

Subbotina V., Belozеров V., Sobol' O.

Phase composition of coatings on the D16 alloy during micro-arc oxidation in alkaline and silicate electrolytes

Субботіна В. В., Білозеров В. В., Соболев О. В.

Фазовий склад покриттів на сплаві Д16 при мікродуговим оксидуванні в лужному і силікатном електролітах

Goal. The influence of electrolysis conditions at different electrolyte compositions on the phase formation of coatings obtained by micro-arc oxidation (MDO) on an aluminum alloy D16 was studied. **Method.** For electrolysis, two types of electrolytes were used: alkaline electrolyte (solution (KOH) in distilled water), silicate electrolyte (with different percentages of Na_2SiO_3 component). **Research results.** It was found that the phase composition of the MAO coatings obtained in an alkaline (KOH) electrolyte mainly consists of γ - Al_2O_3 phases and, to a much lesser extent, the α - Al_2O_3 phases. An increase in the KOH concentration leads to a shift in the γ - $\text{Al}_2\text{O}_3 \rightarrow \alpha$ - Al_2O_3 polymorphic reaction toward the formation of the hardest α - Al_2O_3 phase (corundum). The formation of the preferred orientation of the growth of crystallites of γ - Al_2O_3 and α - Al_2O_3 phases during their formation in an alkaline electrolyte was not detected. **Scientific novelty.** A significant influence on the mechanism and processes of coating formation is made by the addition of liquid glass (Na_2SiO_3) in the electrolyte. In this case, the growth rate of the coating increases significantly, but the size of the ordering regions decreases from crystalline to X-ray amorphous. The phase composition of the MAO coatings, when they are formed in a silicate electrolyte, varies from a mixture of the γ - Al_2O_3 phase and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) with a low content of liquid glass (10 g/l Na_2SiO_3) to the formation of only the X-ray amorphous phase with a high content of liquid glass in the electrolyte (50 g/l Na_2SiO_3).

Practical significance. It was concluded that the use of an alkaline or silicate electrolyte with different percentages allows a wide variation of both the phase composition and structural state (α - Al_2O_3 and γ - Al_2O_3 phases, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) or X-ray amorphous state) and the kinetics of growth the coating itself.

Key words: structural engineering, microarc oxidation, D16 aluminum alloy, alkaline electrolyte, silicate electrolyte, growth kinetics, phase composition

Мета. Досліджено вплив умов електролізу при різних складах електроліту на фазоутворення покриттів, отриманих мікродуговим оксидуванням (МДО) на алюмінієвому сплаві Д16. Для електролізу використовувалися електроліти двох типів: лужний електроліт (розчин (KOH) в дистильованій воді), силікатний електроліт (з різним процентним вмістом Na_2SiO_3 складової). Встановлено, що фазовий склад МДО-покриттів одержуваних в лужному (KOH) електроліті в основному складається з γ - Al_2O_3 фази і в значно меншій мірі α - Al_2O_3 фази. Збільшення концентрації KOH призводить до зрушення реакції γ - $\text{Al}_2\text{O}_3 \rightarrow \alpha$ - Al_2O_3 поліморфного перетворення в бік формування найбільш твердої α - Al_2O_3 фази (корунду). Утворення переважної орієнтації зростання кристалітів γ - Al_2O_3 і α - Al_2O_3 фаз при їх формуванні в лужному електроліті не виявлено.

Істотний вплив на механізм і процеси формування покриття вносить використання рідкого скла (Na_2SiO_3) в складі електроліту. При цьому значно збільшується швидкість росту покриття, проте зменшується розмір областей впорядкування від кристалічної до рентгеноаморфної. Фазовий склад МДО-покриттів, при їх формуванні в силікатном електроліті, змінюється від суміші γ - Al_2O_3 фази і муллиту ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) при малому вмісті рідкого скла (10 г/л Na_2SiO_3) до формування тільки рентгеноаморфної фази при великому вмісті рідкого скла в електроліті (50 г/л Na_2SiO_3).

Зроблено висновок, що використання лужного або силікатного електролітів з різним процентним вмістом дозволяє в широких межах змінювати як фазовий склад і структурний стан (α - Al_2O_3 і γ - Al_2O_3 фази, муллиту ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) або рентгеноаморфний стан), так і кінетику зростання самого покриття.

