efficiency of the Whole Turbine (WT) continuously increases during the increase in turbine load (WT exergy efficiency is the lowest at Load 50% and equal to 91.36%, while at the Load 100% WT exergy efficiency is the highest and equal to 92.93%). Analyzed turbine is projected to operate dominantly on the Load 100% because at that load the exergy efficiencies of all cylinders and Whole Turbine are higher than 91%.

KEYWORDS: EXERGY ANALYSIS, STEAM TURBINE, TURBINE CYLINDERS, VARIOUS LOAD CONDITIONS

1. Introduction

Steam turbines are nowadays constituent components of various power plants: conventional steam power plants [1], nuclear power plants [2], cogeneration and combined cycle power plants [3, 4], marine propulsion power plants [5, 6] and many others [7, 8]. The dominant function of steam turbines is the drive of electric generators and electricity production [9]. However, it should be highlighted that steam turbines can also be used for the drive of various mechanical power consumers (usually, for that function are used low power auxiliary steam turbines) [10, 11].

High power steam turbines are dominantly composed of several cylinders connected to the same shaft which drives an electric generator [12]. Single cylinder steam turbines are dominantly of auxiliary type [13]. Turbine cylinders are usually composed of several turbine stages, while some auxiliary steam turbines can consist only one (Curtis) stage – these steam turbines produce very low mechanical power (of around several hundred kilowatts) [14].

Steam turbine cylinders can be single flow or dual flow cylinders, while dual flow cylinders can be symmetrical and dissymmetrical. In a single flow cylinder, steam expands in one direction from the cylinder inlet until the outlet, while in dual flow cylinders steam enters in the middle of the cylinder and simultaneously expands in two opposite directions. Symmetrical dual flow steam turbine cylinders have identical left and right part, while in dissymmetrical cylinders left and right parts are not identical [15].

This paper presents an exergy analysis of a complex three-cylinder steam turbine and her cylinders at three loads. For each observed load is interesting to investigate which cylinder is the dominant mechanical power producer and which cylinder shows the best operating performance (the lowest exergy destruction and the highest exergy efficiency).

2. Description and operation characteristics of the analyzed steam turbine and her cylinders

Steam turbine analyzed in this paper is a complex turbine composed of three cylinders: High Pressure Cylinder (HPC), Intermediate Pressure Cylinder (IPC) and Low Pressure Cylinder (LPC), Fig. 1. All cylinders are connected to the same shaft which drives an Electric Generator (EG).

HPC gets steam of the highest pressure and temperature from Steam Generator (SG), operating point 1, Fig. 1. HPC has one steam extraction which deliver a certain steam mass flow rate to the High Pressure Feedwater Heating System, operating point 2, Fig. 1. After expansion in HPC, one small steam part is additionally delivered to the High Pressure Feedwater Heating System (operating point 4, Fig. 1), while the dominant part of the steam mass flow rate is delivered to the Re-Heater (RH) mounted inside the SG, operating point 5, Fig. 1. Re-Heater increases steam temperature and deliver steam with an increased temperature to the IPC.

IPC has three steam extractions – the first one deliver a certain steam mass flow rate to High Pressure Feedwater Heating System

(operating point 7, Fig. 1), second extraction delivers a certain steam mass flow rate to Deaerator (operating point 8, Fig. 1), while the last, third steam extraction delivers a certain steam mass flow rate to Low Pressure Condensate Heating System [16] (operating point 9, Fig. 1). Remaining steam mass flow rate after expansion in IPC is delivered directly to the LPC (operating point 10, Fig. 1).

LPC has two steam extractions (operating points 11 and 12, Fig. 1), where both of them deliver a certain steam mass flow rate to Low Pressure Condensate Heating System. After expansion in LPC, remaining steam mass flow rate (operating point 13, Fig. 1) has low temperature and pressure notably below the atmospheric one, that steam cannot be further used in the power plant, so the steam at the LPC outlet is delivered to Main Condenser [17] for condensation.

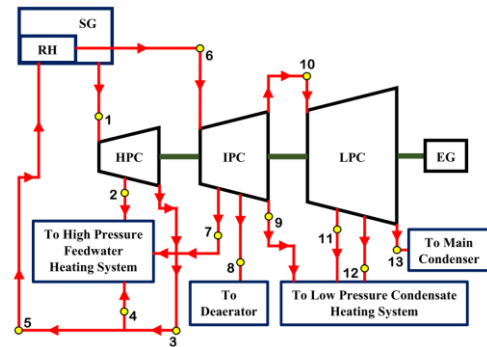


Fig. 1. General scheme of the observed steam turbine and operating points required for the exergy analysis of each cylinder and Whole Turbine

3. Exergy analysis

The main difference between exergy and energy analyses is that exergy analysis considers the ambient parameters (ambient pressure and temperature) in which observed component operates, while in the energy analysis, any ambient parameter is neglected and not considered [18]. The benefit of the exergy analysis is that the ambient parameters can be varied with an aim to investigate its influence on the component exergy efficiencies and destructions [19]. The change in the ambient pressure is usually small and did not have a notable influence on the component exergy efficiencies and destructions, while the change in the ambient temperature is dominant and its change is often observed during the component exergy analysis. Finally, it must be highlighted that exergy analysis of any component requires the definition of the base ambient state.

Exergy analysis of any steam turbine or turbine cylinder is based on the real (polytropic) steam expansion process, which consider all the losses that occur in the turbine stages during the expansion [20].

3.1. Overall exergy equations and balances

In the exergy analysis of any component exist a few equations which should always be satisfied, regardless of the component operating conditions. The overall component exergy balance equation at steady state is defined as [21]:

$$\dot{X} - P = \sum \dot{E}x_{out} - \sum \dot{E}x_{in} + \dot{E}x_D, \quad (1)$$

where P is mechanical power, index in denotes input (inlet), index out denotes output (outlet) and index D denotes exergy destruction. The exergy transfer by heat at the temperature T ($\dot{X}$) is [22]:

$$\dot{X} = \sum (1 - \frac{T_0}{T}) \cdot \dot{Q}. \quad (2)$$

$\dot{E}x$ is a fluid total exergy flow defined by the equation:

$$\dot{E}x = \dot{m} \cdot \varepsilon. \quad (3)$$

In the two above equations, T is a temperature, $\dot{Q}$ is the energy transfer by heat, $\dot{m}$ is fluid mass flow rate, index 0 denotes the base ambient state, while ε is fluid specific exergy which can be defined, according to [23], by an equation:

$$\varepsilon = (h - h_0) - T_0 \cdot (s - s_0), \quad (4)$$

where h is fluid specific enthalpy and s is fluid specific entropy. Mass flow rate balance for any component is:

$$\sum \dot{m}_{in} = \sum \dot{m}_{out}. \quad (5)$$

3.2. Equations for the exergy analysis of Whole observed Turbine and her cylinders

Exergy analysis equations of the Whole Turbine and each turbine cylinder (HPC, IPC and LPC) are arranged according to recommendations from the literature [24, 25]. Presented equations for each cylinder and Whole Turbine remain always the same, regardless of the observed load (only the steam operating parameters are changeable at each load and in each operating point). The numeration of indexes in all equations is related to the operating points presented in Fig. 1. In addition, index WT which is not defined so far is related to the Whole Turbine.

Developed mechanical power

$$P_{HPC} = \dot{m}_1 \cdot (h_1 - h_2) + (\dot{m}_1 - \dot{m}_2) \cdot (h_2 - h_3), \quad (6)$$

$$P_{IPC} = \dot{m}_6 \cdot (h_6 - h_7) + (\dot{m}_6 - \dot{m}_7) \cdot (h_7 - h_8) + (\dot{m}_6 - \dot{m}_7 - \dot{m}_8) \cdot (h_8 - h_9), \quad (7)$$

$$P_{LPC} = \dot{m}_{10} \cdot (h_{10} - h_{11}) + (\dot{m}_{10} - \dot{m}_{11}) \cdot (h_{11} - h_{12}) + (\dot{m}_{10} - \dot{m}_{11} - \dot{m}_{12}) \cdot (h_{12} - h_{13}), \quad (8)$$

$$P_{WT} = P_{HPC} + P_{IPC} + P_{LPC}. \quad (9)$$

Exergy power input

$$\dot{E}x_{in,HPC} = \dot{m}_1 \cdot \varepsilon_1, \quad (10)$$

$$\dot{E}x_{in,IPC} = \dot{m}_6 \cdot \varepsilon_6, \quad (11)$$

$$\dot{E}x_{in,LPC} = \dot{m}_{10} \cdot \varepsilon_{10}, \quad (12)$$

$$\dot{E}x_{in,WT} = \dot{m}_1 \cdot \varepsilon_1 + \dot{m}_6 \cdot \varepsilon_6 + \dot{m}_{10} \cdot \varepsilon_{10}. \quad (13)$$

Exergy power output

$$\dot{E}x_{out,HPC} = \dot{m}_2 \cdot \varepsilon_2 + \dot{m}_3 \cdot \varepsilon_3 + P_{HPC}, \quad (14)$$

$$\dot{E}x_{out,IPC} = \dot{m}_7 \cdot \varepsilon_7 + \dot{m}_8 \cdot \varepsilon_8 + \dot{m}_9 \cdot \varepsilon_9 + \dot{m}_{10} \cdot \varepsilon_{10} + P_{IPC}, \quad (15)$$

$$\dot{E}x_{out,LPC} = \dot{m}_{11} \cdot \varepsilon_{11} + \dot{m}_{12} \cdot \varepsilon_{12} + \dot{m}_{13} \cdot \varepsilon_{13} + P_{LPC}, \quad (16)$$

$$\dot{E}x_{out,WT} = \dot{m}_2 \cdot \varepsilon_2 + \dot{m}_3 \cdot \varepsilon_3 + \dot{m}_7 \cdot \varepsilon_7 + \dot{m}_8 \cdot \varepsilon_8 + \dot{m}_9 \cdot \varepsilon_9 + \dot{m}_{10} \cdot \varepsilon_{10} + \dot{m}_{11} \cdot \varepsilon_{11} + \dot{m}_{12} \cdot \varepsilon_{12} + \dot{m}_{13} \cdot \varepsilon_{13} + P_{WT}. \quad (17)$$

Exergy destruction

$$\dot{E}x_{D,HPC} = \dot{E}x_{in,HPC} - \dot{E}x_{out,HPC}, \quad (18)$$

$$\dot{E}x_{D,IPC} = \dot{E}x_{in,IPC} - \dot{E}x_{out,IPC}, \quad (19)$$

$$\dot{E}x_{D,LPC} = \dot{E}x_{in,LPC} - \dot{E}x_{out,LPC}, \quad (20)$$

$$\dot{E}x_{D,WT} = \dot{E}x_{in,WT} - \dot{E}x_{out,WT}. \quad (21)$$

Exergy efficiency

$$\eta_{ex,HPC} = \frac{P_{HPC}}{\dot{E}x_{in,HPC} - \dot{E}x_{out,HPC} + P_{HPC}} = \frac{P_{HPC}}{\dot{E}x_{D,HPC} + P_{HPC}}, \quad (22)$$

$$\eta_{ex,IPC} = \frac{P_{IPC}}{\dot{E}x_{in,IPC} - \dot{E}x_{out,IPC} + P_{IPC}} = \frac{P_{IPC}}{\dot{E}x_{D,IPC} + P_{IPC}}, \quad (23)$$

$$\eta_{ex,LPC} = \frac{P_{LPC}}{\dot{E}x_{in,LPC} - \dot{E}x_{out,LPC} + P_{LPC}} = \frac{P_{LPC}}{\dot{E}x_{D,LPC} + P_{LPC}}, \quad (24)$$

$$\eta_{ex,WT} = \frac{P_{WT}}{\dot{E}x_{in,WT} - \dot{E}x_{out,WT} + P_{WT}} = \frac{P_{WT}}{\dot{E}x_{D,WT} + P_{WT}}. \quad (25)$$

4. Steam operating parameters required for the exergy analysis at each observed turbine load

Steam operating parameters required for the exergy analysis of each cylinder and Whole Turbine, in each operating point from Fig. 1 and for each load, are found in the literature [26]. Steam operating parameters at each load and in each operating point, which are not found in the literature, are calculated by using NIST-Refprop 9.0 software [27]. Steam operating parameters at turbine load of 50% are presented in Table 1, Table 2 shows steam operating parameters at turbine load of 75%, while Table 3 presents steam operating parameters at turbine load of 100%.

The base ambient state required for the exergy analysis can be defined arbitrarily. In this paper, the base ambient state is defined by the ambient temperature of 25 °C and the ambient pressure of 1 bar.

Table 1. Steam operating parameters at turbine load of 50%

Load 50%						
O. P. *	Temp. (°C)	Pressure (bar)	Mass flow rate (kg/s)	Specific enthalpy (kJ/kg)	Specific entropy (kJ/kg·K)	Specific exergy (kJ/kg)**
1	538.0	135.00	138.69	3434.3	6.5474	1486.70
2	344.0	28.23	6.02	3105.9	6.7551	1096.50
3	299.4	19.46	132.67	3024.3	6.7807	1007.20
4	299.4	19.46	8.04	3024.3	6.7807	1007.20
5	299.4	19.46	124.64	3024.3	6.7807	1007.20
6	538.0	17.51	124.64	3554.7	7.6034	1292.30
7	453.9	9.99	3.55	3379.7	7.6320	1108.80
8	364.8	5.30	3.99	3198.3	7.6559	920.27
9	296.9	3.10	4.73	3063.0	7.6772	778.62
10	296.9	3.10	112.38	3063.0	7.6772	778.62
11	215.1	1.41	5.31	2903.6	7.7364	601.53
12	111.4	0.478	3.65	2705.1	7.7758	391.31
13	54.0	0.150	103.41	2531.9	7.8040	209.65

* O. P. = Operating Point (in accordance to Fig. 1)

** Specific exergy at the base ambient state

Table 2. Steam operating parameters at turbine load of 75%

Load 75%						
O. P. *	Temp. (°C)	Pressure (bar)	Mass flow rate (kg/s)	Specific enthalpy (kJ/kg)	Specific entropy (kJ/kg·K)	Specific exergy (kJ/kg)**
1	538.0	167.00	209.26	3398.5	6.4151	1490.40
2	351.8	41.83	10.78	3093.6	6.5656	1140.60
3	305.6	28.68	198.49	3012.4	6.5918	1051.60
4	305.6	28.68	13.98	3012.4	6.5918	1051.60
5	305.6	28.68	184.51	3012.4	6.5918	1051.60
6	538.0	25.81	184.51	3546.7	7.4170	1339.90
7	452.0	14.61	6.68	3369.6	7.4448	1154.50
8	361.8	7.72	6.48	3187.5	7.4672	965.76
9	293.3	4.50	7.67	3052.0	7.4875	824.19
10	293.3	4.50	163.68	3052.0	7.4875	824.19
11	210.9	2.04	8.41	2892.5	7.5445	647.66
12	108.1	0.693	8.01	2696.1	7.5823	440.04
13	54.0	0.150	147.26	2491.5	7.6807	206.08

* O. P. = Operating Point (in accordance to Fig. 1)

** Specific exergy at the base ambient state

Table 3. Steam operating parameters at turbine load of 100%

Load 100%						
O. P.*	Temp. (°C)	Pressure (bar)	Mass flow rate (kg/s)	Specific enthalpy (kJ/kg)	Specific entropy (kJ/kg·K)	Specific exergy (kJ/kg)**
1	538.0	167.00	287.39	3398.5	6.4151	1490.4
2	380.1	57.12	17.18	3132.5	6.4949	1200.6
3	329.7	38.58	270.21	3045.5	6.5216	1105.6
4	329.7	38.58	21.08	3045.5	6.5216	1105.6
5	329.7	38.58	249.14	3045.5	6.5216	1105.6
6	538.0	34.72	249.14	3538.1	7.2720	1374.5
7	451.0	19.56	10.05	3361.0	7.3005	1188.9
8	359.9	10.28	9.41	3178.7	7.3230	999.9
9	290.8	5.97	11.16	3042.9	7.3427	858.28
10	290.8	5.97	218.51	3042.9	7.3427	858.28
11	208.0	2.56	12.00	2884.3	7.4239	675.43
12	106.0	0.873	13.44	2689.7	7.4600	470.09
13	54.0	0.150	193.07	2444.1	7.5357	201.88

* O. P. = Operating Point (in accordance to Fig. 1)

** Specific exergy at the base ambient state

5. Exergy analysis results and discussion

Produced mechanical power in each cylinder and Whole Turbine at all three observed loads is presented in Fig. 2.

Observing turbine cylinders, it can be concluded that LPC is the dominant mechanical power producer at Load 100% (LPC produces mechanical power equal to 122.26 MW at Load 100%), while at partial loads the dominant mechanical power producer is IPC. HPC produces lower mechanical power in comparison to other cylinders at all three observed loads.

According to presented operating parameters in Table 3, at Load 100% Whole Turbine (WT) produces mechanical power equal to 341.11 MW, Fig. 2.

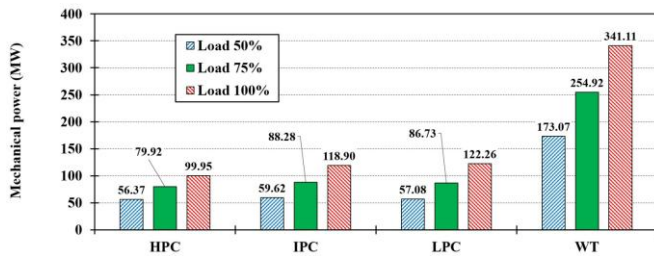


Fig. 2. Produced mechanical power in each cylinder and Whole Turbine at all three observed loads

Exergy power inputs and outputs of each cylinder and Whole observed Turbine at three loads are presented in Fig. 3.

At each load, for each cylinder and Whole Turbine exergy power input must be higher than exergy power output (the difference is exergy destruction), what is confirmed in Fig. 3. Observation of all cylinders shows that HPC has the highest exergy power inputs and outputs at all observed loads, while exergy power inputs and outputs of the LPC are the lowest at all loads. An increase in turbine load results with simultaneous increase in the exergy power input and output of Whole analyzed Turbine and each turbine cylinder, what is clearly visible in Fig. 3.

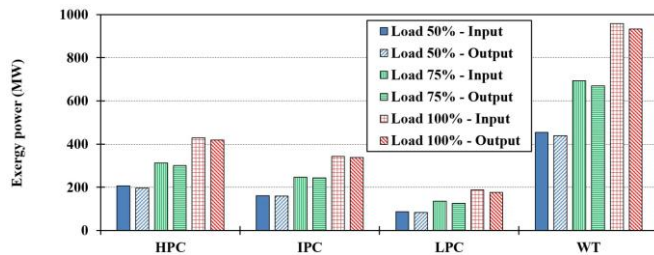


Fig. 3. Exergy power input and output of each cylinder and Whole Turbine at three observed loads

Exergy destructions of each cylinder and Whole Turbine at all three observed loads are presented in Fig. 4.

