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PHASE COMPOSITION AND HARDENING OF CASTABLE Al – Ca – Ni – Sc ALLOYS CONTAINING 0.3% Sc

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The phase composition of aluminum alloys of the Al – Ca – Ni – Sc system containing 0.3 wt.% Sc is studied. It is shown that the aluminum solid solution may be in equilibrium not only with binary phases (Al_4Ca, Al_3Sc and Al_3Ni) but also with a ternary Al_9NiCa compound. The temperature of attainment of maximum hardening due to precipitation of nanoparticles of phase Al_3Sc is determined for all the alloys studied. Principal possibility of creation of castable alloys based on an (Al) + Al_4Ca + Al_9NiCa eutectic, the hardening heat treatment of which does not require quenching, is substantiated.

Key words: Al – Ca – Ni – Sc system, nanoparticles of Al_3Sc, phase composition, eutectic, microstructure, hardening.

INTRODUCTION

Scandium is a very effective hardener of aluminum alloys due to formation of secondary precipitates of phase Al_3Sc (Ll_2) less than 10 nm in size in their structure [1 – 7]. These nanoparticles form in the process of annealing due to decomposition of supersaturated aluminum solid solution (Al). This phenomenon raises substantially the strength of aluminum alloys not subjected to a classical hardening heat treatment (quenching + aging). Deformable magnals, such as alloy 1570, are the most widely applied representatives of this group [3]. Despite the high cost of scandium, the latter is assumed today to be the most promising alloying element for aluminum alloys of the new generation.

In standard castable aluminum alloys the addition of scandium does not produce the same hardening effect as in deformable alloys. This is the most typical for silumins, which constitute the major part of the total production of castings from aluminum alloys [8, 9]. This is explainable by the fact that silicon lowers considerably the solubility of scandium in (Al) and thus makes it impossible to form a sufficient number of nanoparticles of Al_3Sc phase during annealing. However, in aluminum alloys based on other eutectics, for example, nickel-containing ones, the addition of scandium provides considerable hardening [10, 11]. Since the castable alloys should contain an enough content of a eutectic [8], it seems expedient to search for other eutectic-forming elements not lowering the hardening effect due to scandium alloying. One such element is calcium, the eutectic concentration of which in the Al – Ca system is 7.6% at 617°C [12].

It is known that ternary (and more complex) eutectics commonly have a finer structure than binary ones. Specifically, this has been proved experimentally for the Al – Ce – Ni [13] and Al – Mg – Ni – Si systems [14]. We may state that the addition of a second eutectic-forming element may be a kind modifying (like the introduction of strontium into silumins for modifying the aluminum-silicon eutectic). In our opinion, the Al – Ca – Ni system, where a eutectic reaction $L \rightarrow (Al) + Al_4Ca + Al_3Ni$ occurs at 6.7% Ca and 5.7% Ni at 607°C [12], has prospects as a base for castable aluminum alloys hardened by a low addition of scandium without the use of quenching. It should be noted that by the data of later reports, for example [15], this ternary system contains an Al_9CaNi compound that participates in a eutectic reaction $L \rightarrow (Al) + Al_4Ca + Al_9CaNi$ at 610°C. However, the published information on the transformations occurring in aluminum alloys with calcium additions is scarce.

The aim of the present work was to study the phase composition and structure of alloys of the Al – Ca – Ni – Sc system in the aluminum-rich range at a constant concentration

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TABLE 1. Chemical Compositions of Experimental Aluminum Alloys

Alloy	Content of element, wt.%		
	Ca	Ni	Sc
1	–	–	0.3 (0.38)
2	–	6 (5.85)	0.3 (0.29)
3	7.6 (7.53)	–	0.3 (0.28)
4	4 (2.71)	4 (4.20)	0.3 (0.30)
5	4 (2.58)	8 (6.06)	0.3 (0.32)
6	10 (8.32)	4 (4.45)	0.3 (0.31)

Note. The content of impurity elements in the blend (by the data of spectrum analysis) does not exceed 0.01.

TABLE 2. Modes of Annealing of Castings from Experimental Alloys

Notation	Annealing mode
S00	Without annealing (cast condition)
S200	200°C, 3 h
S250	S200 + 250°C, 3 h
S300	S250 + 300°C, 3 h
S350	S300 + 350°C, 3 h
S400	S350 + 400°C, 3 h
S450	S400 + 450°C, 3 h
S500	S450 + 500°C, 3 h
S550	S500 + 550°C, 3 h
S600	S550 + 600°C, 3 h

of scandium (0.3 wt.%) experimentally and by computation and to determine the influence of calcium and nickel on precipitation hardening due to nanoparticles of phase Al_3Sc.

METHODS OF STUDY

We studied six alloys of the Al – Ca – Ni – Sc system containing 0.3% Sc and different contents of Ni and Ca, namely, three quaternary alloys, two ternary alloys and one binary alloy (Table 1). The alloys were melted in a LAC electric resistance furnace in graphite-chamotte crucibles. All the alloys were based on high-purity aluminum A99 (GOST 11069–2001). Calcium, nickel and scandium were introduced into the aluminum melt in the form of aluminum-base alloying additions (Al – 18% Ca, Al – 20% Ni and Al – 2% Sc respectively). The melts were cast into graphite crucibles at 730 – 740°C to obtain flat castings 15 × 30 × 180 mm in size (the rate of the crystallization cooling was about 10 K/sec). The castings were cut into specimens for the study.