Ключові слова: структурна інженерія, мікродугове оксидування, алюмінієвий сплав Д16, лужний електроліт, силікатний електроліт, кінетика зростання, фазовий склад

1. Introduction

Plasma electrolytic oxidation treatment (often referred to as micro-arc oxidation, MAO) allows you to create durable, thick, uniform coatings with high adhesion to complex metal components. Moreover, during the MAO treatment, there is no significant increase in the temperature of the substrate [1, 2].

Unlike anodizing, oxidation during micro-arc oxidation does not occur through continuous ion transfer through the electrolyte (in a thin oxide layer), but through the union of metal and oxygen atoms or ions in the discharge plasma. This mechanism facilitates the preparation of thicker oxide layers and often leads to a harder and larger crystallite structure. The main

reason for this is that the discharges emit a large amount of heat, which contributes to crystallization in the surrounding oxide material [3, 4].

The process of structural surface engineering during micro-arc oxidation is to form a protective ceramic coating on the surface of valve metals (Al, Ti, Mg, Zr, Nb, etc.) and their alloys [5]. It should be noted that valve ones are metals on which oxide films (formed by the electrochemical method) possess unipolar or asymmetric conductivity in the metal – oxide – electrolyte (MOE) system [6]. In this case, the positive potential on the metal (on which the anodic oxide film is formed) corresponds to the blocking or reverse direction, i.e., the system works similarly to a semiconduc-

tor valve.

Thus, MAO simultaneously exhibit features of two different groups of modification methods: coating (i.e. modification with an increase in thickness) and changes in the state, structure, surface properties and surface layers (that is, without an increase in thickness) [7, 8].

The MAO treatment of aluminum alloys allows the formation of coatings with a large thickness (usually up to 400 μm), firmly bonded to the base, consisting of various polymorphic forms of aluminum oxide [9, 10], spinel and other complex oxides.

As a rule, the phase composition of the coatings varies along the thickness of the MAO layer [11]. During MAO treatment of aluminum-based alloys, it was found that high-temperature modifications of aluminum oxide are in its inner layers. Toward the outer surface of the modified layer, the number of low-temperature modifications of alumina increases. It is assumed that the latter is associated with electrolysis conditions at the initial stages of anodic-spark treatment, since the temperature of the metal sections adjacent to the discharge craters is only 400–500 °C [12].

Despite a fairly large number of articles in the field of micro-arc oxidation, however, an understanding of the fundamentals of the formation of MAO coatings on aluminum alloys remains far from certain [13-15].

The aim of this work was to study the effect of two types of electrolytes (alkaline and silicate) on the kinetics and type of phases formed in MAO coatings, as well as the effect of phase composition on properties.

2. Materials and methods for the preparation and study of coatings obtained by MAO processing

Samples in the form of cylinders with a diameter of 30 mm and a height of 10 mm were subjected to MAO treatment. Deformable aluminum alloys D16 (the composition of the main elements Al (90.9 - 94.7%), Cu (3.8-4.9%), Mg (1.2-1.8%), Mn, - in the range of 0.3-0.9%, Fe - not more than 0.5%; Si - not more than 0.5%; Zn - up to 0.25%; Ti - not more than 0.15%) were subjected to microplasma oxidation treatment.

Micro-arc oxidation was carried out in a 100 liter bath. During the MAO process, cooling and sparging of the electrolyte was ensured. The average voltage

value was 380 V. The initial current density was 20 A/dm², and the processing time varied.

As electrolytes were used:

1) Alkaline electrolyte - a solution of potassium hydroxide (KOH) in distilled water;

2) Silicate electrolyte (with different percentages of Na₂SiO₃);

Determination of the phase composition of the MAO coatings was carried out according to the results of X-ray phase analysis. The studies were carried out on the DRON-3 facility (Burevesnik, Russia) in monochromatized K_α – Cu radiation. Diffraction spectra were recorded according to the Bragg – Brentano scheme for reflection [16]. The shooting was carried out both in continuous and in point-by-point mode with a step of 2θ = 0.1 °. The maximum error in determining the content of structural crystalline components (with detectability of 10 vol.%) does not exceed ± 0.7%. The minimum detectability of structural components is about 1 vol. %

The results obtained in this work relate to the main coating layer (the technological layer was removed by polishing on abrasive paper).