Observation of all cylinders shows that IPC is the cylinder with the lowest exergy destruction at all observed loads (the highest exergy destruction of the IPC can be seen at Load 100% and is equal to 5.06 MW). At the highest load (Load 100%), LPC is the cylinder with the highest exergy destruction (equal to 11.88 MW) while at two partial loads (Load 75% and Load 50%) HPC is the cylinder with the highest exergy destruction. For all cylinders and Whole Turbine is valid general conclusion that an increase in turbine load simultaneously increases exergy destruction (the only deviation from this conclusion can be seen for HPC between Load 75% and Load 100% where HPC exergy destruction decreases during the load increase).

Whole observed Turbine has the lowest exergy destruction equal to 16.38 MW at Load 50% and the highest exergy destruction equal to 25.94 MW at Load 100%.

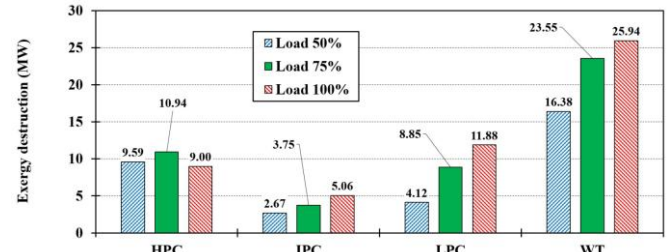


Fig. 4. Exergy destruction of each cylinder and Whole Turbine at three observed loads

The exergy efficiency of each cylinder and Whole analyzed Turbine at three observed loads is shown in Fig. 5.

From Fig. 5 can be easily concluded that IPC is the cylinder which has the highest exergy efficiency in comparison to other cylinders at all observed loads. IPC has a very high exergy efficiency at each load (higher than 95%) what confirms its optimal operation.

From the currently published literature which deal with various complex steam turbines and turbine cylinders [28] can also be confirmed that IPC shows the best performance of all cylinders. This conclusion can be explained by a fact that IPC did not operate with a steam of the highest pressure and temperature (as HPC) and that IPC did not operate by using wet steam in any stage – water droplets in wet steam increase losses in the cylinder (at least a few last stages of the LPC operate with wet steam). LPC has notably higher exergy efficiency in comparison to HPC at partial turbine loads (Load 50% and Load 75%), while at the highest load (Load 100%), LPC has slightly lower exergy efficiency in comparison to HPC.

Whole Turbine exergy efficiency continuously increases during the increase in turbine load (WT exergy efficiency is the lowest at Load 50% and equal to 91.36%, while at the Load 100% WT exergy efficiency is the highest and equal to 92.93%).

Finally, it can be concluded that this turbine is obviously projected to operate dominantly on the Load 100% because at Load 100% the exergy efficiencies of all cylinders and Whole Turbine are the highest (with an exception of LPC) and higher than 91%, Fig. 5.

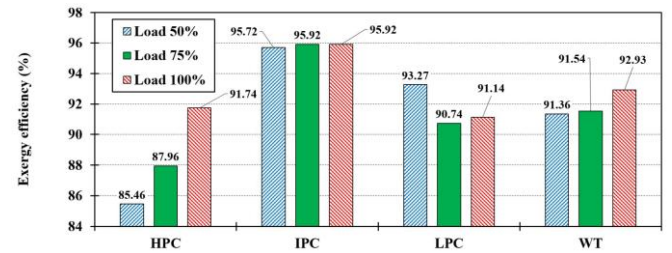


Fig. 5. Exergy efficiency of each cylinder and Whole Turbine at three observed loads

6. Acknowledgment

This research has been fully supported by the Croatian Science Foundation under the project IP-2022-10-2821.

7. Conclusions

In this paper are presented exergy analysis results for the Whole observed steam Turbine and each of her cylinders at three loads. The most important conclusions derived from this analysis are:

- Observation of all cylinders shows that LPC is the dominant mechanical power producer at the highest observed load (LPC produces mechanical power equal to 122.26 MW at Load 100%), while at partial loads the dominant mechanical power producer is IPC. At Load 100% Whole Turbine produces mechanical power equal to 341.11 MW.
- An increase in turbine load results with simultaneous increase in the exergy power input and output of Whole analyzed Turbine and each turbine cylinder.
- IPC is the cylinder with the lowest exergy destruction at all observed loads (the highest exergy destruction of the IPC is obtained at Load 100% and is equal to 5.06 MW).
- Whole observed Turbine has the lowest exergy destruction equal to 16.38 MW at Load 50% and the highest exergy destruction equal to 25.94 MW at Load 100%.
- IPC is the cylinder which has the highest exergy efficiency in comparison to other cylinders at all observed loads (higher than 95%).
- Whole Turbine (WT) exergy efficiency continuously increases during the increase in turbine load (WT exergy efficiency is the lowest at Load 50% and equal to 91.36%, while at the Load 100% WT exergy efficiency is the highest and equal to 92.93%).
- Analyzed turbine is obviously projected to operate dominantly on the Load 100% because at that load the exergy efficiencies of all cylinders and Whole Turbine are higher than 91%.

8. References

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Development of copper wire deformation technology

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Abstract: The paper studies the evolution of microstructure and mechanical properties of copper wire during a new combined deformation process. The essence of the technological process is deformation of wire in a rotating equal-channel step matrix and subsequent drawing. The matrix rotates around the wire axis and thereby creates stress due to equal-channel angular drawing and twisting in the matrix. The deformed copper wire was investigated by transmission electron microscopy and EBSD analysis, as well as tensile tests and microhardness determination. The deformation resulted in an ultrafine-grained gradient microstructure having a high component of high-angle grain boundaries. The tensile strength of the deformed copper wire compared to the undeformed one increases more than twice from 302 to 635 MPa, and the yield strength increases from 196 to 306 MPa, an increase of 56%. The use of such hardened copper wire in construction will reduce the weight of the structure by reducing the diameter.

KEYWORDS: WIRE, DRAWING, TWISTING, COPPER, TECHNOLOGY.

1. Introduction

One of the most promising methods for increasing the strength and plastic properties of metals is the formation of ultradisperse structures in materials using deformation methods. However, despite numerous developments, modern methods have a number of significant limitations in terms of continuity and productivity of process flows [7-8]. One of the most effective methods for obtaining an ultrafine-grained structure is the methods of severe plastic deformation (SPD) [9-10].

Equal channel angular pressing (ECAP), which is probably the most widely used severe plastic deformation technology, is considered as a promising method to achieve the desired high degrees of deformation [11-13]. Recently, based on this method, a large number of its modifications have appeared [14-16], some of which make it possible to obtain high-quality products [16-18].

However, despite numerous developments, the problem of creating a new deformation scheme that is as close as possible to industrial conditions and is of scientific and practical interest from the point of view of mass production remains unresolved. One of such schemes may be a new continuous scheme of equal-channel angular pressing and drawing (ECAP-drawing) [19-21]. Its key feature is that, unlike other combined methods, there is no rolling stage. Continuity of deformation is ensured by the drawing process, which occurs immediately after the ECAP process. Due to this unique deformation pattern, a fairly high level of tensile stress develops in the cross section of the workpiece, and incorrect selection of technological parameters will lead to breakage of deformed wire.

However, despite the listed advantages, ECAP drawing has a disadvantage associated with the manufacturability of the process. To achieve a high level of detailing, several deformation cycles are required. In practice, this means either sequential replacement of the ECA-matrix and drawing tool after each pass (for a single-pass drawing mill), or the creation of a sufficiently long production line (for a multi-pass drawing mill). Therefore, further relevant direction for the combined ECAP-drawing process development is the creation of an additional level of deformation, which will reduce the required number of deformation cycles. In this case, it is necessary to take into account the fact that due to this additional deformation, the cross-section of the wire should not change much, since if the cross-section is reduced, the effect of any existing stage of combined process may decrease, and if it is increased, the deformation process may be impossible. All these parameters correspond to the torsion operation, which, when developing SPD processes, is represented as a classical high-pressure torsion process [4,29,37].

The key difference between the developed technology studied in this work and the ECAP-drawing technology is that in an equal-channel stepped matrix, due to rotation around the axis of the workpiece, it is twisted, which makes it possible to achieve an additional level of deformation in the entire section. When the wire enters the die, its cross-section is calibrated in the die channel. An equal-channel stepped matrix, which stands before drawing, ensures the implementation of transverse and

longitudinal shear deformations, which eliminates the main disadvantage of drawing process - low ductility.

In this regard, the use of an improved deformation method that combines torsion, simple shear and classical drawing process makes it possible to realize a higher level of metal processing and expand the boundaries of traditional structural materials use.

2. Material and research methodology

To implement the combined technology during the process of copper wire deformation, an industrial drum drawing machine V-1/550M was used. The deformation was carried out at room temperature using the Bc route (the rotation of wire after each deformation cycle was carried out at 90°). The number of passes is 3. The reduction in wire diameter after each deformation cycle is 0.5 mm. So after 3 passes of deformation we obtained a wire with a diameter of 5.0 mm.

The technology of twisting process in an equal-channel stepped matrix followed by drawing does not differ significantly from classical drawing (Fig.1). At the first stage, the wire is sharpened on a sharpening machine to the required diameter. Next, the wire is passed through a chamber with lubricant in which the rotation mechanism is installed. The wire passes through the hole in the die bandage and then through the hole in the die. The front end of the wire is fixed in the drawing drum pliers.



Figure. 1 Scheme of wire straining new process: 1 - wire, 2 - drawing block, 3 - bed, 4 - drive gear, 5 - intermediate gear, 6 - bandage, 7 - equal-channel stepped die, 8 - die stand, 9 - die hole

Next, two equal-channel segments are installed around the wire step matrix and are inserted into the bandage according to the wedge principle. At this stage, all preparatory operations are completed. After which the mill is started up, reaching the planned drawing speed, and in parallel the mechanism that rotates equal channel stepped matrix is set in motion.

The preparation of samples for metallographic analysis was carried out using a Struers electrolytic sample preparation unit. All samples were examined in the middle plane of the sample to avoid the influence of peripheral regions. The effectiveness of hardening after deformation was assessed by measuring Vickers microhardness at a random load of 0,5H.

3. Experimental results

Metallographic analysis of deformed copper wire was carried out using an optical microscope to observe structure refinement general appearance. A cross-sectional optical microscope examination shows a gradient structure (Fig. 2). The surface layer is refined to 500 nm to a depth of ≈ 1 mm. Further, the grain size increases towards the central part of the wire and amounts to 4 μm . The longitudinal structure is elongated and parallel to the drawing direction in the surface layer and is more uniform in grain towards the center.

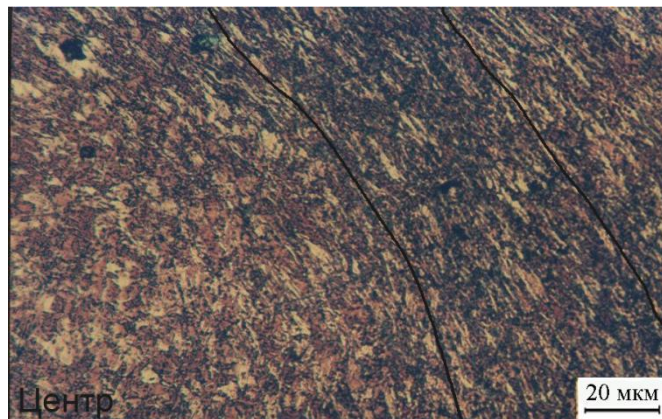


Fig. 2 Microstructure of copper wire after 3 cycles of deformation

The formation of a gradient microstructure after deformation by a combined technology in a rotating equal-channel stepped matrix and subsequent drawing is associated with the existing deformation mechanism. Due to the combination of two deformation processes, large grains are constantly refined on the surface with increasing deformation. Moreover, during drawing, formation of new boundaries does not occur; all fragmentation of structure occurs in an equal-channel stepped matrix during shear deformations due to mechanical twinning. Therefore, the main formation of structure is realized during shear deformation in the matrix, which is inherited during the process of drawing.

After the metallographic analysis, a microhardness study was carried out. The initial microhardness after annealing was 77 HV. After 3 deformation passes, the hardness increased almost 3 times. Thus, the average value of microhardness in the surface layers was 216 MPa, in the middle layers - 174 MPa, and in the center of the wire 155 MPa. This scatter in microhardness can be explained by the formation of a gradient structure and strengthening of grain boundaries due to an increase in the dislocation density.

Considering resulting gradient structure, it was decided to study the change in microhardness along the wire cross section after each pass. In order to construct a microhardness profile, measurements were carried out through each millimeter of the sample cross-section 3 times at each point of the graph. The results for each point were averaged. The graph is shown in Fig. 3. As can be seen from the graph, due to the presence of a gradient structure across the cross section of the rod, a smooth drop in the level of microhardness towards the center of the wire is observed.

5. Conclusion

The work examines copper wire deformed using a new technology, the distinctive feature of which is the combination of a shear pattern and tension pattern in one deformation zone. The alignment was made possible by simultaneous deformation of the wire in a rotating equal-channel stepped matrix and drawing. As a result of deformation, copper wire with a gradient structure was obtained. The surface layer is refined to 500 nm to a depth of ≈ 1 mm. Further, the grain size increases towards central part of the wire and amounts to 4 μm . Analysis of tensile diagrams showed that the tensile strength of deformed copper wire, compared to undeformed copper wire, more than doubles from 302 to 635 MPa, and the yield strength increases from 196 to 406 MPa. Also, after 3

passes of deformation, the hardness increased almost 3 times. Thus, average value of microhardness in the surface layers was 216 MPa, in the middle layers - 174 MPa, and in the center of the wire 155 MPa. This scatter in microhardness can be explained by the formation of a gradient structure and strengthening of grain boundaries due to an increase in dislocation density. Such high microhardness values of the surface layer help to increase the wear resistance of the wire, and the soft center increases its plastic properties.

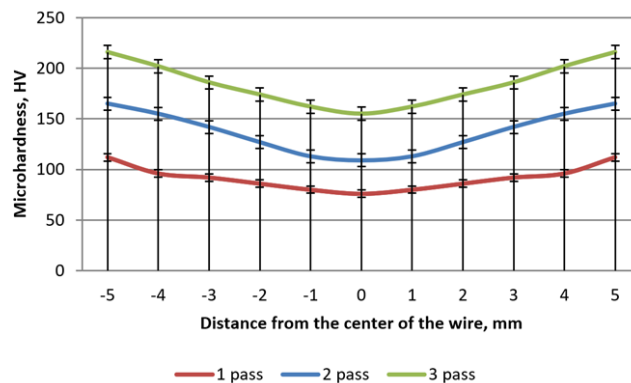


Fig. 3 Microhardness of copper wire in cross section

6. Financing

This research has been/was/is funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP19676903).

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Charge activity of silicon-containing nanophase particles intended for modification of polymer matrices

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Abstract: The article considers the influence of various technological methods for obtaining nanosized silicate-containing particles. Each of the methods has its advantages and disadvantages, none of them is universal. It is shown that, depending on the methods of formation of particles, their activity changes. Silicon carbide particles obtained as a result of the thermolysis process with preliminary chemical treatment from natural raw materials of organic origin are of interest for further research. These particles have an increased charge activity in relation to other studied classes of charged particles.

KEYWORDS: NANOPARTICLES, SILICATES, ACTIVITY, CHARGE, CURRENT

1. Introduction

One of the effective ways to significantly change the performance characteristics of multi-tonnage polymer materials is the introduction of various types of substances in doping concentrations. The presence of a modifier in the polymer matrix significantly affects the physical and mechanical characteristics of polymers and ultimately determines the quality of the products obtained. Based on the available research, it is believed that modified thermoplastics can be processed by all known methods. Usually, when modifying polymer materials, shrinkage decreases or stabilizes, more stable viscosity characteristics are observed, and the course of relaxation processes changes [1-10].

The use of nanoparticles that can be attributed to superhard materials (nanodiamonds, diamond-containing charge, nanoparticles based on tungsten carbide, etc.) in most cases leads to an intensification of the wear process, a faster change in the geometric dimensions of the counterbody in the friction node, due to changes in tribochemical test conditions [11-12]. The use of various types of nanorods can also lead to a change in the performance characteristics of polymers in the direction of deterioration of properties, due to the heterogeneity of the distribution of this type of modifiers in the polymer matrix, as well as by creating local regions with different orientation of the modifier in the volume of a high-molecular compound.

The authors [13] studied the effect of the number of SiO₂ nanoparticles on the physico-mechanical properties, heat resistance and tribological characteristics of flame-retardant polyamide coatings. The absence of oxidative degradation of polyamide with an optimal content of SiO₂ nanoparticles is shown.

It was found in [14] that the introduction of hydrosilicate nanoparticles into the polymer matrix leads to a noticeable increase in the modulus of elasticity of the material.

The authors [15] describe the characteristics of nanoparticles and the effect of nanoparticle sizes on the mechanical properties of composite nanomaterials (strength, elongation, Young's modulus). Mechanisms of modification and evaluation of properties of polymer materials modified by nanoparticles are discussed.

In [16], experimental results show the electrothermopolarization of polymer-nanoparticle-based compositions changes its charge state, the supramolecular structure of the polymer changes, the interfacial interactions between the components of the composition and the thickness of the interfacial layer, as a result of which the strength properties change.

Thus, the use of modifiers and fillers of various dispersities can allow solving various problems of materials science, in the field of creating new structural materials, by optimal selection of a modifying agent. Currently, various types of silicate particles are widely used as modifiers of polymer materials. Depending on the chemical composition, structure, and morphology, these particles have different activity, which determines their degree of modifying effect on the high-molecular matrix [17].

Currently, the main methods for producing nanoparticles are: compaction of isolated nanoclusters obtained by evaporation and condensation, precipitation from solutions or decomposition of precursors; crystallization of amorphous alloys; intense plastic

deformation; ordering of highly nonstoichiometric compounds and solid solutions. Each of the methods has its advantages and disadvantages, none of them is universal [18].

For the modification of thermoplastic polymer matrices, the most promising is the use of nanodispersed particles of silicon carbide obtained by thermolysis technology of natural raw materials containing this chemical compound. Currently, the industry needs for this superhard compound (SiC) are provided by particles obtained by the Acheson method using solid-phase chemical reactions at high temperatures. However, these particles are obtained with a high content of metal compounds used as catalysts in the production of the product. The presence of these additional chemical inclusions degrades the characteristics of low-dimensional SiC particles and complicates their application, in particular, in the radio-electronic industry. The use of the thermolysis process with preliminary chemical treatment of natural raw materials makes it possible to obtain high-purity silicon carbide particles [19-24].

The purpose of this work is to study the activity of silicate particles of various types by the method of thermo-stimulated current spectroscopy.

