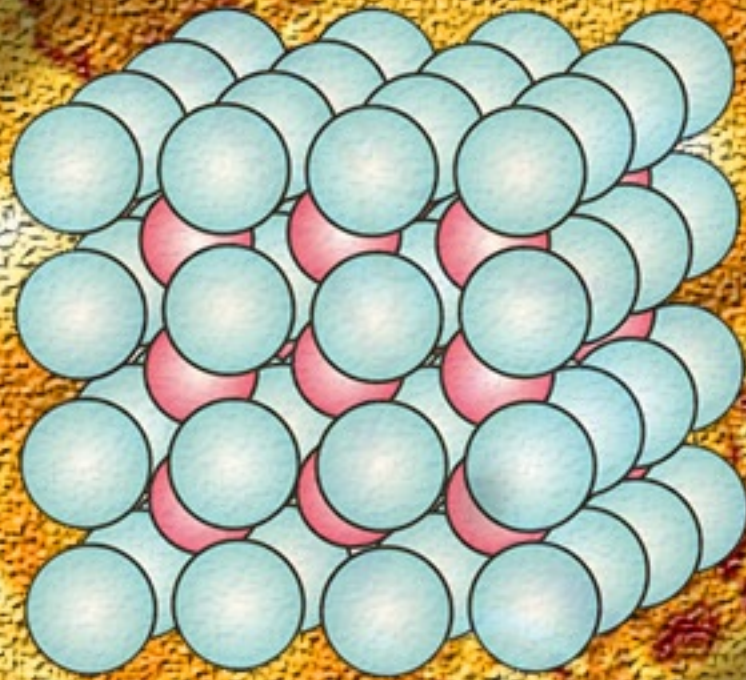


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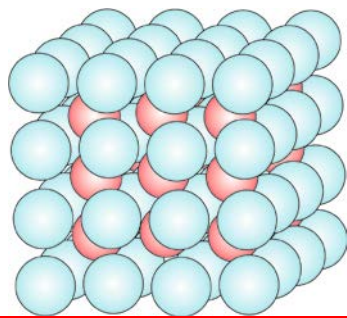
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EFFECT OF STRUCTURE AND TEXTURE ON THE MECHANICAL CHARACTERISTICS OF MAGNESIUM ALLOYS PROCESSED BY EQUAL-CHANNEL ANGULAR PRESSING

ВЛИЯНИЕ СТРУКТУРЫ И ТЕКСТУРЫ НА МЕХАНИЧЕСКИЕ ХАРАКТЕРИСТИКИ МАГНИЕВЫХ СПЛАВОВ, ПОЛУЧЕННЫХ РАВНОКАНАЛЬНЫМ УГЛОВЫМ ПРЕССОВАНИЕМ

PhD Martynenko N.S.^{1,2*}, Tokar A.A.^{1,2}, PhD. Serebryany V.N.¹, PhD. Prosvirnin D.V.¹, Prof., Dr. Sci. Terentiev V.F.¹,

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Abstract: ECAP was carried out with a gradual decrease in temperature and an increase in the number of passes on two medical magnesium alloys: WE43 (Mg-3.56%Y-2.20%Nd-0.47%Zr) and ZX10 (Mg-1.0%Zn-0.3%Ca). It was shown that ECAP leads to a significant refinement of the alloys structure. For ZX10 alloy, the average grain size after ECAP decreased from $\sim 105 \mu\text{m}$ in the initial state to $8 \pm 0.18 \mu\text{m}$ in the longitudinal section and to $4 \pm 0.19 \mu\text{m}$ in the transverse one. For the WE43 alloy, the average grain size was changed from $70 \mu\text{m}$ to $0.69 \pm 0.13 \mu\text{m}$ and the precipitation of particles of the $\text{Mg}_{41}\text{Nd}_5$ phase with an average size of $0.45 \pm 0.18 \mu\text{m}$ was also discovered. At the same time, the grain refinement led to an increase in the strength characteristics of the both alloys (including fatigue strength), and increased prismatic slip activity (along with the formation of an inclined basal texture in ZX10 alloy) led to an increase in their ductility. The alloy structure formed during the ECAP process does not lead to a decreasing in resistance to chemical corrosion.

KEYWORDS: MAGNESIUM ALLOYS, EQUAL CHANNEL ANGULAR PRESSING, ULTRAFINE GRAINED STRUCTURE, TEXTURE, MECHANICAL PROPERTIES, FATIGUE LIFE

1. Introduction

Magnesium alloys have been actively studied in many countries for two decades as medical materials [1-3]. Currently, the most studies are aimed at obtaining the optimal composition and properties of these materials. The development of the compositions of such alloys is complicated by the fact that the selected alloying elements must have good biocompatibility and fulfill their basic properties: strengthen the alloys and increase its corrosion resistance. Therefore, a limited number of elements are now used (Ca [4], Zn [5], Ag [6], Li [7], Sr [8], Mn [9], some rare-earth metals [10-12]), which fall in their characteristics under both criteria. But just only alloying is not enough to obtain optimal properties. Therefore, alloys usually are deformed to improve their mechanical properties. In this sense, severe plastic deformation [13], and in particular equal-channel angular pressing (ECAP) [14], which allows significantly strengthening magnesium alloys by formation an ultrafine grained (UFG) structure, is especially attractive. In addition, the cases of increasing the corrosion resistance of magnesium alloys after formation of UFG structure are known [15, 16]. Therefore, the effect of alloying and ECAP on the structure and properties of two medical magnesium alloys (WE43 and ZX10) was studied in this study.

2. Materials and Methods

Two magnesium alloys were investigated in the work: WE43 (Mg-3.56%Y-2.20%Nd-0.47%Zr) and ZX10 (Mg-1.0%Zn-0.3%Ca). In the initial state, the WE43 alloy was homogenized at 525°C for 8 hours and then air cooled. The ZX10 alloy was also subjected to homogenization at 450°C for 3 hours and then water quenched. The Bc ECAP route was carried out on the machine with a channel intersection angle of 120° with a gradual decrease in the deformation temperature and an increase in the number of passes. For WE43 alloy, the ECAP temperature decreased from 425 to 300°C with a step of 25°C and 2 passes at each temperature ($N_\Sigma = 12$). For the ZX10 alloy, stepwise ECAP was performed with a decrease in temperature from 400 to 300°C with a step of 25°C and also 2 passes at each temperature ($N_\Sigma = 10$) (Figure 1).

The microstructure was examined using an Axio Observer D1m Carl Zeiss optical microscope and an electron microscope JEM-1400 (Jeol, Japan) operating at a voltage of 120 kV . Foils for TEM analysis after ECAP were cut in the longitudinal direction,

mechanically ground up to $180 \mu\text{m}$ and then subjected to ion-bombardment on a GATAN 600 unit. The size of the microstructural units was estimated by the method of random sections using the Image ExpertPro 3 software.

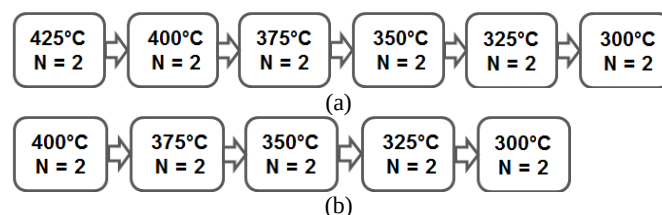


Figure 1 - The ECAP processing regimes employed (N denotes the number of passes at a given temperature)

Texture analysis was carried out using X-ray diffraction in a Rigaku Ultima IV diffractometer with the $\text{CuK}\alpha$ radiation in the reflection mode. Five complete pole figures $\{00.4\}$, $\{20.2\}$, $\{10.2\}$, $\{10.3\}$, $\{11.0\}$ were obtained with a maximum inclination angle $\alpha_{\text{max}} = 70^\circ$ and a step of 5° in the radial angle α and the azimuth angle β on a pole figure. The orientation distribution functions (ODFs) were calculated from the measured pole figures presented as a superposition of a large number (1000) of standard distributions with a small scatter. The centers of standard functions were located on a regular three-dimensional grid in the orientation space [17]. With these ODFs, complete pole figures were also calculated. The volume fractions of the major orientations were estimated using the ODFs as described in [17]. Using the Euler angles and the volume fractions of the orientations, the generalized Schmid factors for the existing deformation systems and the inverse orientation factors were calculated, as described in [18].

The mechanical properties were evaluated through uniaxial tensile tests carried out at room temperature in an Instron 3382 testing machine with an extension rate of 1 mm/min on 33 mm long dog bone-shaped specimens with a gauge length of 15.0 mm and diameter of 3.0 mm . The fatigue tests were carried out under cyclic tension using an ElectroPulsTME3000 machine (testing frequency of 30 Hz , stress ratio $R = 0.1$).

The corrosion properties were investigated by the weight loss method upon immersion of specimens in a 0.9% NaCl solution at

37°C for 4 weeks. Before weighing the specimens after immersion, the corrosion products were removed according to ASTM_G1-03-E.

3. Results and Discussion

The study of the alloys microstructure in the initial state showed that after homogenization in both cases a uniform structure with equiaxed grains is formed (Figure 2 a, b) (an average grain size of $\sim 70 \mu\text{m}$ for the WE43 alloy and $\sim 105 \mu\text{m}$ for the ZX10 alloy). The formation of smaller grains in the case of the WE43 alloy, even despite the longer homogenization duration, is probably associated with the presence of Zr in its composition, which use as a modifier for refinement the structure. In addition, due to the low diffusion rate of rare-earth metal atoms in the case of WE43 alloy, more thermal energy is required to dissolve the phase. ECAP leads to a significant refinement of the structure of both alloys. An ultrafine grained structure with an average grain size of $0.69 \pm 0.13 \mu\text{m}$, as well as globular particles of the $\text{Mg}_{41}\text{Nd}_5$ phase [19] with an average size of $0.45 \pm 0.18 \mu\text{m}$ are formed after ECAP in the WE43 alloy (Figure 2 c). At the same time, ECAP in the ZX10 alloy leads to the formation of a rather inhomogeneous structure elongated along the pressing direction with an average grain size of $8 \pm 0.18 \mu\text{m}$ in the longitudinal section (Figure 2 d) and $4 \pm 0.19 \mu\text{m}$ in the transverse one. The formation of larger grains, in comparison with the previous alloy, is probably associated with a smaller number of ECAP passes, as well as a lower temperature recrystallization of the alloy. The second phase particles were not found in this alloy after ECAP.

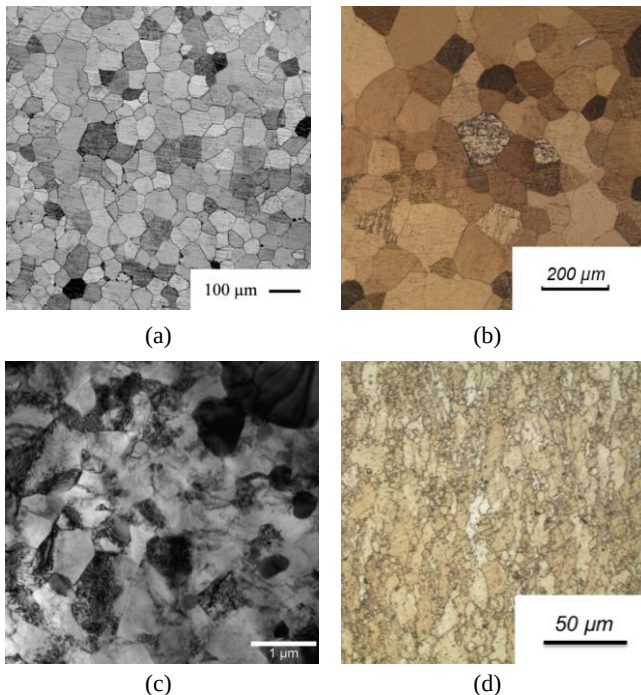


Figure 2 – The microstructure of the WE43 alloy (a, c) and the ZX10 alloy (b, d) in homogenized (a, b) and deformed (c, d) states

The study of the mechanical properties of the alloys showed that the formation of a more dispersed structure after ECAP in the case of the WE43 alloy most significantly strengthened the alloy. So in the initial state, a yield stress (YS) of the WE43 alloy was 161 MPa, an ultimate tensile strength (UTS) - 234 MPa, and an elongation (EL) - 9%. But these characteristics increased to 260 MPa, 300 MPa, and 12.4% after ECAP, respectively. The yield stress was 92 MPa, the ultimate tensile strength - 194 MPa, and the elongation - 12.8% in the case of the initial state of the ZX10 alloy. After ECAP, the ductility is almost doubled to 23.9%, while the strength remains almost unchanged (the yield stress is 106 MPa and the ultimate tensile strength is 215 MPa) (Table 1).

Table 1 – Mechanical properties of WE43 and ZX10 alloys in the initial state and after ECAP processing

	Conditions	UTS, MPa	YS, MPa	El, %
ZX10	Initial state	194	92	12.8
	ECAP	215	106	23.9
WE43	Initial state	234	161	9.0
	ECAP	300	260	12.4

As noted earlier, the increase in strength characteristics is associated with the grain refinement. However, for example, for ZX10 alloy, grain refinement after ECAP more than 10 times does not lead to a significant increase in strength. In addition, for both alloys, despite the refinement of the structure, an increase in ductility is observed. That is, it can be assumed that there are additional factors affecting the final properties. In magnesium alloys, in addition to structure, the transformation of texture also contributes to the change in mechanical properties. Therefore, to assess the contribution of the texture to the change in the mechanical properties of materials, direct pole figures of the alloys were constructed before and after ECAP, and the orientation factors of the main deformation systems and twinning were calculated (Figure 3 and Table 2).

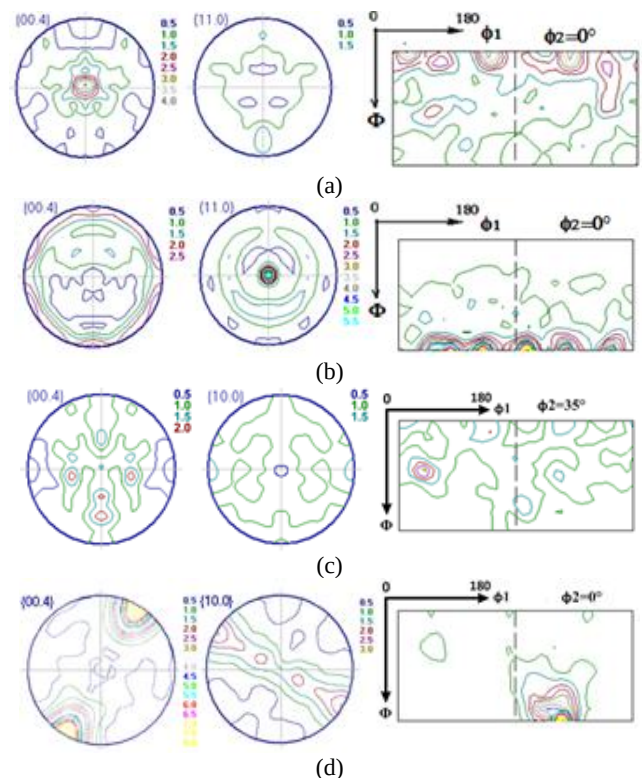


Figure 3 - {00.4} and {11.0} pole figures and ODF sections at $\phi_2 = \text{const}$ for the WE43 (a, b) and ZX10 (c, d) alloys in the initial states (a, c) and after ECAP processing (b, d)

The texture analysis showed that a cardinal change of texture type occurs from a sharp basal texture in the initial state to a sharp prismatic texture in the case of ECAP of the WE43 alloy (Figure 3 a, b). It is known that activation of prismatic slip in magnesium alloys leads to an improvement in their ductility, which we observe for the WE43 alloy. At the same time, the magnesium alloys after ECAP are also characterized by the formation of an inclined basal texture, which has a beneficial effect on the ductility, but does not improve (and often worsens) their strength [19, 20]. We observe a similar situation in the case of the ZX10 alloy, where ECAP leads to the transformation of a diffused basal texture into a sharp basal texture inclined by 80-85° (Figure 3 c, d). At the same time, in the case of alloys with rare-earth metals, fine particles are deposited in the basal planes, which make it difficult to slip dislocations along

them [21]. This leads to partial inhibition of the basal slip and activation of the prismatic one, which does not lead to deterioration in ductility and strength. We observe a similar situation for the WE43 alloy. Moreover, a decrease in the values of orientation factors for prismatic slip planes also indicates an increased likelihood of prismatic slip in the alloys after ECAP (Table 2). The probability of basal and pyramidal slip activity, as well as twinning in the case of WE43 alloy, is reduced. Twinning activity in the case of the ZX10 alloy remains unchanged.

Table 2. Orientation factors for WE43 and ZX10 alloys in the initial state and after ECAP processing

Conditions	Basal {0001} <1120>	Prismatic {1010} <1120>	Pyramidal <c+a>	Twinning {1012} <1011>
Initial state (WE43)	4.6	6.2	4.1	4.0
ECAP (WE43)	6.0	4.3	5.0	5.0
Initial state (ZX10)	4.4	5.1	4.7	4.8
ECAP (ZX10)	5.9	3.9	4.9	4.8

The Figure 4 shows the results of the fatigue life study of the both studied alloys before and after ECAP.

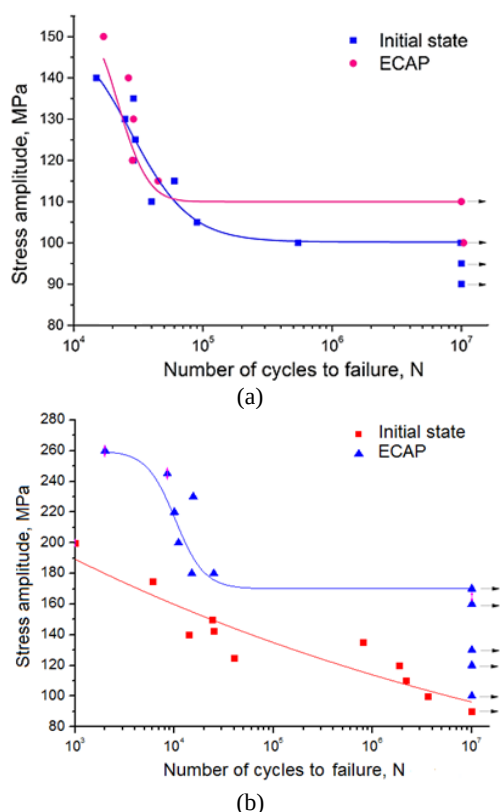
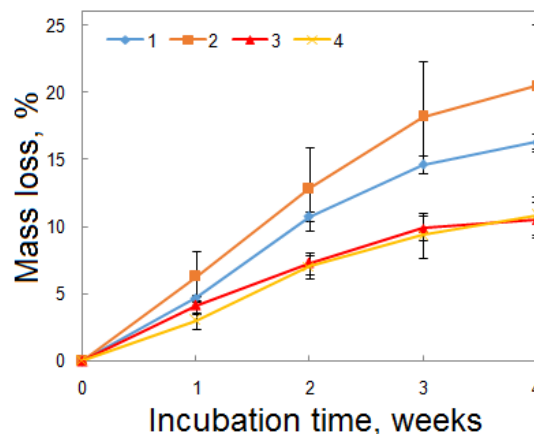


Figure 4 - Fatigue behaviour of the ZX10 (a) and WE43 (b) alloys in the initial states and after ECAP

It was shown that the grain refinement after ECAP leads to an increase in the fatigue limit of both studied alloys. In the case of the ZX10 alloy, the increase in fatigue limit is small, probably due to the formation of an unfavorable texture. So the fatigue limit of the alloy in the initial state was 100 MPa, and after ECAP - 110 MPa. For the WE43 alloy, the increase in the fatigue limit is more substantial: from 90 MPa in the initial state to 170 MPa after ECAP. One of the most important in-service properties of the magnesium medical alloys is their corrosion resistance. The corrosion resistance studies were carried out in a physiological saline solution of 0.9% NaCl at 37 °C in this work (Figure 2).



1 – ZX10 alloy in initial state; 2 – ZX10 alloy after ECAP;
3 – WE43 alloy in initial state; 4 – WE43 alloy after ECAP
Figure 5 – The study of corrosion resistance of the alloys

It was shown that the WE43 alloy has a higher corrosion resistance compared to the ZX10 alloy both in the initial state and after ECAP, apparently, due to the presence of rare-earth metals in the composition. Moreover, ECAP does not lead to a decrease in the corrosion resistance of both alloys. The total mass loss over 4 weeks of testing was 16.3 ± 0.6 and $20.4 \pm 4.7\%$ for the homogenized and deformed states of the ZX10 alloy and 10.5 ± 1.3 and $10.8 \pm 1.5\%$ for the homogenized and deformed states of the WE43 alloy, respectively.

4. Conclusions

1. ECAP leads to significant structure refinement of both studied alloys. For the WE43 alloy an UFG structure is formed with an average grain size of $0.69 \pm 0.13 \mu\text{m}$, as well as $\text{Mg}_{41}\text{Nd}_5$ phase particles with an average size of $0.45 \pm 0.18 \mu\text{m}$ during ECAP. ECAP processing of ZX10 alloy gave rise to grain refinement from $\sim 105 \mu\text{m}$ in the initial state to $4.0 \pm 0.19 \mu\text{m}$ and $8.0 \pm 0.18 \mu\text{m}$ in transversal and longitudinal cross-sections of the billets.
2. The grain refinement caused by ECAP of WE43 alloy result in improved strength characteristics ($\text{YS} = 260 \text{ MPa}$ and $\text{UTS} = 300 \text{ MPa}$), while also raising its tensile ductility to 12.4%. ECAP of ZX10 alloy was shown to moderately increase the mechanical strength of the alloy, while doubling its tensile elongation. The increasing of ductility is believed to be associated with the activation of prismatic slip.
3. A further positive effect of ECAP is an increase of the fatigue limit by $\sim 10\%$ on the ZX10 alloy and $\sim 89\%$ on the WE43 alloy.
4. The above beneficial effects were achieved without ECAP impairing the chemical corrosion resistance.

Acknowledgments

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FUNCTIONALLY GRADED AL MATRIX MATERIALS CONTAINING 10, 20 AND 30 % B₄C_p STACKS

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Abstract: As a relatively new class of materials that exhibits a gradual compositional or microstructural change along one axis, functionally graded materials (FGM) emerged. As a result of this change, properties of the material also vary. This property change can be controlled by tailoring the composition or microstructure of the individual stacks in the FGM.

In the present study, aluminum matrix functionally graded composite materials with increasing amounts of B₄C particles in an aluminum matrix were formed. The functionally graded materials were composed of 4 composite stacks with different compositions; namely, 0, 10, 20 and 30 volume % B₄C particles. The matrix material was aluminum - 4 wt.% copper alloy. Preparation of the functionally graded materials was conducted through powder metallurgical methods including mixing, cold pressing and sintering without pressure. Samples were produced in dimensions according to 3-point bending standards.

Microstructure of the functionally graded materials contained some porosity, amount of which was seen to increase with increasing B₄C reinforcement amount. All the stacks were subjected to Vickers microhardness measurements and it was seen that the hardness of the layers increased significantly with increasing reinforcement amount. The unreinforced layer had a hardness of 55 HV_{0.1} and that of the layer containing 30 % B₄C was 143 HV_{0.1}. On the other hand, the bending strength of the functionally graded material was seen to be lower than that of the unreinforced sample.

Keywords: FUNCTIONALLY GRADED MATERIALS, Al-4Cu

1. Introduction

As a relatively new class of materials that exhibits a gradual compositional or microstructural change along one axis, functionally graded materials (FGM) emerged. As a result of this change, properties of the material also vary. This property change can be controlled by tailoring the composition or microstructure of the individual stacks in the FGM [1].

Chemical composition, porosity or an additional property of the FGM can change gradually in its arrangement. This structure of FGMs prevents formation of any mismatch between the top and bottom surfaces of the material [1].