For quantitative phase analysis, the method of reference mixtures was used [17].

The coating thickness was determined on a VT-10 NTs instrument (Kontrolpribor, Russia). The error in measuring the thickness of the coating is not more than 5% with the smallest coating thickness (about 10 microns). With a larger coating thickness, the accuracy of determining the thickness increases (for example, with a thickness of 50 μm, the measurement error is not more than 2%).

Microhardness was determined on a PMT-3 instrument (AO LOMO, Russia).

3. Results and discussion

3.1. Micro-arc oxidation in an alkaline electrolyte

Alkaline electrolyte is a solution of potassium hydroxide (KOH) in distilled water. The addition of KOH ensures the conductivity of the electrolyte. However, its high concentration determines the aggressiveness of the electrolyte, which is manifested in the etching of the surface of the processed material and the forming coating.

The research results are shown in table 1 and in figures 1 and 2.

Table 1
Characterization of MAO coatings on D16 alloy formed in an alkaline electrolyte

Electrolyte	Processing time, min	Thickness, μm	Phase composition, vol.%	
			α-Al ₂ O ₃	γ-Al ₂ O ₃
KOH-1 g/l	60	20	13	87
KOH-2 g/l	60	50	15	85
KOH-5 g/l	60	80	17	83

An analysis of the results shows that the coating has a crystalline structure, the main phase is γ-Al₂O₃, and the content of the hardest α-Al₂O₃ (corundum) phase does not exceed 15 vol.%. No predominant

orientation of crystallites of γ-Al₂O₃ and α-Al₂O₃ phases has been revealed. Figure 1 shows a typical X-ray diffraction spectrum of such a coating.

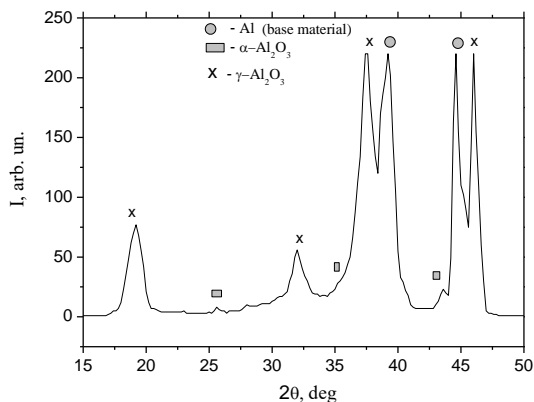


Fig. 1. XRD pattern of the coating on the D16 alloy (K_{α} - Cu radiation, electrolyte - 5 g/l KOH)

An increase in the KOH content in the electrolyte practically does not affect the phase composition, however, it leads to an increase in the coating thickness (Table 1).

The kinetics of the formation of the coating thickness and the volumetric phase content at different times of the MAO treatment are shown in Figure 2.

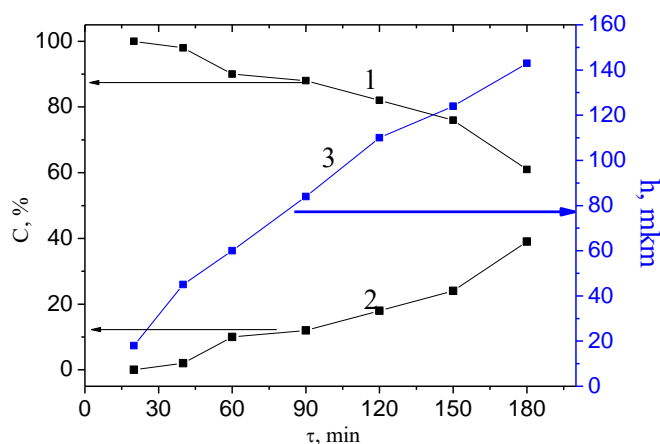


Fig. 2. The phase composition and thickness of the coatings obtained in an alkaline electrolyte with KOH-5g/l: 1 - γ - Al_2O_3 , 2 - α - Al_2O_3 , 3 - coating thickness h .