2. Materials and methods of research

Ultradisperse silicate-containing particles of various production technologies, compositions, and structures were studied using the method of thermally stimulated depolarization (TSD spectroscopy, thermally stimulated current spectroscopy,) [17]. The essence of the method is to study the relaxation of the charge that causes the electret state, that is, a state in which surface charges arise on the surface of the dielectric under the influence of external factors such as an electric field, irradiation with electrons, ions, etc. To ensure rapid relaxation, thermal stimulation of the dielectric discharge is used at a constant heating rate. The analysis is based on the property of charges accumulated by dielectrics to be released when heated and on fixing the parameters of the current flowing at the same time. The current graph in the temperature function is a spectrum of TST, by the nature of which the mechanisms responsible for the manifestation of the effect are judged. The TST analysis was carried out in the range of 20-270 °C using a device for measuring thermally stimulated currents ST-1 (ODO "Microtestmashiny", Belarus, Gomel) (Figure 1) according to the developer's methodology.

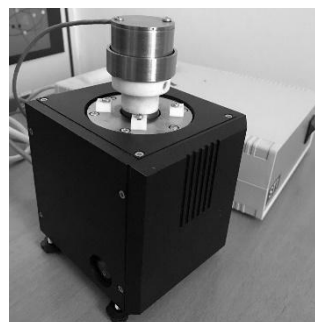


Figure 1 Device for measuring thermally stimulated currents ST-1

3. Results and discussion

The TST spectrum of flint (Figure 2a) is characterized by a weakly expressed peak, the maximum of which is in the region of $\sim 27^\circ\text{C}$ – 29°C and the maximum intensity is 3.2 pA. Flint is most likely characterized by a heterocharge, which decreases over time to a certain constant value determined both by the structure of the material and by the external conditions under which the sample is located. Carrying out mechanical activation of flint (Figure 2b) leads to a shift of the maximum peak of the thermally stimulated currents to the region of 33°C – 37°C and an increase in the intensity of the TST peak by about 3 times ($I_{\text{max}} \sim 10$ pA). In the case of mechanical activation, the flint most likely acquires a homocharge, which passes through the maximum and then changes little.

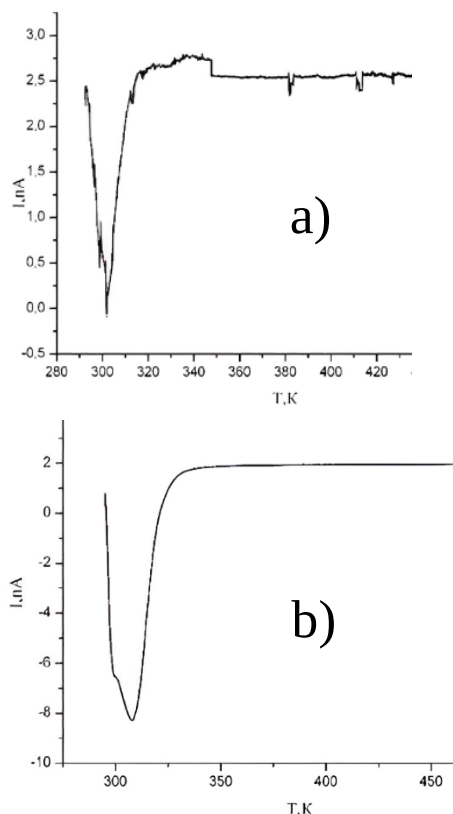


Figure 2 TST spectrum of silicate-containing particles based on flint: a) flint, b) mechanically activated flint

Studies by the method of thermally stimulated depolarization have shown the presence of a maximum in the spectrum of the TST aerosol (Figure 3c), located in the temperature range $T \sim 39^\circ\text{C}$ – 41°C , with an I_{max} peak intensity of ~ 0.32 pA. An aerosil is characterized by a homocharge [17].

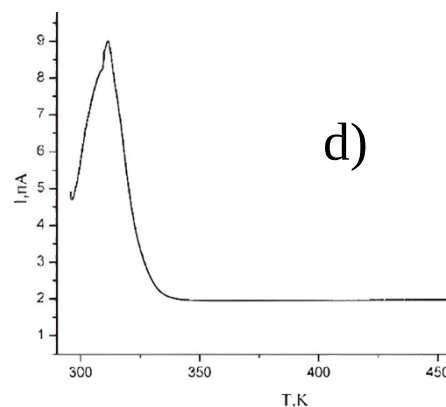
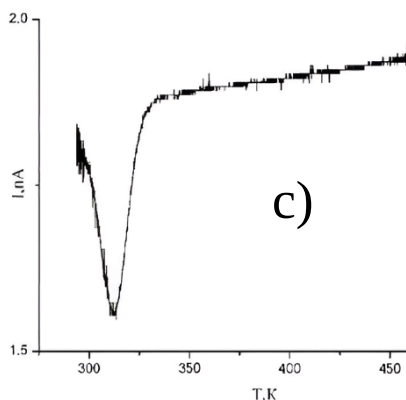


Figure 3 TST spectrum of silicate-containing particles based on aerosil: c) aerosil, d) flint – 65%, SiO_2 – 35%. The composition was mechanically activated for 30 sec at an acceleration of 20 g.

Based on the conducted studies, it can be seen that aerosil is the least active in terms of charging activity; mechanically activated flint has the maximum charging activity. Carrying out mechanical activation enhances the charging effects in the starting materials. The joint mechanical activation of aerosil with silicon (Figure 3d) reduces the charge activity in comparison with mechanically activated silicon, but in comparison with the starting materials, there is a sharp increase in the activity of the resulting composite system [17].

Shungite is characterized by a wide temperature range of charge activity from 20 – 80°C (Figure 4e) and is most likely effective for use in cold-cured composite materials, such as epoxy, polyester, urea-formaldehyde resins, etc.

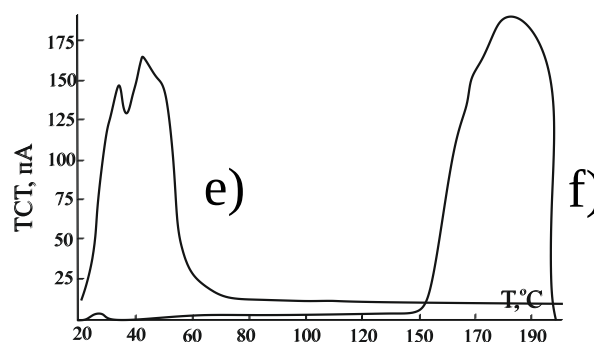


Figure 4 TST spectrum of silicate-containing particles obtained from natural raw materials. e) shungite, f) silicon carbide

Studies conducted to study the charge activity of silicon carbide particles obtained using this technology have shown the presence of an intense peak in the TST spectrum in the region of 150 – 190°C (Figure 4f), which indicates a high charge activity of silicon-containing material. The temperature range of the SiC charge activity is in the processing area of most thermoplastic polymers. It is possible to assume a significant influence of silicon carbide particles obtained from natural raw materials on the structure and physico-mechanical characteristics of thermoplastic polymer composites with the doping content of the modifier. The mechanism explaining the modifying effect of these particles is the formation of a labile network of physical bonds in the polymer matrix between modifier particles and polymer molecules.

The presence of peaks of thermally stimulated currents in silicate-containing particles indicates the activity of the material during heating. These TST peaks are located in the temperature range of processing of high-tonnage polymer materials (polyolefins, polyamides, polyethylene terephthalate). In this regard, these nanophase silicate-containing particles obtained from organic raw materials can be used as modifiers of polymer materials to create

composites with increased resistance to radiation and electromagnetic radiation in the microwave range.

4. Conclusion

Thus, an analysis of the activity of existing low-dimensional silicate-containing particles used to modify polymer matrices has been carried out. The prospects of using ultrafine SiC particles obtained from natural raw materials by thermolysis for modifying thermoplastic polymer materials are shown.

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Processes for wire and arc additive manufacturing (overview)

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Abstract: Wire and arc additive manufacturing is a rapidly developing technology for the production of metal parts used in various industries such as space, automotive, shipbuilding, etc. Today, it is a potential alternative to traditional manufacturing processes due to its shorter lead time, low material losses and cost-effectiveness. In recent decades, this technology has been used to produce components from various materials. This overview examines the methods of realization, the specifics of the technological process, the process parameters and their influence on the formation of the layers and typical.

Keywords: WAAM, GTAW, PAW, GMAW, BEAD FORMATION

1. Introduction

Additive manufacturing, which is known as 3D printing [1], is a technology for producing of details and subject by material depositing layer by layer. Here we are accentuating on using the technology for producing of details from metals and there alloys. This technology is one of the most innovative and includes digital modelling, layer-by-layer deposition and machining. Also, in order to obtain details with the required properties, deep knowledge in materials science is required. The technology of wire and arc additive manufacturing (WAAM) is exploring as a process in last 10 years. It's a development of classic technologies for arc welding and surfacing [2÷5]. The process is shown in Fig.1.

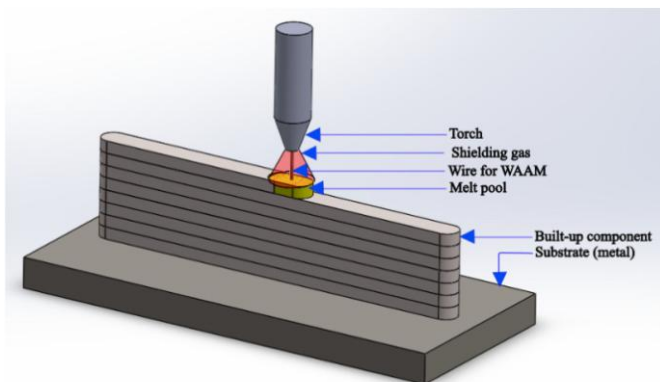


Fig. 1. WAAM process.

The WAAM process makes it possible to: manufacture structures with large dimensions (up to tens of meters); obtaining completely dense details; high production efficiency and low production costs. It is also suitable for restoring and repairing damaged details and parts. Typically, the direct cost of metal wire using WAAM is about 10% of the cost of metal powder of the same weight [5]. Comparative process performance data are given in Table 1.

Table 1. Comparing process performance [6÷7].

Type of AM Process	SLM	EBM	LMD	WAAM
Process performance, (g/h)	40 ÷ 100	100 ÷ 300	150 ÷ 2400	500 ÷ 10000

2. Varieties of the WAAM process.

Depending on the welding method used, the WAAM process has three main technological implementation options [8÷9] – GTAW, PAW and GMAW (Fig.2÷Fig.5).

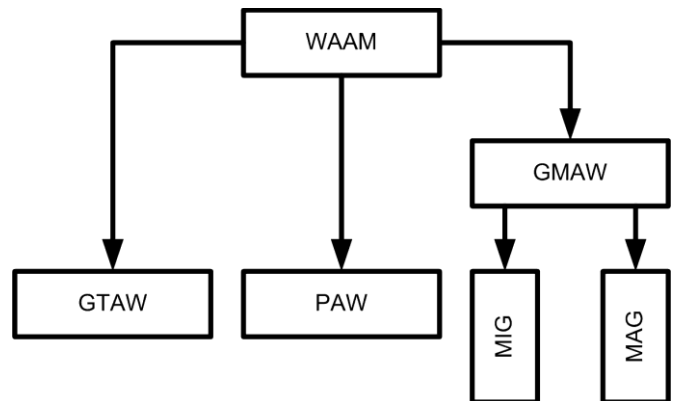


Fig. 2. Technological implementation options of WAAM.

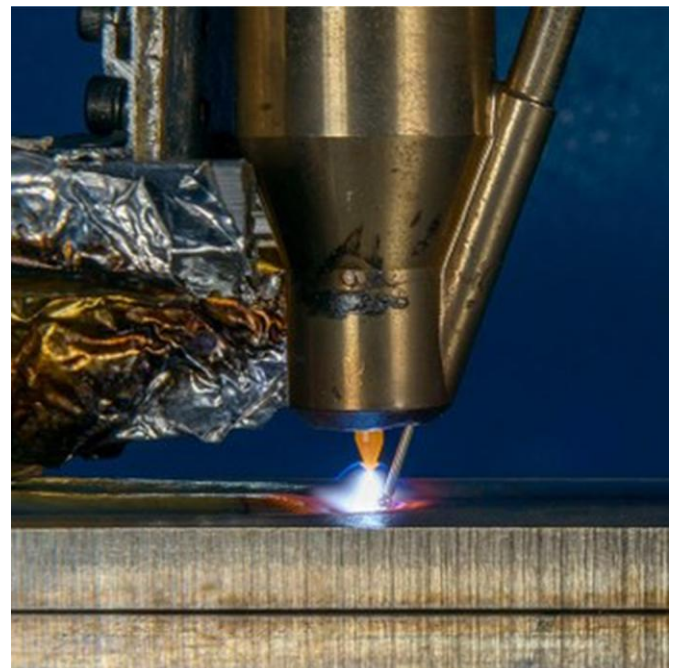


Fig. 3. GTAW WAAM

In GTAW WAAM (GTAAM), the filler wire is melted by the heat of the arc and deposited on the substrate surface to obtain the desired geometry (width, height, cross-section, etc.) and mechanical properties. The PAW process is similar to GTAW in that both processes use a tungsten electrode, but PAW differs from GTAW in the construction of the welding torch and is more efficient than GTAW. However, the initial cost of PAW is very high compared to GMAW and GTAW. Today, GMAW is more widely used as a process for WAAM than other processes due to its high melting performance. In GMAW, the feed rate and arc power are linked,

which reduces the flexibility of the process. Comparative data on melting productivity for these three varieties are given in Table 2.

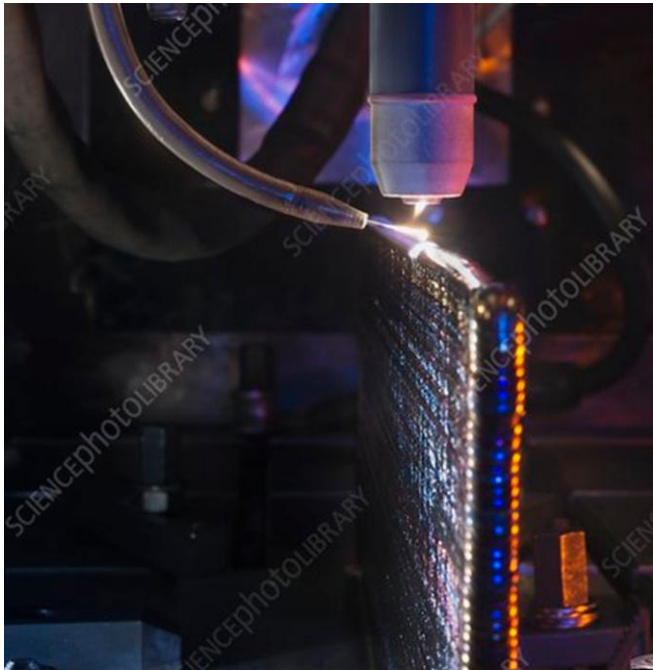


Fig. 4. PAW WAAM (PAAM)

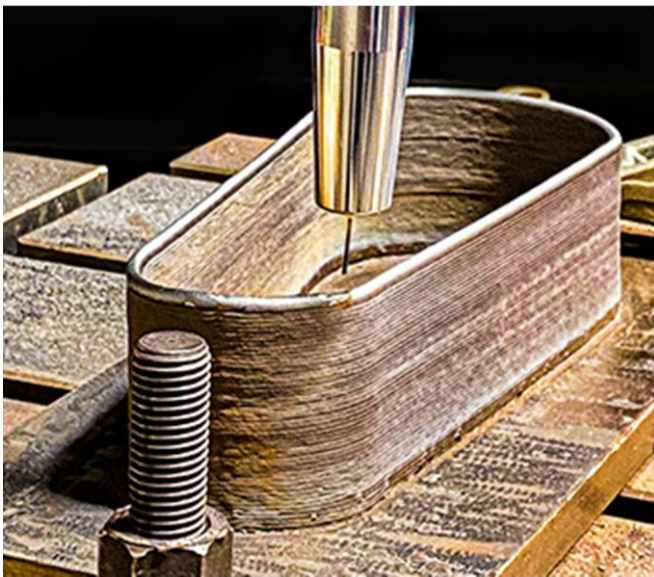


Fig. 5. GMAW WAAM (GMAAM)

Table 2. Comparison of melting performance for GTAW, PAW and GMAW processes [10÷12].

Process	GTAW	PAW	GMAW
Process performance, (kg/h)	1 ÷ 2	2 ÷ 4	7 ÷ 8

Conventional GMAW has four metal transfer modes: short arc (with frequent short circuits), transient arc, long arc, and jet process. Subsequently, such varieties of the process as surface tension transfer (STT), cold arc (CA), cold process (CP), cold metal transfer (CMT) were developed. These processes are oriented to work in the short arc range and to reduce heat input. The most widely used deposition process is CMT. It has the following varieties: conventional, advanced, pulsed and pulsed advanced [13].

3. Implementation and process parameters.

The main stages of the WAAM process, which are reported in the literature [14, 15] are indicated in Table 3.

Table 3. Main stages of implementation.

Before the process.	Arc parameters selection
	Selection of substrate material type and size
	Selection of material and diameter of wire.
	Tool path design
	Choice of shielding gas..
During the process.	If necessary, pre-heat the substrate..
	Realization and control of the tool path.
	Layer-by-layer surfacing with the selected process parameters.
	Rolling or forging (ancillary processing – optional).
After the process.	Quality control.
	Heat treatment (if necessary).
	Mechanical processing.
	Quality control.

The parameters used to WAAM vary depending on the type of process and the wire material. During the deposition of the material, the interlayer temperature rises due to the accumulation of heat as new layers are added. This process is highly dependent on the dimensions of the workpiece, the welding mode and the trajectory of the tool movement (it may include time intervals during which the welding arc does not burn). Process parameters include welding current, arc voltage, torch travel speed, wire feed rate, interlayer temperature, interlayer dwell time, shielding gas composition and flow rate, angle between torch and substrate, electrode diameter, heat input and electrode output. They are decisive for the production of a high-quality part, i.e. without defects with the required mechanical characteristics.

In [16], results were given on the influence of the ratio between the wire feed rate and the torch displacement speed on the geometry of the surfaced layer and the mechanical properties were studied. According to this research, the heat input is linearly related to the characteristic bead geometry, including height, width, depth, melting and surfacing areas for the parameter range analyzed. An inverse relationship was observed between the heat input and the hardness of the single welded beads. Wang et al. [17] have studied the influence of the feed rate of wire and other parameters on the geometry of the welded bead. This study shows that in GTAAM of 4043 aluminum alloy, as the wire feed rate increases, the height of the weld bead increases while its width decreases. It is also reported that the arc energy required to melt wire increases as the wire feed rate increases. This can result in non-fusion and reduced bead width. The dimensions of a typical welded strip are shown in Fig. 6.