In order to produce aluminum matrix functionally graded materials, centrifugal casting has been frequently employed in the literature [2,3]. This technique relies on the difference between the density of the matrix phase and the reinforcement particles. Higher density of the reinforcement particles leads to their accumulation on the outer region of the samples, by the action of centrifugal force. In the study of Rajan, SiC reinforced A356 Al alloy FGM parts were obtained by centrifugal casting. It was reported that the volume % of the SiC particles in the outer rim of the samples were in 40-45 % range. The SiC amount gradually decreased in a region of 8 mm in the outer rim of the sample. Hardness of the outer region was about 110 HB whereas the unreinforced region was 90 HB [3].

Another useful method of obtaining the FGM structure is powder metallurgy. In the study of Erdemir et al. [4], SiC reinforced A2024 matrix FGMs were prepared by powder metallurgy. Microhardness of the layers was assessed and an increase up to a certain amount of reinforcement was reported [4].

In the present study, in order to produce functionally graded composite materials with increasing amounts of B₄C particles in an aluminum matrix, cold pressing and sintering was utilized. Obtained FGMs were composed of 4 composite stacks with different compositions: 0, 10, 20 and 30 volume % B₄C particles. Microstructure and mechanical properties of the obtained FGMs were investigated.

2. Experimental Procedure

Preparation of the functionally graded materials was conducted through mixing, cold pressing and sintering without pressure.

Samples were produced in dimensions according to 3-point bending standards [5], which indicated that the span length is 25 mm and thickness is 6 mm and width of the sample is 12 mm.

The FGMs were produced by stacking technique, in which each layer having a definite composition was prepared and laid in a steel mold. After a gentle pressing, the successive stack was laid and thereby a FGM containing 4 layers of the desired thickness was obtained.

The matrix alloy was Al-%4Cu and reinforcement was B₄C particles. Size of aluminum and B₄C particles were smaller than 10 microns. Powders of aluminum, copper and boron carbide were weighed and mixed. The thickness of each stack was calculated as 1.6 mm.

Samples were pressed at 600 MPa pressure. The green samples were sintered in an atmosphere controlled furnace. Sintering was conducted at 610 °C for 30 min in flowing nitrogen.

Sintered samples were subjected to microstructural examinations by optical microscope (Nicon Eclipse, LV150) after metallographic preparation. For the preparation of the samples, 600, 1200 and 3000 grit sand papers were used. Final polishing was done with 1 micron polycrystalline diamond paste. Microhardness measurements were conducted according to Vickers method and 0.1 kg load was applied for 15 seconds. 3-point bending tests were performed by a Shimadzu AG-IC 50 kN unit.

3. Results and Discussion

The weight of the samples before sintering was about 7.50 g. After sintering, there was an increase in the weight of about 30 mg, which was attributed to nitrogen intake during sintering.

Density of the FGM sample was 92 % of the theoretical density.

Bending Strength and Strain

After 3-point bending tests, stress-strain curves of the samples were obtained. The highest tensile stress on the sample during bending test occurs on the bottom side of the sample. In addition, the unreinforced side of the FGM generally presents higher strength and ductility. On the other hand, the side of the FGM having high amount of reinforcement particles is known to possess lower ductility and strength. The properties of the FGM sample are

anisotropic. Therefore, the orientation of the FGM sample during the 3-point bending operation is important and affects the results of the stress-strain test.

The stress-strain graph of the FGM is presented in Fig.1. This bending test was conducted when the unreinforced side of the FGM was facing up, and the 30 % B_4C containing side was facing down. The FGM sample presented a bending strength of 139 MPa. Bending strain value of this sample was about 4.3 %. These values can be considered to be low for aluminum alloys and composites. In our previous studies, it was found that the bending strength of the unreinforced Al-%4Cu alloy is around 370 MPa and its bending strain is around 25 %. The low strength of the FGM may be attributed to the orientation of the sample. The brittle layer, containing 30 % B_4C has very low ductility and thus, formation of a crack during the bending test is very easy on that side. Once the crack forms, it propagates vertically, along the thickness of the sample, on to the upper layers. The strength of the FGM is expected to be higher when the unreinforced side is facing down, since the unreinforced layer is more ductile and formation of a crack is more difficult.

When the stress-strain plot of the FGM is examined, it can be seen that there are 3 drop points in the strength (as pointed with arrows). The first drop is believed to belong to the formation of the crack at the bottom stack. The second and large drop most probably forms when the level containing 20% B_4C cracks. After that there is a slight increase in stress, which may be related to strain hardening of the remaining 2 layers that are low in B_4C composition.

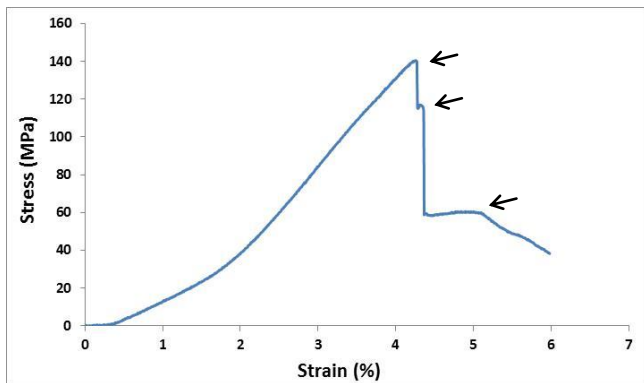


Fig. 1 Stress-strain plot of the FGM sample obtained by three point bending test.

Macrostructure

Macrostructure of the FGM can be visualized in Fig. 2 and Fig. 3. Fig.2 is a macro image of the fracture surface of the FGM after bending test. Fig.3 is a stereo microscope image. In both figures, the levels in the macrostructure of the functionally graded material can be visualized.



Fig. 2 Image of the FGM after bending test, exposing the 4 levels in its structure.

Formation of a delamination defect is seen in Fig.3 (pointed with arrow). This delamination may probably form during bending test, after the formation of vertical cracks. The delamination of levels is undesired in FGMs. Increasing the sintering time or temperature may be useful in order to provide better bonding between the levels.

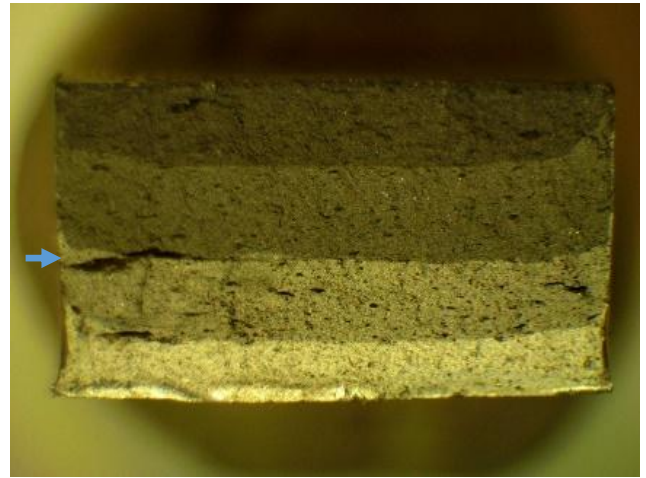


Fig. 3 Stereo microscope image of the FGM having 0, 10, 20, 30 % B_4C . (Total thickness is about 6.5 mm)

Microstructure

After polishing the fracture surfaces of the FGM, they were examined by optical microscope. Microstructure of the FGM is given in Figs. 4-6. Fig.4 presents the transition region of the stacks having 0 and 10 % B_4C . In Fig.5, transition from stack having 10 % B_4C to 20 % B_4C can be seen. Transition zone of the stacks having 20 and 30 % B_4C is given in Fig. 6. In Figs 5 and 6, transition line between different stacks is not easy to distinguish; therefore it was marked with a dash-line. B_4C particles are evenly dispersed in the each level of the FGM.

The black irregular shapes in these micrographs are voids in the structure of the FGM. It can be seen that the amount of the voids increases with the increase in the amount of B_4C particles in the stacks.

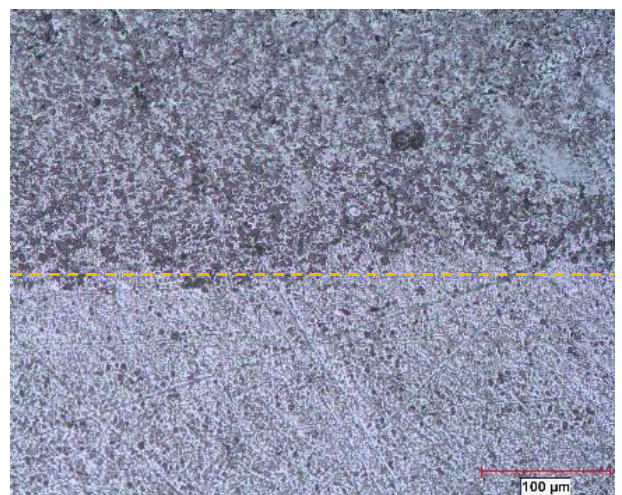


Fig. 4 Optical microscope image of the transition region between the levels containing 0 % and 10 % B_4C .

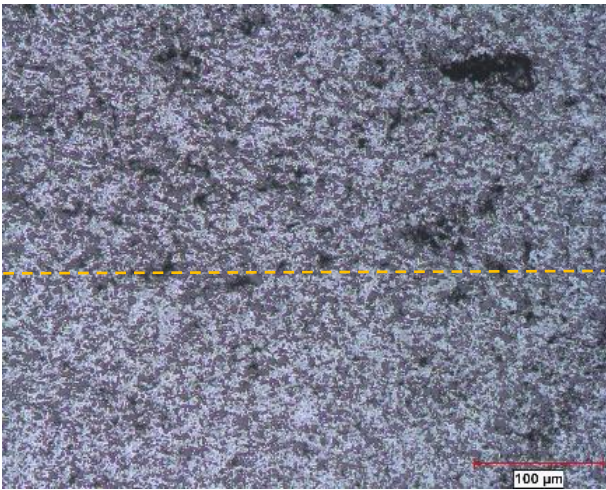


Fig. 5 Optical microscope image of the transition region between the levels containing 10 % and 20 % B_4C .

The voids in the structure become larger in the stacks that have higher amount of B_4C . This may be due to 2 reasons. The first one is that when the amount of hard B_4C particles is high, the transfer of stress to lower regions of the sample during cold compaction is low, which leads to lower green density of these layers. The second reason may be during sintering, due to high amount of B_4C , the aluminum particles that form the matrix need to cover a larger path for merging with each other.

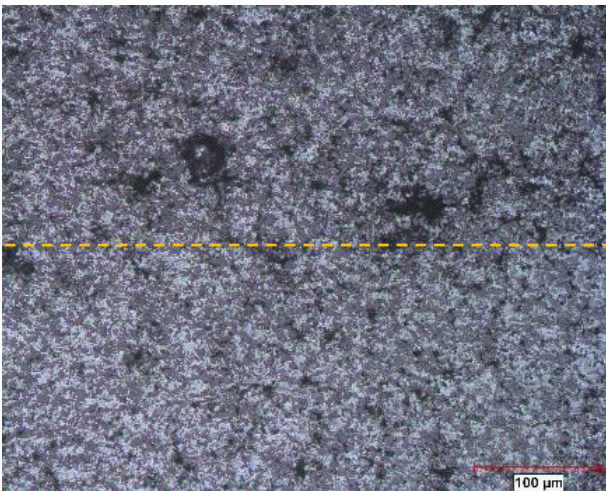


Fig. 6 Optical microscope image of the transition region between the levels containing 20 % and 30 % B_4C .

Hardness

In Fig. 7, microhardness values of the levels are given. The level that did not contain B_4C had an average hardness of about 55 $HV_{0.1}$ and that of the layer containing 30 % B_4C was 143 $HV_{0.1}$. The B_4C reinforcement had a significant effect on the hardness. The wear resistance of the layer containing 30 % B_4C is expected to be the highest.

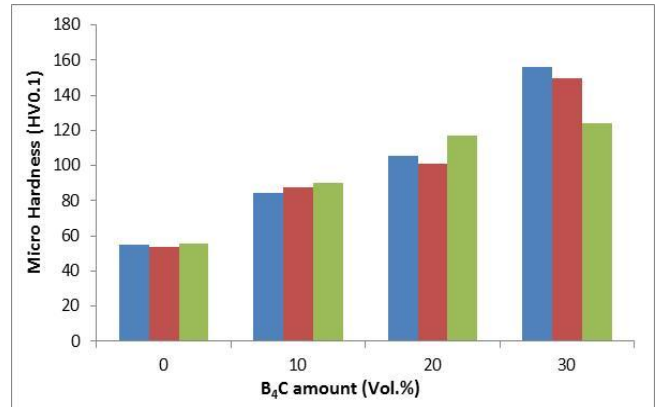


Fig. 7 Vickers microhardness values of the levels of FGM (each group represents 3 measurements)

4. Conclusion

Aluminum matrix functionally graded composite materials with increasing amounts of B_4C particles in an aluminum matrix were formed. The low strength of the FGM was attributed to the position of the high reinforced layer being in the high stress region of the sample during the bending test. On the other hand, the presence of the reinforcement particles was seen to have an important effect on increasing the hardness of the stacks.

Acknowledgements

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THE MODE OF HARDENING HEAT TREATMENT FOR DEFORMABLE PISTON HYPEREUTECTIC SILUMINS

РЕЖИМ ТЕРМИЧЕСКОЙ ОБРАБОТКИ ДЛЯ ДЕФОРМИРУЕМЫХ ПОРШНЕВЫХ ЗАЭВТЕКТИЧЕСКИХ СИЛУМИНОВ

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Abstract: A series of piston hypereutectic silumin based on Al - (15÷20) % Si, alloyed with copper, magnesium, nickel, chromium is investigated. The mechanical characteristics of ingots from experimental alloys were determined: temporary tensile strength, hardness, relative elongation depending on the composition of the alloys, and temperature coefficient of linear expansion (TCLE). It is shown that the tensile strength of forged blanks is 1.5-2.4 times higher than ingots of hypereutectic silumins. The resulting structure of forgings ensures their high plasticity (relative elongation $\delta = 5.7 \div 7.5\%$; relative narrowing $\Psi = 10.3 \div 14.2\%$). The optimal mode of heat treatment of deformed silumin is determined: quenching from step heating and aging, which allows increasing the strength of forgings up to 370-470 MPa. Moreover, the plasticity indicators remain at a high level, and the average thermal expansion coefficient of the alloys is $(18.0 \div 19.2) \cdot 10^{-6} \text{ K}^{-1}$ in the range of $50 \div 200^\circ \text{C}$.

KEYWORDS: HYPEREUTECTIC SILUMIN, STRUCTURE, FORGING, HEAT TREATMENT, TENSILE STRENGTH, HARDNESS, TEMPERATURE COEFFICIENT OF LINEAR EXPANSION.

1. Introduction

Analysis of operation conditions of modern heavy-duty engines [1-3] shows that in the course of operation they take significant dynamic loads that vary within one cycle in sign and direction. With that, pressure of gases onto piston could reach 800 MPa. Another specific feature of piston operation conditions is high temperature of fuel combustion products ($\sim$ up to 2000°C). That preconditions heating of piston head up to $350\text{--}400^\circ \text{C}$ in certain operation modes. With due account for piston operating conditions and strict requirements set to piston alloys the hypereutectic alloyed silumins are currently one of the most advanced materials for manufacturing of internal combustion engine pistons. This is determined by favorable combination of light weight, low thermal coefficient of linear expansion (TCLE) and good mechanical and process properties. However, presence of coarse crystals of primary silicon in the structure of hypereutectic silumins reduces their plasticity and makes it impossible to manufacture pistons by pressure shaping in industrial conditions [2-5]. Besides they adversely affect dynamic and static strength of pistons and disallow high values of fatigue endurance characteristic of deformable alloys. In order to ensure necessary package of physical and mechanical properties of piston alloy blanks it is mandatory to apply finishing heat treatment [3,6]. Therefore studies of susceptibility of developmental high silicon deformable silumins to heat treatment hardening is of practical interest and is the purpose of this study.

2. Material and methods

A series of developmental ingots has been manufactured from hypereutectic silumins on the basis of Al – (15÷20) % Si, alloyed with copper, magnesium, nickel, chromium and other elements. In order to ensure good deformability and high value package of

mechanical values the alloys were modified with phosphorus and hydrogen containing reagents.

Developmental ingots were manufactured with weight range of 32-40 kg, diameter of 190 mm, height of 500-550 mm, their deformation was performed and heat treatment impact studied. Chemical composition of alloys is exhibited in table 1.

Preparation of developmental alloys was performed in commercial induction furnace in graphite crucible of 40 kg capacity. Alloys were prepared on aluminum A7 (GOST 11063), Silicon Kr0 (GOST 2163). Alloy additives used were pure metals and compositions. Melt hydrogenation was performed by means of wet asbestos wads at $700\text{--}760^\circ \text{C}$. Phosphorus was introduced into alloys in form of phosphorous copper MF-1 [3,7]. Technological process of alloy preparation included the following main operations: charging into furnace and melting the estimated amount of aluminum, alloying, hydrogenation, modification, melt settling, skimming, casting. Melt was cast into steel cylindrical ingot (casting mold), covered with refractory paint. Alloys casting temperature was $700\text{--}730^\circ \text{C}$ (for alloys based on Al-15-18 % Si) and $730\text{--}750^\circ \text{C}$ (for alloys based on Al-20 % Si).

After mechanical machining (removal of cast surface, cutting into blanks) ingots underwent plastic deformation (free forging). Overall deformation degree amounted to $\varepsilon = 94\%$, and overall forging ratio $R_{\text{ovr}} = 28$. Blanks were forged on compressed air forging hammer MB 412 with head weight of 160 kg and hit energy not less than 2,5 kJ. Prior to forging the blanks underwent annealing in order to acquire equilibrium structure. Annealing temperature and exposure time were sorted out experimentally and equaled $450\text{--}470^\circ \text{C}$ and 1,5-3 h. In progress of forging intermediate annealing was performed at the temperature of $450 \pm 10^\circ \text{C}$ during 0,5-1 h [8-10].

Table 1. Chemical composition of developmental hypereutectic piston silumins

№ alloy	Components of alloys, % (wt.)									
	Si	Cu	Mg	Ni	Mn	Cr	Ti	P	H	Al
1	15	3	0,2	-	-	-	-	0,01	0,00008	rest
2	15	3	0,2	1,0	-	-	-	0,01	0,0001	rest
3	15	5	1,1	1,0	-	-	-	0,01	0,0003	rest
4	18	4	0,6	-	-	-	-	0,02	0,0003	rest
5	18	4	0,6	1,0	-	-	-	0,02	0,0006	rest
6	20	5	1,1	-	-	-	-	0,03	0,0006	rest
7	20	1,0	0,4	-	0,8	0,3	0,1	0,01	0,00008	rest

Heat treatment of forgings was performed in resistor furnaces SNOL 2.2, 5.2/12.5-II and electric drying ovens SNOL 3.5.3.5.3.5/3.5-II2. To perform metallographic analysis of ingots and forgings an optical microscope OLYMPUS GX-51F was applied. Studies of ingot microstructure were performed on transverse template micro-sections cut at equal distance from ingot bottom part. True and mean TCLE of alloys were determined with the assistance of high temperature dilatometer DIL 402C. TCLE error equaled $0,1 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$.

3. Results and discussion

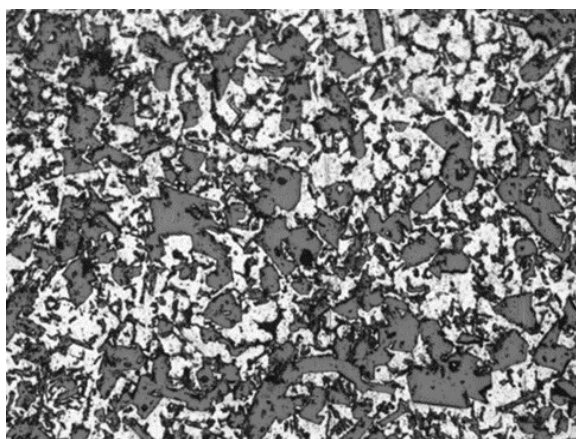
3.1 Structure specifics and properties of ingots

Microstructure of developmental ingot from alloyed hypereutectic silumin based on Al-18 % Si is exhibited in figure 1.

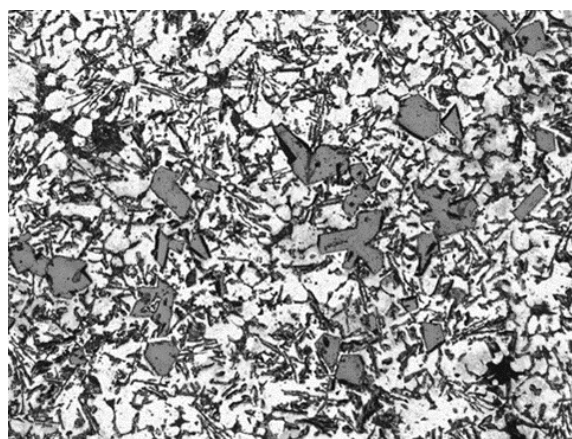
It is established that microstructure of alloys in as-cast condition is non-homogeneous in section of ingot. Along its cross-section three

specific zones can be identified:

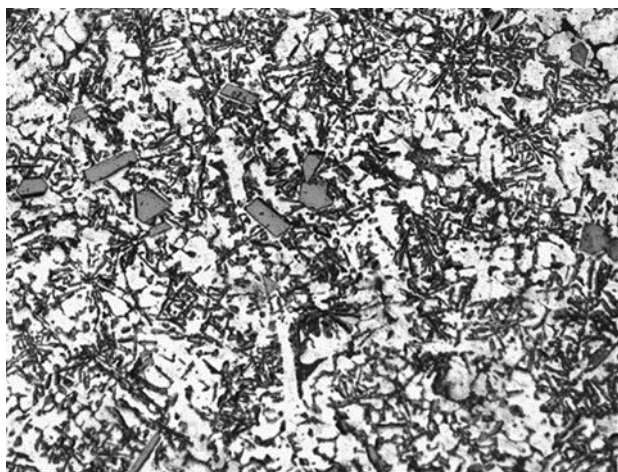
- surface – is represented by coarse crystalline band with 3÷5 mm width and maximal volume ratio of PSC;
 - intermediate – consisting of acicular eutectics, areas of α -solid solution and primary silicon crystals. Also clearly seen are Mg_2Si phase dark precipitates and CuAl_2 light spheroidal precipitates;
 - central – microstructure of which consists of two or more complex eutectics, areas of α -solid solution of complex composition and primary silicon crystals (PSC). With that PSC volume ratio in central zone is significantly less compared to intermediate.
- Table 2 exhibits mechanical properties and thermal coefficient of linear expansion of as-cast alloys. It is apparent that that despite the structural differences between the edge (intermediate zone) and the central parts of the ingots, their hardness differs insignificantly insignificantly and amounts to 840-1020 and 813-1006 MPa respectively. Tensile strength of ingots from developmental hypereutectic silumins is within the range of 80 -153 MPa.



a



b



c

Fig. 1. Microstructure of ingot from developmental alloyed silumin Al-18 % Si-4 % Cu-0,6 % Mg: a – surface; b – intermediate; c – central zones; $\times 100$

Table 2. Physical and mechanical properties of ingots from alloyed hypereutectic silumins

№ alloy	Hardness, HB, MPa		σ_{ts} , MPa	TCLE, $\alpha \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$ at temperature, $^\circ\text{C}$								
	edge	centre		50	100	150	200	250	300	350	400	450
1	873	853	153	17,4	18,9	19,7	20,5	21,0	22,5	22,3	20,1	18,6
2	840	813	148	17,1	18,8	19,5	20,0	19,8	20,7	21,0	19,5	16,9
3	1020	1006	125	18,1	19,2	19,7	19,8	20,1	20,4	21,5	21,1	20,4
4	986	928	138	18,0	19,2	20,0	20,7	21,5	21,9	22,6	21,9	19,8
5	980	876	124	18,1	17,1	16,9	16,7	16,3	19,0	19,3	16,6	18,8
6	943	941	86	17,4	18,4	19,3	19,8	19,8	20,2	20,5	20,7	18,3
7	958	950	80	17,0	18,9	19,7	20,3	20,5	20,9	21,2	20,5	19,8

Their mean value of linear expansion coefficient determined within the interval of 50-200 °C, amounts to $(17,2 \div 19,5) \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, and within the interval of 200-450 °C – $(17,7 \div 21,4) \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ respectively.