As can be seen from the obtained data, the process of coating formation begins with the formation of the γ - Al_2O_3 phase. An increase in the treatment time leads to the appearance of α - Al_2O_3 , apparently, as a result of the thermodynamically favorable polymorphic transformation γ - $Al_2O_3 \rightarrow \alpha$ - Al_2O_3 [10]. Such a process becomes possible due to an increase in the power of microdischarges with an increase in the coating thickness.

It was established (by visual observation) that when processing for more than 60 minutes (thickness 70-80 microns), the process goes into the arc discharge mode. In this case, pits are formed on the surface, which are recesses on the surface of the coatings.

A qualitative assessment of wear resistance (by grinding on an abrasive) showed that coatings formed in an electrolyte containing 5 g/l KOH possess the

best properties. Therefore, for the case of coating formation with a thickness of about 70-80 microns, this type of electrolyte can be recommended. Note that an increase in the KOH content of more than 5 g/l does not ensure the implementation of the process in the mode of micro-arc discharges.

3.1. Micro-arc oxidation in silicate electrolyte

Promising from the point of view of technology and the ecology of coating, is an aqueous solution of sodium or potassium liquid glass. Sodium liquid glass was used (GOST 13078-81), the concentration of which varied in the range of 10-50 g/l.

The results of studies of the formation of coatings in a silicate electrolyte are shown in table 2 and in figures 3 and 4.

Table 2
Characterization of MAO coatings on an D16 alloy formed in a silicate electrolyte

Electrolyte	τ , min	h, μm	Phases, %		
			γ	M	AF
10 g/l Na_2SiO_3	30	30	45	55	–
	60	70	45	55	–
	120	130	25	45	30
25 g/l Na_2SiO_3	30	75	8	14	78
	60	140	10	7	83
	120	270	10	5	85
50 g/l Na_2SiO_3	5	35	–	17	83
	15	70	–	10	90
	30	200	–	5	95

Note: τ is the processing time, h is the total thickness, γ is $\gamma\text{-Al}_2\text{O}_3$, M - $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mullite), AF is an X-ray amorphous phase

As can be seen from Figure 3, the typical form of the X-ray diffraction spectrum is characterized mainly by the formation of $\gamma\text{-Al}_2\text{O}_3$, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and an amorphous-like phase. An increase in the duration of the process for silicate electrolyte mainly leads to an increase in the content of the X-ray amorphous phase. Thus, in the silicate electrolyte there is a significant decrease in the size of the regions of formation and the transition from the crystalline structure of the coating to nanodispersed (X-ray amorphous). Whereas, an increase in the concentration of Na_2SiO_3 by more than 25 g/l leads to the formation of an almost X-ray amorphous coating (Table 2).

In this case, a layer-by-layer study of the phase composition by coating thickness ($h \approx 200 \mu\text{m}$, electrolyte 50 g/l Na_2SiO_3) showed its uniformity in thickness.

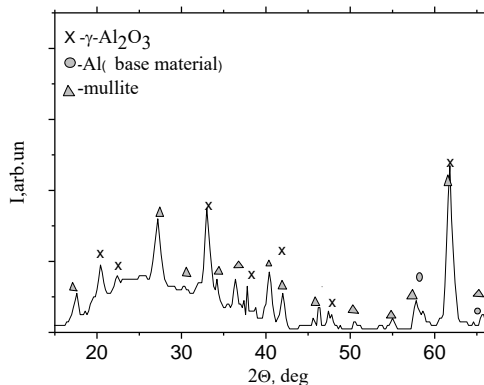


Fig. 3. X-ray pattern of the coating on the D16 alloy (K_α - Cu radiation, electrolyte - 10 g/l Na_2SiO_3)

An analysis of the results showed that the concentration of the electrolyte significantly affects not only the phase composition of the coating (Table 2, Fig. 3), but also the kinetics of its growth (determined by the thickness of the coating, Fig. 4).