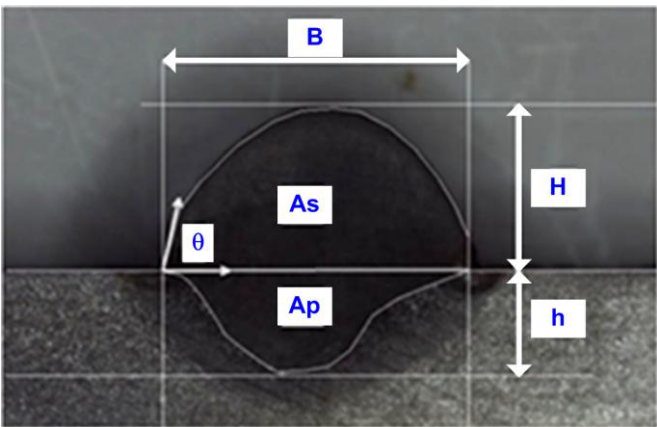


Fig. 6. Schematic representation of the weld bead dimensions (material R120S-G), where: B is the width; h - penetration depth; H - height; Ap - melted area; As - deposited area; θ - contact angle.

Dinowitzer et al. [18] investigated the effect of torch speed and other parameters on the microstructure and layer geometry in

WAAM of Hastelloy X alloy. In this study, regression analysis was used to determine the effect of process parameters (feed rate, welding speed, arc current and argon flow) on the microstructure and geometry of the welded bead (shape and size of the bead, roughness, penetration depth and degree of oxidation). It is shown that the magnitude of the current and the deposition rate significantly affect the microstructure and geometry of the resulting bead. The microstructure of the workpiece depends on the welding speed, which is explained by the change in heat input. In addition, the welding speed has a stronger effect on the width than on the height of the bead. This is explained by the authors by the influence of the deposition rate on the contact angle (wetting angle).

The heat input is critical to the WAAM process. This relates to bead shape and volume, mechanical properties and microstructure [19, 20] as well as internal defect formation, phase transformations, residual stresses and strains [21]. The linear energy has a significant influence on the danger of hot crack formation [22].

The substrate preheat temperature determines the shape of the first layer mainly. When it increases, the width increases and the height of the deposited bead decreases [22, 23]. The appropriate interlayer temperature is crucial for obtaining a smoother surface, higher mechanical properties of raw parts and magnitude of residual stresses [24, 25]. This is related to the trajectory of the torch and the dwell time between layers. This means that a trade-off may have to be made between the performance and the obtained characteristics of [26].

4. Imperfections.

Common imperfections in the wire and arc additive manufacturing process include residual stresses and distortion, cracks and porosity. The ratio of wire feed speed to torch travel speed, heat input, electrode stickout and gas flow rate affect the risk of their formation. Since when using GMAW the magnitude of the current is related to the feed rate and the electrode stickout it has more possibilities for problems, e.g. spatter, porosity and overheating, compared to GTAW and PAW based technologies [27].

Aluminum alloys are prone to pore formation. The technology for WAAM is no exception. An example of this is given in Fig. 7 [28]. In the same work, the distribution of pores by size was also investigated (Fig. 8) - the essential amount of pores is of small size. To avoid the problem, a clean and smooth wire, a suitable shielding gas (or gas mixture) and a suitable gas flow rate should be used [29, 30]. Mechanical processing (rolling) during the application of the layers or in the waiting periods between layers can also reduce this defect in the case of aluminum alloys [31]. The defect can also be reduced by increasing the cooling time of the molten pool as much as possible so as to allow time for trapped gases to escape [32].

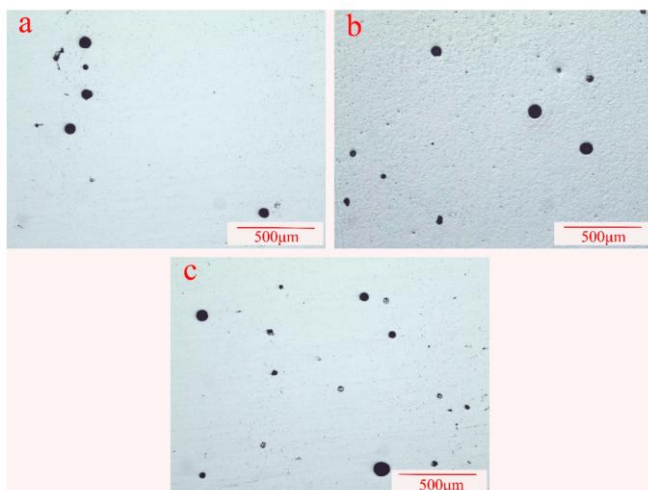


Fig. 7. Porosity in aluminum alloys using different methods of realizing the process: CMT+A (a), CMT (b) and CMT+P (c).

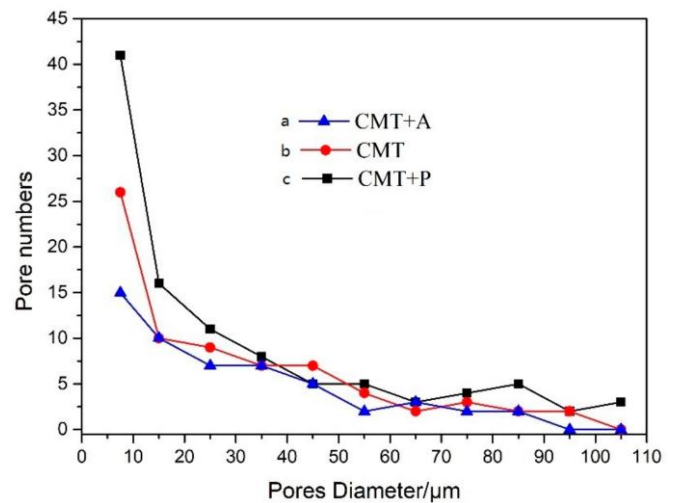


Fig. 8. Pore size distribution in different variants of the cold metal transfer method.

Layer waviness (Fig.9) is a specific imperfection for the WAAM process. Usually, the cause is an inappropriate ratio of the wire feed rate to the torch travel speed [33]. It negatively affects the subsequent application of layers. It appears in the form of humps and depressions. Gratzke et al. [34] through a theoretical analysis came to the conclusion that avoiding this imperfection can be achieved when the length to width of the weld pool is smaller than a certain critical value.

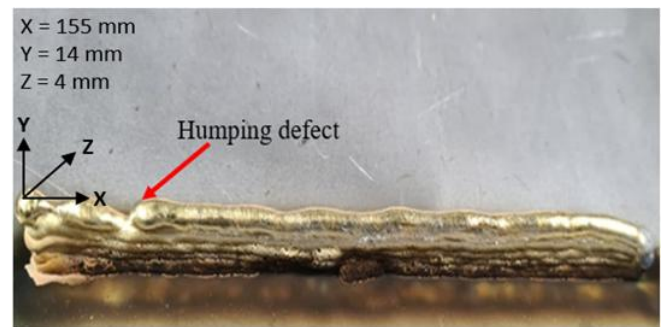


Fig. 9. Humping defect (material: copper alloy CuAl8).

5. Conclusions.

WAAM is a promising technology for obtaining details/components with complex geometry. It has been studied to a considerable extent, but even with the use of conventional materials there are problems to be solved. In this brief overview, only the formation of layer geometry is considered and the main conclusions that can be drawn are:

- The production of details by WAAM is related to the use of one of the welding processes GTAAM, PAAM and GMAAM, the latter being the most common.
- Typical imperfections can be avoided by appropriate selection of technological parameters and tool (torch) movement strategy.
- The operations during the process, e.g. rolling, can improve the microstructure and mechanical properties of a simple article, but are not applicable to articles of complex shape.
- Operations performed after the layer-by-layer building process can also result in improved microstructure and mechanical properties.
- The relationship between process parameters and part quality has not yet been sufficiently investigated.

ACKNOWLEDGMENTS:

The authors are grateful to the financial support of the Bulgarian National Science Fund, Contract No KP-06-H57/10, for carrying out the necessary research.

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Use of gamma irradiation processing for decomposition of aflatoxins in wheat flour

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Abstract: The article presents the effects of different doses of gamma irradiation on the degradation of aflatoxins B₁, B₂, G₁ and G₂ in wheat flour. The experiment was conducted after contamination of wheat flour samples with mixture of aflatoxins with concentrations from 3 µg/kg to 12 µg/kg using reference material. Irradiation of flour aliquots with absorbed doses from 5.8 kGy to 27 kGy was carried out in an industrial gamma irradiation facility BULGAMMA. The concentrations of the aflatoxins before and after the radiation processing were measured by HPLC. The results showed that gamma irradiation with 27 kGy caused the highest degree of destruction of aflatoxins B₂ (82 %) and G₂ (81 %), followed by aflatoxin G₁ (65 %) and to the lowest extend of aflatoxin B₁ (59 %). Gamma irradiation with the maximum allowable dose for commercial food irradiation of 10 kGy was not sufficient to destroy the studied aflatoxins to the maximum permissible concentrations in wheat flour.

Keywords: AFLATOXINS B₁, B₂, G₁, G₂, GAMMA IRRADIATION, DECOMPOSITION, WHEAT FLOUR, HPLC

1. Introduction

Aflatoxins are mycotoxins that are produced by naturally occurring species of fungi [1] and can be found in various foodstuff [2]. Numerous studies have been devoted to the methods for their determination and decomposition due to the serious danger they pose to human health [3-12].

Aflatoxins B₁, B₂, G₁ and G₂ are the most common mycotoxins and have proven highly carcinogenic effects. They are produced by strains of *Aspergillus flavus* and *Aspergillus parasiticus*. According to their chemical nature, they are furocoumarins. Furocoumarins are a class of organic chemical compounds with phototoxic properties, found naturally in many types of plants, some of which are commonly consumed by humans. Furocoumarins are synthesized by plants through the fusion of a coumarin and a furan ring [13, 14], generating linear or angular isomers. The two main isomers of furocoumarins are psoralens and angelicins (isopsoralens), depending on the position of the furan ring [5]. Chemical structures of psoralen and isopsoralen and aflatoxins B₁, B₂, G₁ and G₂ are presented on Figs. 1-2.

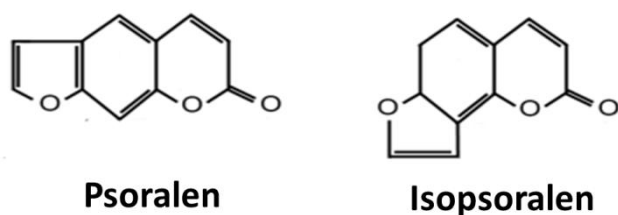
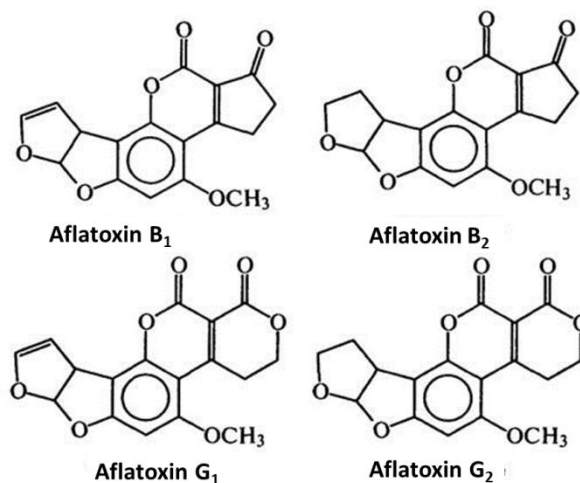


Fig. 1 Chemical structures of psoralen and isopsoralen

Furocoumarins are produced by plants as a defense mechanism against various types of pests, such as insects, fungi and bacteria. They react with their DNA thus disrupting their replication when exposed to UV light. In this way, they inhibit microbial growth and increase insect mortality [5].

The basis of all physico-chemical methods for qualitative and quantitative determination of aflatoxins is their ability to fluoresce under the influence of UV rays [5]. Aflatoxins that fluoresce in blue are designated as B₁ and B₂, and those that fluoresce in yellow-green light are designated as G₁ and G₂.

Fig. 2 Chemical structures of aflatoxins B₁, B₂, G₁ and G₂



Aflatoxins are low-molecular compounds that are persistent and do not break down in the process of technological treatment of infected substrates. They are not destroyed during steam treatment, granulation, drying, as well as during long-term storage. They are also resistant to the action of acids and bases.

Aflatoxin B₁ has been classified by the International Agency for Research on Cancer (IARC) as a class 1 human carcinogen [9].

Aflatoxin B₁ is the most toxic metabolite. Its share is about 80% of the total amount of aflatoxins, and aflatoxin G₁ is the least toxic. It has been established that aflatoxin B₁ occurs most often in cereals - corn, wheat and rice. It has a pronounced hepatocarcinogenic effect on humans and animals [6].

Radiation processing of contaminated foodstuff has been studied as a method of toxin degradation. However the results obtained are not unambiguous and depend on the studied product.

In 2003, at the Congress of Microbiology in Brazil, a report was presented on the effect of gamma irradiation on the levels of aflatoxin B₁ and fungal infection, examining samples of peanuts, variety Tatu Vermelho. At a radiation dose of 10 kGy, mold growth was completely stopped, and doses of 15, 20, 25 and 30 kGy were sufficient to decompose aflatoxin B₁ by 55-74%. The results showed that decontamination of molds by gamma irradiation, before the formation of aflatoxin B₁, is the most acceptable method for preserving peanuts [11].

Another study showed that the degradation of aflatoxin B₁ in food samples depended on their oil content. Thus, in peanuts, which have the highest oil content, the percentage of degradation of aflatoxin B₁ at 10 kGy is no more than 60%, while in maize, which has the lowest oil content, it reaches 80%. The reported results show the possibility of using gamma radiation as a means of degrading aflatoxin B₁ in food and feed crops to levels lower than the maximum permissible [9].

According to [10] gamma irradiation is a suitable technique that reduces aflatoxin B₁ levels in cereal samples without affecting nutritional values. The absorbed dose of 4 kGy led to reduction of aflatoxin B₁ with nearly 16% for maize, 22 % for wheat, and 27% for rice, while at 6 kGy, the percent reduction of aflatoxin B₁ was 32%, 44%, and 56%, respectively. A radiation dose of 8 kGy removed about 60% of the toxin in corn, 65% in rice, and 69% in wheat samples. The authors concluded the higher radiation doses of 8 kGy are required to remove the toxin until it reaches the legal limit [10].

The aim of the present study is to present the applicability of gamma-irradiation processing with doses from 5.8 kGy to 27 kGy for decomposition of aflatoxins B₁, B₂, G₁ and G₂ in wheat flour.

2. Materials and Methods

2.1. Samples

For conducting the research, white wheat flour was contaminated in the laboratory with the aflatoxins under investigation. Five samples of white wheat flour were prepared, with three repetitions each. 25 grams of each sample were weighed on an analytical balance, transferred to glass vials and contaminated with mixture of the four toxins at concentrations between 3 µg/kg and 12 µg/kg using reference material Romer Labs L18492M/06.2019.

2.2. Sample preparation

2.2.1. Solid phase extraction, using immunoaffinity columns: Contaminated flour from each sample was transferred to 500 mL iodine flasks with stoppers. 5 grams of sodium chloride and 125 ml of methanol/water were added in a ratio of 70/30. The entire mixture was homogenized and extracted for one hour on a shaking machine.

Dilution of the extract: The entire amount of sample was filtered through Whatman No. 4 filter paper. 15 mL of the filtrate was measured into a graduated cylinder and 30 mL of deionized water (1) was added.

Purification by immunoaffinity column: The immunoaffinity column AFLAPREP® was connected to the solid phase extraction system by means of adapters. 15 mL of the filtrate (1) were passed through the column under the influence of gravity. After the entire amount of filtrate has passed, the column is washed with 30 mL of deionized water at a flow rate of 1-2 drops per second, and finally the column is dried by passing air.

Elution: The column was moved to the position of the solid phase extraction system, which was equipped with a vial. Aflatoxins were eluted with 2 mL of methanol passed through the column under gravity. After the eluate had flowed out, a vacuum was created in the system to drive off the methanol.

Concentration of the extract: The methanol extract was evaporated in a stream of nitrogen at 40°C. The dry residue was dissolved in 1 mL of methanol/water, in a ratio of 50:50, immediately before analyzing the sample. It was homogenized on a vortex and transferred to a vial for liquid chromatography separation.

All chemicals and solutions were high purity grade and purchased from Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, MO, US).

2.3. Gamma-irradiation

Gamma-irradiation was carried out with the industrial gamma-irradiator BULGAMMA, based on the JS-850 ⁶⁰Co type gamma-irradiator, located at Sopharma JSC, Sofia, Bulgaria. The device was validated by the manufacturer NORDION (Canada). Doses applied to the irradiated samples were determined using ethanol-chlorobenzene dosimeters.

2.4. Instrumentation

The concentrations of aflatoxins B₁, B₂, G₁ and G₂ were measured using HPLC 1100 Series Agilent Technologies. The analysis was carried out according to BDS EN ISO 16050:2011 "Foodstuffs. Determination of aflatoxin B₁, and the total content of aflatoxins B₁, B₂, G₁ and G₂ in cereals, nuts and derived products - High-performance liquid chromatographic method".

A Zorbax Eclipse Plus C18 chromatographic separation column (3 mm x 150 mm, particle size 5 µm) equipped with a pre-column and a fluorescence detector with a wavelength of 362-455 nm was used for the quantification of aflatoxins. The temperature of the column thermostat was set at 30°C. The mobile phase for the quaternary pump (1) consisted of a mixture of deionized water (channel A), methanol (channel B) and acetonitrile (channel C) in a ratio of 62% : 28% : 10%. The mobile phase for the isocratic pump (2) was pyridine perbromide. 100 µL of the sample was injected into the apparatus; the flow rate was 0.6 mL/min for pump (1) and 1.25 mL/min for pump (2). The time for analysis of one sample was 17 minutes.

The retention times of the aflatoxins under investigation were as follows: 8.35 min for G₂, 10.24 min for G₁, 12.03 min for B₂ and 15.08 min for B₁, as shown on Fig. 3.

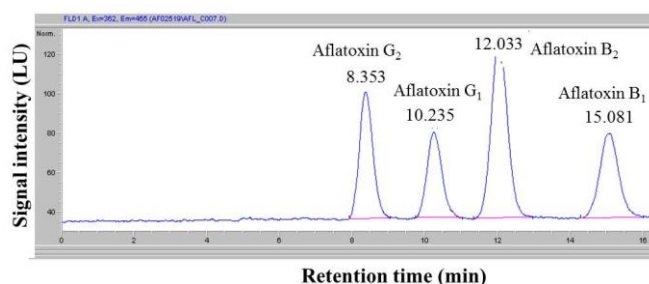


Fig. 3. Chromatogram of non-irradiated sample of wheat flour, contaminated with aflatoxins B₁, B₂, G₁ and G₂

3. Results and Discussion

The concentrations of aflatoxins in the samples of wheat flour before and after gamma irradiation with different doses are established in Table 1. The presented data are expressed as the means of three replicates ± standard deviations (SD).