3.2. Ingots deformation.

Prior to forging the blanks underwent annealing at 450-470 °C during 1,5-3 h. During annealing the heterogeneity of the structure and composition of the alloys is partially eliminated by diffusion, siliceous precipitates coagulation occurs. At that there is significant lattice stress reduction in aluminum α -solid solution, which facilitates the process of metal deforming.

In the structure of forgings there are fragmented fine-crystalline uniformly distributed crystals of primary silicon and granular structure eutectics. Under hot deformation and annealing, coagulation and spheroidization of eutectic particles of silicon and other phases occurs (fig. 2).

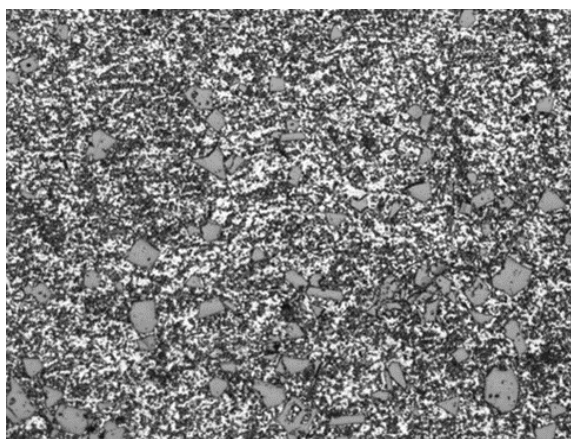


Fig. 2. Microstructure of forging from developmental hypereutectic silumin Al-18 % Si-4 % Cu-0,6 Mg; $\times 100$

Mechanical characteristics and mean TCLE of alloys in deformed state are shown in table 3. It is apparent that tensile strength of deformed blanks amounts to 227-306 MPa depending on composition of hypereutectic silumins. In addition, hot forging of alloys forms finer-grained microstructure of blanks with spheroidized precipitates of eutectic silicon and other phases.

Microstructure of forgings from silumin Al-18 % Si-4 % Cu-0,6% Mg is exhibited in fig. 2. Such structure provides rather high plasticity of forgings compared to as-cast alloys (relative elongation $\delta = 5,7 \div 7,5 \%$; relative reduction $\Psi = 10,3 \div 14,2 \%$).

3.3. Heat treatment of forgings.

Heat treatment of forgings from alloyed hypereutectic silumins included quenching and ageing. Hardening in this case is achieved by fixing the maximally supersaturated α -solid solution of aluminum during quenching and its decomposition during subsequent ageing due to decrease in the solubility of the alloying components with temperature reduction.

It is known that quenching parameters (heating temperature and exposure time) depend on nature of the alloys, their phase composition. Constitutional diagram analysis of Al-Si-Cu-Mg system, to which the given alloys are referred, shows that they possess complex phase composition. Seven phases can remain in equilibrium with aluminum solid solution: Si, θ (CuAl_2), β (Al_2Mg_3) or (Al_3Mg_5), Mg_2Si , S (Al_2CuMg), T (Al_6CuMg), W ($\text{Cu}_2\text{Mg}_8\text{Si}_6\text{Al}_5$) [11]. The main strengtheners are phases CuAl_2 , Mg_2Si , S (Al_2CuMg) and partially W ($\text{Cu}_2\text{Mg}_8\text{Si}_6\text{Al}_5$). The complex phase composition of the alloys preconditions occurrence possibility of vast number of nonvariant reactions in a broad temperature range 444-577 °C and, therefore formation becomes possible of complex low-melting eutectics, the melting point of which determines the heating conditions for quenching. Such specific feature of alloys causes increased alloys susceptibility to burning. To ensure the complete dissolution of the alloying elements and to avoid the possibility of burning, it is recommended to apply staged heating for quenching. The necessity of such heating for these alloys is confirmed by the results of experiments on the effect of heating temperature for cold water quenching and exposure time onto the mechanical properties of the alloys (ageing mode - 150 °C, 5 hours), listed in table 4 for the composition of alloy No. 4 (see table 1).

Table 4 data analysis shows that satisfactory combination of strength and plasticity is achieved after quenching according to modes 2 and 3, providing for staged heating for quenching at temperatures of 480 ± 10 °C (stage one) and 490 and 500 ± 10 °C (stage two) with exposure at these temperatures during 0,5-1 h and subsequent ageing. Upon execution of indicated heat treatment modes tensile strength of forgings equals 450-460 MPa, relative elongation – 4 %, relative reduction 5,8-8,3 %.

Table 3 Physical and mechanical properties of alloys in deformed state (forging, $\varepsilon = 94 \%$)

№ alloy	Mechanical properties			Average TCLE, $\alpha \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ in the temperature range, °C	
	σ_{ts} , MPa	δ , %	Ψ , %	50-200	200-450
1	245	7,5	14,2	19,8	20,9
2	227	5,7	13,1	19,8	19,8
4	306	7,2	13,4	18,6	20,8
5	291	5,8	10,0	19,3	19,4

Table 4. Mechanical properties of forgings from Al-18 % Si-4 % Cu-0,6 % Mg alloy depending on quenching modes (ageing 150°C, 5 h)

№	Quenching temperature and holding time	Mechanical properties		
		σ_{ts} , MPa	δ , %	Ψ , %
1	Без обработки	306	7,2	13,4
2	480 ± 10 °C, 2 h $\rightarrow$ 490 ± 10 °C, 2 h	450	4,0	5,8
3	480 ± 10 °C, 2 h $\rightarrow$ 500 ± 10 °C, 0,5 h	460	3,8	8,3
4	480 ± 10 °C, 2 h $\rightarrow$ 500 ± 10 °C, 1 h	425	1,0	0
5	490 ± 10 °C, 1 h	437	1,2	0
6	490 ± 10 °C, 3 h	437	1,0	0

After quenching according to modes 5 and 6, that do not provide for staged heating, there are burning processes occurring in alloys, which causes rapid plasticity reduction down to 1-1,2 %.

Thus the following heat treatment mode was adopted as optimal for piston alloys: quenching – staged heating 480 ± 10 °C → $(490-500) \pm 10$ °C, with exposure 2 and 1 h respectively at earlier and later stages, cold water cooling and subsequent artificial ageing at 150 °C within the period of 5 h. Table 5 exhibits physical and mechanical properties of studied deformable alloys post heat treatment according to the indicated mode.

Table 5. Physical and mechanical properties of forgings after quenching and ageing

№ сплава	Mechanical properties			Average TCLE, $\alpha \cdot 10^{-6} \text{ K}^{-1}$ in the temperature range, °C	
	σ_{ts} , MPa	δ , %	Ψ , %	50-200	200-450
1	425	6,4	9,9	18,6	22,4
2	372	4,6	7,4	19,0	22,1
4	450	4,0	5,8	18,0	20,6
5	400	2,8	6,1	19,2	21,5
6	470	5,0	5,2	18,8	22,0
7	400	3,5	-	19,0	22,7

It is evident out of table data that resulting from quenching and ageing there is a significant increase in tensile strength of deformed hypereutectic aluminum-silicon alloys up to 370-470 MPa. At that the plasticity values remain at the high level for piston silumins, and mean TCLE of alloys post heat treatment equals $(18,0 \div 19,2) \cdot 10^{-6} \text{ C}^{-1}$ in the interval of 50÷200 °C and $(20,6 \div 22,7) \cdot 10^{-6} \text{ C}^{-1}$ in the interval of 200÷450 °C.

Metallographic research of deformable alloyed hypereutectic silumins post quenching and ageing showed that particles of primary and eutectic silicon adopt more rounded and spheroidized shape in microstructure of heat-treated forgings. Mg_2Si and CuAl_2 phases that have not fully dissolved during heating and deformation of blanks do dissolve after quenching in α -solid solution of aluminum. Moreover, this process leads to enhancement of inhomogeneous etchability of α -solid solution.

4. Conclusions

Study has been performed of mechanical characteristics and TCLE of ingots and forgings from developmental hypereutectic silumins based on Al – (15÷20) % Si, alloyed with copper, magnesium, nickel, chromium and other elements and modified by phosphorus- and hydrogen-containing reagents. Due to application of optimal heat treatment modes (quenching and ageing) the possibility has been demonstrated to improve the package of physical and mechanical properties of deformed hypereutectic piston silumins. At that significant strength gain for such alloys has been acquired with retained high plasticity values as compared to cast piston silumins and low TCLE value as related to deformable alloys.

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STRUCTURE, PHASE COMPOSITION AND HYDROGEN SORPTION PROPERTIES OF EUTECTIC ALLOY $\text{Ti}_{47.5}\text{Zr}_{30.2}\text{Mn}_{22.5}$ OBTAINED USING TITANIUM SPONGE

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Abstract: The microstructure and phase composition of the eutectic alloy $\text{Ti}_{47.5}\text{Zr}_{30.2}\text{Mn}_{22.5}$ obtained using titanium sponge, as well as the phase composition of hydrogenation product were investigated by scanning electron microscopy and X-ray phase analysis. It was found that when iodide titanium was completely replaced by titanium sponge, the alloy structure remained eutectic and consisted of bcc solid solution and Laves phase. It was shown that after a sorption-desorption cycle the alloy was in activated state and was capable to absorb hydrogen at room temperature and low pressure (0.21 MPa) starting from the first seconds of contact with hydrogen atmosphere, with hydrogen capacity of 2.61 wt.%.

KEYWORDS: LAVES PHASE, BCC SOLID SOLUTION, EUTECTIC, TITANIUM SPONGE, SORPTION/DESORPTION, HYDROGEN CAPACITY.

1. Introduction

Previously, the prospect of using eutectic alloys of the Ti-Zr-Mn system as a material for the safe storage and transport of hydrogen in a bound state (hydride) was shown [1]. The use of eutectic alloys based on the Ti-Zr-Mn system, which consist of bcc solid solution with high hydrogen capacity and Laves phase (acceptable operating temperatures, sorption capacities ~ 1.0 H/Me and high hydrogenation rates), leads both to a significant increase in the sorption capacity and to the improvement of kinetic and thermodynamic parameters of hydrogenation and dehydrogenation processes due to combining the advantages of both phases.

According to the literature, the processes of hydrogen sorption and desorption in the alloys designed for hydrogen storage are affected by many factors: production techniques (mechanical doping or induction melting [2], arc melting or formation of thin strips from melt [3]), heat treatment parameters [3-4], structure and phase composition of the initial alloys [5-6]. The main common feature of all alloys proposed for hydrogen storage is the use of high-purity materials (not lower than 99.5%) [1-7]. These materials are quite expensive, that significantly increases the cost of the resulting hydride. The cost of the resulting hydride can be reduced by replacing the expensive components by cheaper ones.

The purpose of the present work was to assess the possibility of reducing the cost of the resulting hydride by replacing the high-purity components by cheaper ones. For this goal, previously investigated [1] alloy $\text{Ti}_{47.5}\text{Zr}_{30}\text{Mn}_{22.5}$ was melted, wherein iodide titanium (\$70 for 1 kg) was replaced by cheap grades of titanium sponge (TG-110, TG-130, TG-TV, \$10 for 1 kg).

2. Materials and methods

The alloy was produced by electric arc melting in a laboratory furnace with a non-consumable tungsten electrode in an atmosphere of purified argon. Titanium sponge, iodide Zr (99.975%), and electrolytic Mn (99.9%) were used as initial components. The deviation of chemical composition of the alloy from the nominal one was determined by XRF (VRA-30 unit). It coincided with the nominal one within the measurement error (0.03%).

Differential thermal analysis was performed at a VDTA-8M thermoanalyzer [8] at a heating rate of 40 °C/s in a high-purity helium atmosphere using Y_2O_3 crucibles. The solidus and liquidus were determined with accuracy ± 7 °C.

Metallographic examinations were performed with a scanning electron microscope JSM-6490 LA.

The phase composition and lattice parameters were determined by X-ray phase analysis at a Dron-3M diffractometer with a standard GUR-8 goniometer at monochromatic $\text{Cu-K}\alpha$.

The hydrogen adsorption properties were studied on the alloy in a cast solid state. The interaction of the alloy with hydrogen was studied by the Sieverts method at IVGM-2M unit [9] at room temperature and upon heating at a rate of 0.125 °C/s at absolute pressure ~ 0.6 MPa. The hydrogen desorption was studied at an automated dilatometric complex (ADC) with a mass spectrometer [10].

3. Results and discussion

As seen from DTA curves (Fig. 1), only one thermal effect is observed regardless of initial state of titanium, and the temperature of the phase transformation (melting, solidification) coincides within the measurement error. Previously we showed [1] that the structure of the alloy is close to eutectic, since there is only one thermal effect on the heating and cooling DTA curves, and the difference between the temperatures of start of melting and solidification is minimal (15 °C).

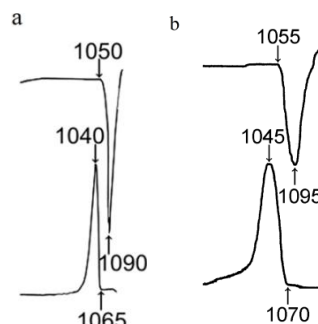


Fig. 1. DTA curves of $\text{Ti}_{47.5}\text{Zr}_{30}\text{Mn}_{22.5}$ alloys: a – iodide titanium [1]; b – titanium sponge.

The data of scanning electron microscopy confirmed the conclusion drawn from DTA studies: the complete replacement of iodide titanium by titanium sponge does not change the structure of the alloy (Figs. 2a, b).

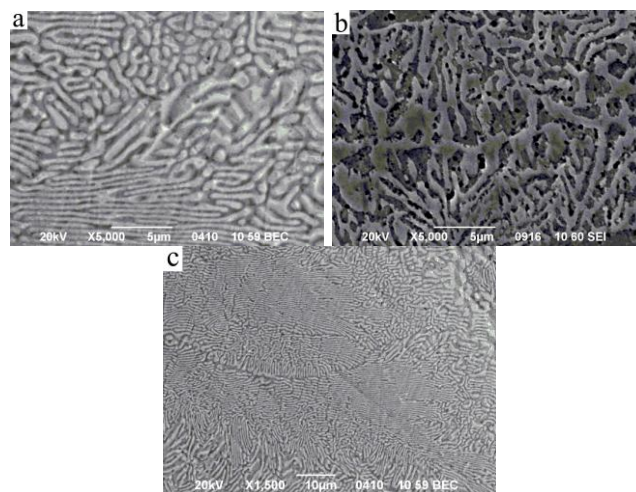


Fig. 2. Microstructure of $\text{Ti}_{47.5}\text{Zr}_{30}\text{Mn}_{22.5}$ alloys: a – iodide titanium [1]; b – titanium sponge; c – a typical eutectic structure.

The eutectic consists of bcc solid solution and Laves phase and has a skeletal structure in which the Laves phase plays role of a nucleating phase that initiates eutectic solidification. It grows in the

form of a branched backbone and forms a framework of colony; it has bright color on back-scattered electron images (Fig. 2c). The fact that the Laves phase initiates solidification is clearly seen from the rounding of its fibers in the joints of eutectic colonies. As the eutectic colonies grow towards one another, heat is released, and the cooling rate drops sharply, therefore the transition from the fibrous structure to the formation of globules at the end of the fibers is observed. The guided phase is bcc solid solution which forms a colony matrix. Thus, as in most metal-intermetallic systems, the phase that initiates and leads the eutectic solidification is the phase with a higher melting enthalpy and a higher anisotropy of interatomic bonds due to directed bonds between atoms of different types. The formation of the framework of eutectic colony and its subsequent growth are typical for the eutectic polyhedron-dendrite.

The results of X-ray phase analysis confirmed the data of scanning electron microscopy on the consistency of the alloy phase composition (Fig. 3). As expected, there is hexagonal Laves phase of C14 type and space group $P6_3/mmc$ (structural type $MgZn_2$) with lattice parameters $a=0.5200 \pm 0.0009$ (nm) $c=0.8542 \pm 0.0009$ (nm) (for previously investigated alloy $a=0.5215 \pm 0.0009$ (nm) $c=0.8581 \pm 0.0009$ (nm) were obtained), and $\beta(Ti,Zr,Mn)$ solid solution with space group $1m-3m$ (structural type W) with lattice parameters $a=0.3374 \pm 0.0009$ (nm) (for previously investigated alloy $a=0.3383 \pm 0.0009$ (nm) were obtained) [1], and traces of ω -phase.

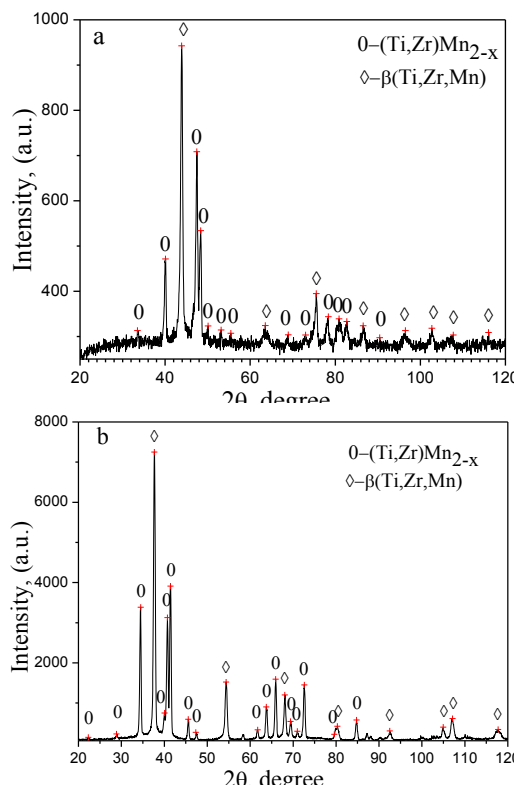


Fig. 3. Diffraction patterns for cast $Ti_{47.5}Zr_{30}Mn_{22.5}$ alloy: a – iodide titanium [1]; b – titanium sponge.

The alloy obtained using titanium sponge was kept at room temperature at hydrogen absolute pressure of 0.6 MPa for 24 hours; however, these hydrogenation conditions did not lead to surface activation and hydrogen absorption. Active absorption of hydrogen was observed only when the alloy was heated up to 565 °C. The start of intense hydrogen absorption during the first hydrogenation was estimated by deviation of the curve “pressure change vs. temperature” from straight line. For the present and previously investigated alloys intense hydrogen absorption started at ~ 525 °C and at ~ 540 °C, respectively (Fig. 4). The maximum rate of hydrogen absorption for both alloys was observed at 565 °C. A major amount of hydrogen at 565 °C was absorbed by the present and previously investigated alloys in ~ 7 min and ~ 12 min [1], respectively. When two alloys reached the maximum absorption rate, a substantial (by 30 °C) increase of the reactor temperature was observed, which indicated the exothermic nature of the reaction of

hydride formation. The total hydrogen content for the present alloy was 2.61 wt.% (H/Me=1.66), while for the previously investigated alloy it was 2.58 wt.% (H/Me=1.64) [1].

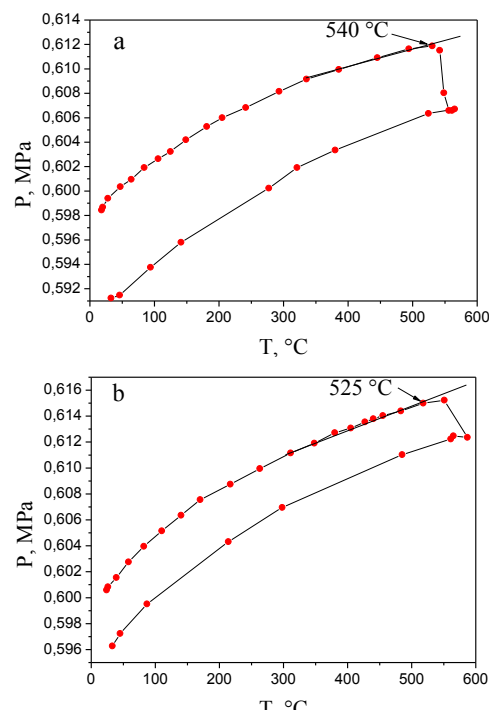


Fig. 4. Dependence of hydrogen pressure on temperature: a – iodide titanium [1]; b – titanium sponge.

Basing on the temperature of the start of active absorption, it can be suggested that the process of hydrogen absorption by both alloys starts in the β solid solution [11]. Regardless of the initial state of titanium, the interaction with hydrogen leads to complete destruction of solid samples to powder due to large internal stresses caused by hydrogen dissolution (Fig. 5).

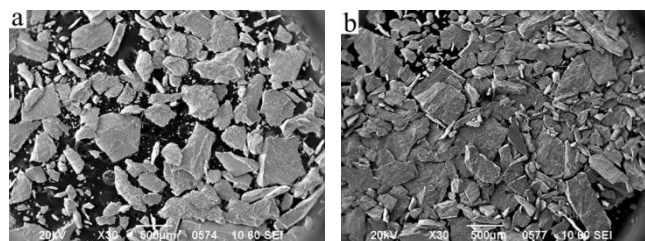


Fig. 5. Appearance of the product of hydrogenation: a – iodide titanium [1]; b – titanium sponge.

According to the data of X-ray phase analysis, during hydrogenation of the alloy obtained using titanium in different initial states hydrides are formed only on the basis of the original phases (Fig. 6.). The resulting hydrogenation product consists of a hydride based on the Laves phase with lattice parameters $a=0.5590 \pm 0.0009$ (nm) $c=0.9182 \pm 0.0009$ (nm) (for previously investigated alloy $a=0.5598 \pm 0.0009$ (nm) $c=0.9192 \pm 0.0009$ (nm) were obtained [1]), and δ -hydride on the basis of mixture of solid solution and ω -phase with lattice parameters $a=0.4591 \pm 0.0009$ (nm) (for previously investigated alloy $a=0.4597 \pm 0.0009$ (nm) were obtained, [1]). These results allow to suggest that the saturation of the alloys by hydrogen does not lead to phase decomposition.

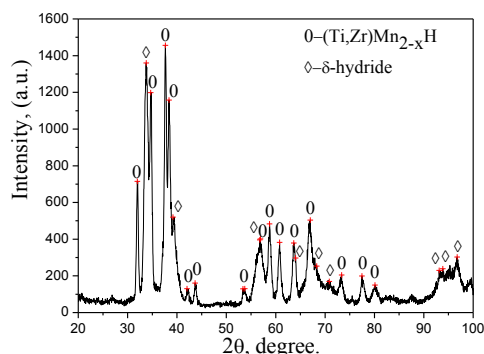


Fig. 6. Diffraction pattern for $Ti_{47.5}Zr_{30}Mn_{22.5}$ alloy obtained using a titanium sponge after hydrogenation.

Mass-spectrometry of hydrogenation products obtained by saturation of the alloys by hydrogen showed that hydrogen desorption at an initial pressure of $4 \cdot 10^{-3}$ Pa in both alloys started at ~ 80 °C, and at 350 °C the reverse capacity was 67% of absorbed amount (1.75 wt.%), whereas at 550 °C complete desorption of the alloys occurred (Fig. 7.).

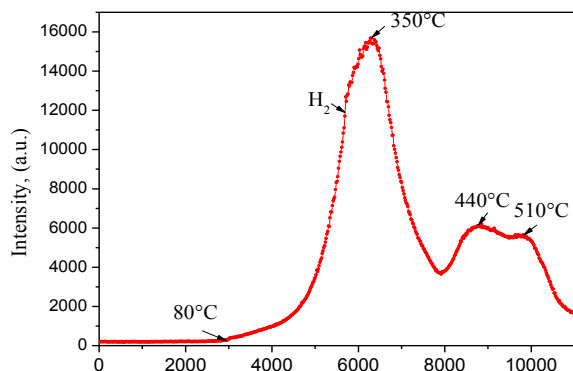


Fig. 7. Dependence of intensity of hydrogen desorption from temperature.

