# Analysis of the phase composition and microstructure of a TNM-type alloy by using thermodynamic calculation

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Using both thermodynamic calculations and experimental analyses, the phase composition and microstructure of the new TNM-type alloy with the following actual compositions, % (at.): TNM - 40.05 Al, 4.51 Nb and 1.05 Mo have been analysed. According to thermodynamic calculation, equilibrium solidification of the new alloy proceeded via the  $\beta$ -phase, i. e.  $L \rightarrow L + \beta \rightarrow \beta$ , followed by the solid-state transformations, the main of which is the eutectoid reaction  $\alpha \rightarrow \alpha_2 + \beta + \gamma$ . The microstructure of the alloy in the as-cast state and after high-temperature vacuum annealing was examined by means of scanning electron microscopy and electron microprobe analysis. Experimental studies have shown that the main structural component is the lamellar  $\gamma/\alpha_2$ -colonies (with a thickness of individual plates of about 300 nm) surrounded by the  $\beta$ - and  $\gamma$ -phase crystals, the total fraction of which does not exceed 30% (vol.). According to the electron microprobe analysis,  $\beta$ -phase contains the largest amount of molybdenum, while the concentration of aluminium is the smallest. In contrast, the  $\gamma/\alpha_2$ -colonies (initial  $\alpha$ -phase) and  $\gamma$ -phase have higher aluminium and minimum molybdenum content. The observed results are in a good agreement with the results of the thermodynamic calculation. Experimental quantitative analysis of the phase fraction after vacuum annealing at 1250 °C of the new alloy has revealed that the total amount of  $\beta$ -phase does not exceed 8% (vol.), what practically corresponds to the base TNM (Ti43.5Al4Nb1Mo) alloy after similar heat treatment. However, the base alloy also contains up to 14% of the  $\gamma$ -phase, which is not observed in the new alloy. After annealing at 1100 °C, new alloy contains up to 24% (vol.)  $\beta$ -phase and 4% (vol.)  $\gamma$ -phase, while the base TNM alloy contains up to 14% (vol.)  $\beta$ -phase and 21% (vol.)  $\gamma$ -phase. In general, we can conclude that a reduction of aluminum content from 43.5 to 40.0% (at.) leads to a considerable increase in the amount of  $\beta$ -phase and decrease the γ-phase content. It is necessary to note, the calculated quantitative data of the phase fraction depending on the alloy annealing temperature are far from experimentally obtained data. However, a qualitative analysis of the change the phase relationship depending on the annealing temperature or chemical composition of the alloy, as well as the chemical composition of the phases is available.

*Key words:* titanium aluminides,  $\gamma$ -alloys, thermodynamic calculations, solidification, microstructure, phase composition, annealing.

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### Introduction

Titanium aluminide (TiAl) based alloys (hereafter referred to as  $\gamma$ -alloys) are considered as promising for manufacturing the blades of next generation gas turbine engines instead of nickel super-alloys [1–4]. These alloys should possess advanced technological properties [5–10] combined with appropriate strength, ductility, fatigue resistance and, most importantly, high temperature strength [4, 11, 12]. In order to achieve the required technological and mechanical properties (at room and elevated temperatures), the so-called 3rd generation  $\gamma$ -alloys such as the TNM alloy (with a nominal composition of Ti43.5Al4Nb1Mo0.1B (in % (at.))) [13–15] have been developed. This class of alloys has compositions that stabilize the  $\beta$ -phase so that this is the first phase to

precipitate on solidification and is the only phase present immediately after solidification is complete (so called  $\beta$ -solidifying alloys) [16]. The fine as-cast microstructure, oxidation resistance and hot workability of these types of alloys have led to significant interest [17–19].

The phase composition of the  $\gamma$ -alloys is characterized by a high sensitivity to small changes in the concentration of alloying elements and heat treatment parameters [20–23]. Since the phase composition determines the structure of the alloys and, ultimately, their properties, its control is required for providing the specified operating characteristics. To analyse the phase composition of the TNM alloys we need to consider a phase diagram of at least four-components: Ti, Al, Nb and Mo. This had been partially studied in [1, 22, 24]. Phase diagrams of more complicated systems (with five or more components) have not been considered

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in the literature at all. The traditional way to assess phase equilibrium for complex alloys, determined by annealing heat treatments followed by metallographic examination of the microstructure, can be onerous and expensive (this is especially true of alloy melting). On the other hand the combination of thermodynamic calculations [25, 26] with some experimental data is usually the preferred approach to determining the phase equilibria in complicated systems.