Significant decrease of the concentrations of the four aflatoxins with the increase of absorbed dose was measured as shown on Fig. 4. The decomposition [%] of the aflatoxins as a result of the absorbed doses gamma irradiation are established on Figs. 5, 6.

From the data presented, it can be seen that aflatoxins B₂ and G₂ are degraded most efficiently, and aflatoxin B₁ undergoes the least degradation. The results showed that at the maximum absorbed dose of 27 kGy, aflatoxins B₂ and G₂ are destroyed to the greatest extent - 82% and 81%, respectively, followed by aflatoxin G₁ (65%) and aflatoxin B₁ (59%). Applying such a high dose, however, is not recommended for food, and is only permissible for sterilization. Lower radiation doses resulted in 14% to 28% toxins destruction (at 5.8 kGy) and 27% to 42% toxins decomposition (at 10.9 kGy).

Although gamma irradiation has been proven to be an effective method for destroying toxic pollutants [5, 9-12, 15, 16], the application of high doses is not always possible when it comes to food products. The maximum allowable dose for commercial food irradiation in many countries is 10 kGy [17].

Table 1: Concentrations of the aflatoxins B_1 , B_2 , G_1 and G_2 in wheat flour before and after gamma-irradiation with different absorbed doses.

Concentrations [$\mu\text{g/kg}$] of aflatoxins before and after different absorbed doses					
Aflatoxin	0 kGy	5.8 kGy	10.9 kGy	20 kGy	27 kGy
B_1	10.93 ± 0.17	9.40 ± 0.20	7.95 ± 0.13	6.51 ± 0.14	4.47 ± 0.16
B_2	3.47 ± 0.15	2.51 ± 0.15	2.06 ± 0.14	1.60 ± 0.13	0.63 ± 0.17
G_1	11.66 ± 0.13	9.21 ± 0.14	8.43 ± 0.15	7.43 ± 0.15	4.10 ± 0.14
G_2	7.12 ± 0.14	5.23 ± 0.14	4.10 ± 0.14	2.78 ± 0.16	1.36 ± 0.13

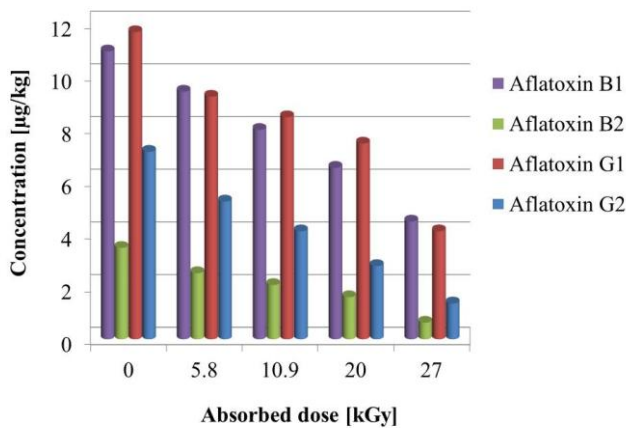


Fig. 4. Decrease of the concentrations of aflatoxins B_1 , B_2 , G_1 and G_2 in wheat flour as a result of gamma irradiation

According to European Commission regulations [18] the permitted maximum levels of aflatoxin B_1 and total sum of aflatoxins in all cereals and all products derived from cereals, including processed cereal products is $2 \mu\text{g/kg}$ and $4 \mu\text{g/kg}$, respectively. As can be seen from Table 1, the maximum permissible concentrations of aflatoxins are not reached even after applying a radiation dose of 27 kGy.

The need of high doses gamma irradiation for decomposition of aflatoxins was found in other investigations. Khalil et al [15] have studied the reduction of aflatoxins and ochratoxin A in maize by irradiation and found maximum degradation of the formed aflatoxins and ochratoxin A in maize occurred at 20 kGy, with best reduction rates of 40.1%, 33.3%, and 61.1% observed for aflatoxin B_1 , aflatoxin B_2 , and ochratoxin A, respectively. Therefore the authors recommended grains irradiation by gamma radiation at 6.0 kGy to decontaminate mycotoxin-producing molds before they produce mycotoxins [15].

Iqbal et al [16] summarized that more than 10 kGy radiation dose is required to achieve complete sterilization in dried chilli. Decontaminating viable mold spores by gamma irradiation before aflatoxin production appeared to be the most acceptable method to preserve dried chilli from aflatoxin contamination [16].

Obviously, the effectiveness of gamma irradiation to neutralize contaminants to acceptable levels also depends on the initial concentrations of toxins in food products.

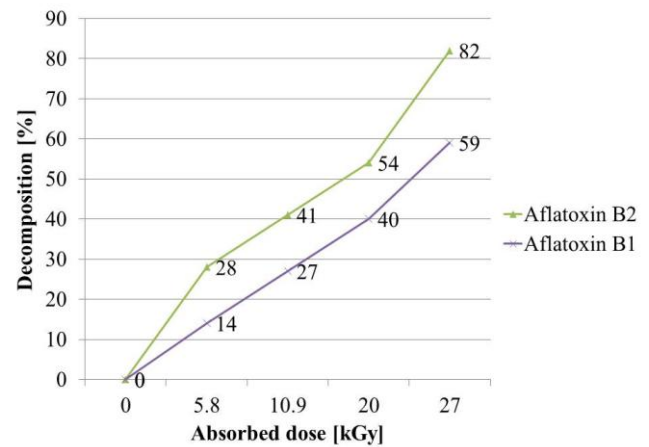


Fig. 5. Decomposition, [%] of aflatoxins B_1 and B_2 after different absorbed doses.

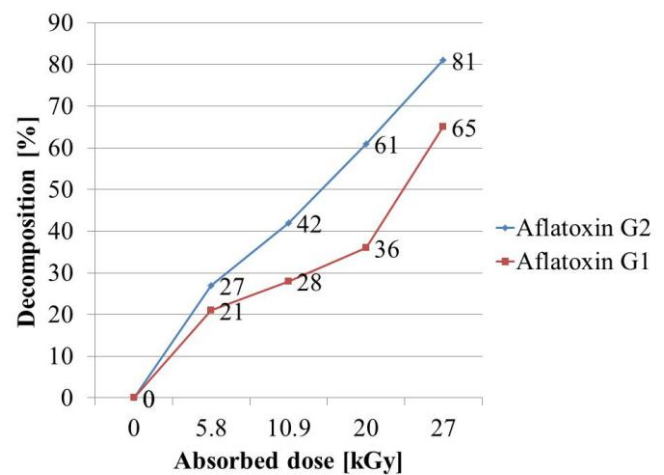


Fig. 6. Decomposition, [%] of aflatoxins G_1 and G_2 after different absorbed doses. .

When the concentrations of the contaminants are higher than the permitted levels for foodstuff, other methods for decontamination can be combined with gamma irradiation processing.

4. Conclusions

The present study showed that gamma irradiation of wheat flour, contaminated with aflatoxins B_1 , B_2 , G_1 and G_2 , with doses up to 27 kGy led to their decomposition from 59 % (for aflatoxin B_1) to 82 % (for aflatoxin B_2). The effective destruction of the toxins, present in concentration levels $3 \mu\text{g/kg}$ – $12 \mu\text{g/kg}$ to the permissible concentration levels in wheat flour was not possible only by applying gamma irradiation processing, but combined methods are necessary. The application of gamma irradiation with doses significantly higher than 27 kGy could result in successful decomposition of mycotoxins however is not recommended for processing of food products. Such an approach could be used in the disposal of unfit for consumption contaminated food products before their disposal, in order to prevent further spread of contaminants. Timely prevention of aflatoxin production, however, is still the best way to avoid these toxins from entering food products.

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Technological characteristics of composite mixtures for the preparation of thermal insulation structural elements

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Abstract: *The technological characteristics of suspensions used in the development of new thermal insulation composite structural elements based on foam materials and inorganic binders (Portland cement) are investigated. The role of the components of the compositions, the parameters of the technological regime and other factors in ensuring adequate workability of the prepared cementitious solutions is considered. Determination of the necessary technological characteristics of composite mixtures ensures their effective distribution in the formwork moulds when forming the specimens, cost-effective performance at production stage and obtaining products with the planned functional properties. The existing opportunities for potential application in modern construction of the developed composite elements are analyzed.*

Keywords: HYDRATION, PLASTICITY, DENSITY, VISCOSITY

1. Introduction

The construction of external thermal insulation systems of buildings of different types are widely used in modern construction to ensure adequate energy efficiency [1-7]. At the same time, in a number of cases, only partial thermal insulation of individual parts of old multi-family residential buildings is carried out (large-area formwork, large-panel residential buildings, etc.), which has a limited energy-saving effect and has an unaesthetic impact on the facades [1,3]. Other types of building insulation are also used: combined (internal and external), internal insulation of sandwich type (wall/insulation/wall). Some of the thermal insulation materials that have gained considerable popularity (EPS, XPS, etc.) actively used in the renovation of existing buildings and the construction of new ones are characterized by relatively low fire resistance and limited service life [1-3]. This inevitably reduces the safety of buildings and requires the replacement of thermal insulation systems after a certain period. In order to overcome the existing risks and problems, it is appropriate to use products based on durable, non-flammable and non-combustible materials complying with the building technical norms for fire safety.

The increasing production capacities in various industries and the intensive use of the resulting products in various economic and household spheres are accompanied by the generation of significant quantities of waste materials of different origins [8-11]. The existing quantities of waste products represent a significant environmental problem with worrying long-term forecasts. Efficient and safe waste management requires the existence of established waste landfills and an organised system of collection and transport by specialized transport equipment [12-14]. One possibility for a partial solution to the problem is the development and implementation of production technologies for the zero-waste recycling of a range of waste products through their application as primary raw materials in the production of a wide range of products. Due to their high durability, significant chemical resistance and specific thermo physical and mechanical properties, glassy waste materials are considered as a complete feedstock [15]. In industrial conditions, production methods have been implemented for the recovery of waste glass raw materials and the production of thermal insulating foam glass materials [16,17]: panels, profiles, granules and chips. The resulting products are mainly used in construction and industry for thermal insulation of buildings and equipment. The use of durable foam-silicate materials eliminates the need to replace thermal insulation systems throughout the life cycle of buildings and increases the fire safety of facilities. A team from IMSETCH-BAS is improving the technology for foam glass production and is developing innovative facilities for producing foam glass thermal insulation materials [18-22] with a cellular structure based on waste glass. The role of various technological factors and the mechanism of granulation and foaming processes are investigated in the paper. The individual technological stages of the production cycle are optimized. Adequate heat treatment regimes have been developed, tailored to the specificity of the waste raw materials and the foaming agent used [19]. Increased efficiency is ensured by

equipment designed on the basis of original construction solutions which improve some unsatisfactory operating characteristics of previous generations of machines [18-22].

An additional possibility for the application of different fractions of foam glass granules is their introduction in the role of lightweight admixtures for the preparation of lightweight thermal insulation concretes [23].

Innovative composite materials involving granulated foam glass and inorganic binders have been developed [24-26]. By their characteristics they represent a potential alternative to a number of traditional and standard thermal insulation building products. An experimental industrial line has been developed for the production of thermal insulation composites, panels and other materials with potential applications in construction.

The technological cycle for the preparation of composite products is carried out through several successive stages [27]:

- mechanical processing of the required quantities of waste glass by crushing and grinding to obtain the final granulometric composition of the raw material;
- preparation of a primary granulate from the resulting charge containing powdered glass fraction, blowing agent, etc.;
- thermal foaming of the primary granulate to form foamed glass granules with a specific cell structure;
- preparation of composite mixtures based on the obtained foam glass aggregate fractions and cement solutions;
- moulding of specimens using specialised moulds, removal of the products from the moulds after a period of technological downtime and further processing if necessary.

To further modify the material, a variety of research data with a broad thematic scope were analyzed [28-49]. At the same time, the experimental results obtained in additional laboratory studies represent a prerequisite for further development of technologies for the preparation of new composite products. A promising direction for further functional application of the composites is the development of structural elements for construction with more specialized purpose, such as fire-resistant insulation elements, etc.

The aim of the present study is to investigate the technological characteristics of composite mixtures applicable to the preparation of various modifications of experimental specimens. The research work carried out is in accordance with the existing experience in the field of composite materials [31,42-44] and the laboratory analysis methods used as presented in the specialized literature [42-46].

2. Studies on experimental thermal insulation composites

2.1. Creation of thermal insulation compositions series A, developed on the basis of foam glass granules, Portland cement CEM I 42.5 N and other components

Table 1 shows the experimental compositions (series A.1) developed on the basis of CEM I 42.5 N Portland cement, foam glass granules and water at a water cement ratio (W/C) of 0.7 and the compositions (series A.2) developed on the basis of CEM I 42.5

N Portland cement, foam glass granules, activated zeolite (clinoptilolite, fraction below 63 μm) and water at a water cement ratio (W/C) of 0.7.

Table 1. Experimental compositions (series A.1) developed on the basis of Portland cement CEM I 42.5 N and compositions (series A.2) developed on the basis of Portland cement CEM I 42.5 N.

Compositions A.1.	Compositions A.2.
Composition A.1.1. cement : granules, W/C 1 : 1, W/C = 0.7	Composition A.2.1. cement : granules : zeolite, W/C 1 : 1 : 0.1, W/C = 0.7
Composition A.1.2. cement : granules, W/C 1 : 2, W/C = 0.7	Composition A.2.2. cement : granules : zeolite, W/C 1 : 2 : 0.1, W/C = 0.7
Composition A.1.3. cement : granules, W/C 1 : 3, W/C = 0.7	Composition A.2.3. cement : granules : zeolite, W/C 1 : 3 : 0.1, W/C = 0.7
Composition A.1.4. cement : granules, W/C 1 : 4, W/C = 0.7	Composition A.2.4. cement : granules : zeolite, W/C 1 : 4 : 0.1, W/C = 0.7

Table 2. Experimental compositions (series A.3) developed on the basis of CEM I 42.5 N Portland cement and compositions (series A.4) developed on the basis of CEM I 42.5 N Portland cement

Compositions A.3.	Compositions A.4.
Composition A.3.1 cement : granules : perlite, W/C 1 : 1 : 0.5, W/C = 0.7	Composition A.4.1. cement : granules : perlite : zeolite, W/C 1 : 1 : 0.5 : 0.1, W/C = 0.7
Composition A.3.2. cement : granules : perlite, W/C 1 : 2 : 0.5 W/C = 0.7	Composition A.4.2. cement : granules : perlite : zeolite, W/C 1 : 2 : 0.5 : 0.1, W/C = 0.7
Composition A.3.3. cement : granules : perlite, W/C 1 : 3 : 0.5, W/C = 0.7	Composition A.4.3. cement : granules : perlite : zeolite, W/C 1 : 3 : 0.5 : 0.1, W/C = 0.7
Composition A.3.4. cement : granules : perlite, W/C 1 : 4 : 0.5, W/C = 0.7	Composition A.4.4. cement : granules : perlite : zeolite, W/C 1 : 4 : 0.5 : 0.1, W/C = 0.7

In Table 2 are presented experimental compositions (series A.3) developed on the basis of Portland cement CEM I 42.5 N, foam glass granules, perlite (fraction up to 3 mm) and water at water-cement ratio (W/C) 0.7 and compositions (series A.4.) developed on the basis of Portland cement CEM I 42.5 N, foam glass granules, perlite (fraction up to 3 mm), activated zeolite (clinoptilolite, fraction below 63 μm) and water at a water-cement ratio (W/C) of 0.7.

2.2. Data for determining the parameters of the composite mixture: normal viscosity, bonding time of the cement mixture, etc.

2.2.1. Viscosity

Normal viscosity is determined by the amount of water in the cement mixture, sufficient to ensure hydration of the cement. On the other hand, the mixture must have sufficient mobility and be easy to handle. The theoretical quantity of water to ensure complete hydration of the cement is relatively small, but it should be kept in mind that significant quantities of water are retained in the gel masses without being directly involved in the chemical process of hydration. In practice, considerably larger than theoretical quantities of water are used to ensure optimum mobility of the cement mixture. Some of this adsorption-bound water evaporates over time and causes the cement product to dry out. Another part serves as a reserve for the hydration processes in the depth of the cement grains. The greater the excess of water in the cement mixture, the greater the drying deformation will be. Moreover, delamination of the cement mixture can occur, which severely deteriorates its properties. For example, the water layers that form can freeze in winter working conditions and cause the cementitious product to crack and disintegrate.

Determination of the optimum amount of water to obtain a mixture of normal density, i.e. viscosity, is the subject of some of

the most important physical and mechanical tests of cement. The normal viscosity of a cement mixture is expressed by the percentage of water in relation to the cement in the mixture.

Determination of the normal density, is carried out with the Vicat apparatus (Fig. 1).

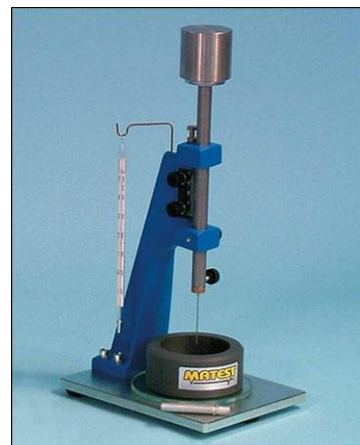


Fig. 1. Vicat's handheld apparatus.

The free moving part of the device, fitted with a cylindrical metal cartridge with a diameter of 10 mm, weighs a total of 300 grams. The normal viscosity is determined by the depth of sinking of the cartridge under the action of the weight of the entire movable part of the instrument in a sample of cement mixture prepared in a standard manner. The reading is done on a scale graduated in millimeters and is converted to Poise (P).

The mixture's specimen weighs 400 g according to international standard. The mixture is prepared and stirred for 5 minutes. The amount of water in a standard mix with Portland cement is 25÷27% of the weight of the cement.

The apparatus is set so that when the cartridge reaches the glass plate the arrow points to zero division. The mixture is considered to have normal consistency, i.e. viscosity, when the cartridge stands 5÷7 millimeters from the plate. If a thicker or thinner mixture is obtained, the experiment is repeated with a mixture with other W/C ratio.