Investigation of the effect of sorption-desorption-sorption cycles on the hydrogen sorption properties of the alloys, regardless of the initial state of titanium, showed that hydrogenation in the second and subsequent cycles occurred already at room temperature and hydrogen pressure of 0.21 MPa starting from the first seconds of contact of the sample with hydrogen atmosphere. Basing on the temperature of hydrogenation, it can be suggested that after sorption-desorption cycle absorption started within the Laves phase [12]. This improvement in the hydrogen sorption properties (lowering hydrogenation temperature from 565 °C to room temperature) of the alloys, regardless of the initial state of titanium, can be explained by the destruction of solid samples to powder, as well as by the decrease in the concentration of oxygen on the surface of the particles as a result of its interaction with atomic hydrogen released.

4. Conclusion

Complete replacement of iodide titanium by titanium sponge does not affect the structure, phase composition and hydrogen sorption properties of the eutectic alloy $Ti_{47.5}Zr_{30}Mn_{22.5}$, and it allows to reduce the cost of the resulting hydride due to different costs of the source materials.

5. Acknowledgement

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COMPUTER MODELING OF INFLUENCE OF PREVIOUS DEFORMATION DEGREE AND STRAIN RATE ON CARBONITRIDES PRECIPITATION KINETICS IN LOW-CARBON MICRO-ALLOYED STEEL

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Abstract: Using computer modelling with originally developed semi empirical physical grounded models a study was carried out to investigate influence of previous hot deformation on carbonitrides formation from austenite in low-carbon micro-alloyed steel. Studied in the article is an influence of degree and rate of the deformation on processes of nucleation and growth of Nb and Ti carbonitride particles. The model helps to predict not only process of changing in number and average size of the particles but also to estimate their final size distribution. One of additional peculiarities of the developed model is its ability to predict composition of the carbonitrides formed in certain conditions. The model takes into account process of recrystallization and returning, which affect carbonitrides precipitation and are influenced by it. Acceleration was shown of both nucleation and growth rates of the particles due to increasing of deformation degree and strain rate. Another result is that previous deformation significantly affects size distribution function of the particles precipitated with rather lesser effect on their average size. Kinetic curves and final size distribution plots are given.

KEYWORDS: STEEL, CARBONITRIDES, MODELLING, DEFORMATION

1. Introduction

The objective of the research is to demonstrate the developed model ability in prediction of processes of carbonitrides precipitation and show an influence of deformation on the particles size distribution.

Precipitation from solid solution (austenite) of carbonitride phases occurs in steels micro alloyed with Ti, Nb, V and Zr. Stimulating for the precipitation is previous deformation, which leads to increase in inner stress and dislocation density of the material. But owing to high temperature of the processes there have a place phenomena of returning and recrystallization [1].

A mathematical model and sufficient computational program was developed to describe kinetics of carbonitrides precipitation from austenite after deformation. The model takes into account returning and recrystallization their influence on carbonitrides nucleation and vice versa. Detailed description of the model can be found in our previous work [2], some information is also in our book [3] (in chapter 1). Here we do not consider on the essence of the model and its realization. It is a semiempirical but physical based model. Finite differences method was used for realization of the processes calculation.

Successful enough preempts were made before to describe theoretically kinetics of recrystallization and carbonitrides precipitation in deformed steel [4-6]. Even a program was developed [4], but it is not an open source. So program code realization for the model implementation was made originally by us. A remarkable feature of our model, qualitatively distinguishing it from the above one is including of thermodynamic calculation of the carbonitrides composition. For instance in the work [4] they consider carbonitrides as stoichiometric composition, which is a rather rough approximation and does not correspond to the composition of real inclusions. As a bases of thermodynamic module for carbonitrides composition calculation was taken our previously developed program. It was completely rewritten using Python language (original was in Delphi), program code optimization were made and precision increased (the nonideality of carbonitride as a mutual solid solution of the corresponding carbide and nitride is better taken into account). Another feature of current investigation is consideration on size distribution of the carbonitrides precipitated. In particular the influence of deformation degree and strain rate on the particles size distribution was studied using the model developed. In other papers known to us, the average indicators were modeled and investigated, but not the distribution functions. There are many others lesser particularities our model consisting in a more accurate consideration of many quantities and their dependencies but their description will lead to detail that make it difficult to understand.

2.1. Studied material

Chemical composition of the studied steel in this work is given in table 1.

Table 1

Chemical composition of the studied steel								
Fe	C	Mn	Si	Mo	Ti	V	Nb	N
base	0.10	2.00	0.25	0.15	0.015	0.02	0.045	0.006

The given composition is quit similar to one from our work [2] but amounts of Mn and Mo are higher and concentration of carbon is lesser. It's seen that the steel is low-carbon one and has rather high amount of Mn. It is micro alloyed with strong carbide and nitride forming elements, which are Ti, Nb and V. It is a typical strip steel.

2.2. Calculation and its results

The process modelling was carried out for four regimes of deformations that differ by deformation degree and strain rate. Values of the deformation degree and strain rate are given below in table 2.

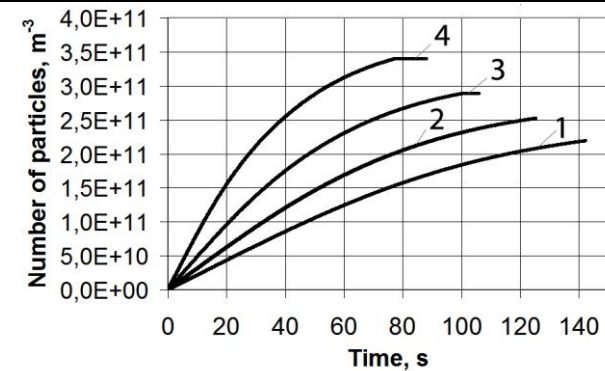
Table 2

Regimes of deformation		
No.	Deformation degree	Strain rate, sec ⁻¹
1	0.10	0.5
2	0.10	3.5
3	0.30	0.5
4	0.30	3.5

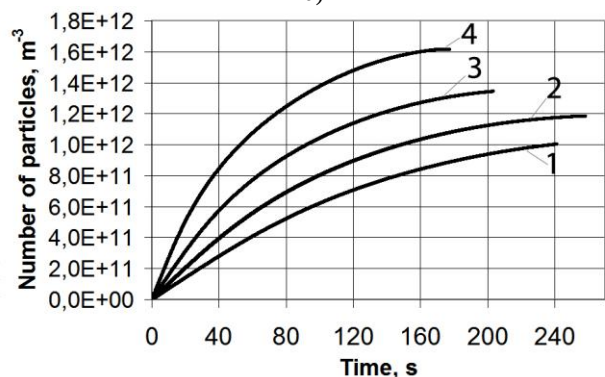
Deformation temperature, which also was considered as the temperature of precipitation was 950 °C for all the regimes modelled.

Computation shows that only carbonitrides of Ti and Nb can form at the temperature. Carbides and nitrides of V have significantly lesser temperature of precipitation, so they do not occur under the considered conditions. According to thermodynamic calculations compositions of the carbonitrides formed are as follows: $\text{TiC}_{0.58}\text{N}_{0.42}$ and $\text{NbC}_{0.76}\text{N}_{0.24}$.

Primary studied were processes of the particles nucleation and growth. Figure 1 shows increasing of number of the particles by time flowing for Ti and Nb carbonitrides depending on the deformation regime.



a)



b)

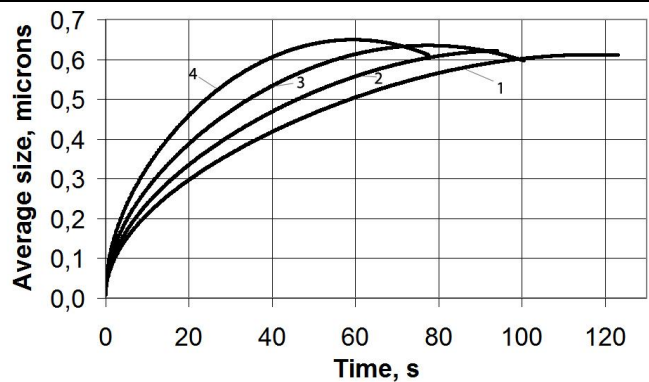
Figure 1 – Changing by time of number Ti(CN) – (a) and Nb(CN) – (b) particles depending on deformation regime. Numbers near curves correspond to the regimes listed in table 1

Increasing in number of particles occurs owing to nucleation process. When nucleation stops, the increasing stops too. According to the theory accepted in the model, the sites of nucleation of particles are the intersection sites of dislocations. So increasing of dislocation density during deformation leads to more places of nucleation. Besides increasing of precipitated particles number intensification of deformation also leads to acceleration of nucleation – the process goes faster. Significantly more particles of Nb(CN) precipitate than particles of Ti(CN), which is mostly owing to higher concentration of Nb competing with Ti in initial chemical composition of the steel. Increasing both of deformation degree and strain rate has significant and similar influence. This distinguishes current situation from that considered in paper [7], where the influence of the strain rate on the kinetics of phase transformations was significantly less than the effect on the deformation degree on it.

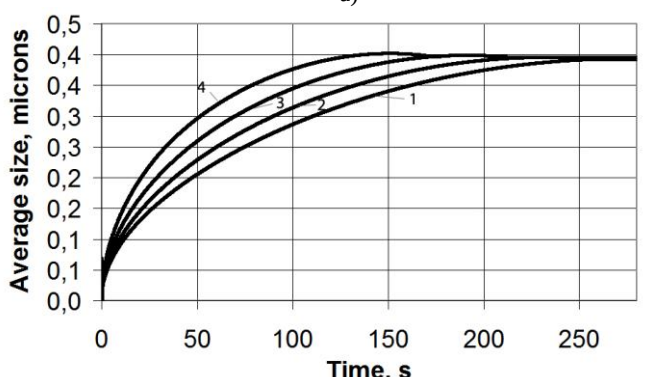
In addition to the nucleation process, this model also describes the growth of carbonitride particles. Figure 2 demonstrates changing of the particles average size by the time flowing.

On figure 1 (a) – for Ti(CN) a strange effect is seen. In cases of higher deformation degree, at a certain time the average size of the particles begins to decrease. It is important to note that it's about average size only. Size of each particle grows. This effect is because of new particles nucleation during all the period. The larger a particle is the slower it grows. Intensive deformation makes better conditions for the emergence of a larger number of particles. Hence a situation is possible when originated at an early stage particles are already grown enough to slower their following growth but new ones are keeping appear. This is an explanation of the observed effect of decreasing of average size when all the particles grow. The same effect but significantly lesser is seen for Nb(CN) also that is shown on figure 2 (b).

Another interesting result is that despite the average size growth acceleration intensification of deformation does not affect significantly its final value.



a)



b)

Figure 2 – Changing by time of average size of Ti(CN) – (a) and Nb(CN) – (b) particles depending on deformation regime. Numbers near curves correspond to the regimes listed in table 1

Below in table 3 are given predicted values of final average sizes of the particles obtained at each of the considered deformation regimes.

Table 3

Final average sizes of particles (in nm)

Regime No.	Ti(CN)	Nb(CN)
1	626	401
2	614	397
3	607	391
4	594	382

In spite of a little difference in an average size the particles number differs significantly. This effect has the following explanation. Deformation affects more the particle size distribution function than their average size. Plots of the final size distribution density functions predicted using the model are shown on figure 3.

The distribution function is lognormal for all of the cases. More significant influence of deformation regime on size distribution function is observed for Nb(CN) particles. With a lower intensity and degree of deformation, the particle size distribution function looks more smeared. That is, both smaller and larger particles will equally be present in the metal. An increase in the degree and rate of deformation leads to a narrowing of the distribution function and a smaller scatter of medium size. A large role in the narrowing of the distribution function plays an increasing of deformation degree than strain rate, which effect is additional. Deformation effect on distribution function for Ti(CN) particles is lesser but it is also observed. It is noteworthy that in terms of size distribution change for Ti(CN) in this case the effects of strain rate increasing with lower deformation degree is almost to deformation degree magnification but with lesser strain rate.

Thus, the model shows that an increase in the intensity of deformation leads not only to an increase in the number of carbonitride particles, but also narrows the range of variation of their sizes.

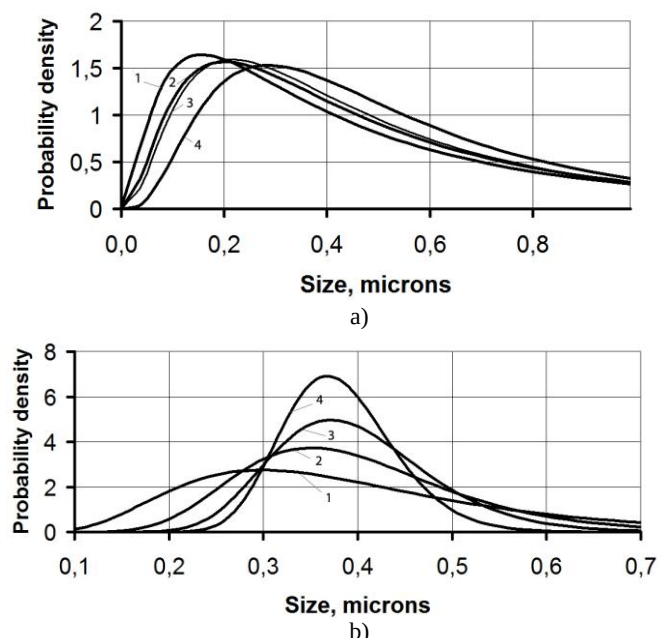


Figure 2 – Final size distribution function of Ti(CN) – (a) and Nb(CN) – (b) particles depending on deformation regime. Numbers near curves correspond to the regimes listed in table 1

The normal growth of particles at a given temperature stops when the system reaches equilibrium between the carbonitrides and solid solution. That is, simply put, when all that could have precipitated was already precipitated. After that the process of Ostwald ripening begins. It is when particles with smaller size become even smaller and then disappear and larger particles grow taking on material from smaller ones. Ostwald ripening stage of process is also included in the developed model but is out of consideration in current article. It is only to be said that this process is much slower than the nucleation and growth considered above.

3. Conclusions

Using a developed computer model a study was carried out to estimate influence of deformation on kinetics of Ti and Nb carbonitrides precipitation from austenite in low-carbon micro alloyed steel. An influence of the degree and rate of deformation on the number of carbonitride particles, the rate of their nucleation at a temperature of 950 °C was studied.

Composition of Ti and Nb carbonitrides was predicted for the invalidated conditions, it is $\text{TiC}_{0.58}\text{N}_{0.42}$ and $\text{NbC}_{0.76}\text{N}_{0.24}$. Information of chemical composition of carbonitrides is useful to conduct more precise kinetics computation.

It was shown that in spite of small difference in average particles size their amount differs significantly depending on deformation regime. Found here was that degree and rate of deformation affects significantly an obtained size distribution function of the particles precipitated. Especially increasing of both deformation degree and strain rate leads to the dispersion of the distribution becomes smaller.

The obtained results present in the paper are useful for developing of controlled rolling regimes for low-carbon steels micro alloyed with strong carbide and nitride forming elements.

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PROPERTIES AND PERFORMANCE OF POLYETHERSULFONE MEMBRANES MODIFIED WITH HALLOYSITE AND TITANATE NANOTUBES

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Abstract: Ultrafiltration polyethersulfone (PES) membranes were prepared by wet phase inversion method. Halloysite nanotubes (HNTs), hydrothermally synthesized titanate nanotubes (TNTs) or their mixture (HNTs/TNTs, weight ratio 50/50) were applied as nanofillers (NFs). *N,N*-dimethylformamide was used as a solvent, and deionized water was applied as a non-solvent. Some well dispersed aggregates as well as larger agglomerates of the NFs were observed on the surface of the membranes examined by atomic force microscopy. The retention of poly(ethylene glycol) (20 kDa) applied as a model organic compound, by the modified and unmodified membranes was similar and did not exceed 10%. The rejection of 500 kDa dextran ranged from 84 to 92%, and was the highest for the membrane modified with HNTs. A 71% improvement of pure water flux, compared to the neat membrane, was observed in the case of the membrane modified with the HNTs/TNTs. The best antifouling performance during bovine serum albumin filtration exhibited the HNTs-modified membrane.

Keywords: POLYETHERSULFONE, MEMBRANE, HALLOYSITE NANOTUBES, TITANATE NANOTUBES, FOULING, SEPARATION

1. Introduction

The membranes used in pressure-driven membrane techniques are usually made of polymers, mainly due to simple procedure of their fabrication at various characteristics as well as low price of their manufacturing [1]. Polyethersulfone (PES) is one of the polymers used to prepare ultrafiltration (UF) and microfiltration (MF) membranes. However, PES membranes have relatively low hydrophilicity which can lead to membrane fouling [2]. Fouling is one of the major problems in membrane processes. The colloids, particles and organic solutes present in feed can be deposited on the membrane surface or within its pores which leads to a decrease of permeability or damage of the membrane [3,4]. To reduce fouling and improve membrane properties, various modifications are used. One of the very common attempts is the introduction of a filler into a casting solution. In case of PES membranes the nanofillers as halloysite nanotubes (HNTs), carbon nanotubes (CNTs), TiO₂, SiO₂, Al₂O₃, silver and copper nanoparticles (NPs) and titania/titanate nanotubes (TNTs) have been proposed for the modification purpose [5,6].

Halloysite nanotubes are natural inorganic aluminasilicates with the general formula Al₂Si₂O₅(OH)₄•nH₂O [7]. HNTs have natural tubular structure, large surface, porous microstructure, chemically active internal and external surface, high ion exchange capacity, and possess hydrophilic groups on the surface [8,9]. TNTs can be synthesized by hydrothermal method, electrochemical oxidation or soft chemical method. The titanate nanotubes derived from the hydrothermal method have ion exchange properties, high surface area and pore volume and possess hydrophilic -OH groups on their surface [10]. The literature reports show that both HNTs and TNTs have positive influence on hydrophilicity of membranes, they can improve water flux and separation properties [5,6].

The main aim of the present study was to examine the effect of HNTs and TNTs on physicochemical properties, pure water flux, separation properties and antifouling performance of mixed matrix membranes. The PES membranes and modified membranes were prepared by wet phase inversion method using *N,N*-dimethylformamide as a solvent. The membranes were characterized based on contact angle (CA), atomic force microscopy (AFM), scanning electron microscopy (SEM) and pure water flux measurements. Membrane fouling resistance was evaluated using bovine serum albumin (BSA). Separation properties were examined by separation of poly(ethylene glycols) (PEGs) and dextrans.

2. Materials and methods

Polyethersulfone (Ultrason E6020P) was supplied by BASF SE (Germany). *N,N*-dimethylformamide (DMF) was provided by Avantor Performance Materials Poland S.A. Halloysite nanotubes were purchased from Sigma Aldrich. Titanate nanotubes were prepared using hydrothermal treatment [6] from TiO₂ powder (Aeroxide®TiO₂ P25, Evonik Industries). Bovine serum albumin (Probumin) was obtained from Merck, poly(ethylene glycols) were provided by Sigma Aldrich. In all experiments pure (deionized) water (type 2, 0.006 µS/cm) from Elix 3 (Millipore) was applied.

The membranes were prepared by wet phase inversion method. In case of the unmodified membrane (NM) the 15 wt% of PES were dissolved in DMF. The casting dope was casted on a glass plate using an automatic film applicator (Elcometer 4340) with the knife gap of 0.1 mm, and immersed in pure water bath to complete the phase inversion process. The modified membranes were prepared by mixing a dispersion containing 1 wt% of HNTs, TNTs or their mixture (Table 1) in 10 cm³ of DMF with previously prepared solution of polymer in DMF (40 cm³). The NPs dispersion was prepared by sonication for 30 min using ultrasonic probe (Vibra-cell VCX-130, Sonic, USA, amplitude 80%). After addition of the NPs dispersion to PES solution, the casting dope was mixed alternately (15 min by turns) using a magnetic stirrer and sonication in ultrasonic bath (Sonic-6D, Polsonic, Poland) for 2h.

Table 1: Weight ratio of HNTs and TNTs in casting solutions.

Membrane	HNTs	TNTs
NM	0	0
PES/HNTs	100	0
PES/TNTs	0	100
PES/HNTs/TNTs	50	50

The morphology of HNTs and TNTs was analyzed using transmission electron microscope (TEM) FEI Tencai F20.

Topography of the membranes was analyzed using atomic force microscope (AFM, NanoScope V Multimode 8, Bruker Corp.) with silicon nitride probe in the ScanAsyst mode. Roughness of membranes (R_a) was calculated using the NanoScope Analysis Software. The hydrophilicity of membranes surface was determined by water static contact angle measurement using goniometer (type 260 ramé-hart instruments co.) by the sessile drop method. The volume of the water drop was 10 µl, and the results are mean values of 10 measurements. Morphology of membranes was analyzed using ultra-high-resolution field-emission scanning electron microscope (UHR FE-SEM Hitachi SU8020) in the secondary electrons mode (SE, accelerating voltage 5kV) and dispersive X-ray spectroscopy EDX NSS 312 (Thermo Scientific). A small piece of a membrane (dehydrated in ethanol) was broken in liquid nitrogen

and sputtered with a chromium layer before SEM analysis. The pure water flux was determined with application of a laboratory scale cross-flow unit by ultrafiltration of pure water at transmembrane pressure of TMP = 1, 2 and 3 bar. The membrane (0.0025 m^2) was mounted in a stainless steel membrane module with a 1.19 mm feed spacer. Antifouling properties were determined by ultrafiltration of BSA solution (1 g/dm^3) at TMP = 2 bar and feed cross flow velocity of 1 m/s. Separation properties were evaluated on a basis of rejection of model organic compounds: PEGs (4, 10, 20, 35 kDa) and dextrans (70, 110, 200, 500 kDa) at TMP = 1 bar. The concentration of the model solutions was 0.5 g/dm^3 . Concentration of PEGs and dextrans were measured using HPLC LaChrom Elite (Hitachi, Japan).

3. Results and discussion

2.1 Characteristics of HNTs and TNTs

HNTs and TNTs were characterized using TEM technique, and the results are presented in Fig. 1.

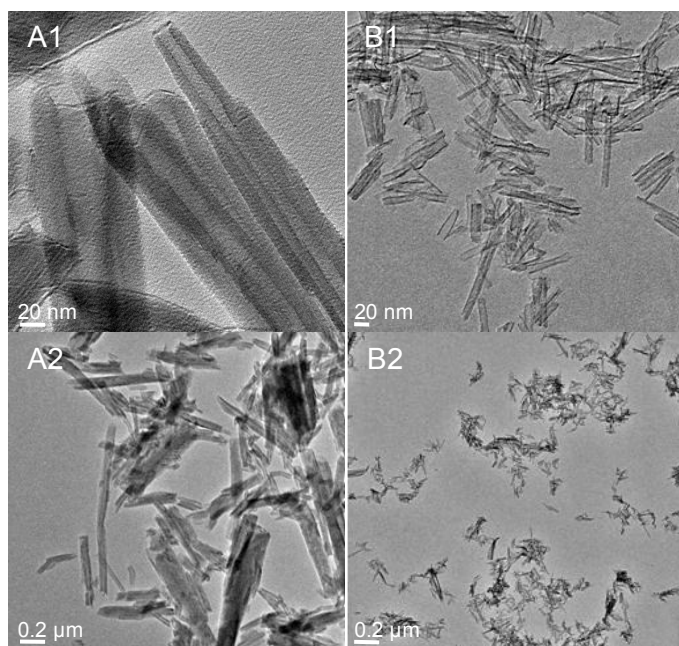


Fig. 1 TEM images of HNTs (A1-2) and TNTs (B1-2)

The commercial HNTs and the hydrothermally synthesized TNTs are multi-walled and open-ended. The length of HNTs was in the range of 15–1250 nm, the internal diameter and wall thickness changed from 11 to 28 nm and from 5 to 23 nm, respectively. The length of TNTs was in the range of 29–164 nm, the internal diameter changed from 4 to 8 nm and external from 8 to 13 nm.

2.2 Contact angle

Fig. 2 shows results of contact angle measurement.