This paper primarily focused on the thermodynamic calculations and experimental verification of phase equilibria (transformation temperatures) during solidification and subsequent heat treatments of the new Ti - 40Al - 4Nb - 1Mo TNM-type  $\gamma$ -alloy with reduced aluminum content. For a comparative evaluation, the calculated and experimental results were compared with the standard TNM alloy (Ti43.5Al4Nb1Mo) [27], the results for which were obtained in [28].

Thermodynamic calculations were performed using a commercially available database [12, 13].

### **Experimental methods**

The alloy was prepared using a vacuum induction furnace with a cold crucible. The ingots were melted twice to ensure composition homogenization. The diameter and the length of the ingot were 12–20 mm and 100–150 mm, respectively. The nominal chemical composition of the alloys and results of the chemical analyses by spectral analysis (ARL 4460 OES) are summarized in Table 1. The total fraction of interstitial impurities (O, N, C, H) was smaller than 1000 wt.-ppm.

The specimens were heated in a VE316 vacuum resistance furnace with a graphite heater at 1100 and 1250 °C for 3 h. After annealing, the samples were cooled within the furnace.

The microstructure was examined by means of transmission electron microscopy (TEM, JEM-2100), scanning electron microscopy (SEM, TESCAN VEGA 3) and by electron microprobe analysis (EMPA, OXFORD AZtec). Polished samples were used for the studies. Mechanical polishing was used, as well as electrolytic polishing, which was carried out at a voltage of 12 V in an electrolyte containing six parts  $C_2H_5OH$ , one part HClO<sub>4</sub> and one part glycerin. The initial analysis of the microstructure of the samples was carried out using OM and detailed metallographic studies were performed using SEM. The thin foils for TEM were prepared by ion thinning with a PIPS (Precision Ion Polishing System, Gatan) machine and studied at 160 kV.

For the experimental determination of the volume fraction of the alloy structural components, a metallographic approach was implemented using high contrast microstructural images processed with appropriate software (Adobe Photoshop CS6 and ImageJ). First, using the Adobe Photoshop CS6 software, one can transform the initial image into an image of uniform elevated conTable 1

Nominal (Top Row) and Actual (Bottom Row) Chemical Composition of the Alloys

A.U	AI	Nb	Мо	AI	Nb	Мо	
AllOy	% (at.)			% (wt.)			
TNM	40	4	1	25.81	8.89	2.48	
	40.05	4.51	1.05	25.57	9.61	2.33	

trast, since insufficient contrast of the analysed figures can cause a high measurement error. Further, this image was processed with the ImageJ software. To obtain reliable data, we analysed at least 10 fields of the microstructure to define the content of each structural component.

The quantitative analysis of the phase composition (applied to the actual composition of the alloy) was also determined using thermodynamic calculations in the Thermo-Calc program (version TCW5, database TTTIAL).

### **Results and their discussion**

**Thermodynamic calculation.** According to thermodynamic calculations, equilibrium solidification of the new alloy proceeded via the  $\beta$ -phase, i. e.  $L \rightarrow L + \beta \rightarrow \beta$  (Fig. 1, *a*), followed by a multitude of solid-state transformations and reactions. Cooling in the  $\beta$ -range should be accompanied by a polymorphic  $\beta \rightarrow \alpha$  transformation and then by segregation of secondary  $\gamma$ -crystals. This should then be followed by the eutectoid reaction which proceeds via the four-phase reaction  $\alpha \rightarrow \alpha_2 + \beta + \gamma$ .

However, actual solidification of most alloys usually occurs with substantial deviations from equilibrium. As a result, the estimation of the phase composition of alloys in real-life casting conditions requires special approaches. One of the most popular approaches is the Sheil-Gulliver model, implemented in the Thermo-Calc software. Using the Sheil model it is possible to calculate the temperatures of liquids and non-equilibrium solids in conditions close to the real, non-equilibrium solidification. Fig. 1, b presents the curves of non-equilibrium solidification computed by this model for the alloy in the form of a dependence of the total mass fraction of the solid phases on the temperature.