2.2.2. Bonding time

After the cement mixture is obtained, it must retain its plasticity for some time in order to be used and processed. The determination of the bonding time is carried out on the same sample with which the normal density has previously been determined. The metal cartridge of the Vicat apparatus is replaced by a needle with a circular cross-section and an area of 1 mm². The difference in weight between the cartridge and the needle is compensated by additional weights which are added to the movable part of the apparatus so that the total weight of the movable part is brought back to 400 g. The time from the moment of mixing the cement with the water until the moment when the needle of the Vika apparatus stops sinking and stands 3 to 5 millimeters from the tile is considered the start of bonding. The end of bonding is considered to be the time from the moment the cement is mixed with water until the needle sinks no more than 0.5 mm into the cement mixture. The start of bonding shall be established by dropping the needle every 5 minutes and the end - by dropping the needle every 15 minutes.

According to the relevant Portland Cement Standard, the start of bonding shall occur no earlier than one hour and the end no later than 10 hours after mixing the cement with the water.

2.2.3. Volumetric change

During the process of hydration of the cement solution, a certain change in its volume is observed. In some cases, the changes occurring are of such a nature as to greatly reduce the mechanical strength of the obtained articles and render the cement unfit for use. The main factors causing the volume changes are of a chemical and physico-chemical nature. In the first place, it should be pointed out that a number of substances give, on hydration, products of greater

specific volume. In cement solution there are certain quantities of free lime and other oxides and sulphites not absorbed in the firing process, expressed in the gross analysis as SO_3 . In addition, a certain amount of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is added to the solution as a binding time regulator. These substances are the main contributors to the volumetric inconsistency of cement hydration and their amounts in cement are therefore strictly limited by the standards.

The amount of sulphur trioxide in cement, which is characterized by CaSO_4 , is limited by the Bulgarian Standard to 3%. In many countries this value is lower. The volumetric consistency of cement can be ensured by complying with the limiting norms for the content of free lime, magnesium oxide and sulphur trioxide in the relevant standards.

Other sources of volumetric changes of the hardened cement solution are thermal deformations due to the exothermicity of the hydration processes and the drying and swelling phenomena and the associated change in the surface tension of the cement mortar. This phenomenon is combated by limiting the C_3S , C_3A content of the cement solution because their hydration is highly exothermic process.

2.2.4. Swelling and drying

The swelling and drying of the cement solution are determined by the state of the gel masses in it. Evaporation of physical water from the gel masses leads to drying. Conversely, in continuous contact with water (drying under water), the amount of water in the gel masses increases and swelling occurs. The drying phenomena are particularly strong and harmful in cement solutions which contain a greater amount of water than the normal determined by the Vicat instrument (Fig. 1).

2.3. Investigation of the viscosity and bonding time of the A-series composite cement mixture used for the preparation of thermal insulation panels

The standard prescribes that the water content of cement compositions should be up to 30% of the weight of the cement. In the present work, compositions with water contents of 5, 7.5 and 15% above the standard quantity were investigated. The standard quantity is 25-27 %. The 3 % increase from the standard is for wetting of additional substances such as perlite, zeolite, the granules themselves, etc.

The measured viscosity at 30 % water content in the cementitious composite mixture is presented in Table 3.

Table 3. Viscosity data of cement composite mixtures of series A

Series	Subspecies of series A1				Subspecies of series A2			
Composition	A1.1.	A1.2.	A1.3.	A1.4.	A2.1.	A2.2.	A2.3.	A2.4.
Viscosity	cP mN.s/m ²	cP mN.s/m ²	cP mN.s/m ²	cP mN.s/m ²	cP mN.s/m ²	cP mN.s/m ²	cP mN.s/m ²	cP mN.s/m ²
Measurement	mm	mm	mm	mm	mm	mm	mm	mm
Normal at 30% water	70	70	70	70	70	70	70	70
+ 5 % water	65	65	65	65	65	65	65	65
+ 7.5% water	60	60	60	60	60	60	60	60
+ 15 % water	50	50	50	50	50	50	50	50
Bonding time, h	4	7	6	5.5	7	6	5.5	5
Compressive strength, kg/cm ²	280	280	280	280	240	240	240	240
Series	Subspecies of series A3				Subspecies of series A4			
Composition	A3.1.	A3.2.	A3.3.	A3.4.	A4.1.	A4.2.	A4.3.	A4.4.
Viscosity	cP mN.s/m ²	cP mN.s/m ²	cP mN.s/m ²	cP mN.s/m ²	cP mN.s/m ²	cP mN.s/m ²	cP mN.s/m ²	cP mN.s/m ²
Measurement	mm	mm	mm	mm	mm	mm	mm	mm
Normal at 30% water	70	70	70	70	70	70	70	70
+ 5 % water	70	70	70	70	65	65	65	65
+ 7.5% water	60	60	60	60	55	55	55	55
+ 15 % water	55	55	55	55	50	50	50	50
Bonding time, h	6	6	6	6	5.5	5.5	5.5	5.5
Compressive strength, kg/cm ²	250	250	250	250	270	270	270	270

Fig. 2 shows a test specimen made of composition A.2.1 cast with a composite mixture containing 5% water in excess of the

normal 30%. The slump is relatively small. Additional edge strengthening is possible depending on the specific application of the product.



Fig. 2. Test specimen

3. Conclusions

As the water content of the composite mixtures increases from 30 to 45%, the viscosity decreases from 70 to 50÷55 mN.s/m².

With the increase of heat and sound insulation additives (foam glass granules, perlite, zeolite, etc.) the bonding time decreases from 6 to 5.5 h.

With the increase of the additives in the composite material the compressive strength decreases from 280 to 240 kg/cm².

Summing up the results from the investigations, a correlation can be made between the obtained dynamic characteristics regarding thermal and acoustic insulation of the composite materials and the static characteristics - the compressive strength of the specimens of the different formulations, the bonding time of the hydrating ingredient (cement), the viscosity, etc., i.e. a decrease in one of the parameters is at the expense of an increase in the other and vice versa.

Acknowledgments

The authors express their gratitude to the Bulgarian National Innovation Fund and the Bulgarian Small and Medium Enterprises Promotion Agency (BSMEPA) for funding the scientific and applied project / contract № 13 IF-02-21/12.12.2022 between contracting authority BSMEPA and contractors - beneficiary "MAG" Ltd. with partner Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre "Acad. A. Balevski".

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Cathodic protection for cooling water system

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Abstract: The aim of this research was the installation of a cathodic protection system for the inlet and outlet steel sea water pipeline respectively DN 1800 and DN 1600 mm in Adriatic Sea. It is extremely important to maintain the integrity of metallic structures in contact with aggressive effluents for both economic and environmental reasons. The proper design of cathodic protection system can help maintain this integrity and increase the useful service life of metallic structures. All cathodic protection systems should be installed with the intent of conducting uninterrupted, safe operations. When cathodic protection is applied, it should be operated continuously to maintain polarization for this purpose were calculated the protection current density, coating breakdown, protection current demand, sacrificial material weight, anode contact resistances, anode current outputs and number of anodes to be installed.

KEY-WORDS: COATING BREAKDOWN, SACRIFICIAL ANODE, PROTECTION CURRENT, ELECTROLYTE RESISTIVITY

1. Introduction

The Cooling Water System is one of the components of the Thermal Power Plant that is in the bay of Vlore, Adriatic Sea. Its scope is to provide the Plant with the required quantity of water for the necessity of cooling circuit of the engines and to return to sea, after use, the warm water.

The pipelines installed there are hereby listed:

- 1800 mm I.D., approx 1455 m long Water Intake pipeline
- 1600 mm I.D., approx 1050 m long Outfall Water Discharging pipeline.

It is extremely important to maintain the integrity of metallic structures in contact with aggressive effluents for both economic and environmental reasons. The proper design, installation, and maintenance of cathodic protection system can help maintain this integrity and increase the useful service life of metallic structures. Cathodic protection can be installed to protect new or existing structures, but can not protect metallic surface that are not in contact with an electrolyte. All cathodic protection system should be installed the intent of conducting uninterrupted, safe operations. When cathodic protection is applied, it should be operated continuously to maintain polarization.

The cathodic protection system is designed to reach the following objectives:

- To protect the steel surfaces of Sea Water Intake and Outlet components in contact with corrosive electrolyte (sea water)
- To provide sufficient and uniformly distributed current
- To provide system life commensurate with the design life of the Sea Water Intake
- To locate and install system components where the possibility of damage is minimal

The cathodic protection system protect the steel components of Sea Water Intake and Outlet at Thermal Power Plant located in the Adriatic Sea (Albanian Coast).

2. Design data

- The cathodic protection system is designed to provide full protection for 30 (thirty) years.
- An electrolyte resistivity of 20 Ω -cm is assumed for the design calculations of the cathodic protection system.
- The cathodic protection system shall be sacrificial anodes type and the anodes shall be made of aluminum-zinc-indium alloy.
- Polarization potential and anodes characteristics:

According to the Reference Document [1], [2] and [3], the following values has been used (potentials are referred to Ag/AgCl reference electrode):

Protection potential of Carbon Steel : -0.80 V

Anodes potential (at close circuit)	: -1.05 V
Anodes alloy	Zinc = 3.00% ÷ 6.00%
	Indium = 0.010% ÷
0.040%	
	Iron = 0.12% max
	Silicious = 0.15% max
	Copper = 0.006% max
	Titanium = 0.010% max
	Others = 0.020% max each
	Aluminum = balance
Anodes electrochemical efficiency (at 20 °C)	: 2500 Ah/kg
Anodes utilization factor	: 0.85

- Structures to be protected.

The main steel surfaces to be protected are the followings:

- ❖ Steel components of Suction Chamber (Reinforcing plates, Filtering Screens, Manhole, etc.)
- ❖ Steel Pipe $\varnothing_{\text{INN}}$ 1800mm
- ❖ Steel Pipe $\varnothing$ 1600mm
- ❖ Steel Pipe $\varnothing$ 1150mm
- ❖ Steel Pipe $\varnothing$ 14"

The above surfaces shall be in contact with sea water, and they shall be coated surfaces.

- Protection current density

According to the Reference Document [2] and [3], the following protection current densities shall be assumed for ensure the protection of bare steel:

	Initial value [mA/m ²]	Maintenance value [mA/m ²]	Repolarization value [mA/m ²]
STEEL IN SEA WATER	110	60	80

Table 1. Current density

- Coating Breakdown

The coating breakdown factor (CB) describes the anticipated reduction in cathodic current density due to the application of an electrically insulating coating. CB = 0 means that the coating is 100% electrically insulating, CB = 1 implies that the coating has no protective properties [4]. The coating breakdown factor is a function of coating properties, operational parameters, and time. The coating properties are dependent on coating materials, surface preparation and the coating application.

As indicated in the literature [3], the coating breakdown factor can be described as:

$$CB = k_1 + k_2 \cdot t$$

where t is the coating lifetime in years, k_1 and k_2 are constant that are dependent on the coating.

As indicated in the literature [3], for cathodic protection design purposes the initial, average, and final coating breakdown factors are to be calculated. Introducing on the above formula $t = 0$ for initial coating breakdown, $t = [\text{Design Lifetime} / 2]$ for average

coating breakdown and t = Design Lifetime for the final coating breakdown.

The surfaces in contact with sea water have been coated by marine paint coating type JAMSUB having 1200 μ m DFT as minimum. As indicated in the literature [3], this type of coating can be classified as Coating Category III.

As indicated in the literature [3], the constant k_1 and k_2 of Coating Category III to be assumed are: $k_1 = 0.020$ and $k_2 = 0.008$. Consequently, the CB values to be assumed for the design calculations of the cathodic protection system are the followings:

- CB(INITIAL) = 0.02
- CB(AVERAGE)..... = 0.14
- CB(FINAL) = 0.26

3. Cathodic Protection Design

3.1 Surfaces to protect.

With reference to the Sea Water Intake arrangement and dimensions, the surfaces area to be cathodic protection shall be about 176 m². Consider a safety factor of 1.10 (to consider other steel structures not quantifiable), the total surface area [SW] of steel structures in sea water to be protected shall be about 194 m².

With reference to the Sea Water Outlet the steel structures in sea water to protect have the following characteristics:

- ✓ Steel Pipe $\varnothing$ 1600mm
 - Outside diameter [$\varnothing_{OUT}$] = 1644 mm
 - Total length [L] $\cong$ 34 m
 - Surface to protect [SP] $\cong$ 176 m²
- ✓ Steel Pipe $\varnothing$ 1150mm
 - Outside diameter [$\varnothing_{OUT}$] = 1194 mm
 - Total length [L] $\cong$ 23 m
 - Surface to protect [SP] $\cong$ 86 m²
- ✓ Steel Reduction from Pipe $\varnothing$ 1600mm to Pipe $\varnothing$ 1150mm
 - Total length [L] $\cong$ 2 m
 - Surface to protect [SP] $\cong$ 9 m²
- ✓ Steel Pipes $\varnothing$ 14"
 - Outside diameter [$\varnothing_{OUT}$] = 355.6 mm
 - Total length [L] $\cong$ 12 m
 - Surface to protect [SP] $\cong$ 14 m²

Consider a safety factor of 1.10 (to consider other steel structures not quantifiable) [5], the total surface area [SSTR] of steel structures in sea water to be protected shall be about 314 m².

3.2 Protection current demand

The protection current demand is the current needed to maintain an efficient polarization level during the design life [6]. It is calculated by the following formula:

$$I_p = \delta_w \cdot S_w \cdot CB$$

where: I_p = total protection currents (initial, average and final)
 δ_w = protection current densities (initial, maintenance and final) for bare steel in sea water

S = surface area in sea water to protect = 314 m²

CB = coating breakdown (initial, average, final) of steel structures in sea water.

Considering the above symbology and carrying out the calculations for the initial, average, and final life of cathodic protection system, the protection currents shall be:

PROTECTION CURRENT		
Initial value [mA]	Maintenance value [mA]	Repolarization value [mA]
427	1630	4035

Table 2. Protection current sea water intake

PROTECTION CURRENT		
Initial value [mA]	Maintenance value [mA]	Repolarization value [mA]
691	2638	6531

Table 3. Protection current sea water outlet

3.3 Sacrificial material weight

The sacrificial material weight necessary to maintain the protection level during all the design life for the sea water intake line is given by the following formula:

$$W_T = \frac{I_p t 8760}{1000 \varepsilon u} = 201.6 \text{ kg}$$

where: I_p = maintenance protection current = 1630 mA
 t = design lifetime = 30 years
 ε = anode electrochemical efficiency = 2500 Ah/kg
 u = anodes utilization factor = 0.85

The sacrificial material weight necessary to maintain the protection level during all the design life for the sea water outlet line is given by the following formula:

$$W_T = \frac{I_p t 8760}{1000 \varepsilon u} = 326.2 \text{ kg}$$

where: I_p = maintenance protection current = 2638 mA
 t = design lifetime = 30 years
 ε = anode electrochemical efficiency = 2500 Ah/kg
 u = anodes utilization factor = 0.85

3.4 Sacrificial Anodes

3.4.1 Anodes Type

For the cathodic protection system of the Sea Water Intake line, the following type of anode has been selected.

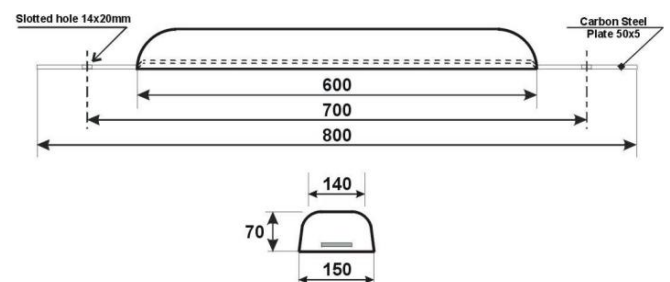


Figure 1. The anode type and dimensions

The anode weights shall be:

- Net Weight = 14.6 kg
- Gross Weight = 16.0 kg

The anodes shall be painted on the surface facing the steel structure surface by Pure Epoxy and they shall be mounted by means of bolts (M12x50) on suitable "C" brackets NP 120 (150 Long) welded on upper and lower steel surfaces of suction chamber.

For the cathodic protection system of the Sea Water Outlet line, the following type of anode has been selected.

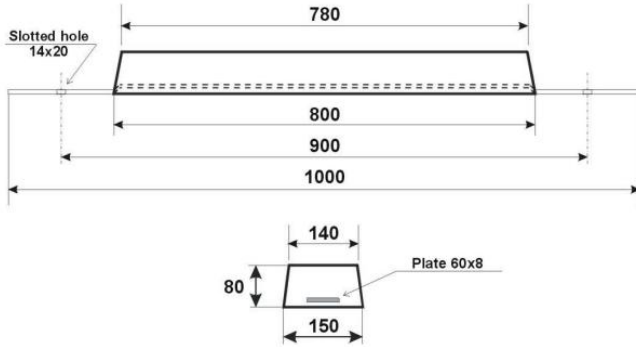


Figure 2. The anode type and dimensions

The anode weights shall be:

- Net Weight = 24.1 kg
- Gross Weight = 27.9 kg

The anodes shall be painted on the surface facing the steel structure surface by Pure Epoxy and they shall be mounted by means of bolts (M12x50) on suitable "C" brackets NP 120 (150 Long) welded on steel pipes Ø 1600 mm and Ø 1150 mm.

3.4.2 Anodes contact resistances.

The calculation of the anodes contact resistances for the Sea Water Intake line is shown below.

As indicated in the literature [3], the selected anode is defined as "short-flush mounted anode" (Length ≤ 4 Width). The contact resistance of this type of anode is given by the following formula:

$$R_A = \frac{0.315 \rho}{\sqrt{A}}$$

where: ρ = electrolyte resistivity = 20 $\Omega \cdot \text{cm}$

A = exposed anode surface area

This calculation has been carried out for the initial and final design life and considering the painted anode surface (as indicated in previous paragraphs).

As indicated in the literature [3], for the final life shall be considered the following assumptions:

- anode consumption = 85%
- the final exposed surface area shall be assumed to be equivalent to the initial area facing the surface to protect.

Considering as above specified, the anodes contact resistances shall be:

- Initial life anode contact resistance = 0.157 Ω
- Final life anode contact resistance = 0.210 Ω

The calculation of the anodes contact resistances for the Sea Water Outlet line is shown below.

As indicated in the literature [3], the selected anode is defined as "long-flush mounted anode" (Length ≥ 4 Width). The contact resistance of this type of anode is given by the following formula:

$$R_A = \frac{\rho}{2 A}$$

where: ρ = electrolyte resistivity = 20 $\Omega \cdot \text{cm}$

A = the arithmetic mean of anode length and width = (790 + 145) / 2 = 467.5 mm

This calculation has been carried out for the initial and final design life and considering the painted anode surface (as indicated in previous paragraphs).

As indicated in the literature [3], for the final life shall be considered the following assumptions:

- anode consumption = 85%
- for long-flush mounted anode the final shape shall be assumed to be a semi-cylinder; the length reduction shall be 8.5% (1% for each 10% of anode consumption)

Considering as above specified, the anodes contact resistances shall be:

- Initial life anode contact resistance = 0.214 Ω
- Final life anode contact resistance = 0.250 Ω

3.4.3 Anode currents output.

The anode current output (I_A) is dependent on the anode contact resistance and the driving voltage between structure and anode potential.