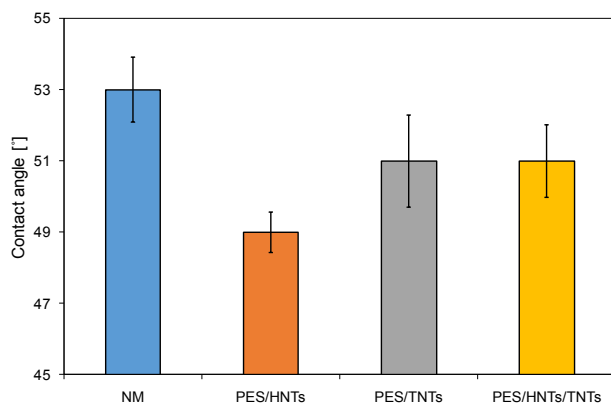


Fig. 2 Contact angle of obtained membranes.

The introduction of HNTs and TNTs into membrane matrix affected hydrophilicity of membranes. The contact angle value was in the range of 49 to 53° being the highest for the unmodified membrane and the lowest for membrane modified with HNTs. The increase in hydrophilicity of the modified membranes was attributed to the presence of –OH groups in the structure of both HNTs and TNTs nanoparticles. A positive influence of the introduction of the nanofillers on hydrophilicity of membranes was also reported by Buruga et al. [11] in case of polystyrene membranes modified with HNTs and Padaki et al. [12] in case of polysulfone membrane modified with TNTs.

2.3 Topography and morphology of membranes

Fig. 3 shows AFM images of membranes surface visualized in 2D mode.

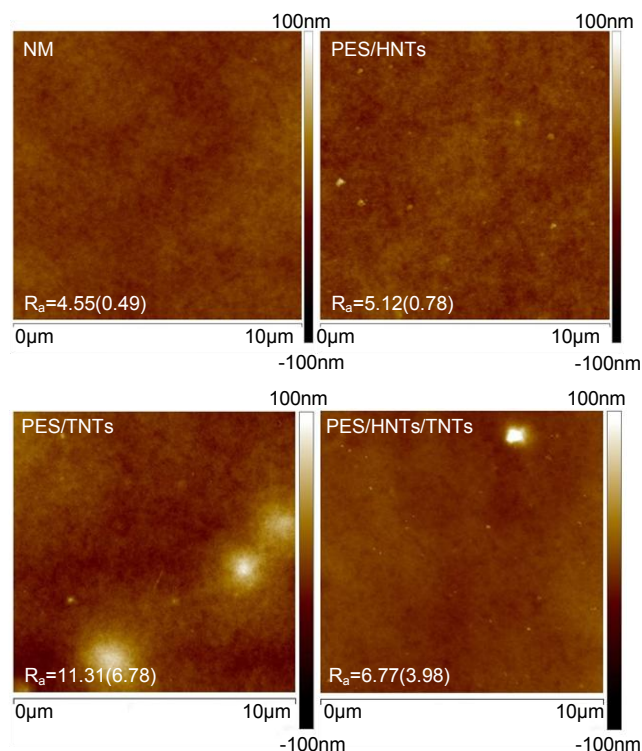


Fig. 3 AFM images of the surface of the obtained membranes.

In case of the membranes containing only halloysite nanotubes some well dispersed NPs agglomerates with diameters in the range of ca. 30–270 nm are present. On the skin layer of the PES/TNTs membrane the small NPs aggregates possess diameters in the range of ca. 15–100 nm, however, also larger agglomerates with diameters even up to $2.5 \mu\text{m}$ are observed. Similar results were obtained previously [6] in case of Ag-TNTs modified membranes. On the surface of the membrane containing both HNTs and TNTs nanoparticles, the diameters of the small agglomerates are in the range of ca. 15–150 nm, while some larger agglomerates with diameters up to $1 \mu\text{m}$ are also present. The obtained results show that when a mixture of HNTs/TNTs was used, the diameters of agglomerates formed on the membrane surface were reduced compared to PES/TNTs membrane. This can be attributed to a lower weight loading of TNTs in the PES/HNTs/TNTs membranes compared to PES/TNTs one (Table 1), resulting in a lower NPs agglomeration.

Based on AFM images, the surface roughness of the prepared membranes was determined. The R_a value calculated for the NM membrane was 4.55(0.49) nm. The highest surface roughness was observed in case of PES/TNTs membrane (11.31(6.78) nm). The application of a mixture of HNTs and TNTs resulted in a decrease of surface roughness to 6.77(3.98) nm compared to PES/TNTs membranes. The lowest R_a amongst the mixed matrix membranes exhibited the PES/HNTs (5.12(0.78)).

SEM images of the membranes cross section taken using SE mode are shown in Fig. 4. All of the membranes exhibit asymmetric

structure with a dense thin separation layer in the top of the membrane, narrow finger-like pores in the middle part and spongy structure in the bottom part of the membrane and between the finger-like pores. In case of the modified membrane some clusters of NPs can be observed (circles in Fig. 4).

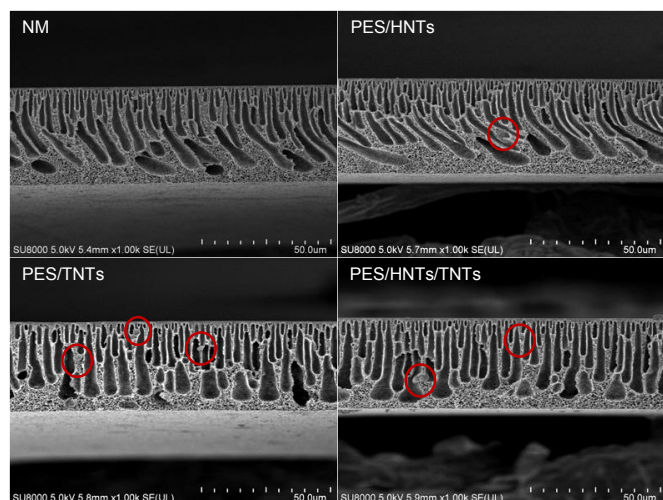


Fig. 4 SEM images of membranes cross-section. The NPs agglomerates are marked with circles.

Furthermore, the membrane modified with a mixture of HNTs and TNTs nanoparticles was analyzed using SEM-EDX method. The results are presented in Fig. 5.

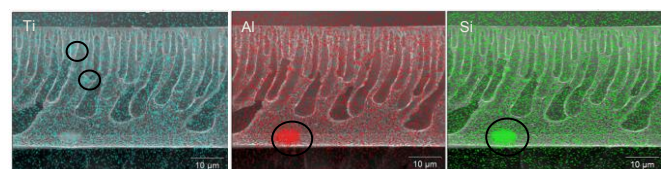


Fig. 5 Results of SEM-EDX analysis for PES/HNTs/TNTs membranes.

Despite application of thorough sonication and mixing at the stage of preparation of the casting dope, both types of NPs did not form joint agglomerates. Separate spots of halloysite nanotubes and titanate nanotubes are visible in the cross-section of the membrane.

2.4 Permeability and fouling resistance of the membranes

A comparison of pure water flux (PWF) measured for the prepared membranes is presented in Fig. 6.

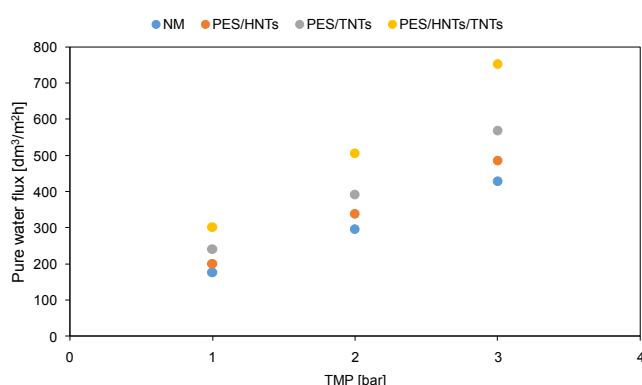


Fig. 6 The influence of transmembrane pressure on the pure water flux through the prepared membranes.

The introduction of different types of the nanofillers affected the PWF values of the modified membranes to a various extent. The least improvement of permeability compared to the unmodified membrane was found in case of PES/HNTs sample. That did not correspond with the hydrophilicity, which was in case of this membrane the highest (Fig. 2). A more significant increase of PWF values was found in case of PES/TNTs membrane. The increase in PWF may be related to the distribution of nanoparticles. The NPs can create additional pores which could increase the permeability of

membranes [5]. In addition, some additional pores are present due to the tubular structure of TNTs, which also contributes to the improved PWF of the membrane. The use of a mixture of halloysite and titanate nanotubes caused an increase in PWF by 71% in relation to the unmodified membrane and by 55 and 33%, respectively, in relation to PES/HNTs and PES/TNTs membranes. The increase in the permeate flux may be associated with an increase in the dispersion of the particles in the membrane matrix that can be seen in Fig. 3.

The influence of the NPs on fouling of the membranes was determined using bovine serum albumin as a model foulant (Fig. 7). After 2h of the BSA ultrafiltration the decrease of permeate flux through the NM membrane in comparison to PWF reached 54%. The introduction of 1 wt% of HNTs led to an improvement of the antifouling properties of the PES membrane resulting in a 46% decrease in permeate flux compared to PWF. On the opposite, the application of TNTs caused a deterioration of the antifouling performance in comparison to the unmodified membrane, and the permeate flux declined for 70% with reference to PWF. The sample containing a mixture of HNTs and TNTs was characterized by better antifouling properties compared to PES/TNTs, however, the flux decline was more severe (64%) than that observed for PES/HNTs membrane (46%).

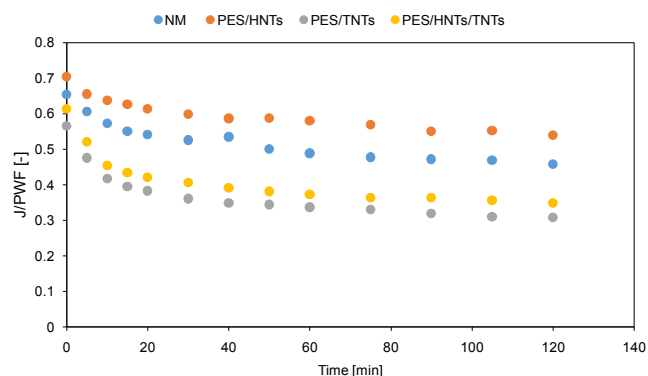


Fig. 7 The effect of HNTs and TNTs on BSA fouling of the PES membranes. Initial BSA concentration: 1 g/dm³; TMP = 2 bar.

The observed results revealed much better antifouling properties of the membrane containing HNTs compared to the other types of the fabricated mixed matrix membranes. One reason can be its higher hydrophilicity (Fig. 2) compared to the other samples. Another factor can be its relatively low permeability in comparison to the PES/TNTs and PES/HNTs/TNTs membranes. At higher flux, the enhanced transport of BSA molecules towards the membrane occurs during initial stages of filtration, which contributes to the intensity of the fouling phenomenon [14]. Other reason can be surface roughness. In case of PES/HNTs membrane the R_a value was the lowest amongst the mixed matrix membranes what was reflected by the best fouling resistance of this sample. Moreover, the roughness of PES/HNTs/TNTs membrane was lower compared to that of PES/TNTs which also resulted in its better antifouling performance. Both Liu et al [15] and Hobbs et al [16] reported that relatively smooth surfaces were more resistant to fouling. Incorporating HNTs into membrane containing TNTs results in higher dispersion of NPs and decrease in surface roughness what affects the fouling resistance of that membrane.

2.5 Separation properties

Fig. 7 shows the rejection of model organic compounds by the obtained membranes. The introduction of HNTs and TNTs into the membranes improved their separation properties. The highest influence of the modification was found in the case of the PES/HNTs membrane. The retention of dextran 110 kDa increased from 50% for the unmodified membrane to 69% after modification with halloysite. In the case of PEGs, the average increase in retention was 4 percent points (p.p.), being the lowest for PEG 35 kDa (2 p.p.) and the highest for PEG 20 kDa (6 p.p.).

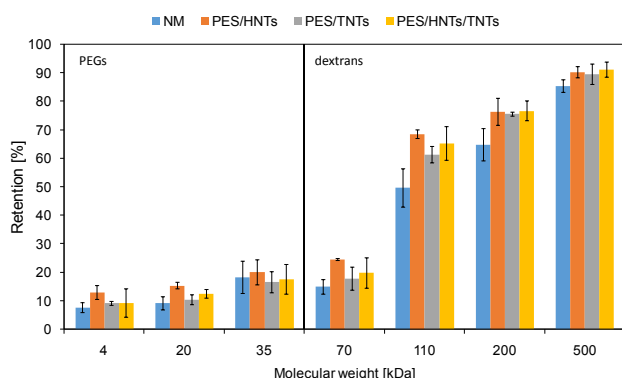


Fig. 7 Separation properties of the obtained membranes.

The use of the mixture of halloysite and titanate nanotubes resulted in an improvement of the separation properties of the membrane compared to the membrane containing TNTs only. The lowest effect was observed for PEGs. More significant changes can be seen in case of dextrans, e.g. the retention of dextran 110 kDa increased by 15 p.p compared to the unmodified membrane.

3. Conclusions

The incorporation of halloysite nanotubes, titanate nanotubes or their mixture into PES membrane matrix affected its physicochemical properties, water permeability, fouling resistance and separation characteristics. The use of both HNTs and TNTs nanofillers caused an increase of hydrophilicity and pure water flux of the PES membrane. The membrane prepared using TNTs as a filler exhibited higher pure water flux than the membrane prepared with HNTs. The highest water permeability was observed for PES/HNTs/TNTs membrane. Application of HNTs resulted in an improvement of the fouling resistance and separation properties of the membranes. However, the membranes modified with TNTs and HNTs/TNTs mixtures were more prone to BSA fouling compared to the unmodified membrane. Nonetheless, the PES/HNTs/TNTs was less fouled than the PES/TNTs membrane confirming a positive effect of HNTs on membrane fouling mitigation. The highest improvement of separation properties of the membranes was obtained by application of HNTs nanofiller.

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THE EFFECT OF PHASE TRANSFORM ON CREEP RESPONSES OF FGM ROTATING DISK

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Abstract: In many applications, FGM rotating discs are subjected to severe operating temperature and high rotational speeds. In such conditions the incidence of creep is inevitable. To study some aspects of this phenomenon, using the Sherby's law the creep relaxation of a group of FGM rotating discs is modeled. Results show that even though the temperature is uniform entirely, the stress variation leads to a phase transformation and so the creep mechanism is changed. In this paper the effect of this change of creep mechanism on the steady state creep behavior of FGM rotating discs made of Al-SiC is studied.

KEYWORDS: CREEP, FGM, ROTATING DISK, PHASE TRANSFORM

1. Introduction:

In many types of machineries such as the turbines, pumps, compressors and jet engines, rotating discs are the basic part. Generally it happens that such instruments are subjected to severe simultaneous thermo-mechanical loads. In these cases the study of creep as a kind of mechanical behavior makes sense. While considering the creep is one aspect of this research, the other standpoint is the study of non-homogeneity effects upon the load carrying capacities of the rotating discs.

Now a day in various industries, productivity implies that many efforts must be made to improve the quality of the manufactured parts and the performance of different machineries while keeping the costs as low as possible. This in turn leads to an essential need for the optimization of different material characteristics such as the weight, thermal and mechanical durability and strength. A new technique to overcome this requirement is the administrated use of FGMs (Functionally Graded Materials). In a structural view FGMs are inhomogeneous materials usually composed of the mixture of seemingly homogenous parts or particles. These compositions can bring about different physical characteristics and functional capabilities such as the light weight, high strength, high conductivity and thermal strength as well as the resistance against the wear, corrosion or burning. So in severe thermo-mechanical loadings their FGM compositions can behave ideally.

At high temperatures the creep deformations are inevitable and consequently the creep must be considered in a careful modeling attempt. The first studies of the creep phenomenon as a mechanical property dates back to the early 1920s. The importance of the material high temperature time dependent behavior or creep relaxation has been recognized during the World War II and following the development of the jet engines [1]. Schweiker [2] has investigated the creep relaxation of high temperature pressurized thick-walled tubes which is necessary to ensure a safe operational condition of the vessels. Owing to the extensive utilization of the discs in rotating machineries, the study of creep in rotating discs covers a wide range of the researches and investigations. Among the first studies we can refer to the work of Wahl et al. [3] in 1954, which has theoretically analyzed the steady state creep deformations of a rotating turbine disc using the von-Mises and Tresca's yield criteria and evaluating the results by comparing with experimental data. In 1959, Ma [4] analyzed the creep deformations and stresses in a rotating gas turbine disc with variable thickness exposed to isothermal conditions and high temperatures, using the maximum shear stress theory. In 1960 and 1964, Ma [5, 6] studied the creep relaxation in the variable thickness discs operating under the conditions of radial temperature gradients. In this analysis Ma used both exponential and power law creep models to find the steady state creep relaxations. Using a time hardening creep law in 1979 Arya and Bhatnagar [7] investigated the creep of orthotropic

rotating discs. They have indicated that by increasing the anisotropy of the disc material, the tangential stresses at any radius and the tangential strain rate at the inner radius are decreased. In 1986, Biakiewicz [8] offered a theoretical method to find the finite strains of a rotating disc using the damage and creep rupture front motion as described by Kachanov's theory [9]. In 1986, Bhatnagar et al. [10] studied the steady state creep behavior of the orthotropic rotating discs comprising the linear and hyperbolic types of thickness variations. By selecting a certain type of anisotropy they derived the best profile of the disc such that stresses are decreased and life expectancy is increased. In 1999, Durodola and Attia [11] obtained the creep results for several forms of the reinforcement gradation with unique overall volume fraction.

In 2002, Singh and Ray [12] studied an FGM disc with linear distribution of silicon carbide particles in the radial direction, reinforced in aluminum matrix. They concluded that the FGM disc having linearly reducing particle contents along the radial direction exhibits significantly lower strain rates when compared to a similar disc but with uniform distribution of particles and the same total amount of particle contents. In 2003, Jahed and Bidabadi [13] presented a general axisymmetric method by using the variable material properties (VMP) method to analyze the primary and secondary creep in the axisymmetric rotating discs and pressure vessels. In 2004, Singh and Ray [14] studied the steady state creep in an anisotropic composite disc considering the Bauschinger's effect, Norton's creep power law and a new yield criterion. They have also considered the disc with residual stress to study the secondary creep. In 2004, Gupta et al. [15], used the Sherby's law to examine the steady state creep behavior of a constant thickness disc, made of isotropic functionally graded material. The disc is composed of linear distributions of the silicon carbide particles in a matrix of pure aluminum. The disc is assumed to operate under a radial thermal gradient and the results are compared with the creep relaxation of a disc with uniform particle distribution. The steady state creep behavior in an isotropic rotating disc made of Al-SiC has been analyzed by Gupta et al. [16] in 2004. They have used Sherby's creep law to look into the trends of the stress and strain rate variations in a particulate composite disc. In recent years Hafeez et al. [17] investigated the creep compliance of straight run (neat) and polymer-modified asphalt binders at their high performance grade temperature using a multi-stress creep recovery test.

In all references exist in the literature the effect of creep mechanism change is ignored. In this paper we intend to study the effects of the change of creep mechanism on the creep behaviors that can occur at the disc made of Al-SiC composite. For this purpose, the steady state creep is modeled and analyzed in FGM rotating disc.

2. Creep mathematical modeling

Similar to the procedures outlined in earlier works [15, 16], a mathematical model is developed to study the second order creep relaxation in a rotating FGM disc. Further, it is assumed that the material of the disc is isotropic and incompressible. With these assumptions we will have,

$$\dot{\epsilon}_r + \dot{\epsilon}_\theta + \dot{\epsilon}_z = 0 \quad (1)$$

In which the subscripts r , θ and z indicate the radial, tangential and axial directions and dot symbol designates the time derivative. Compared to other dimensions, the disc thickness is assumed to be small. So, we can suppose that the problem is plane stress and the assumption of $\sigma_z = 0$ is prevailing.

Moreover it is assumed that, in comparison with creep deformations, the elastic or plastic deformations of the disc are negligible. The study of creep is limited to the analysis of the secondary phase or steady state creep relaxations. In keeping with these assumptions, the Sherby's law [18] has been used for the description of material behavior. That is,

$$\dot{\epsilon} = A_s \left[\frac{\bar{\sigma} - \sigma_0}{E} \right]^n \quad (2)$$

Where $\dot{\epsilon}$, $\bar{\sigma}$, n , E and σ_0 are effective strain rate, effective stress, stress exponent, Young's modulus and threshold stress respectively. A_s is a constant defined as,

$$A_s = \frac{AD_L \lambda^3}{|b|^5} \quad (3)$$

λ stands for the sub-grain size, $|b|$ is the magnitude of the Burgers vector, A is a definite constant and D_L is the lattice diffusivity. The strain rate relation in Sherby's law can be written as,

$$\dot{\epsilon} = [M(\bar{\sigma} - \sigma_0)]^n \quad (4)$$

In which, M equals $\frac{A_s n}{E}$ and according to the von-Mises isotropic yield criterion the effective stress is given as [15],

$$\bar{\sigma} = \frac{1}{\sqrt{2}} [\sigma_r^2 + \sigma_\theta^2 + (\sigma_r - \sigma_\theta)^2]^{1/2} \quad (5)$$

In a particulate composite, the creep parameters M and σ_0 are related to the particle size P , particle distribution $V(r)$ and local temperature T . Following the experimental data reported by Pandey et al. in 1992 [19] and regression technique developed by Gupta et al. [16], the parameters of Sherby's law in Eqs. (6) and (7) are found to be,

$$\ln M = -35.38 + .2077 \ln P + 4.98 \ln T - 0.622 \ln[V(r)] \quad (6)$$

$$\sigma_0 = -0.03507 P + 0.01057 T + 1.00536 V(r) - 2.11916 \quad (7)$$

Here and similar to [16], the size of SiC particles P is assigned the value $1.7 \mu m$. The prevailing temperature T is considered to be $700^\circ K$. It is clear that creep parameters M and σ_0 are functions of the FGM disc radius r .

The structure under study is assumed to be an isotropic FGM disc made of 6061 Al-SiC constituents. In the analysis linear radial distributions of SiC particles are considered. The distribution of the volume fraction in the disc is designated as,

$$V(r) = 100 \times \left[0.4 - 0.3 \times \left(\frac{r-a}{b-a} \right) \right] \quad (8)$$

In which, r is a typical radius of the disc. Moreover a and b are the inner and outer radii of the disc respectively. A profile of the disc and its parameters are shown in Fig. (1).

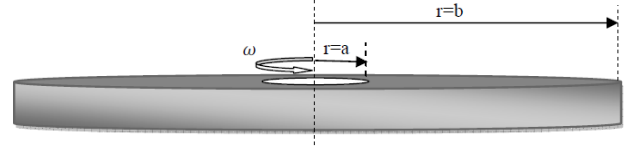


Fig. 1: Studied disc and its parameters

While any point of a heterogeneous FGM compound may seem like a unique substance, in fact it is a mixture of two or more phases. A mixture rule is a formula which shows how the property of a mixture is obtained from the dissimilar properties of its components. For instance, based on the level of volume fraction, a linear mixture rule for the density function, used in this study is,

$$\rho(r) = \rho_m + (\rho_d - \rho_m) V(r) \quad (9)$$

In our application of Eq. (9) and similar to Gupta et.al. [16], $\rho_m = 2698.9 \text{ kg/m}^3$ is the density of the pure aluminum matrix and $\rho_d = 3210 \text{ kg/m}^3$ is the density of the dispersed SiC particles.

In an isotropic disc under the planar state of stress, the creep constitutive equations are [16]:

$$\dot{\epsilon}_r = \frac{\dot{\epsilon}}{2\bar{\sigma}} (2\sigma_r - \sigma_\theta) \quad (10)$$

$$\dot{\epsilon}_\theta = \frac{\dot{\epsilon}}{2\bar{\sigma}} (2\sigma_\theta - \sigma_r) \quad (11)$$

$$\dot{\epsilon}_z = \frac{\dot{\epsilon}}{2\bar{\sigma}} (-\sigma_r - \sigma_\theta) \quad (12)$$

Where $\dot{\epsilon}_r, \dot{\epsilon}_\theta, \dot{\epsilon}_z, \sigma_r, \sigma_\theta, \sigma_z$ are the strain rates and stress components in radial, tangential and axial directions respectively. Besides $\dot{\epsilon}$ and $\bar{\sigma}$ are the effective strain rate and effective stress defined in Eqs. (4) and (5).