In accordance with Fig. 1, *b*, the non-equilibrium solidification proceeded via the peritectic reaction:  $L + \beta \rightarrow \alpha$ , which lead to the appearance of the non-equilibrium  $\alpha$ -phase. The corresponding displacement of the phase regions is shown schematically in Fig. 1, *a*. In accordance with it, in addition to  $\beta$ -phase, the as-cast structure of the alloy should contain  $\alpha$ -phase crystals. In contrast to the equilibrium conditions, the non-equilibrium solidification of the alloy ends at a lower temperature, which corresponds to non-equilibrium solidification range of the new alloy exceeds 320 °C, while for the base TNM alloy only 220 °C [26]. Reducing the solidus temperature

during non-equilibrium solidification should be taken into account for choosing the mode for high temperature processes of as-cast ingots.

Cross sections provide a qualitative assessment of the influence of the alloying elements and heating temperatures on the phase composition of alloys. To obtain quantitative estimates the calculations of the alloy phase composition and chemical composition were performed for three temperatures: 1400, 1250 and 1100 °C. These data show the temperature effects on the mass fractions of the phases ( $Q_m$ ) and their chemical composition. The results of the calculations are given in Table 3.



Fig. 1. The politermal cross section of the quaternary Ti - AI - Nb - Mosystem calculated at element contents (% (at.)): 4.51 Nb and 1.05 Mo (% (at.)) and variable aluminum concentration. The vertical line indicates the average composition of the alloy. The dashed lines schematically describes the displacement of the phase regions during non-equilibrium solidification of the alloy (*a*). Dependence of solid phase fracture on temperature in the range of the non-equilibrium solidification of the TNM-alloy. The numbers indicate the sequence of the phase transformations (*b*):  $I - L; 2 - L \rightarrow \beta; 3 - L + \beta \rightarrow \alpha; 4 - L \rightarrow \alpha$ 

The TNM-allov equilibrium phase composition at 1400 °C should consist of single  $\beta$ -phase (Table 3). The equilibrium phase composition of the base TNM alloy at the same temperature consists of ~64% (wt.)  $\beta$ -phase and ~36% (wt.) of  $\alpha$ -phase [26]. When the temperature is decreased from 1400 to 1250 °C, the phase composition of new alloy consists of two  $\alpha + \beta$  phases. The fraction of  $\beta$ -phase is significantly reduced (up to 26% (wt.)), while  $\alpha$  becomes the main phase. Moreover, the difference between the chemical compositions of the phases is essential. In particular, the molvbdenum content in  $\beta$ -phase is about three times larger than in  $\alpha$ -phase. The base alloy at the same temperature also consists of two  $(\alpha + \beta)$  phases. However, the  $\beta$ -phase fraction is lower and reaches about 12% (wt.). The distribution of elements in the phases is generally similar. At 1100 °C, the phase composition of new alloy changes slightly in comparison to the 1250 °C. The amount of  $\alpha$ -phase is additionally increased up to 83%. At the same time, a small amount of  $\gamma$ -phase appears. The base alloy at 1100 °C should consist of about 40%  $\gamma$ - and  $\alpha$ -phases and the remai-

Table 2

The calculated equilibrium and non-equilibrium temperatures of the phase transformations and experimental data of the eutectoid transformation temperature of the TNM and TNM + CZ alloys

Phase transformation	Temperatures of the phase transformations of the TNM-alloy, °C
Liquidus. $L \rightarrow \beta + L(T_L)$	1650
$\beta \rightarrow \alpha (T_{\alpha})$	1375
$\beta + \alpha \rightarrow \beta + \alpha + \gamma (T\gamma)$	1120
$\alpha \rightarrow \alpha_2 + \gamma (T_{eu})$	1073
Equilibrium solidus. $L + \beta \rightarrow \beta (T_S)$	1560
Non-equilibrium solidus ( <i>T<sub>NS</sub></i> )	1330
The equilibrium solidification temperature range ( $\Delta T$ )	90
The non-equilibrium solidification temperature range ( $\Delta T_{NS}$ )	320