Considering the following parameters (versus Ag/AgCl electrode):

- Protection potential of Carbon Steel: -0.80 V
- Anodes potential (at close circuit) : -1.05 V

The driving voltage considered is 0.25 V.

The anode current output is calculated by the following formula:

$$I_A = \frac{\Delta V}{R_A}$$

where: ΔV = driving voltage = 0.25 V

R_A = anode contact resistance

Also, this calculation has been carried out for the initial and final life of anodes. Considering as above specified, the anode current output shall be:

For the Sea Water Intake line

- Initial life anode current = 1592 mA
- Final life anode current = 1190 mA

For the Sea Water Outlet line

- Initial life anode current = 1168 mA
- Final life anode current = 1000 mA

3.5 Number of anodes to install.

The number of anodes shall satisfy both the current requirements to protect the surfaces of components of Sea Water Intake and Sea Water Outlet and the sacrificial material weight requirement which is needed to ensure the protection during the lifetime. The number of anodes is given by the highest results of the following ratios:

$$N_{A[initial]} = \frac{I_{P[initial]}}{I_{A[initial]}}$$

$$N_{A[final]} = \frac{I_{P[final]}}{I_{A[final]}}$$

$$N_{A[weight]} = \frac{W_T}{W_A}$$

where: $N_{A[initial]}$ = number of initial anodes
 $N_{A[final]}$ = number of final anodes
 $N_{A[weight]}$ = number of anodes for to ensure the weight needed
 $I_{P[initial]}$ = initial protection current
 $I_{P[final]}$ = final protection current
 $I_{A[initial]}$ = anode initial life current
 $I_{A[final]}$ = anode final life current
 W_T = total net weight of anodes
 W_A = anode net weight

Considering the above symbology and replacing the numerical values previously calculated, the number of anodes for Sea Water Intake shall be:

$I_{P[initial]}$ [mA]	$I_{A[initial]}$ [mA]	$N_{A[initial]}$ [No.]	$I_{P[final]}$ [mA]	$I_{A[final]}$ [mA]	$N_{A[final]}$ [No.]	W_T [kg]	W_A [kg]	$N_{A[weight]}$ [No.]
427	1592	1	4035	1190	4	201.6	14.6	14

Table 4. Number of anodes for sea water inlet

Consequently, for the cathodic protection of steel components of Sea Water Intake, 14 (fourteen) anodes must be installed.

Considering the above symbology and replacing the numerical values previously calculated, the number of anodes for Sea Water Outlet shall be:

$I_{P[initial]}$ [mA]	$I_{A[initial]}$ [mA]	$N_{A[initial]}$ [No.]	$I_{P[final]}$ [mA]	$I_{A[final]}$ [mA]	$N_{A[final]}$ [No.]	W_T [kg]	W_A [kg]	$N_{A[weight]}$ [No.]
691	1168	1	6531	1000	7	326.2	24.1	14

Table 5. Number of anodes for sea water outlet

Consequently, for the cathodic protection of steel components of Sea Water Outlet, 14 (fourteen) anodes must be installed.

4. Results and discussion

The difference between the calculated and measured anode current was very low. Measurements of protective current flows from electrolyte into the structure were taken every week to check the variation by time of the current value.

Anode performance depends on the electrolyte resistivity as well as the anode material and size. The sea water resistivity of 300 Ω has a better conductivity than in soils. The aluminum-zinc-indium alloy anode that used is suitable for water application, because of its high driving voltage and low consumption rate.

The used anode is composed of a metals more active in the Galvanic Series than the structure to be protected. It serves essentially as a source of portable electrical energy. The potential difference of zinc with respect to steel is about 1,03V and hence current output per anode is also less. This low voltage is sometimes considered as an advantage over higher impressed voltages in that the danger of overprotection to some portion of the system is less.

From the current output line chart, there is a decrease in current output relative to the time. This is due to the reduced anode surface during the life of the system. The dissolving anode must also obey Faraday's law that the wasting of the anode will be proportional to the total current delivered. Therefore, as the anode dissolves, the resistance it presents to the circuit increased and the current measured decreased.

5. Conclusion

The calculation of the cathodic protection system with sacrificial anode was presented in this paper. The design for sacrificial anode makes use of the corrosive potential for different metals. The current required for carbon steel pipe is supplied by the corrosion of the zinc anode that has a higher positive charge than the protected structure. This electric potential (voltage) difference causes a greater attraction of negative free electrons than the ions in the carbon steel pipe. The result is that the zinc anode gets sacrificed (corrode) and the corrosion process in the carbon steel pipe is interrupted and hence protected.

The calculation principles and measurements of cathodic protection are quite straightforward and based on assumption. However, their application in real systems is often sufficiently complex to prelude quantitative determinations.

The installation of the cathodic protection system was carried out successfully. The water intake and outlet pipelines are still working properly.

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The influence of aging parameters on thermal, mechanical and structural properties of the EN AW-6060 aluminum alloy

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Abstract: This paper investigates the influence of aging parameters (temperature and time) on thermal, mechanical and structural properties of the EN AW-6060 aluminum alloy. Thermal diffusivity and hardness were measured after applied heat treatments followed by investigation on scanning electron and transmission electron microscopes. Heat treatments included: solutionizing at 550°C for 1 hour followed by quenching in ice water; after quenching samples were aged at two separate temperatures of 180°C and 200°C for 1-8 hours. The results show that hardness gradually increases with aging time achieving peak value of 95 HV₁₀ after aging at 180°C for 5 hours. Thermal diffusivity also increases with both aging time and temperature achieving peak values after aging at 200°C for 4 hours. SEM/EDS analysis show the existence of finely distributed precipitates containing Mg, Si and Fe. TEM investigation confirms the existence of rod-shaped precipitates several nanometers in length.

Keywords: EN AW-6060, AGING, HARDNESS, THERMAL DIFFUSIVITY, MICROSTRUCTURE

1. Introduction

The EN AW-6060 aluminum alloy belongs to the Al-Mg-Si alloy system. Alloys from this system are of particular interest to the researchers due to their technological importance and exceptional increase in hardness due to precipitation hardening [1-3]. Besides mechanical properties, other properties like electrical conductivity, thermal diffusivity, and thermal conductivity can also be improved by aging [4]. The change in mechanical, thermal, and structural properties is due to the precipitation of different metastable phases, but primarily by the precipitation of β'' precipitates (Mg_5Si_6) [5]. Formed precipitates cause severe lattice distortion due to incoherency with the matrix, which in turn leads to inhibition of dislocation movement and an increase in the alloy's hardness [6].

The alloys from this system are usually aged for a very long time at temperatures below 200°C in order to achieve the desired hardening. Many authors investigated this type of aging parameter on mechanical, structural, and other properties [1, 3, 5-9]. The EN AW-6060 aluminum alloy is a great candidate for the production of thermal components that require, besides satisfactory values of hardness, high thermal diffusivity. Because of that, some researchers investigated the influence of precipitation on the thermal properties of the Al-Mg-Si system [4, 10-14]. The authors showed that the thermal properties of Al-Mg-Si alloys are highly influenced and can be enhanced by different aging parameters.

Based on the reviewed literature, it can be concluded that there is a great influence of aging parameters on thermal and mechanical properties; therefore, it is very important that research in this area continues. Accordingly, our interests were focused on investigating the aging parameters, which included one conventional aging temperature (180°C) and one aging temperature that was higher than the conventional ones (200°C). At both aging temperatures, the aging time was from one to eight hours, after which thermal diffusivity, hardness, and microstructure were investigated.

2. Experimental procedure

For this investigation an EN AW-6060 alloy was chosen. The alloy was delivered in aged condition in the form of the extruded rectangular bars. The chemical composition was determined by optical emission spectrometer "Belec Compact Port". Results of the chemical analysis are given in Table 1.

Table 1: Chemical composition of the investigated alloy (mass %)

Si	Mg	Fe	Cu	Mn	Cr	Zn	Ni
0.49	0.594	0.182	0.012	0.006	<0.003	0.01	0.028
Ti	Pb	V	Co	Sn	Zr	Al	
0.005	<0.003	0.014	<0.003	<0.003	<0.003	98.62	

In order to remove the as-received condition, all samples were annealed at 550 °C for 6 h in the electric resistance furnace Heraeus K-1150/2, and cooled in air. To prepare the samples for the aging treatment, samples were heated again at 550°C for one hour and quenched in ice water in order to obtain a supersaturated solid solution (α_{SSS}). After quenching, samples were isothermally aged at 180°C and 200°C for 1–8 hours. Properties of the aged samples were compared to the as-quenched sample for comparison (annotated as quenched state in the presented figure). After the heat treatment, samples were subjected to different characterizations. Hardness was measured on the VEB Leipzig Vickers hardness tester with a 10 kg load and a 15 s dwelling time, according to the ASTM E384 standard [15].

On the TA Instruments DXF 500 thermal conductivity meter, the xenon flash method was applied to determine the thermal diffusivity of the investigated samples after different heat treatments by irradiating the disc-shaped specimens with a diameter of 12.7 mm with the xenon lamp in a nitrogen atmosphere. The thermal conductivity as a function of temperature was calculated according to the equation:

$$\lambda(T) = \rho(T) \times c_p(T) \times \alpha(T) \quad (1)$$

where, λ - thermal conductivity; (W/m·K), ρ - density; (kg/m³), c_p - specific heat capacity; (J/kg·K), α - thermal diffusivity; (mm²/s), T - temperature; (°C).

For thermal diffusivity measurements, four different samples were chosen based on the hardness measurements: underaged samples (aged for 1 hour at 180°C and 200°C) as well as peak aged samples (aged for 4 or 5 hours at 180°C and 200°C) were chosen for the investigation. The aging condition was determined by hardness measurements. These samples were investigated at four different temperatures (25°C, 75°C, 150°C, and 250°C).

The TESCAN Vega 3 LMU scanning electron microscope equipped with an EDS X-act detector by Oxford Instruments was used for metallographic investigation of the samples. The preparation of the samples included wet grinding on a series of SiC papers and polishing with alumina suspension with two different granulations of Al₂O₃: particle sizes of 0.3 μ m and 0.05 μ m. Dix-Keller solution was used for the etching of the samples by immersion to reveal the microstructure.

Transmission electron microscopy was used to analyze the microstructure at the nanolevel. For this analysis, the sample with the highest hardness was chosen (aged at 180°C for 5 hours). In order to obtain transparent TEM foils, "Gatan PIPS 691" was used for sample preparation. TEM analysis was performed on a "Jeol JEM 2010F" transmission electron microscope.

3. Results and discussion

Figure 1 shows the change in hardness values as a function of time during isothermal aging of EN AW-6060. Looking at the graphs shown in Figure 1, it can be concluded that the aging time has a great influence on the hardness values. With the increase in aging time, the hardness of the aged samples gradually reaches its maximum value and then decreases. The maximum hardness value was reached after aging at 180°C for 5 hours. The obtained value was 95 HV₁₀, which was 69.6% higher than the hardness value of the quenched sample (56 HV₁₀). It can be assumed that, in the first four hours of aging, the precipitation of the pre-β" metastable phase occurs. After quenching, a large number of vacancies were created, promoting the nucleation of the pre-β" phase. During aging, Mg and Si atoms diffuse from the solid solution and move towards the pre-β" phase, exchanging places with Al atoms. As a result, there is a growth of precipitates and a gradual loss of coherence with the Al lattice. With the increase in aging time, the exchange of atoms of alloying elements with Al atoms increases, so the phase transformations continue according to the precipitation sequence [5]. The hardness maximum shown in Fig. 1 is obtained due to the formation of the β" metastable phase (Mg₅Si₆). This has been confirmed by many authors [1-3, 5, 7-9, 16]. According to Marioara et al. [1], although the precipitate density during the precipitation of the β" phase is low, the hardness reaches a maximum because the incoherency with the lattice increases. After aging for 6–8 h, precipitates of the β" phase grow and coagulate, which leads to a decrease in the hardness values.

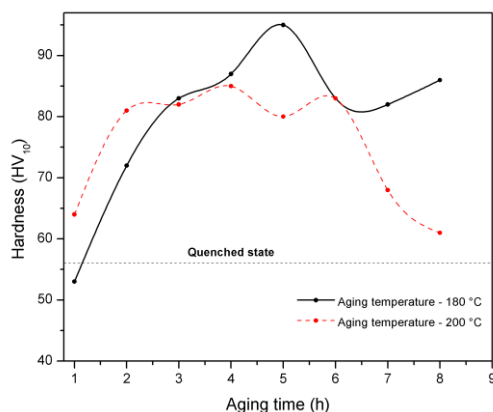


Fig. 1 Change in hardness values as a function of aging time at two different temperatures

From the further analysis of the graphs in Fig. 1, it can be concluded that aging at higher temperatures leads to faster attainment of maximal hardness values. However, the maximum values of hardness achieved after aging at a higher temperature are lower than those obtained after aging at lower temperatures. In the first 2 hours of aging, the achieved hardness values are higher during isothermal aging at 200°C compared to 180°C. This is explained by the fact that with an increase in the aging temperature, there is also an increase in the diffusion rate, so the precipitation of the pre-β" phase and the loss of coherence occur faster. Nevertheless, in order to achieve a true peak aged state, a lower aging temperature with longer aging times must be used.

Thermal diffusivity of the aged samples was investigated at four different temperatures as shown in tables 2 and 3.

Table 2: Change in thermal diffusivity after aging at 180°C for different times at different measuring temperatures

Temperature (°C)	Thermal diffusivity (mm ² /s)	
	After aging at 180°C for 1 hour	After aging at 180°C for 5 hours
25	78.51	87.38
75	77.07	85.94
150	76.88	84.45
250	78.5	83.25

Table 3: Change in thermal diffusivity after aging at 200°C for different times at different measuring temperatures

Temperature (°C)	Thermal diffusivity (mm ² /s)	
	After aging at 200°C for 1 hour	After aging at 200°C for 4 hours
25	81.75	96.53
75	81.49	96.55
150	80.75	93.76
250	81.01	90.6

* Thermal diffusivity of the quenched sample = 85 mm²/s

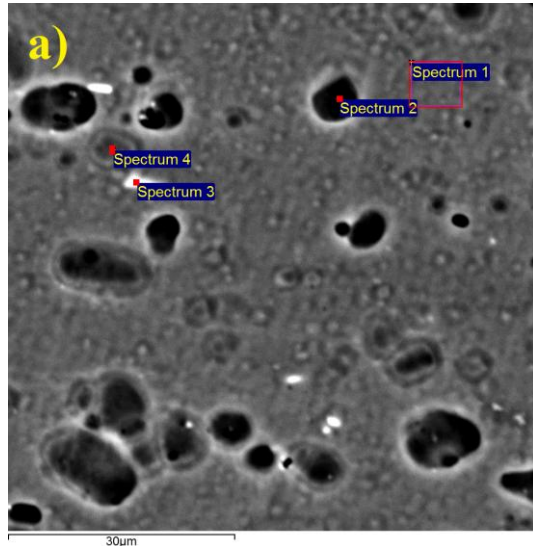
These temperatures were chosen to represent two different stages in the precipitation process. Samples aged for one hour represent the underaged samples and, samples aged for 4 or 5 hours represent the peak aged state, according to the hardness graph given in Fig. 1. By reviewing the results given in Tables 2 and 3, it can be concluded that the thermal diffusivity of underaged samples is lower, while the thermal diffusivity of peak aged samples is higher than those obtained for the quenched sample. Peak aging had a positive effect on thermal diffusivity values. The maximum value of thermal diffusivity was obtained after aging at 200°C for 4 h, and it is 13.6% higher in comparison to the quenched sample. When aging for 1 hour, the thermal diffusivity values are lower than those obtained for the quenched sample. At these aging parameters, the pre-β" phase (GP-zones) is formed. This type of precipitate has the effect of scattering electrons, which leads to a decrease in thermal diffusivity. With an increase in aging time (4 or 5 hours), the amount of precipitate increases due to the reduction of alloying elements in the solid solution; consequently, the thermal diffusivity increases [4, 10].

Thermal diffusivity is highest when the saturation of the solid solution is lowest, and in this case, that was achieved by the precipitation of the β" phase. Also, by comparing the results in Tables 2 and 3, it can be concluded that at higher aging temperatures, diffusion is accelerated, so the precipitation intensifies, which leads to a faster reduction of alloying elements in the solid solution, leading to an increase in thermal diffusivity. By increasing the measurement temperature (represented by the rows in the tables), the thermal diffusivity decreases due to thermal vibrations in the lattice. This was confirmed in peak aged samples. In underaged samples, this phenomenon is not observed. In these samples, a sudden increase in thermal diffusivity values can be observed at 250°C. This increase can be attributed to additional aging. Given that these samples are underaged, reheating the samples at higher temperatures, at which precipitation takes place according to the precipitation sequence, can result in additional aging. Additional aging causes a new amount of precipitates to be formed, which leads to the reduction of alloying elements in the solid solution, leading to an easier flow of electrons.

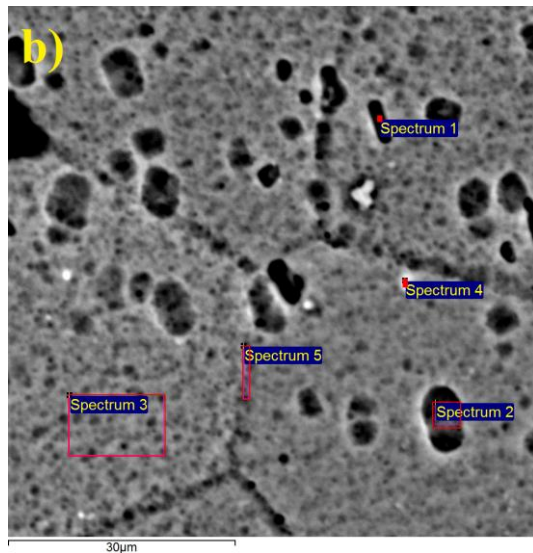
For a deeper analysis, the sample with the highest value of hardness (aged for 5 hours at 180°C) was investigated on TEM. Additionally, SEM-EDS analysis was performed on samples underaged and peak aged at 200°C that were subjected to thermal diffusivity analysis.

Fig. 2a-b show the SEM-EDS analysis of the on samples underaged and peak aged at 200°C, respectively. By analyzing figures 2a–b, it can be assumed that the microstructure of the peak aged sample is covered with finely distributed precipitates of the metastable β" phase, which is shown by spectrum 3 in Figure 2b. This can also be stated for the sample that was underaged because this is a possibility due to the high aging temperature combined with the short aging time (Fig. 2a). Analysis of spectrum 1 (Fig. 2a) shows precipitates containing Mg and Si. Also, an AlFeSi phase appears in both analyzed samples, represented by spectrum 3 in Fig. 2a and spectrum 4 in Fig. 2b. Also, somewhat larger particles containing silicon with and without magnesium were analyzed in the microstructures. Those particles are represented by spectrums 2 and 4 in Fig. 2a and spectrums 1 and 2 in Fig. 2b.