By replacing effective strain rate from Eq. (4) and effective stress from Eq. (5) into Eq. (10) and Eq. (11) one obtains,

$$\dot{\epsilon}_r = \frac{d\dot{u}_r}{dr} = \frac{\{M(r)[\bar{\sigma} - \sigma_0(r)]\}^8}{\sqrt{2}[\sigma_r^2 + \sigma_\theta^2 + (\sigma_r - \sigma_\theta)^2]^{1/2}} (2\sigma_r - \sigma_\theta) \quad (13)$$

$$\dot{\epsilon}_\theta = \frac{\dot{u}_r}{r} = \frac{\{M(r)[\bar{\sigma} - \sigma_0(r)]\}^8}{\sqrt{2}[\sigma_r^2 + \sigma_\theta^2 + (\sigma_r - \sigma_\theta)^2]^{1/2}} (2\sigma_\theta - \sigma_r) \quad (14)$$

Defining a stress ratio as $x(r) = \frac{\sigma_r(r)}{\sigma_\theta(r)}$ and simplifying the above equations provides,

$$\dot{\epsilon}_r = \frac{d\dot{u}_r}{dr} = \frac{[2x(r)-1]\{M(r)[\bar{\sigma} - \sigma_0(r)]\}^8}{2[x(r)^2 - x(r) + 1]^{1/2}} \quad (15)$$

$$\dot{\epsilon}_\theta = \frac{\dot{u}_r}{r} = \frac{[2-x(r)]\{M(r)[\bar{\sigma} - \sigma_0(r)]\}^8}{2[x(r)^2 - x(r) + 1]^{1/2}} \quad (16)$$

Dividing Eq. (15) by Eq. (16) and integrating the resulted quotient, consequences,

$$\int_a^r \frac{d\dot{u}_r}{\dot{u}_r} dr = \int_a^r \frac{1}{r} \left[\frac{2x(r)-1}{2-x(r)} \right] dr \quad (17)$$

So,

$$\dot{u}_r = \dot{u}_{ra} \exp \left[\int_a^r \frac{f(r)}{r} dr \right] \quad (18)$$

Where $\dot{u}_{ra}$ is the radial displacement rate in the inner radius of the disc and $f(r)$ is,

$$f(r) = \frac{2x(r)-1}{2-x(r)} \quad (19)$$

Dividing both sides of Eq. (18) by r , we obtain:

$$\frac{\dot{u}_r}{r} = \frac{\dot{u}_{ra}}{r} \exp\left(\int_a^r \frac{f(r)}{r} dr\right) = \frac{[2-x(r)]\{M(r)[\bar{\sigma}-\sigma_\theta(r)]\}^8}{2[x(r)^2-x(r)+1]^{1/2}} \quad (20)$$

After substituting $\bar{\sigma}$ from Eq. (5) into Eq. (20) and simplifying the answer, the tangential stress in each arbitrary radius of the disc is obtained as,

$$\sigma_\theta(r) = \frac{(\dot{u}_{ra})^{1/8}}{M(r)} \lambda_1(r) + \lambda_2(r) \quad (21)$$

Where in this equation,

$$\lambda_1(r) = \frac{\lambda(r)}{[x(r)^2-x(r)+1]^{1/2}} \quad (22)$$

$$\lambda_2(r) = \frac{\sigma_\theta(r)}{[x(r)^2-x(r)+1]^{1/2}} \quad (23)$$

and

$$\lambda(r) = \left[\frac{2}{r} \frac{[x(r)^2-x(r)+1]^{1/2}}{[2-x(r)]} \exp\left(\int_a^r \frac{f(r)}{r} dr\right) \right]^{1/8} \quad (24)$$

Now, as in Fig. (2) considering an element of rotating disc which rotate by an angular velocity ω , which is considered to be 180 rad/s in this analysis, the equilibrium of a disc element implies,

$$\frac{d}{dr}(r\sigma_r) - \sigma_\theta + \rho(r)r^2\omega^2 = 0 \quad (25)$$

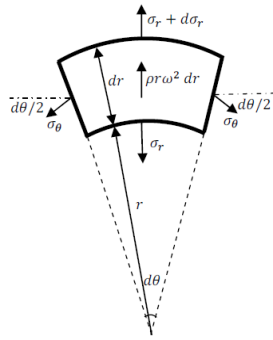


Fig. 2: Schematic pictures of a disc and a disc element

The boundary conditions of the rotating disc are,

$$\sigma_r(r=a) = 0 \quad (26)$$

$$\sigma_r(r=b) = 0 \quad (27)$$

Integrating the equilibrium equation between $r=a$ and $r=b$ results in,

$$\int_a^b \sigma_\theta dr = \omega^2 \int_a^b \rho(r)r^2 dr \quad (28)$$

To obtain $\dot{u}_{ra}$ (i.e., the radial displacement rate at the inner radius of the disc), we can integrate Eq. (21) from $r=a$ to $r=b$. It provides,

$$(\dot{u}_{ra})^{1/8} = \frac{\int_a^b M(r)\sigma_\theta(r)dr - \int_a^b M(r)\lambda_2(r)dr}{\int_a^b \lambda_1(r)dr} \quad (29)$$

To solve this problem, the computational procedure presented henceforward is employed. In this practice primarily in each step a uniform distribution of temperature and definite amount of angular velocity is assumed. These quantities can be selected independently. In the first step we can assume that the distribution of tangential stress is uniform. In this case we can write $\sigma_\theta(r) = (\sigma_\theta)_{ave}$, in which $(\sigma_\theta)_{ave}$ is obtained from the following equation.

$$(\sigma_\theta)_{ave} = \frac{1}{(b-a)} \int_a^b \sigma_\theta dr \quad (30)$$

Then we can obtain σ_r from the equilibrium equation as:

$$\sigma_r = \frac{1}{r} \int_a^r \sigma_\theta dr - \frac{\omega^2}{r} \int_a^r \rho(r)r^2 dr \quad (31)$$

When σ_r is obtained, we can find the ratio of σ_r and σ_θ which has already been defined as $x(r)$. Now the radial distributions of $f(r)$, $\lambda_1(r)$, $\lambda_2(r)$, $\bar{\sigma}_r$ functions and the amount of $\dot{u}_{ra}$ can be found. Afterwards Eq. (21) is used to obtain a new estimation of σ_θ field. This loop is repeated until a desirable convergence for the tangential stress distribution in the radial direction is achieved. So we can calculate the strain creep rate and stress fields in the steady conditions of uniform ambient temperature throughout the rotating disc.

3. Results and discussions

Based on the analytical techniques introduced in the previous section and using a self-developed computer code some calculations are performed to find the radial distributions of the stress and strain rates for FGM rotating disc. But there is a challenge in this condition which ignored in the literature. In a rotating disc the stress field is varied in different sections it means despite of the constant temperature the phase of creep can be changed in various areas of rotating disc so the creep mechanism changed in different section of rotating disc.

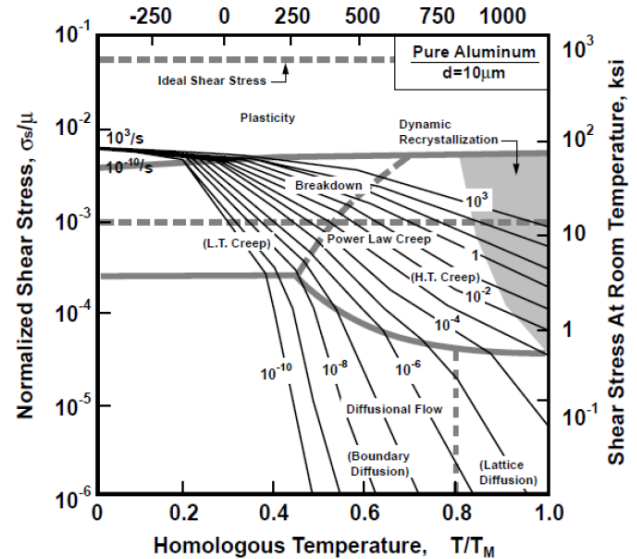


Fig. 3: Creep mechanism map of Aluminum

Mechanical behavior of disc is depended to stress fields, beside the stress field completely dependent on the material behavior, so an analytical and repetitive cycle is required. Referring the creep mechanism map (please see Fig. (3)) it is obvious that in 0.75 of melting temperature of aluminum, if the stress ratio σ_e/G is lesser than the 5×10^{-4} the diffusion mechanism is governed and if the stress ratio is higher than the 5×10^{-4} the governing mechanism is dislocation climb. The creep mechanism change is effective on stress power component means n in Eq. (4). For diffusion mechanism, the stress exponent is 3 and for the dislocation mechanism 5 is considered.

Fig. (4) and Fig. (5) show the radial and tangential stress distribution in disc with and without considering the creep mechanism change. Based on these figures, the effect of creep phase transform on the stresses is negligible. Also the relatively higher levels of tangential stress occur near the inner radius, while lower amounts are seen near the outer radius of the disc. The radial stress at inner and outer radius reached to zero because of the free-free boundary condition which is considered.

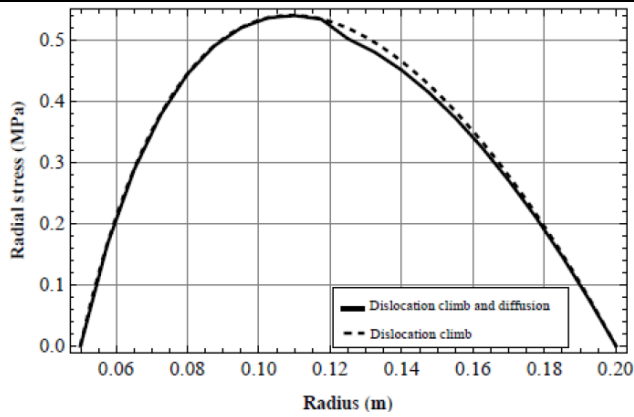


Fig. 4: Radial stress distribution

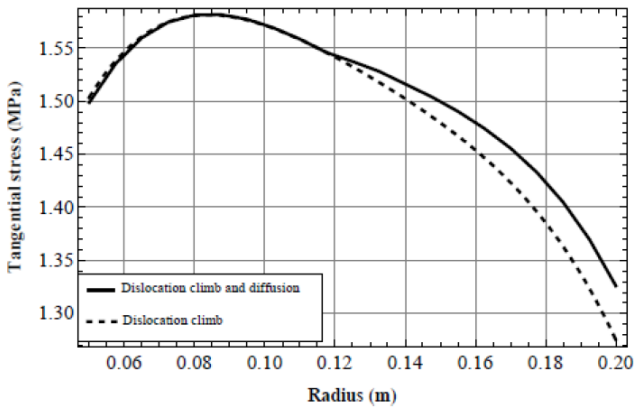


Fig. 5: Tangential stress distribution

Fig. (6) presents the radial displacement rate distribution of FGM rotating disc with two distinct creep behavior model and without considering this changing. The figure shows that the change of creep mechanism is completely affected on radial displacement rate.

Radial and tangential creep rates are investigated in Figs. (7) and (8). As it can be seen nearly in the middle of the disc which the creep mechanism is changed from dislocation climb to diffusion mechanism, the creep rate distributions also have tremendous changes. It is obvious that ignoring this changing mechanism lead to significant errors. Radial and tangential creep rates have a decreasing trend via radial direction and the maximum values of both rates occurs at inner radiuses.

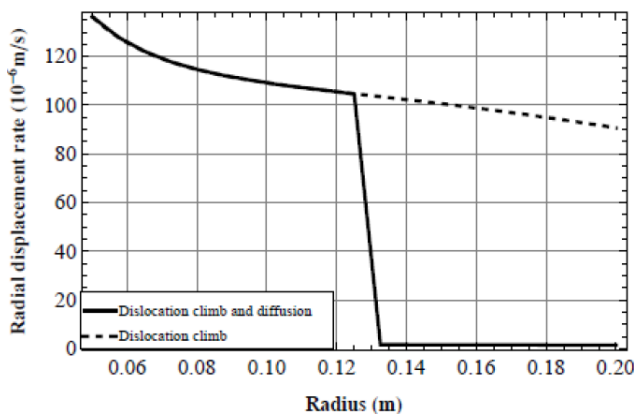


Fig. 6: Radial displacement rate

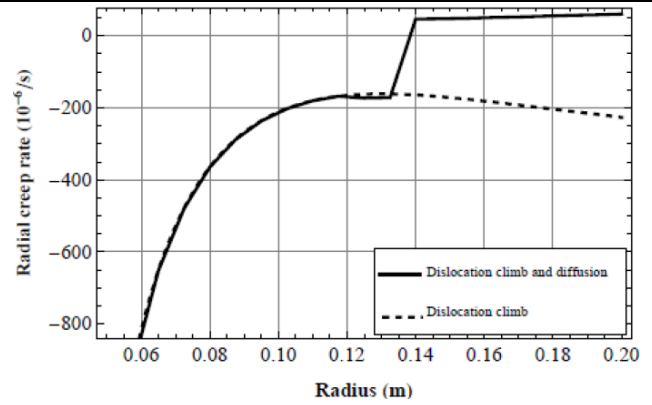


Fig. 7: Radial creep rate distribution

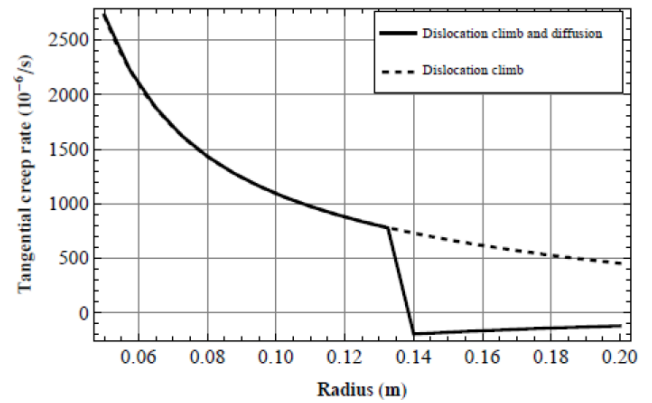


Fig. 8: Tangential creep rate distribution

4. Conclusion

In high rotational speeds the creep relaxation phenomena can affect the performance of FGM rotating disc. Creep behavior is depended to stress and temperature fields, time, loading history, temperature history and microstructure type of materials. Therefore, through the various parameters which are effective on creep behavior, it is usual to exist two distinct creep mechanism in a single substance and results show that creep response is very sensitive to the governing creep mechanism in FGM rotating disc and also considering only one governing mechanism in all parts of rotating disc results the large errors.

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IRON POWDERS WITH INSULATING LAYERS: STRUCTURE AND MAGNETIC PROPERTIES

ПОРОШКИ ЖЕЛЕЗА С ИЗОЛИРУЮЩИМИ ПОКРЫТИЯМИ: СТРУКТУРА И МАГНИТНЫЕ СВОЙСТВА

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Abstract: The development and study of the composite magnetic soft material, the magnetic properties of which are close to the laminated metal magnets and the remagnetization losses is lower than that one of metal magnets is very relevant. The study of magnetic properties and magnitude of losses on the remagnetization of the developed low-frequency composite magnetically soft material, comprising separate iron $20 \div 100$ mkm particles, covered by insulating layers (films) with thickness $3 \div 10$ nm, in comparison with similar parameters of electrical steel 3412 (E320) was performed in this work.

KEYWORDS: SOFT MAGNETIC MATERIALS, COMPOSITES, CRYSTAL STRUCTURE, MAGNETIC PROPERTIES

1. Introduction

The wide application of valve inverter drive type electric motors, for which the operating remagnetization frequency is significantly higher than the industrial frequency, required the development of new magnetic-soft materials.

Over the past few years, many research centers have been intensively conducting research on soft magnetic composite (SMC) materials based on the use of soft magnetic particles, usually based on iron with an electro-insulating coating on each particle.

In [1] the isolated powder is obtained by treating the iron powder with a solution containing phosphoric acid and chromic acid. The pressed product obtained from isolated powders is then subjected to heat treatment.

Another type of coating is described in [2]. In accordance with the patent, the core from magnetic powder is obtained by iron powder treating with an aqueous solution of potassium dichromate, drying, pressing the powder and heat treatment of the product at a temperature of 600°C approximately. In another known method, the particles of magnetically soft iron are coated with thermoplastic materials before pressing [3].

Significant progress in creating the composite soft magnetic material made up company "Hoganas" [4-7]. Individual products of this company, for example with the use of powder "Somaloy 500, 750", approximate by the parameters of the device from electrical steel. However, the results of these studies do not allow to clearly speaking about the successful solution of the problem of developing a composite magnetic soft material.

2. Experimental technique

Further improvement of the properties of a soft magnetic material based on iron powders coated with a ferrite layer was achieved through the use of HF synthesis of metal-dielectric-metal (MDM)-structures. The fundamental difference between the HF synthesis of MDM-structures and the previously described method of rapid thermal sintering is the formation of MDM-structures. The process of forming thin-layer MDM-structures with the formation of channel effects at the interfaces is considered in paper [8].

When exposed on MDM-structure of high-frequency radiation, for which the depth of the skin-layer is comparable to the size of the sample, in the ferrite coating separating the iron grains, conduction channels are formed. The size of the channels is usually from one to several microns.

As a result of the formation of conduction channels in ferrite boundaries between iron grains in a two-phase crystalline system, a single electronic structure is formed, which corresponds to ferromagnetic ordering in the entire system (Fig.1).

Progress in magnetic properties improving of composite materials and reducing of the remagnetization losses has been achieved in this work by using of various magnetic oxides as insulating coatings, where the thickness of iron particle coatings has been reduced to a fraction of nanometers [8]. The technology of

manufacturing powders of composite magnetically soft materials consisted in the reactive application of insulating coatings from the gas phase in a vacuum at a temperature of $150\text{--}200^\circ\text{C}$ [9]. In this paper, we studied a low-frequency composite material based on ASC100.29 iron powder, with an average coating thickness based on phosphorus oxide $d < 0.3\text{--}0.5$ nm, marked in a work as SMC-LF.

Samples of the composite magnetic material were made by powder metallurgy method by pressing the prepared isolated iron powder with addition of zinc stearate in an amount of 0.25% of the total mass under pressure of $7\text{--}8$ t/cm² and then were annealed by vacuum at a temperature of 400°C during 2 hours.

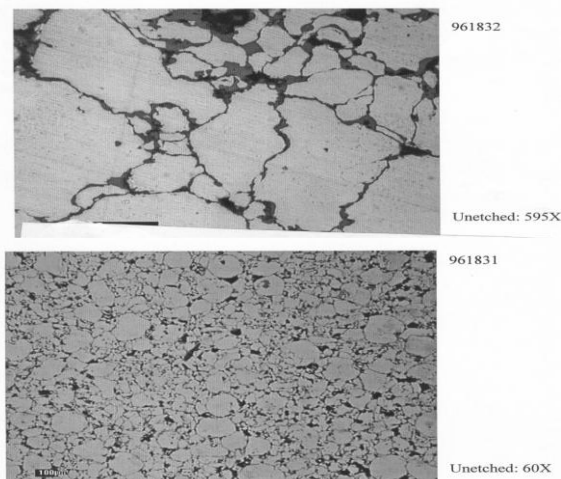


Fig. 1. Results of metallographic study of the structure of the MDM-alloy

Study of basic magnetic properties of composite magnetic materials using iron powders ASC100.29 (Hoganas) [10] is performed in comparison with the same parameters for electrical steel 3412 (E320). With this purpose were made cores $24 \times 13 \times 10$ mm from a set of tape drives electrically insulated steel and composite magnetic material of density $\rho = 7.7$ g/cm³, were investigated the static, dynamic magnetic properties and hysteresis loss of the static characteristics were studied using microperimetry F5050, and dynamic performance and losses – by flaxmere and Express magnetometer in the frequency range up to 10 kHz and magnetic fields up to 30 kA/m.

3. Results and discussion

On Fig. 2 the static magnetization curves of a composite magnetic material based on iron powder ASC100.29 (curve 1) and electrical steel (curve 2) are given. The figure shows that the magnetic induction of the composite material in the fields up to

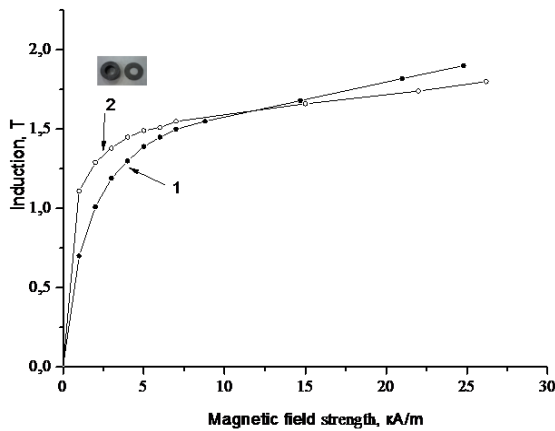


Figure 2. Curves of magnetization of the magnetic composite material based on powder ASC100.29 (curve 1) and on steel strip 3412(Э320) (curve 2)

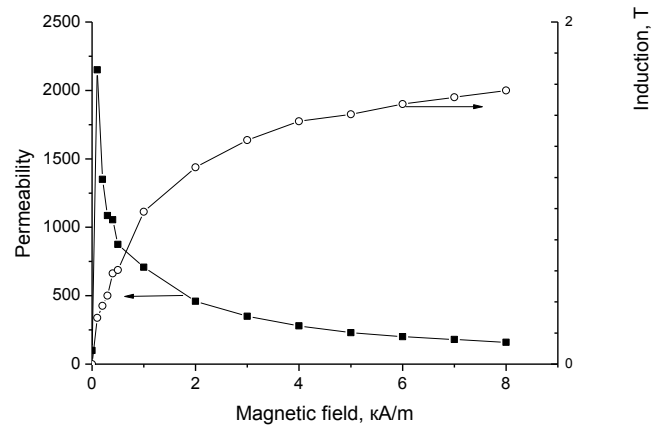


Figure 3. Magnetic permeability and magnetic induction depending on the field of composite magnetic material based on ASC100.29 powder

$H = 5 - 6$ kA/m is inferior in value to the induction of electrical steel, and at higher fields it exceeds the parameters for electrical steel.

Magnetic induction at a strength $H = 25$ kA/m for a composite magnetic material is $B_m = 1.95 - 2.0$ Tesla, and for steel in the same field – $B_m = 1.84$ Tesla at the same density of samples $\rho = 7.7$ g/cm³.

The initial magnetic permeability for the composite magnetic material is $\mu_m = 100-110$, the magnetic permeability maximum is, respectively, $\mu_m = 2100-2300$ (Fig. 3).

The dynamic reversal curves for a composite magnetic material at a frequency of 1 kHz are shown in Fig. 3 (curve 1). The induction of the composite material is higher than the induction of steel in the fields of large 5 – 6 kA/m.

In Fig. 4 is shown the dynamic curve of magnetization reversal at a frequency of 1 kHz in weak fields, from which it is possible to take the value of the coercive force of the composite material equal to $H_c = 30 - 40$ A/m.

The losses in steel increase quadratically with increasing magnetic induction. Losses in electrical steel are largely determined by eddy currents [4]:

$$P_c = (\pi B_m f h)^2 6 \rho, \quad (1)$$

where f – remagnetization frequency, h – grain size, ρ – resistivity, B_m – the magnetic induction.

At the same time in the composites losses on eddy currents are practically absent, only magnetic losses remain, which increase linearly with induction to the order of 1.5 Tesla. The losses in the composite material at a frequency of 1 kHz and induction $b = 1.8$ T are $W = 120$ W/kg, then for the steel under the same conditions the loss is 1.5 times higher $W = 170$ W/kg.