Table 3

# Quantitative parameters of the phase compositions of the TNM alloy at the annealing temperatures

T, ⁰C	Phase	<i>Q</i> <sub>m</sub> ,	Content of elements, % (at.) (% (wt.))				
		% (wt.)	Ti	AI	Nb	Мо	
1400	β	100	54.82 (62.49)	39.82 (25.57)	4.34 (9.61)	1.02 (2.33)	
1250	α	74	55.0 (64)	40.5 (26)	3.8 (8.5)	0.64 (1.5)	
1250	β	26	53.5 (59)	38.5 (24)	5.9 (12.6)	2.1 (4.7)	
	α	83	55.5 (64)	40.0 (26)	4.0 (8.7)	0.7 (1.7)	
1100	β	13.5	51.4 (55.4)	38.6 (23.4)	7.0 (14.7)	3.0 (6.0)	
	γ	3.5	47.3 (56)	47.7 (32)	4.4 (10.1)	0.5 (1.2)	

ning ~20% is  $\beta$ -phase. For the both alloys, the  $\gamma$ -phase contains the largest proportion of aluminum. Niobium is quite uniformly distributed between the phases (the partition coefficients of niobium is do not exceed 1.5) while molybdenum is preferentially in the  $\beta$ -phase. From the obtained data, we can concluded that a reduction in aluminum content from 43.5 to 40.0% (at.) leads to a considerable increase in the amount of  $\beta$ -phase and decrease in the  $\gamma$ -phase content. While the distribution of elements in the phases remains almost unchanged.

### Microstructure and phase analysis

The results of an experimental study of the alloy structure in as-cast state in a good agreement with the results of thermodynamic prediction by the Sheil model (Fig. 1, *b*). In particular, the microstructure of the alloy in the as-cast state (Fig. 2) has a mixed nature and consists of lamellar  $\gamma/\alpha_2$ -colonies (initial  $\alpha$ -phase at elevated temperature) and  $\beta$ -phase crystals. The  $\beta$ -phase is bright in appearance and easily identified. In accordance with the results of energy dispersive microanalyses (Fig. 3),  $\beta$ -phase contains the largest amount of molybdenum and least of aluminium. Niobium is distributed relatively evenly, with a slight excess in the  $\beta$ -phase. It should be noted that the obtained experimental data for the distribution of elements between the phases in a good agreement with the results of thermodynamic calculations (Table 3).

The as-cast microstructure is fine grained due to the high cooling rate in the solidification range of the alloy and the  $\gamma/\alpha_2$ -lamella cannot be resolved at the magnification used. In accordance with the metallographic analysis, the total fraction of  $\beta$ -phase is about 40% (vol.), what is more than three times than in the base TNM alloy (12% (vol.)) [26].

The microstructure of the alloy after annealing at 1250 °C is shown in Fig. 4. As can be seen, the structure of the alloy contains  $\beta$ -grains situated at the lamellar  $\gamma/\alpha_2$ -colonies boundaries. Lamellar colonies become the main structural component and retain a fine structure (Fig. 4, *b*),

with a thickness of individual plates of about 300 nm (Fig. 5). Annealing leads to a significant decrease in the  $\beta$ -phase fraction, the total amount of which does not exceed 8% (vol.), what practically corresponds to the base alloy after similar heat treatment. However, the base alloy also contains up to 14% of the  $\gamma$ -phase, which is not observed in the new alloy.

The experimentally determined chemical composition of the  $\gamma/\alpha_2$ -colonies (initially  $\alpha$ -phase) and  $\beta$ -phase (Fig. 6) are close to the calculated compositions of the phases (Tables 3). According to the experimental data,



Fig. 2. SEM image of the TNM-alloy microstructure in the as-cast state



Spectrum	Chemi	ical comp	osition, 9	Sum	Phase	
	AI	Ti	Nb	Мо	Sum	Identification
1	27.75	62.67	7.96	1.62	100.00	α <sub>2</sub> /γ
2	24.07	63.05	10.21	2.67	100.00	β
3	27.96	62.86	7.83	1.34	100.00	α <sub>2</sub> /γ
4	23.60	62.64	10.69	3.07	100.00	β
5	24.14	63.89	9.78	2.18	100.00	β
6	24.13	62.95	10.07	2.86	100.00	β
7	27.05	63.45	8.16	1.35	100.00	$\alpha_2/\gamma$

**Fig. 3.** Results of electron microprobe analysis of the TNM-alloy in as-cast state



Fig. 4. SEM image of the TNM-alloy microstructure after annealing at 1250 °C



Fig. 5. Microstructure of the lamellar  $\gamma/\alpha_2$ -colonies after annealing at 1250 °C of the TNM-alloy. TEM (dark field)