The additional analysis was performed using a transmission electron microscope on the samples aged for 5 hours at 180°C.



Spectrum	Mg	Al	Si	Fe
1	0.41	99.13	0.46	
2	0.48	99.18	0.34	
3		89.18	3.51	7.32
4		99.5	0.49	



Spectrum	Mg	Al	Si	Fe
1		99.51	0.49	
2		99.4	0.57	
3	0.31	98.64	0.83	0.23
4		91.97	2.72	5.31
5		99.41	0.59	

Fig. 2 SEM-EDS analysis of the samples underaged and peak aged at 200°C for 1 and 4 hours, respectively

The peak aged sample was subjected to TEM analysis. The TEM microphotograph (Figure 3) shows the precipitation in the peak aged sample. The SAED (selected area of electron diffraction) image (Figure 4) shows the orientation of the precipitates in the crystal lattice. TEM micrograph was imaged in the [0 0 1] zone axis of Al in order to visualize the precipitates. Looking at Figs. 3 and 4, it can be concluded that small needle-shaped precipitates with a size of several tens of nanometers are visible. The density of the precipitates is high, and they are distributed quite evenly throughout the microstructure of the investigated sample [1, 5, 6, 8].

The presented microstructures in figures 2-4 are in agreement with the results given for hardness and thermal diffusivity measurements.

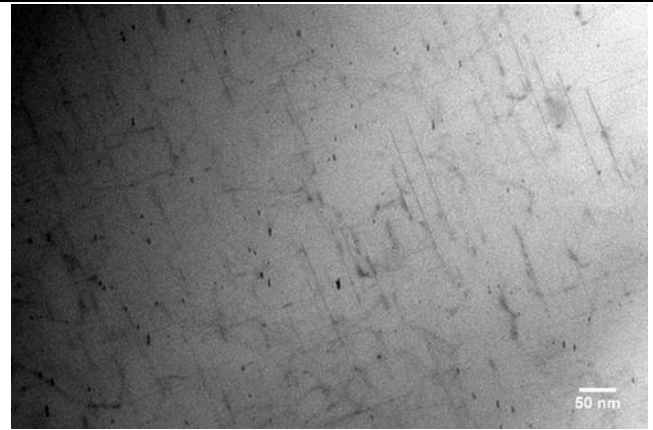


Fig. 3 TEM microphotograph of the sample peak aged at 180°C for 5 hours

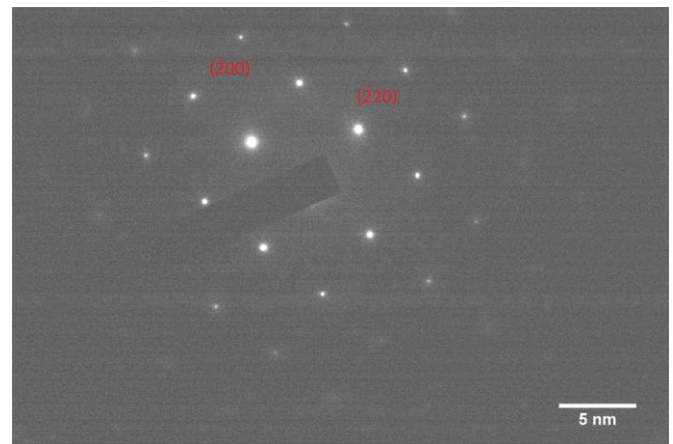


Fig. 4 SAED diffraction pattern of the sample peak aged at 180°C for 5 hours

4. Conclusions

Based on the results obtained during the investigation of the influence of aging on the thermal, mechanical, and structural properties of the EN AW-6060 aluminum alloy, the following conclusions were drawn:

- Isothermal aging caused significant increase in mechanical and thermal properties. The highest improvement in hardness values was obtained after aging at 180 °C for 5 hours. It can be assumed that hardening effect was caused by the precipitation of metastable β'' phase.
- Thermal diffusivity was measured in four different samples that represent underaged and peak aged states. The underaged samples showed lower values of thermal diffusivity in comparison to the quenched sample due to precipitation of electron scattering phases. The highest values of thermal diffusivity were obtained after aging at 200°C for 4 hours, when the highest degree of precipitation from the solid solution was caused.
- Microstructural investigation confirmed the existence of finely dispersed metastable phases which caused the enhancement of thermal and mechanical properties. The responsible phase is believed to be the β'' phase.

5. Acknowledgments

The research presented in this paper was done with the financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-47/2023-01/200131.

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Experimental coatings for photovoltaic panels obtained by the sol-gel method based on compositions with the participation of Y_2O_3 and ZrO_2

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Abstract: A summary study of the development of solar energy and the main factors determining the productivity of photovoltaic systems has been carried out. The predominant surface contaminants of solar panels, reducing the efficiency of photovoltaic installations, and the existing different design types of cleaning systems for their effective removal are examined. The main trends in the development of single-layer and multi-layer hydrophobic and other oxide coatings with diverse performance indicators suitable for solar panels are traced. In laboratory conditions, experimental self-cleaning coatings (based on compositions with the participation of Y_2O_3 and ZrO_2) deposited by the sol-gel method on vitreous samples were obtained. The structure and morphology of the prepared thin films and the technological conditions for the deposition of nanoscale layers with different functional characteristics were investigated. The experimental results represent a prerequisite for the development of a series of additional compositions and a detailed technological regime for obtaining various modifications of resistant, long-lasting self-cleaning coatings, potentially applicable to photovoltaic panels.

Keywords: PHOTOVOLTAIC SYSTEMS, SOLAR ENERGY, SURFACE CLEANING, Y_2O_3 and ZrO_2

1. Introduction

As a promising energy alternative, new generations of ecological and efficient systems for electricity production based on renewable energy sources are being developed [1]: photovoltaic, wind generator, hydroelectric, geothermal, hybrid and other plants. In recent decades, there has been a trend of increasing interest in the construction of photovoltaic plants of various capacities [2-6]: from relatively small installations intended for single-family or multi-family residential and business buildings to systems for manufacturing enterprises, as well as extensive solar parks. According to the distribution of the produced electricity, solar power plants are divided into several groups [2,5,6]: stand-alone systems (providing power supply only to isolated sites), photovoltaic installations integrated with the existing electricity distribution network and combined systems combining the functional capabilities of the previous ones.

The working capacity and efficient functioning of photovoltaic installations is determined by the operating conditions and the condition of the facilities [2,7,8]: positioning of the systems, orientation of the solar modules, climatic characteristics of the designated region, seasonal weather fluctuations, dynamics of solar activity, presence of adjacent objects shading the modules, serviceability and depreciation of the facilities and others. An essential factor having a significant effect on the performance of solar systems is the condition of the working surface of the photovoltaic panels and the presence of contaminants. The main pollutants are dust particles [7] (of technogenic or other origin), heterogeneous surface deposits formed under the influence of dynamic weather conditions, products of the life cycle of a number of organisms and others.

Cleaning systems (manual, robotic and automated) with different functional capabilities and specific operating requirements are used to remove deposited pollutants from solar panels [2,8]. The designed manual cleaning systems are mostly suitable for relatively small PV installations, but are not an appropriate solution for large solar parks. At the same time, automated and robotic cleaning systems require significant capital investments and qualified service. On the other hand, to ensure high efficiency of photovoltaic systems, the use of self-cleaning coatings deposited on the working surface of the solar panels is an expedient option [5]. This allows the reduction of losses (from pollution of the photovoltaic modules) in the production of electricity. Commercially available products for the impregnation (by the users themselves) of photovoltaic panels have a limited effect within a certain period of use. The resulting coatings are characterized by an uneven distribution on the surface

of the panels and gradually deteriorate and lose their functional properties in the process of operation.

In this aspect, an effective solution to the problem is the application of technological methods [9-25], ensuring the production of long-lasting resistant coatings (for photovoltaic panels) combining different operational characteristics.

By means of atmospheric pressure chemical vapour deposition [12,13], antireflective TiO_2 coatings have been deposited, increasing the efficiency of monocrystalline and polycrystalline silicon solar cells.

Self-cleaning [18], antireflective monolayer TiO_2 [14], bilayer ($\text{SiO}_2/\text{TiO}_2$ and $\text{SiO}_2\text{-TiO}_2/\text{SiO}_2\text{-TiO}_2$) [16,18] and trilayer ($\text{SiO}_2/\text{SiO}_2\text{-TiO}_2/\text{TiO}_2$ and $\text{SiO}_2/\text{TiO}_2/\text{SiO}_2\text{-TiO}_2$) [15,17] oxide coatings for solar cells have been obtained using the sol-gel method [14-18].

Self-cleaning and weather resistance nano- SnO_2 /modified silicone oil coating suitable for photovoltaic (PV) glass have been developed [19]. Superhydrophobic self-cleaning composite coatings [20] synthesized in the binary oxide system rGO-TiO_2 were investigated. Various modifications of nanoscale antireflective experimental coatings for solar energy have been obtained: $\text{WO}_3\text{-TiO}_2$ [21], TiO_2/Ni [22], NPs/TiO_2 [23], $\text{Al}_2\text{O}_3/\text{In}$ [23] and others.

Multilayer $\text{TiO}_2/\text{SiO}_2/\text{Ag}$ thin films with self-cleaning properties [24] and high reflectivity suitable for solar reflectors were deposited by magnetron sputtering. The antireflective properties of multilayer $\text{TiO}_2\text{-SiO}_2/\text{SiO}_2/\text{SiN}_x$ coatings (with a specific stacks-structure) applicable for polycrystalline silicon solar cells were investigated [25].

The sol-gel method represents [14-18] a competitive and expedient technological solution for the deposition of coatings, ensuring the production of thin films with the presence of diverse functional properties at lower synthesis temperature values (when compared with other technological approaches) and without the need from using high-tech equipment. The sol-gel technology allows effective control of the parameters of the reaction medium and of the individual technological stages and is applicable for obtaining of long-lasting nano-sized mono- and polyphase, single-layer or multilayer thin films with different structural characteristics.

The use of materials with specific and unique characteristics, successfully applied in various technical fields, can be considered as a perspective possibility for obtaining new self-cleaning coatings for photovoltaic panels. In this regard, materials obtained on the basis of ZrO_2 with proven high operational properties in a variety of working environments are a suitable option.

Three phases are characteristic of ZrO_2 [26-28]: monoclinic (m- ZrO_2 , below 1170°C), tetragonal (t- ZrO_2 , in the interval from 1170°C to 2370°C) and cubic (c- ZrO_2 , above 2370°C). The transformation from one structural form to another is accompanied by the occurrence of stresses and destructive changes in the material [29,30]. The introduction of limited amounts of oxide additives (Y_2O_3 , Ce_2O_3 , MgO , CaO , etc.) allows stabilization of the tetragonal or cubic phase [27,31,32]. Therefore, ZrO_2 finds use mainly in the form of a stabilized phase, being characterized by significant wear resistance and high mechanical, thermal and other characteristics [27]. Materials based on ZrO_2 are applicable in the production of oxygen sensors, fuel cell membranes, microelectronic devices, thermal barrier coatings, refractory, insulation, abrasive and dental products. Experimental double-layer $\text{ZrO}_2/\text{SiO}_2$ antireflective coatings for silicon solar modules have been developed and investigated for the photovoltaic industry [33].

The aim of the present work is to present the characteristics of experimental self-cleaning coatings obtained on the basis of compositions with the participation of ZrO_2 and Y_2O_3 , deposited by the sol-gel method on vitreous samples. In laboratory conditions, the structure and morphology of the prepared thin films and the role of the technological conditions in the formation of their operational properties were investigated. The experimental data obtained are a prerequisite for developing an optimal technological regime for obtaining various modifications of self-cleaning coatings for photovoltaic panels.

2. Experimental procedures

Preparation of stabilized sols from Y_2O_3 doped ZrO_2 .

We strive to:

1. Obtaining stable sols or solutions that will last (with proper preservation) for months and years.
2. Obtain samples with high permeability.
3. Obtaining samples resistant to high temperatures and with high chemical stability.
4. Obtaining samples with evenly applied layers and relatively low roughness (unevenness).

Way of acting:

In this case, sol-gel technology was applied. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ is dissolved in absolute alcohol - so that a 0.3 - 0.4 molar solution is obtained. $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is added to it slowly with vigorous stirring. During hydrolysis, nitric acid is added or stirred until it becomes clear, i.e. until complete dissolution. As a last resort, acetyl acetone or diethanol amine can also be used, which further stabilize the synthesized sol. The resulting liquid is stored in a refrigerator. Instrumental physicochemical study of the synthesized sol.

The figures show layers on glass based on the experiments, and the samples are numbered GLS -0, 3 and 5, where the number is the number of layers.

3. Results and Discussion

Optical characterization was performed with UV-VIS-NIR Shimadzu 3600 double-beam spectrophotometer (Shimadzu Corporation, Kyoto, Japan) in the spectral region of 280-1800 nm. The transmittance spectra of the samples were taken against air. The reflectance spectra were measured by using the specular reflectance attachment (5° incidence angle) and Al coated mirror as reference.

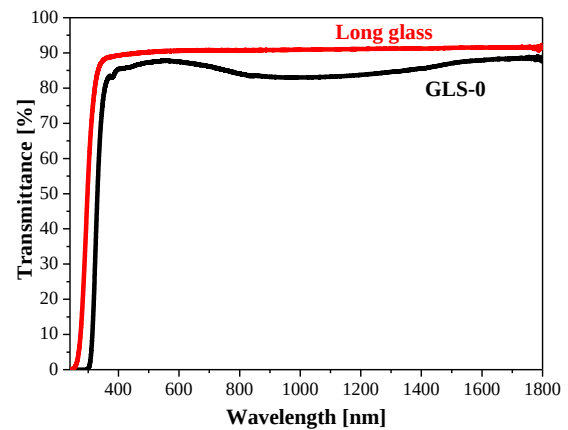


Figure 1. The figure shows the transmission spectrum of a clean GLS-0 substrate

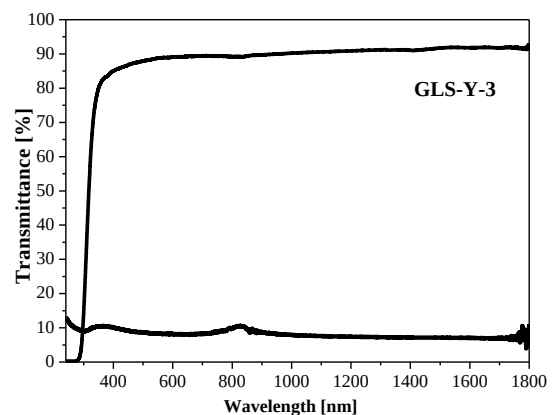


Figure 2. The figure shows the transmission spectrum of a GLS-Y-3

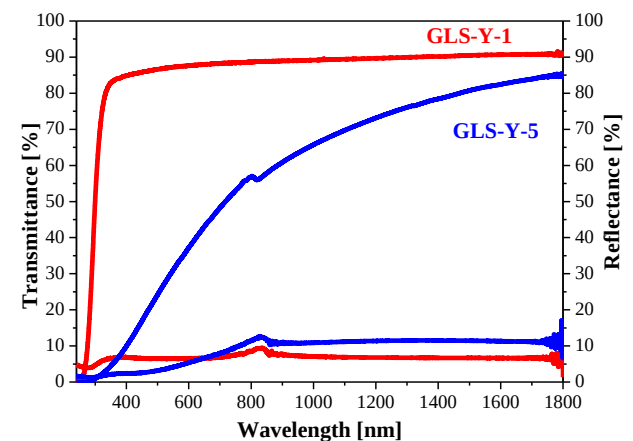


Figure 3. The figure shows the transmission spectrum of a GLS-Y-1 u GLS-Y-5

An X-ray diffractometer with a Bragg-Brentano θ -2 θ focusing system was used. The samples were examined at room temperature with $\text{Cu-K}\alpha$ radiation (monochromatic radiation with wavelength $\lambda = 154178\text{\AA}$) in the interval $20^\circ < 2\theta < 65^\circ$, at a step of 0.025° for 10 seconds. A graphite monochromator was used for better peak resolution (better signal-to-noise ratio).

The size of the ZrO₂ crystallites is calculated according to the Scherrer formula:

$$D = 0.9\lambda / B \cdot \cos\theta$$

D - average crystallite size /Average Crystallite size/

λ - wavelength (in angstroms) - 1.54178 Å /X-Ray wavelength/

θ - Bragg angle (degrees) - $2\theta/2$ /Bragg angle/

B - line broadening FWHM (2 θ), /Line broadening/ must be of dimension radians (rad=20* π /180)

The positions of the X-ray diffraction peaks correspond to tetragonal ZrO₂, according to standard JCPDS card 069-1771. According to Scherrer's formula, the average crystallite size corresponding to the 111 orientation (the peak with the highest intensity) was calculated. It is 31 nm.

The layer thickness was determined on an EPSILON 1 Malvern PANalytical B.V. X-ray Energy Dispersive Spectrometer for X-ray Fluorescence Analysis. (The X-ray energy dispersive spectrometer for X-ray fluorescence analysis, model EPSILON 1 Malvern PANalytical B.V.). Stratos layer analysis software module was used for this purpose.

With this definition, a thickness of the investigated layer of 82nm was established.

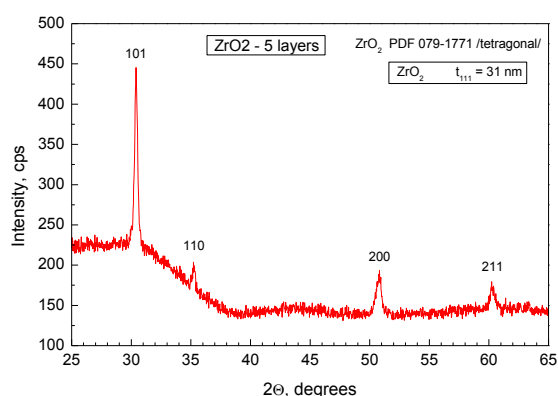


Figure 4. The figure shows the X-ray diffractometer of GLS-Y-5

4. Conclusions

1. Coatings are prepared by the sol-gel method using a dip coating technique. The present study characterizes self-cleaning ZrO₂ and Y₂O₃ thin films for photovoltaic application.

2. Tests were conducted at different layers of the included components, application rate of the solution on the glass substrate and different drying temperatures.

3. The studies were conducted by XRD studies and optically transparent according to the UV-VIS-NIR spectra

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