The iron particles have a size $d > 100$ nm and are multi-domain. Losses in the motion of the domain boundary occur when it is inhibited on defects in the structure and, first of all, on defects in induced anisotropy that occurs during uniaxial pressing of products. At high magnetic field values of order $H = 15 - 20$ kA/m the effect of anisotropy on the magnitude of the losses is affected to a lesser extent, and on the dependence of losses on the induction of the observed deviation from linearity with the transition to saturation.

Comparative data of the main characteristics of electrical steel 3412 (E320) and composite material SMC-LF based on iron powder ASC100.29 are summarized in table 1.

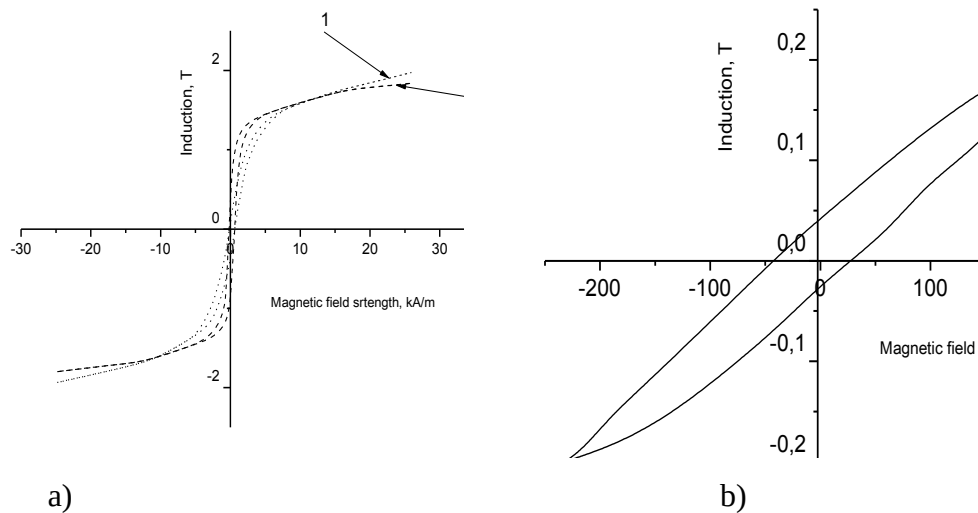


Figure 4. Dynamic hysteresis loops at the remagnetization frequency of 1 kHz: a-for composite material based on ASC100.29 (curve 1) and electrical steel 3412 (E320) (curve 2), b — for the composite material based on ASS100.29 in weak fields

Table 1. Comparative data of the main characteristics of electrical steel 3412 (E320) and composite material SMC-LF based on iron powder ASC100.29

Magnetic material	Density, g/cm ³	HC, A/m	μm	B, T 10000 A/m	Losses, W/kg 1 T, 1000 Hz	Losses W/kg 1,75 T, 1000 Hz
Steel 3412 0,35 mm	7,7	8 – 10	7000	1,59	100	170
SMC-LF	7,7	30 – 40	2000	1,59	60	110

Comparative studies of composite materials based on iron powders sprayed with air and water are carried out. For all selected iron powders the thickness of the phosphate insulation coating was 0.3-0.5 nm while maintaining identical conditions for their production. For example, an sprayed with air iron powder Laiwu Taidong Powder (China) significantly differs from water-sprayed

ASC100.29 (Sweden) by the content of basic impurities such as manganese, carbon, phosphorus [10].

Table 2 shows the comparative data on losses for composite materials based on some iron powders, which shows the advantage of composite materials based on ASC100.29.

Table 2. Comparative data on losses for composite materials based on iron powders

Type of iron powder	The relative losses in the field 2 kA/m	The relative losses in the field 10 kA/m
PGR 2 (Russia)	1,33	1,27
LaiwuTaidon (China)	1,25	1,5
ASC100.29 (China)	1,01	1,12
ASC100.29 (Sweden)	1,06	1,17
ABC100.30 (Sweden)	1	1

4. Conclusion

As a result of the research it is shown that the magnetic induction of the developed composite material in the fields up to $H = 5 - 6$ kA/m is inferior in the induction value of electrical steel, and at higher fields it exceeds the parameters for electrical steel. Magnetic induction at a strength $H = 25$ kA / m for a composite magnetic material is $B_m = 1,95-2,0$ T, and for steel in the same field- $B_m = 1,84$ T at the same density of samples $\rho = 7,7$ g/cm³

The advantages of the composite magnetic material over the electrical steel, first of all, is the reduction of remagnetization losses, for example at a frequency of 1 kHz and induction $B = 1,8$ T with $W = 170$ W/kg for steel to $W = 120$ W/kg for the composite material, as well as the manufacturability of products, waste-free production, lower cost parameters, allow us to consider this material as an alternative product to metal magnets. In particular, the use of composite magnetically soft materials will have significant advantages due to lower losses in electrical machines, transformers and other products with increased specific power and high speed of rotation, where electrical steels have higher losses.

The study of remagnetization losses of composite materials showed that the hysteresis losses are 25 – 30% higher for composites based on iron powders sprayed with air (columns 1 and 2 of the table.2), compared with losses for composites based on powders, sprayed with water, such as the ASC100.29. First of all, this is due to the purity of the iron powder ASC100.29, for which the impurity content is less than 1.0%.

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CRYSTALLIZATION REGULARITIES OF A HIGH AND LOW DENSITY POLYETHYLENE BLEND AND COMPOSITE MATERIALS ON ITS BASIS

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Abstract: The results of studies of the regularities and mechanism of crystallization of polymer mixtures of high and low-density polyethylene in various proportions and composite materials based on blends of high and low density polyethylene taken in a 50/50 ratio are given. In filled composites, aluminum hydroxide was used in concentrations of 1, 3, 5, 10% wt. and bentonite in concentrations of 1, 3, 5, 10, 20, 30% wt. Dilatometric studies were carried out on an IIRT-1 device, in the process of stepwise cooling of samples with a load of 5.3 kg.

Keywords: CRYSTALLIZATION, DILATOMETRY, LOW DENSITY POLYETHYLENE, HIGH DENSITY POLYETHYLENE, POLYMER BLEND, BENTONITE, ALUMINUM HYDROXIDE.

1. Introduction

As the engineering, aviation, shipbuilding, and automotive industries developed and improved, increasingly stringent requirements began to be placed on the quality of polymeric materials. It is clear that, according to their characteristics, base polymers produced in the polymer industry are not always able to meet the increased requirements of modern technology. In this regard, the modification methods undertaken in the direction of improving the structure and complex of the properties of polymers allow one to come closer to the accomplishment of the task to one degree or another. One of the most common methods for modifying polymers is blending a polymer with a polymer [1, 2]. In recent years, polyethylene-polyethylene mixture has been the subject of great scientific and practical interest, in which not only quality problems were solved, but also the cost of products derived from them [3, 4]. By varying the ratio of high density polyethylene / low density polyethylene (HDPE / LDPE), it is possible to obtain relatively strong and flexible polymeric materials. Along with this, the loading of fillers into their composition actually allows to obtain relatively new types of polymer composites with improved deformation and strength properties, in which the filler plays the role of an amplifier of polymers.

The research task was to study by dilatometry method the regularities and mechanism of crystallization of polymer mixtures of HDPE / LDPE (at 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10 ratios) and composite materials based on HDPE + 50% wt. LDPE and fillers, differing in their nature and particle size.

2. Results and discussion

Industrial objects of HDPE, LDPE, fillers — aluminum hydroxide and bentonite — were used as an object of research. The choice of these fillers in the composition of polymer mixtures was due, above all, the need to obtain fire-resistant composite materials. The HDPE / LDPE ratio in the filled composite materials was 50/50. The choice of this ratio was due to the fact that it is by using an equal amount of HDPE and LDPE in the mixture that their best technological miscibility and mutual dispersibility is achieved.

Composite materials were obtained by mixing the components on laboratory rollers at a temperature of 150°C within 8-10 minutes. Then, at a pressing temperature of 170-180°C, plates were molded from which the corresponding samples were cut down for testing.

Dilatometric studies were carried out on an IIRT-1 instrument during stepwise cooling with a load of 5.3 kg and in the temperature range from 180°C to room temperature.

Studies of the influence of the ratio of the considered polymer components on the density and crystallization onset temperature, which characterizes the first-order phase transition, showed that up to 50% wt. content of LDPE in the composition, the crystallization onset temperature does not undergo any changes and remains within

114°C. At the same time, as expected, there is a regular decrease in the density of samples with increasing concentration of LDPE in the composition. When the concentration of LDPE in a mixture of more than 50% wt. the crystallization onset temperature of the polymer composition begins to decrease. The latter circumstance confirms our understanding of phase inversion at 50% wt. content of LDPE in the composition. The results of studies of the kinetic regularities of crystallization of the original LDPE, HDPE and their mixtures at various ratios showed that all changes in the dilatometric curves of polymer mixtures are concentrated between the curves of the initial components of the mixture (Figure 1).

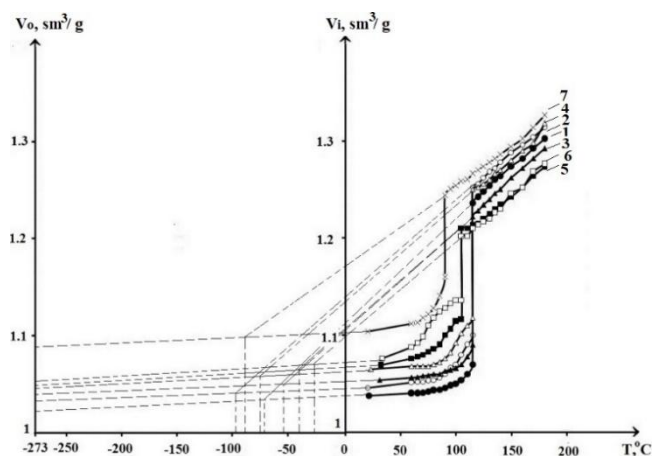


Fig. 1. Kinetic regularities of crystallization of the original LDPE, HDPE and their mixtures at different ratios: 1(●) – 100% wt. HDPE, 2(o) – 10% wt. LDPE + 90% wt. HDPE, 3(▲) – 20% wt. LDPE + 80% wt. HDPE, 4(Δ) – 50% wt. LDPE + 50% wt. HDPE, 5(■) – 80% wt. LDPE + 20% wt. HDPE, 6(□) – 90% wt. LDPE + 10% wt. HDPE, 7(x) – 100% wt. LDPE

It should be noted that the melting point of HDPE is 125°C and that of LDPE is 95°C. This means that in the process of cooling samples of polymer mixtures, the HDPE macromolecules will first crystallize at 110 - 114°C, and then LDPE. The development of the crystallization process is promoted by such factors as the flexibility of the polymer chains, the symmetry of the molecular structure, the absence of bulky side substitutes in the polymer chain, the presence of potential possibilities for fixing orderly arranged macromolecules. It can be assumed that in the process of cooling the samples, the crystallization of HDPE macromolecules and the growth of spherulite formations is accompanied by the displacement of relatively branched LDPE macromolecules into amorphous regions. It is not excluded that, depending on the amount loaded into the composition of the LDPE, the mechanism of crystallization and the packing of its macromolecules may change significantly. Apparently, at low concentrations of LDPE (up to 20% wt.), the crystallization process of the HDPE macromolecules is

accompanied by the formation and growth of its own spherulite formations, which push the LDPE macromolecules into the amorphous regions. Compaction and concentration of LDPE macromolecules in the amorphous regions of the crystalline phase of HDPE create certain steric difficulties for crystallization and folding of branched macrochains into more ordered and perfect crystalline formations. The further crystallization process of LDPE macromolecules in the cramped conditions of the amorphous regions of HDPE becomes excessively difficult. That is why, the process of crystallization of compositions up to 50% wt. LDPE content proceeds at the same temperature close to the crystallization temperature of HDPE, i.e. 114°C. There is reason to believe that the process of melting and crystallization for each of the components of the mixture proceeds independently of each other. Only, in this case, distortions or shifts in the temperature ranges of melting and crystallization are possible. It is possible that with a ratio of components (HDPE / LDPE) within 40-60 / 60-40, the process of formation of crystalline formations under phase inversion proceeds in a slightly different way. It can be assumed that with such a ratio of mixture components a certain parity is achieved, in which the formation and growth of spherulite formations of HDPE and then LDPE are not accompanied by interference in the placement of macromolecules in ordered regions. In addition, we can assume the appearance of "concentration compatibility" of the components of the mixture in the range of 40/60 - 60/40 ratios.

Crystallization of polymers is a spontaneous process. This process is reflected in the change in the characteristic properties of polymers: its density increases, the modulus of elasticity increases, i.e. polymer stiffness, other characteristics change. The filler particles can increase or decrease the crystallization rate of the semi-crystalline polymer, affect the growth of polymer matrix crystals, and the effect of nucleation in the melt. It was interesting to study the effect of aluminum hydroxide and bentonite on the regularities of crystallization of composite materials based on mixtures of high and low density polyethylene.

Studies based on a mixture of HDPE / LDPE (50/50) and bentonite were carried out with different concentrations (1, 3, 5, 10, 20 and 30% wt.) of bentonite. 1% wt. the content of bentonite in a mixture of LDPE / HDPE does not have any change on the temperature of the beginning of the crystallization process, and is equal to 114°C. For composite materials with a concentration of bentonite in the range of 3–30% wt. phase transition of the first kind occurs at 110-113°C. The density corresponding to room temperature for these materials naturally increases. The upper branches of the isotherm (Figure 2) directly reflect a decrease in the specific volume and, accordingly, an increase in the melt density of the composites with an increase in the amount of bentonite in the composition. The loading of bentonite in the composition of the polymer mixture helps to reduce the free specific volume. This fact suggests that the filler particles are mainly embedded in the free volume of the polymers.

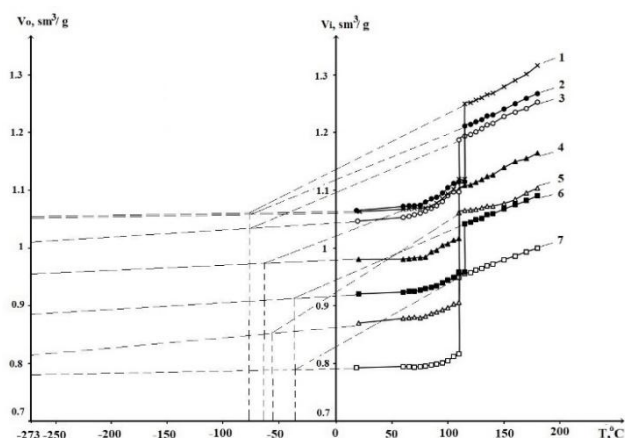


Fig. 2. Regularities of change in specific volume from temperature for nanocomposites based on bentonite / HDPE / LDPE: 1(×)–50% wt. LDPE+ 50% wt. HDPE, 2(●)– HDPE / LDPE+1% wt.

bentonite, 3(○)– HDPE / LDPE+3% wt. bentonite, 4(▲)– HDPE / LDPE+5% wt. bentonite, 5(Δ)– HDPE / LDPE+10% wt. bentonite, 6(■)– HDPE / LDPE+20% wt. bentonite, 7(□)– HDPE / LDPE+30% wt. bentonite

Studies based on a mixture of HDPE / LDPE (50/50) and aluminum hydroxide were carried out with composite materials containing 1, 3, 5, 10% wt. aluminum hydroxide. Loading 1% wt. aluminum hydroxide has almost no effect on the onset temperature of crystallization of the initial LDPE / HDPE mixture and is equal to 114°C. With an increase in the concentration of aluminum hydroxide to 10%, the onset temperature of crystallization of the composites does not undergo any changes and corresponds to a value of 110°C (Figure 3). With an increase in the concentration of aluminum hydroxide, the specific volume of the composite materials decreases, that is, compaction of the material is observed.

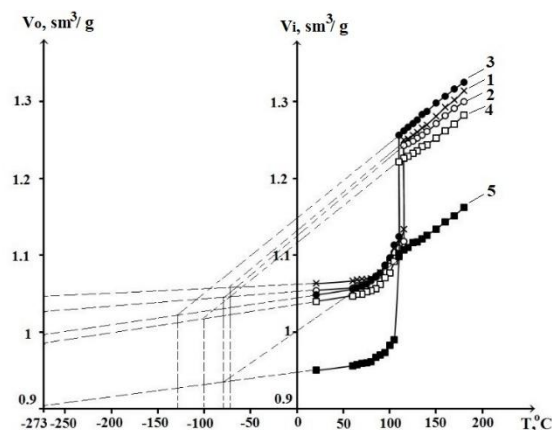


Fig. 3. Graphical dependence of specific volume on temperature for composites based on $\text{Al}(\text{OH})_3$ / HDPE / LDPE: 1(×)–50% wt. LDPE+ 50% wt. HDPE, 2(○)– HDPE / LDPE + 1% wt. $\text{Al}(\text{OH})_3$, 3(●)– HDPE / LDPE + 3% wt. $\text{Al}(\text{OH})_3$, 4(□)– HDPE / LDPE + 5% wt. $\text{Al}(\text{OH})_3$, 5(■)– HDPE / LDPE + 10% wt. $\text{Al}(\text{OH})_3$

The data obtained showed that at low concentrations of aluminum hydroxide, it contributes to the complete crystallization process, but at concentrations of 5-10% wt. on the contrary, the process of crystallization in filled composites is somewhat more difficult. Comparative analyzes have shown that the value of free specific volume for composites filled with aluminum hydroxide is higher than for the original HDPE / LDPE mixture. This can be explained by the fact that aluminum hydroxide particles, by creating steric hindrances for the complete crystallization of macromolecules in the region of the phase transition, contribute to the loosening of the material.

3. Conclusion

Based on the above, it can be stated that a change in the ratio of components in a mixture of HDPE + LDPE leads to an ambiguous change in the structure and properties of polymer blends. In the ratio 40/60 - 60/40, phase inversion occurs, under which conditions are created for the formation of an optimal crystalline structure. In filled composites, the loading of 1% wt. filler does not affect the crystallization onset temperature of the initial mixture of LDPE / HDPE. With a further increase in the concentration of the filler in the polymer mixture, a decrease in the crystallization onset temperature is observed.

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PHASE TRANSFORMATIONS AT HEATING OF Sn–Ni–Zn POWDERS OBTAINED BY CEMENTATION FROM SOLUTIONS

ФАЗОВЫЕ ПРЕВРАЩЕНИЯ ПРИ ПРОГРЕВЕ ПОРОШКОВ Sn–Ni–Zn, ПОЛУЧЕННЫХ ЦЕМЕНТАЦИЕЙ ИЗ РАСТВОРОВ

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Abstract. The low-temperature method of Sn–Ni–Zn powders synthesis by cementation of tin and nickel with zinc powder from acidic solutions with the formation of “zinc core – porous nickel shell – external tin layer” structures has been proposed. The method provides metals ratio control in wide ranges (7–41 at. % of tin, 38–86 at. % of nickel and 7–24 at. % of zinc) by variation of the process duration. X-ray phase analysis data give evidence on the presence of β -Sn and Zn phases as well as NiZn₃ and NiSn intermetallics in the powders obtained. Differential scanning calorimetry data show the availability of Sn–Zn eutectic with the melting point at 171.2 °C in the powders with high tin content (30–40 at. %). The formation of the ternary intermetallic τ_1 phase (Ni_{3+x}Sn₄Zn) has been established to occur as a result of the powders heating at 260 °C. The discovered low-temperature phase transformation in Sn–Ni–Zn system at 260 °C is of interest for electronic equipment assembly processes that include consecutive stages of soldering and resoldering.

Keywords: CEMENTATION, POWDER, NICKEL, TIN, ZINC, PHASE COMPOSITION, INTERMETALLIC, SOLDER.

1. Introduction

The formation of soldered joint (seam) between the metal to be brazed and the solder heated to a temperature slightly above the solder melting point (T_m) is one of the key stages of the soldering technological process. The formation of intermetallic compounds, solid solutions or eutectics occurs in the seam as a result of the interdiffusion and subsequent crystallization processes. The main requirements for soldered joints are their high mechanical strength and acceptable structural characteristics that provide reliable contact with the surface, corrosion resistance, good thermal and electrical properties as well as the possibility of heat treatment of elements containing such joints without causing damage to them [1]. To fulfill these requirements it is necessary to use solders with definite chemical composition. Powder solders have recently become popular on the world market. Their application provides the reduction of labor intensity in the soldering technological process, accurate material dosing, mechanization and miniaturization of the soldering procedure. Naturally, additional requirements are imposed on the particle size in powder solders.

The rejection of the solder based on Sn–38.1wt%Pb eutectic alloy (T_m 183 °C) use and intensive search for alternative tin-containing solders with low melting point began after the adoption of the Directive 2002/96/EC on Waste Electrical and Electronic Equipment (WEEE) by the European Parliament and the Council in 2003 [1, 2]. Sn–0.7wt%Cu (T_m 227 °C), Sn–3.5wt% Ag (T_m 221 °C), Sn–8.8wt%Zn (T_m 198.5 °C), Sn–57wt%Bi (T_m 139 °C), Sn–51.7wt%In (T_m 120 °C) eutectic alloys as well as a number of multicomponent alloys based on tin, silver, copper, zinc, bismuth and indium proved to be the most demanded among the founded candidates [2, 3]. Sn–8.8wt%Zn eutectic alloy has a special place among them since it is cheaper and has good mechanical properties although it is inferior to Sn–57wt%Bi and Sn–51.7wt%In alloys in melting point. However, the practical use of this alloy as a solder in its pure form is hindered by tin and zinc oxidation during crystallization and existence in eutectic phase since intermetallic compounds are not formed in Sn–Zn binary system.

To overcome this problem the alloying metals such as copper, nickel, silver, antimony or bismuth are added to the solder. Nickel is considered to be most suitable alloying metal since stable binary intermetallic compounds are formed in Ni–Zn system. They improve the wettability with Sn–8.8wt%Zn alloy of nickel coatings which are widely used as a diffusion barrier in electronics [4]. Moreover, the addition of nickel can lead to the formation of ternary intermetallic compounds and, consequently, it can improve mechanical properties and corrosion resistance of the joint [5].

In this regard, some methods of Zn–Sn–Ni ternary alloy coatings deposition have been developed. These coatings are

characterized by higher corrosion resistance, excellent solderability and electrical conductivity in comparison with coatings based on Sn–Zn and Ni–Zn binary alloys [6, 7]. As for Zn–Sn–Ni powder alloy, there is no information on its preparation and properties in the literature.

Different researchers have mainly studied the phase equilibria in this ternary system at various temperatures [8–10] as well as the crystal structures of ternary intermetallic compounds formed during heating [11]. This information is important for understanding the processes occurring at the interface “solder Sn–8.8wt%Zn – nickel substrate” during the formation of soldered joint. The principal possibility of Zn–Sn–Ni alloy application as a high-temperature solder is only noted. It is supposed that on purpose to reduce the melting point it is necessary to obtain an alloy with high tin and low nickel content.

In industry powder solders are mainly obtained by dispersion of pure metallurgical bars or spraying of melts with gas or high pressure water steam. However, these methods are material- and energy-intensive. Therefore the actual task is to search and develop simpler, less expensive, materials saving and low-temperature methods of powder materials production which are not inferior to industrial analogues in quality. Cementation processes are one of such methods. They are widely used in hydrometallurgical recovery of metals from solutions and purification of technological solutions and industrial effluents from metal ions, especially heavy ones [12]. Cementation reactions are characterized by high process rates and implementation simplicity. However, cementation has not yet found wide industrial application as a method of powder materials obtaining. Firstly, it is difficult to control chemical composition and particle size of the resulting powder product because of high process rates. Secondly, the additional purification (washing) of powders obtained by cementation from solution components is required in contrast to metallurgical methods.

The rate of cementation depends on many factors, which include solution concentration, pH and temperature, organic substances additives such as surfactants, cementing metal nature, process duration, stirring speed. On the one hand, the diversity of these factors provides difficulties in control of powder products composition. But thanks to these factors the possibilities of powders composition variation are opened up. The cementation processes advantage is the possibility of low-temperature alloy formation which already proceeds during the reduction of metal ions from solutions [13].