Spectrum	Chem	ical compo	Sum	Phase		
	AI	Ti	Nb	Мо	Sum	Identification
1	28.90	64.86	4.97	1.27	100.00	β
2	38.16	56.35	4.33	1.16	100.00	β
3	40.06	55.24	3.64	1.06	100.00	β
4	40.40	54.63	4.15	0.82	100.00	α <sub>2</sub> /γ
5	40.87	54.16	3.96	1.02	100.00	α <sub>2</sub> /γ
6	40.66	54.29	4.15	0.90	100.00	α <sub>2</sub> /γ
7	40.47	54.70	3.93	0.90	100.00	α <sub>2</sub> /γ

Fig. 6. Results of electron microprobe analysis of the alloy after vacuum annealing at 1250  $^{\rm o}{\rm C}$ 

![](_page_4_Picture_6.jpeg)

Fig. 7. SEM image of the TNM-alloy microstructure after annealing at 1100 °C

the  $\beta$ -phase contains the largest amount of molybdenum, while the concentration of aluminium is the smallest. The opposite situation is observed for the  $\gamma/\alpha_2$ -colonies. They have higher aluminium and minimum molybdenum content. The observed results are qualitatively in a good agreement with the results of the calculation.

The microstructure of the alloy after annealing at 1100 °C, as shown in (Fig. 7), is an assembly of lamellar  $\gamma/\alpha_2$ -colonies and a mixture of  $\gamma$ - and  $\beta$ -grains. The experimentally determined chemical composition of the  $\gamma/\alpha_2$ -colonies,  $\beta$ -phase and  $\gamma$ -phase are also close to  $\alpha$ -,  $\beta$ - and  $\gamma$ -phase calculated composition at this annealing temperature (Tables 3). After this heat treatment, except lamellar colonies the alloy contains up to 24% (vol.)  $\beta$ -phase and 4% (vol.)  $\gamma$ -phase. After a similar heat treatment, the base TNM alloy contains up to 14% (vol.)  $\beta$ -phase and 21% (vol.)  $\gamma$ -phase.

From the obtained qualitative and quantitative data on the phase composition of the new alloy after various heat treatments, we can conclude that, in comparison with the base TNM alloy, a decrease in the aluminum concentration by 3% (at.) leads to a certain increase the amount of  $\beta$ -phase and reduction of  $\gamma$ -phase amount. The effect of changing in the phase relationship of the new alloy on its mechanical properties requires careful experimental analysis. At this stage, based on general considerations, we can only assume some of the changes. On the one hand, an increase the amount of  $\beta$ -phase should lead to a decrease the ductility of the alloy, but an increase its heat resistance. The same effects can be obtained by reducing the amount of  $\gamma$ -phase. However, some increase the amount of  $\beta$ -phase at a temperature of 1250 °C, which is used for high-temperature annealing of TNM-type gamma alloys, can leads to more effective inhibition of the growth of  $\alpha$ -phase crystals. It is one of the necessary conditions for obtaining a fine structure of the lamellar colonies, which largely determines the ductility of the  $\gamma$ -alloys at low temperatures.

It is also necessary to note, in general, the calculated quantitative data of the phase fraction depending on the alloy annealing temperature are far from experimentally obtained

data. However, a qualitative analysis of the change the phase relationship depending on the annealing temperature or chemical composition of the alloy, as well as the chemical composition of the phases is available. For instance, as it was shown by calculation and confirmed experimental results, a reduction aluminum content by 3% (at.) increases the amount of  $\beta$ -phase and decreases the  $\gamma$ -phase content.

## Conclusions

1. By using the thermodynamic calculation in the Thermo-Calc program, an analysis of the phase transformations during equilibrium and non-equilibrium solidification of the TNM-type alloy with reduced aluminum content has been conducted. To obtain quantitative estimates, the calculations of the alloy phase composition and chemical composition were performed for three temperatures: 1400, 1250 and 1100  $^{\circ}$ C.