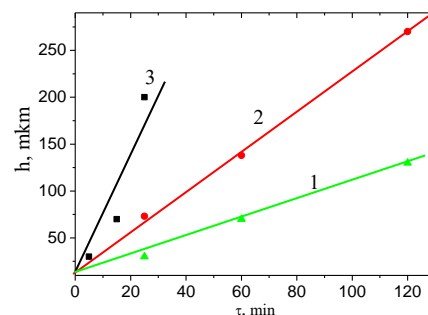


Fig. 4. Kinetics of coating thickness formation on D16 alloy in silicate electrolyte: 1 - 10 g/l Na_2SiO_3 , 2 - 25 g/l Na_2SiO_3 , 3 - 50 g/l Na_2SiO_3

It is seen (Figure 4) that, with a relatively small content of 10 g/l Na_2SiO_3 (dependence 1), in order to achieve a working thickness of 100 μm , it is necessary to carry out the MAO process for 120 minutes. In an electrolyte containing 25 g/l Na_2SiO_3 47 minutes of the MAO process are already sufficient to reach a thickness of 100 μm , and with the highest content of 50 g/l Na_2SiO_3 , only 15 minutes are enough to reach a thickness of the MAO coating of 100 μm .

3.3 Discussion of results

An analysis of the results indicates that the choice of the type of electrolyte and the conditions of the micro-arc oxidation process can significantly change the phase-structural state and surface properties. The use of alkaline electrolyte (KOH) can significantly increase the power of micro-arc discharges, which contributes to the formation of the hardest phase of $\alpha\text{-Al}_2\text{O}_3$ (corundum). This is a consequence of the completeness of the $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ polymorphic transformation during coating formation. Moreover, with an increase in the concentration of KOH, the content of the $\alpha\text{-Al}_2\text{O}_3$ phase increases. Thus, in the absence of silicate in the electrolyte, an electrolytic mechanism of coating formation is realized [10]. However, there is a limit on the percentage of KOH content associated with the conditions for the formation of micro-arc discharges. As we have established, an increase in the KOH content of more than 5 g/l does not ensure the

implementation of the process in the micro-arc discharge mode.

The main disadvantage of the MAO process in alkaline electrolyte is the low rate of coating formation.

In silicate (liquid glass Na_2SiO_3), the growth rate of the coating increases significantly. However, in this case, an increase in the growth rate is accompanied by an increase in the nucleation centers. This leads to a significant relative decrease in the average size of the ordering regions (to the transition to the X-ray-amorphous state in which the size of the regions of ordering is less than 2 nm). The formation of such a phase, as we established [10], leads to a significant decrease in hardness.

Thus, depending on the task, it is possible to vary widely the phase-structural state of the MAO coatings by using different concentrations of alkaline or silicate electrolyte.

CONCLUSIONS

1. It was established that the phase composition of the MAO coatings obtained in an alkaline (KOH) electrolyte mainly consists of the γ - Al_2O_3 phase and, to a much lesser extent, the α - Al_2O_3 phase. An increase in the KOH concentration leads to a shift in the γ - Al_2O_3 → α - Al_2O_3 polymorphic reaction toward the formation of the hardest α - Al_2O_3 phase (corundum).

Thus, in the absence of silicate in the electrolyte, an electrolytic coating formation mechanism is realized.

2. A significant effect on the mechanism and processes of coating formation is made by the addition of liquid glass (Na_2SiO_3) in the electrolyte. In this case, the growth rate of the coating increases significantly, but the size of the ordering regions decreases from crystalline to X-ray amorphous.

3. With an increase in liquid glass content from 10 g/l Na_2SiO_3 to 50 g/l Na_2SiO_3 , the time required to reach a coating thickness of 100 μm decreases from 120 min (10 g/l Na_2SiO_3) to 15 minutes (50 g/l Na_2SiO_3).

4. The phase composition of the MAO coatings, when they are formed in a silicate electrolyte, varies from a mixture of the γ - Al_2O_3 phase and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) with a low content of liquid glass (10 g/l Na_2SiO_3) to the formation of only an X-ray amorphous phase with a high content of liquid glass in the electrolyte (50 g/l Na_2SiO_3).

5. The use of an alkaline or silicate electrolyte with different percentages makes it possible to vary widely both the phase composition (α - Al_2O_3 and γ - Al_2O_3 phases, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) or X-ray amorphous state), as well as the growth kinetics of the coating itself.