The purpose of this work was to develop a method of Zn–Sn–Ni powder obtaining by cementation of Ni(II) and Sn(II) with zinc from solutions, to study its phase composition and phase transformations during heat treatment.

2. Experimental procedure

Sn–Ni–Zn ternary powder alloy was obtained by two-stage synthesis providing metals ratio control [14]. At the first stage Ni(II) ions were reduced with zinc powder from aqueous solution containing 0.42 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at $\text{Ni}^{2+} : \text{Zn}$ molar ratio equal to 1 : 1, pH 1.2, 50 °C and stirring. As a result, Ni–Zn powder formation of “zinc core – nickel shell” type occurred.

After thorough washing with distilled water the obtained powder was filtered and placed in aqueous solution (pH 1.2) containing 0.05 M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The second step of synthesis (tin deposition) from this solution was also carried out at 50 °C and stirring. The deposition of external tin layer on Ni–Zn core with the formation of Sn–Ni–Zn powder was initiated by zinc remained after the first stage of synthesis. We varied the duration of Ni(II) reduction with zinc (t_{Ni}) from 30 s to 20 min at fixed time of tin deposition on Ni–Zn core ($t_{\text{Sn}} = 10$ min). The duration of tin deposition on this core was also varied from 30 s to 20 min at the specified $t_{\text{Ni}} = 3$ min. The resulting Sn–Ni–Zn powders were thoroughly washed with distilled water, filtered and dried to constant weight. A low pH value of solutions was necessary to prevent hydrolysis of Ni(II) and especially Sn(II) compounds.

The elemental composition of the powders was determined by energy dispersive X-ray microanalysis (EDX) using attachment (Rontec) to the scanning electron microscope (LEO 1420, Germany). The probing depth was about 2 μm .

The powders obtained were pressed into tablets with diameter of 1 cm by cold pressing under the pressure of about 2721 $\text{t} \cdot \text{m}^{-2}$ for efficient proceeding of phase transformations during their heat treatment.

The phase composition of the samples was studied by X-ray phase analysis (XRD) using X-ray diffractometer (DRON-3.0, Russia). XRD patterns were recorded at the rate of one degree per minute using CoK_α radiation ($\lambda = 1.78897$ Å). The position of the analyzed lines maxima in XRD patterns was measured with an accuracy of ± 0.01 degrees. The lines were identified using JCPDS card files.

The behavior of the samples during heating was studied in the temperature range of 30–400 °C by differential scanning calorimetry (DSC) method with NETZSCH STA 449 F3 Jupiter (Germany). Heating was carried out in nitrogen atmosphere at the rate of 10 $\text{K} \cdot \text{min}^{-1}$.

To study phase transformations the tablets were heated for 3 h in a tube-type furnace in argon atmosphere at 260 °C. The temperature choice was based on the data in the work [15] where the formation of triple intermetallic phases at stated temperature was observed in the study of Sn–Zn–Ni alloys obtained from metallurgical metal powders.

3. Results and discussion

The effect of t_{Ni} time at fixed t_{Sn} value (10 min) on the elemental composition of Sn–Ni–Zn powders obtained is illustrated by EDX analysis data presented in Table 1.

Table 1. Metal content change (± 5 at. %) in Sn–Ni–Zn powders depending on t_{Ni} ($t_{\text{Sn}} = 10$ min) and t_{Sn} ($t_{\text{Ni}} = 3$ min)

Metal	t_{Ni} (min) at $t_{\text{Sn}} = 10$ min				t_{Sn} (min) at $t_{\text{Ni}} = 3$ min			
	0,5	5	10	20	0,5	5	10	20
Ni	38	67	62	86	50	43	44	47
Sn	38	23	30	7	34	40	41	34
Zn	24	10	8	7	16	17	15	19

It can be seen that an increase in t_{Ni} from 30 s to 20 min provides the growth of nickel content in the powders from 38 to 86 at. %, herewith zinc and tin percentages decrease from 24 to 7 at. % and from 38 to 7 at. % accordingly. The change in tin and nickel content in the powders with t_{Ni} increase is not monotonous. This fact can be caused by reasons related to the mechanism of cementation reaction. They are changes in the area and structure of

the reaction front, the decrease in the area of zinc microanodes and the rise of diffusion difficulties and ohmic losses in the pores of nickel shell which contain solution.

The variation of tin deposition duration at fixed time of nickel cementation (3 min) caused only slight change in content of this metal (within 34–41 at. %). This fact can indicate that the area of microanodes in Ni–Zn core is limited and rapidly decreases.

From the data in Table 1 it follows that in order to obtain Sn–Ni–Zn powders with high tin quota (30–40 at. %) it is necessary to carry out synthesis at minor t_{Ni} time (up to 10 min).

XRD analysis of freshly obtained samples with high tin content (for example, $\text{Sn}_{41}\text{Ni}_{44}\text{Zn}_{15}$ powders) shows the availability of β -Sn crystalline phase (intense peaks) together with NiZn_3 and NiSn intermetallic compounds (Fig. 1a). Note, that NiSn phase is absent on the equilibrium state diagram of Sn–Ni system [16].

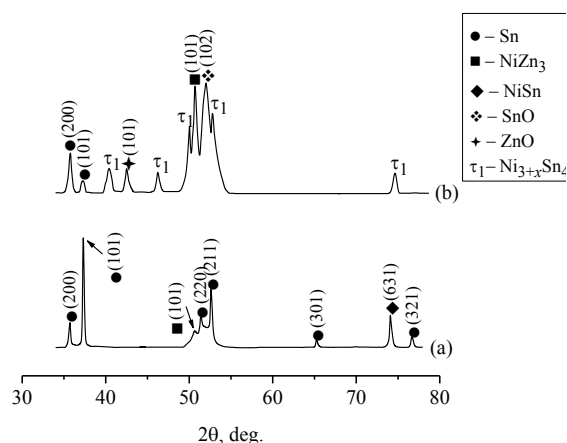


Fig. 1. XRD patterns of tablets made from $\text{Sn}_{41}\text{Ni}_{44}\text{Zn}_{15}$ powders: freshly obtained (a) and heated at 260 °C for 3 h (b).

The broadening of phase reflections in XRD patterns in the range of 2θ angles about 50–54 degrees can indicate their amorphous state. Note, that nickel is often deposited from solutions in amorphous or poorly crystallized state. The reflections of Zn phase are not clearly expressed in XRD patterns. That is due to shielding of zinc core with nickel and tin shells formed successively.

As mentioned above, Sn–Ni–Zn powders can be of interest in soldering processes, and therefore information on their thermal behavior at heating is needed. The results of thermal analysis of tablets pressed from $\text{Sn}_{41}\text{Ni}_{44}\text{Zn}_{15}$ powders before and after their heat treatment are shown in Fig. 2.

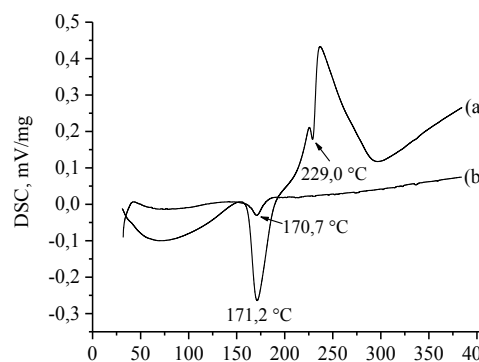


Fig. 2. DSC curves illustrating thermal behavior of tablets pressed from $\text{Sn}_{41}\text{Ni}_{44}\text{Zn}_{15}$ powders: freshly obtained (a) and heated at 260 °C for 3 h (b)

Two endothermic peaks are observed on DSC curve during heating of freshly obtained samples (Fig. 2a). One quite intense peak with a maximum at the temperature of about 171 °C can indicate the melting of Sn–Zn eutectic. The temperature of the end of this peak coincides with the reference data on the melting point

of Sn–Zn eutectic. The shift of the peak to lower temperatures as compared with the melting point of the eutectic can be caused by ultrafine state of the resulting powders [14]. One more endothermic peak is observed at the temperature of 229 °C. This peak can arise owing to melting of metallic tin, the presence of which was proved by XRD data. It is worth noting that in case of Sn–Ni–Zn powders with low tin content (up to 30 at. %) obtained at $t_{Ni} > 10$ min these peaks on DSC curves are of extremely low-intensity or completely absent.

There is a broad exothermic peak on the DSC curve of freshly obtained $Sn_{41}Ni_{44}Zn_{15}$ powders in the region of 230–300 °C (Fig. 2a). Its appearance can indicate the formation of intermetallic compounds during heating of samples above the melting point of tin. Indeed, XRD pattern reveals peaks of τ_1 ternary intermetallic phase (Fig. 1b) after heating of tablets at 260 °C for 3 h. $Ni_{3+x}Sn_4Zn$ composition is attributed to this phase [11]. Chen et al. [15] have also discovered τ_1 -phase during the heating at 250 °C of metallurgical powder mixtures with the composition close to the composition of the samples we studied. Since there is no XRD data in JCPDS on ternary intermetallic compounds in Sn–Ni–Zn system the values of interplanar spacing (d_{lit}) obtained by the authors of [9] were used as reference data to confirm the presence of τ_1 -phase in the heated samples. In turn, we calculated d_{calc} from the experimental values of $2\theta_{exp}$ angles corresponding to the assumed τ_1 -phase reflections using the Bragg's law and compared with d_{lit} . The calculation results are shown in Table 2.

Table 2. The values of interplanar spacing corresponding to τ_1 -phase calculated from XRD experimental data and published in [9]

$2\theta_{exp}$, deg	d_{calc} , Å	d_{lit} , Å [9]
40,403	2,59	2,59
46,237	2,28	2,28
50,036	2,11	2,11
52,790	2,01	2,01
74,640	1,47	1,46

As can be seen from Table 2 the complete coincidence of interplanar spacing values confirms our assumptions about the correspondence of some reflections in XRD pattern of the heated samples to τ_1 -phase. At the same time $2\theta_{exp}$ experimental values shown in Table 2 do not coincide with the data given in JCPDS for individual phases of nickel, tin, and zinc as well as binary intermetallic compounds and oxide phases based on them that eliminates the correlation of the detected reflections to these phases.

The study of thermal behavior of tablets heated at 260 °C showed that an endothermic peak of tin melting is absent on DSC curve of these samples (Fig. 2b) and the intensity of Sn–Zn eutectic melting peak is significantly reduced compared to the same peak on DSC curve of freshly obtained sample (Fig. 2a). These data indicate that during heating of tablets at 260 °C most quantity of Sn–Zn eutectic and metallic tin completely were melted and consumed in the process of ternary intermetallic compound (τ_1) formation. Melting processes are not observed during the repeated heat treatment of these samples. This is very important for resoldering processes since the formed soldered joint will not melt during subsequent technological operations in this case.

The low-temperature phase transformation at 260 °C discovered by us as well as some researchers [8, 15] is undoubtedly of interest in soldering technology taking into account the perspectivity of Sn–Ni–Zn powder alloy use as a high-temperature solder. Unlike published works our powders were synthesized from solutions by simple and low-cost method. Their ultrafine state provided a slight reduction of melting point in case of Sn–Zn eutectic.

4. Conclusions

The low-temperature method of Sn–Ni–Zn powders synthesis by successive cementation of Ni(II) and Sn(II) with zinc powder from acidic solutions and the formation of “zinc core – porous nickel shell – external tin layer” structures has been proposed. The method provides metals ratio control in wide ranges by variation of

the process duration. The possibility to obtain Sn–Ni–Zn powders containing 7–41 at. % of tin, 37–87 at. % of nickel and 7–24 at. % of zinc has been revealed. It has been shown that cementation process provides to obtain not only individual metals (nickel and tin) but also binary alloys of these metals with zinc. Sn–Ni–Zn powders with a high tin quota (30–40 at. %) contain β -Sn and Zn phases, $NiZn_3$ and $NiSn$ intermetallics as well as Sn–Zn eutectic with the melting point (171 °C) less than the reference value (198.5 °C). The formation of the ternary intermetallic τ_1 -phase ($Ni_{3+x}Sn_4Zn$) occurs as a result of the powders heating at 260 °C. The discovered low-temperature phase transformation in Sn–Ni–Zn system at 260 °C is of interest for electronic equipment assembly processes that include consecutive stages of soldering and resoldering. This transformation is necessary to preserve soldered joints during subsequent heat treatments.

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SIMULATION PHASE-STRUCTURE TRANSFORMATIONS IN ALLOY STEELS FOR THE PIERSED TOOLS

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Abstract: In this work are presented the development of simulation methods of analysis the phase-structural transformations and properties in alloy steels. The analytical dependencies of this simulation were applied to the calculation of ferritic, pearlitic and bainitic transformations in carbon and alloy steels. To calculate the amount of martensite, the authors used a new equation that has been successfully used in others works too. Based on the developed regression model, isothermal and structural diagrams for 20CrNi4V and 25Cr2Mo1V steels have been constructed. The analysis is performed of the aerial quenching of tools from alloy steels 20CrNi4V and 25Cr2Mo1V, according to the recommended heat treatment schedules in the tools production. For steels 20CrNi4V and 25Cr2Mo1V, it is possible to obtain a bainitic structure in a wide range of cooling rate. Corrections of heat treatment schedule were proposed.

KEYWORDS: HEAT TREATMENT, PHASE- STRUCTURAL TRANSFORMATION, PROPERTIES, SIMULATION METHODS, ALLOY STEEL, PIERSED TOOLS

1. Introduction / Введення

Improvement of heat treatment process is efficient, if a complete picture is known of the main features and characteristics of processed alloys. Important information is about the kinetics of supercooled austenite transformation, on which the basis issues are addressed of hardenability, heat treatment schedules and the mechanical properties (YTS, UTS, E% and HB).

Experimental study of microstructure components in the heat treatment of alloy steels consists of the building of time-temperature (TTT) and continuous cooling (CCT) transformation diagrams, as well as in the study of steels hardenability.

Modern researches are implemented in the special purpose software packages like JMatPro or ESI Group products for steels modelling. User is able to calculate phase changes for an assigned chemical composition of steel and different modes of treatment, e.g. continuous heating and tempering. That makes it possible to predict the details of the structure after heat treatment [1-3] including large-scale rolls [4-6]. User needs to integrate own routines for calculating diagrams of phase transformations, for example, when heat treatment is combined with cryogenic processing [7].

The aim of this work is development of simulation methods of analysis the phase-structural transformations in alloy steels for the pierced tools.

2. Analytical models phase-structure transformations

Analytical model of austenite transformation was applied for the steel structure modelling based on the results obtained in [7]. The M. Avrami equation was used of the phase transformation kinetics, written in the following form:

$$P_{\alpha} = 1 - \exp(-(V\tau)^n), \quad (1)$$

where P_{α} – result of the phase transformation (amount of formed ferrite, pearlite or bainite); V – relative rate of transformation; n – degree of equation; τ – time of transformation (below critical point Ac_3 for the ferrite, Ac_1 for the pearlite and Ac_0 – for bainite).

The relative rate of conversion is given by [8, 9]:

$$V = K \cdot \Delta T \exp(-Q/2RT), \quad (2)$$

where $\Delta T = T_c - T$, T – current temperature; T_c – temperature critical points of transformation; Q – the activation energy of carbon diffusion in the alloy steel; K – constant coefficient; R – universal gas constant, 1,987 [cal K⁻¹ mol⁻¹]. Parameter Q for ferrite and pearlite is equal to the activation energy of carbon diffusion in the austenite of steel, and for bainite, it is equal to the activation energy of carbon diffusion in steel ferrite. Temperature Ac_0 for roll steels is calculated from the condition that the maximum of the bainite growth rate coincides according to temperature, calculated from equation (2) and its experimental value on an isothermal diagram. This value is 600°C for steel 25Cr2Mo1V and 580°C for steel

20CrNi3V. The steel used for model verification is 25Cr2MoV with known diagrams of austenite transformation and the structure after treatment.

The improved model explicitly contains the rate of phase and structure transformation (ferrite, pearlite, bainite) that allows more clearly to interpret physical coefficients. To describe the process of martensite formation, the model includes both the start and end temperature of transformation.

3. A technique for simulation phase-structural transformations in alloy steels

Special alloy steels 20CrNi4V and 25Cr2Mo1V are used for the rolling and piercing tool. The chemical compositions of alloy steels are given in Table. 1.

Table 1. The chemical composition of alloy steels.

Steels	Chemical composition, %						
	C	Mn	Si	Cr	Ni	Mo	V
20CrNi4V	0.20	0.35	0.41	0.85	4.1	0.16	0.12
25Cr2Mo1V	0.29	0.37	0.45	2.75	0.25	1.1	0.37

The analytical equation of phase transformations was adopted to be applicable in the computer simulation. The algorithm for simulation phase transformations in alloy steels is as follows.

- 1) Calculation of critical points of phase transformations according to the regression model developed for certain range of chemical compositions of alloy steels.
- 2) Building of TTT for the calculated critical points.
- 3) Construction of a CCT by the proposed calculation method.
- 4) Calculation the cooling curves and the boundaries of phase transformations at surface of tools and their comparison with experimental data.
- 5) Calculation the number and fractions of microstructure components in the steel at the end of cooling.

The analytical TTT and CCT diagrams are currently determined for a given range of chemical composition of steels by the statistical processing of the highly alloyed steel grades. That is resulted in a possibility to take into account the complete list of alloying elements and enough wide range of their mass fraction. This is the advantage of the developed analytical models in contrast to the experimental methods of the TTT and CCT determination by the dilatometric measurements.

4. Simulation phase-structural transformations in alloy steels

Under isothermal conditions, an alloy steel 20CrNi4V and 25Cr2Mo1V undergoes three austenite transformations: ferritic, pearlitic and bainitic (Figure 1).

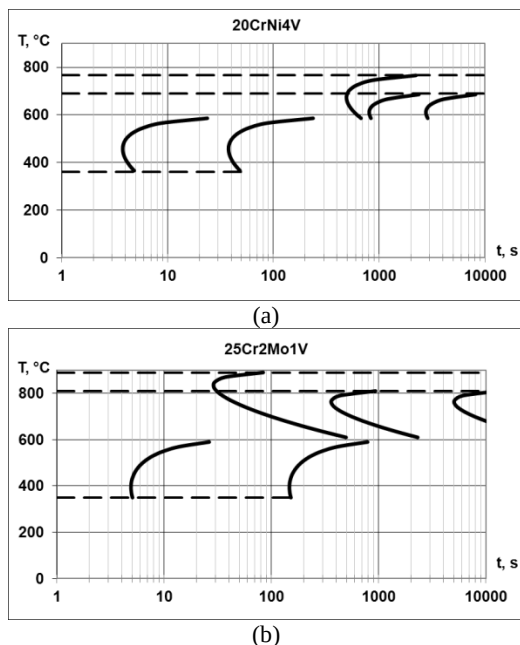


Figure 1. TTT diagrams of alloy steels: (a) 20CrNi4V ($A_{c3}=780^{\circ}\text{C}$, $A_{c1}=690^{\circ}\text{C}$, $M_s=350^{\circ}\text{C}$); (b) 25Cr2Mo1V ($A_{c3}=895^{\circ}\text{C}$, $A_{c1}=810^{\circ}\text{C}$, $M_s=350^{\circ}\text{C}$)

Differences in alloy elements of these steels determine the type of structures diagrams (Figure 2).

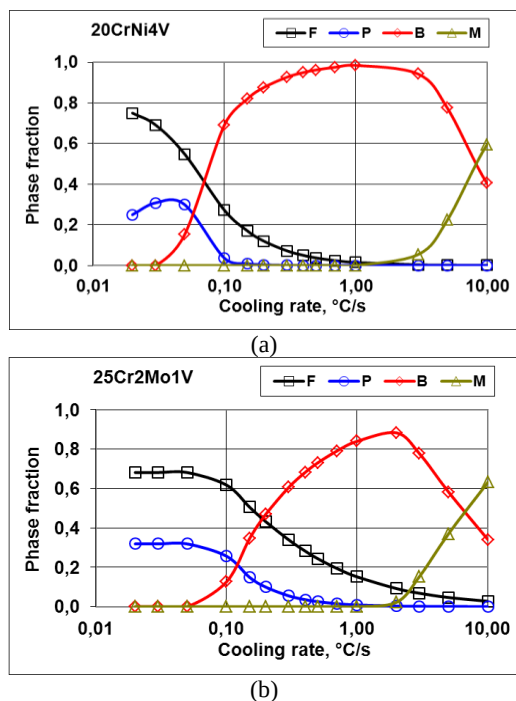


Figure 2. Structures diagrams of steels 20CrNi4V (a) and 25Cr2Mo1V (b) depending on the cooling rate (F – ferrite P – pearlite; B – bainite; M – martensite).

In steel 20CrNi4V (Figure 1a) there is temperature range of austenite stability between the areas of pearlite and bainite, which formation begins earlier than in 25Cr2Mo1V steel. The region of pearlite transformation is shifted to the right side, which indicates an increased stability of austenite due to alloying elements. In alloy steel 25Cr2Mo1V between pearlitic and bainitic areas (Figure 1b) exists of area increased stability of austenite in the temperature near 600°C .

The steel structure 20CrNi4V cooled at a rate 0.5°C/s (corresponds to tools surface cooling) has at 20°C ferrite (5%) and bainite (92%) and retained austenite (3%) (Figure 2a). Steel

25Cr2Mo1V cooled at a rate 0.5°C/s includes at room temperature ferrite (27%), pearlite (3%) and bainite (70%) (Figure 2b).

The calculated CCT of steel 20CrNi4V has an intersection of bainite and pearlite regions at the temperature at 450°C , where these microstructure components are formed simultaneously (Figure 3a).

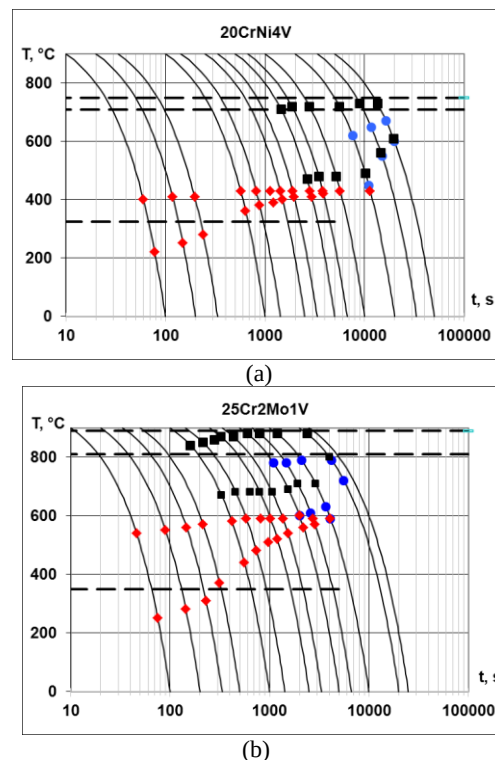


Figure 3. CCT diagrams of alloy steels 20CrNi4V (a) and 25Cr2Mo1V (b)

The areas of ferritic and pearlitic transformations for steel 20CrNi4V are shifted to the region of lower temperatures and cooling rates compared to steel 25Cr2Mo1V (Figure 3b).

Thus, for steels 20CrNi4V and 25Cr2Mo1V, it is possible to obtain a bainitic structure in a wide range of cooling rate.

CONCLUSIONS

In this work are presented the development of simulation methods of analysis the phase-structural transformations and properties in alloy steels for piercing tools. The analytical dependencies of this simulation were applied to the calculation of ferritic, pearlitic and bainitic transformations in carbon and alloy steels. To calculate the amount of martensite, the authors used a new equation that has been successfully used in others work too.

Based on the developed regression model, isothermal and structural diagrams for 20CrNi4V and 25Cr2Mo1V steels have been constructed; their correspondence to experimental data has been established. The analysis is performed of the aerial quenching of tools from alloy steels 20CrNi4V and 25Cr2Mo1V, according to the recommended heat treatment schedules in the tools production.

For steels 20CrNi4V and 25Cr2Mo1V, it is possible to obtain a bainitic structure in a wide range of cooling rate. Corrections of heat treatment schedule were proposed.

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