2. According to the thermodynamic calculations, equilibrium solidification of the new alloy with the following actual compositions, % (at.): TNM – 40.05 Al, 4.51 Nb and 1.05 Mo proceeded via the  $\beta$ -phase, i. e.  $L \rightarrow \Delta L + \beta \rightarrow \beta$ , followed by the solid-state transformations – polymorphic  $\beta \rightarrow \alpha$  transformation, then followed by segregation of secondary  $\gamma$ -crystals and then the eutectoid reaction via the four-phase reaction  $\alpha \rightarrow \alpha_2 + \beta + \gamma$  occurred.

3. Experimental studies have shown that the microstructure of the new alloy in the as-cast state consists of lamellar  $\gamma/\alpha_2$ -colonies (initial  $\alpha$ -phase at elevated temperature) and  $\beta$ -phase crystals, the total fraction of which is about 40% (vol.). After vacuum annealing in the temperature range 1100–1400 °C the main structural component is the lamellar  $\gamma/\alpha_2$ -colonies (with a thickness of individual plates of about 300 nm) surrounded by the  $\beta$ - and  $\gamma$ -phase crystals, the total fraction of which does not exceed 30% (vol.).

4. According to the electron microprobe analysis, the  $\beta$ -phase contains the largest amount of molybdenum, while the concentration of aluminium is the smallest. The opposite situation is observed for the  $\gamma/\alpha_2$ -colonies (initial  $\alpha$ -phase) and  $\gamma$ -phase. They have higher aluminium and minimum molybdenum content. The observed results are in a good agreement with the results of the calculation.

5. Experimental quantitative analysis of the phase composition at the possible heat treatment temperatures of the new alloy in comparison with the base TNM alloy has revealed that a reduction in aluminum content from 43.5 to 40.0% (at.) leads to a considerable increase in the amount of  $\beta$ -phase and decrease in the  $\gamma$ -phase content. While on the distribution of elements in the phases this almost does not affect.

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# Microstructure and phase composition of the eutectic Al – Ca alloy, additionally alloyed with small additives of zirconium, scandium and manganese

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Using both thermodynamic calculations and experimental analyses, the Al – Ca – Mn – Fe – Zr – Sc phase diagram near the aluminum corner has been studied. Based on the obtained results, the optimal concentrations of calcium (about 4%) and manganese (about 0.7%) at an allowable iron content of up to 0.3–0.4% were chosen. According to the thermodynamic calculations, during solidification of the Al4Ca0.7Mn0.4Fe alloy, after formation of a the (Al) primary crystals, the eutectic reaction  $L \rightarrow$  (Al) + + Al<sub>6</sub>(Fe, Mn) should occur. Solidification of this alloy should be completed via the ternary eutectic reaction  $L \rightarrow$  (AI) + AI<sub>6</sub>(Fe, Mn) + AI<sub>4</sub>Ca. The addition of 0.2–0.4% zirconium should leads to the formation of primary crystals of the Al<sub>3</sub>Zr aluminide. However, it is known that at the cooling rates typical for the casting in metal moulds (5–20 °C/s), the concentration boundary is shifted toward higher zirconium concentrations. Therefore, it was assumed that the total amount of Zr should enter into the (AI) composition and consequently have no influence on the phase composition of the alloy. When zirconium addition is present, the casting temperature should be higher than for the base alloy. The microstructure of two alloys with different content of zirconium and scandium: Al4Ca0.7Mn0.4Fe0.2Zr0.1Sc and Al4Ca0.7Mn0.4Fe0.4Zr was examined by means of optical microscopy, scanning electron microscopy and by electron microprobe analysis. The obtained results have revealed that for both alloys microstructure consists of the (AI) primary crystals and eutectic colonies with a fine structure. Calcium and iron are concentrated in the eutectic, while scandium, zirconium and manganese were detected in the both eutectic composition and (AI) primary crystals. Analysis of the hardness and specific electrical conductivity together with transmission electron microscopy has revealed that joint alloying with zirconium and scandium (0.20% Zr and 0.1% Sc) leads to the precipitation hardening due to the decomposition of (AI) and further precipitation of the coherent  $L1_2 - AI_3(Zr, Sc)$  phase nanoparticles. The highest hardness is observed after step annealing at 250 °C, 3 h plus 300 °C, 3 h.

*Key words:* Al – Ca alloys,  $Al_3(Zr, Sc)$  nanoparticles, thermodynamic calculations, phase transformations, microstructure, annealing, hardening.

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