REFERENCES

1. Gu W.C., Shen D.J., Wang Y.L., et al. Deposition of duplex Al_2O_3 /aluminum coatings on steel using a combined technique of arc spraying and plasma electrolytic oxidation. *Appl Surf Sci.* 2006;252:2927–2932.
2. Tseng C.C., Lee J.L., Kuo T.H., et al. The influence of sodium tungstate concentration and anodizing conditions on microarc oxidation (MAO) coatings for aluminum alloy. *Surf Coat Technol.* 2012;206:3437–3443.
3. Martin J., Leone P., Nomine A., et al. Influence of electrolyte ageing on the plasma electrolytic oxidation of aluminium. *Surf Coat Technol.* 2015;269:36–46.
4. Jovović J., Stojadinović S., Šišović N.M., et al. Spectroscopic characterization of plasma during electrolytic oxidation (PEO) of aluminium. *Surf Coat Technol.* 2011;206:24–28
5. Yerokhin, A.L., Nie, X., Leyland, A., Matthews, A., Dowey, S.J. (1999) Plasma electrolysis for surface engineering. *Surf. Coat. Technol.*, 122, 73–93
6. Asadi S., Kazeminezhad M. (2017) Multi Directional Forging of 2024 Al Alloy After Different Heat Treatments: Microstructural and Mechanical Behavior. *Transactions of the Indian Institute of Metals*, 70, 7, 1707-1719
7. Dunleavy C.S., Curran J.A., Clyne T.W. Self-similar scaling of discharge events through PEO coatings on aluminium. *Surf Coat Technol.* 2011;206:1051–1061.
8. Matykina E., Arrabal R., Pardo A., et al. Energy-efficient PEO process of aluminium alloys. *Mater Lett.* 2014;127:13–16.
9. Belozarov V., Sobol O., Mahatlova A., Subbotina V., Tabaza T.A., Al-Qawabeha U.F., Al-Qawabah S.M. (2018) Effect of electrolysis regimes on the structure and properties of coatings on aluminum alloys formed by anode-cathode micro arc oxidation *Eastern-European Journal of Enterprise Technologies*, **1(12-91)**, 43-47,
10. Subbotina V., Al-Qawabeha U.F., Belozarov V., O.V. Sobol', Subbotin A., Tabaza T.A., Al-Qawabah S.M (2019) Determination of influence of electrolyte composition and impurities on the content of α - Al_2O_3 phase in mao-coatings on aluminum, *Eastern-European Journal of Enterprise Technologies*, **6(12-102)**, 6-13
11. Belozarov V., Mahatlova A., Sobol' O., Subbotina V., Subbotin A. (2017) Investigation of the influence of technological conditions of microarc oxidation of magnesium alloys on their structural state and mechanical properties. *Eastern-European Journal of Enterprise Technologies*, 2, 5(86), 39-43
12. Lv P.X., Chi G.X., Wei D.B., Di S.C. (2011) Design of scanning micro-arc oxidation forming ceramic coatings on 2024 aluminium alloy. *Advanced Materials Research*, 189-193, 1296-1300
13. Curran J.A., Clyne T.W. Thermo-physical properties of plasma electrolytic oxide coatings on aluminium. *Surf Coat Technol.* 2005;199:168–176.
14. Javidi M., Fadaee H. Plasma electrolytic oxidation of 2024-T3 aluminum alloy and investigation on microstructure and wear behavior. *Appl Surf Sci.* 2013;286:212–219.
15. Matykina E., Arrabal R., Mohedano M., et al. Recent advances in energy efficient PEO processing of aluminium alloys. *Trans Nonferrous Metals Soc China.* 2017;27:1439–1454.
16. O.V. Sobol', O.A. Shovkoplyas (2013) On advantages of X-ray schemes with orthogonal diffraction vectors for studying the structural state of ion-plasma coatings, *Technical Physics Letters*, **39(6)**, 536–539
17. Klopotov A.A., Abzaev Yu.A., Potekaev A.I., Volokitin O.G. (2012) Osnovi rentgenostrukturnogo analiza v materialovedenii. Tomsk: Izd-vo Tom. gos. arhit.-stroit. Un-ta, 276 p.