The specimens were heat treated in SNOL 8.2/1100 and SNOL 58/350 muffle electric furnaces with about 3°C accuracy of keeping of the temperature. We used multistage annealing modes in the range of 200 – 600°C at a step of 50°C and a hold for 3 h in each stage (Table 2). The stage modes were chosen in order to be able to study the effect of the heating temperature on the structure for one specimen. This method has proved to be both informative and efficient as applied to aluminum alloys hardened due to precipitation of particles of Ll_2 nanophase [16].

The laps were prepared by mechanical polishing of the specimens and etching with Keller reagent. The primary analysis of the microstructure was performed using an Olympus GX51 optical microscope (OM); the detailed metallographic studies were performed using a TESCAN VEGA 3 scanning electron microscope (SEM). The TESCAN microscope equipped with an Oxford Instruments energy dispersive attachment for microanalysis and AZtec software was also used for microscopic x-ray spectrum analysis (MXRSA).

The Brinell hardness was measured according to the GOST 9012–59 Standard using a Wilson Wolpert 930N hardness meter with ball diameter 2.5 mm at a load of 306 N and a hold time of 30 sec. The phase composition of the Al – Ca – Ni – Sc system was computed with the help of the Thermo-Calc software (the TTAL5 database) [17].

RESULTS AND DISCUSSION

We will explain the choice of the composition of the experimental alloys (Table 1) below. Alloy *1* containing only a scandium additive, which has been studied well [1 – 7], played the role of a standard. Alloys *2* and *3* contained eutectic concentrations of nickel and calcium, which follows from the Al – Ni (Fig. 1*a*) and Al – Ca (Fig. 1*b*) diagrams. The concentration of Ca and Ni in alloys *4*, *5* and *6* was chosen on the basis of computation of the liquidus surface of the Al – Ca – Ni phase diagram (Fig. 1*c*), i.e., alloy *4* near the eutectic polytherm, and alloys *5* and *6* in the regions of sure presence of primary crystals of phases Al_3Ni and Al_4Ca, respectively. It should be noted that the computed concentration of nickel at the point of ternary eutectic was about twice lower with respect to the data of [12].

The effect of nickel on the phase composition of alloys of the Al – Ca – Ni – Sc system at different temperatures matches the polythermal section computed for 4% Ca and 0.3% Sc. It can be seen from Fig. 2 that even at low contents of this element we should expect appearance of primary crystals of phase Al_3Sc. It is obvious that their presence should lower the concentration of scandium in (Al) and, as a consequence, the capacity of the alloy for precipitation hardening due to phase Ll_2. It also follows from Fig. 2 that independently of the content of nickel all the alloys of this section should finish crystallization at 607°C, i.e., at the temperature of ternary eutectic.

Analysis of the cast structure of alloys *2* and *3* shows that the presence of 0.3% Sc virtually does not affect the morphology of the binary eutectics (Al) + Al_3Ni (Fig. 3*a*) and

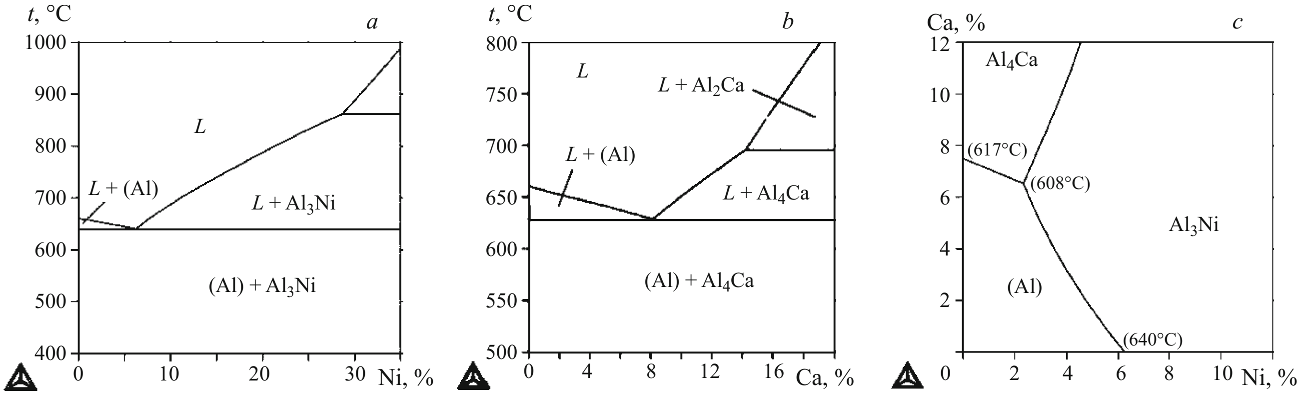

Fig. 1. Binary Al – Ni (*a*) and Al – Ca (*b*) diagrams and liquidus surface of the Al – Ca – Ni diagram (*c*) (designed with the help of Thermo-Calc).

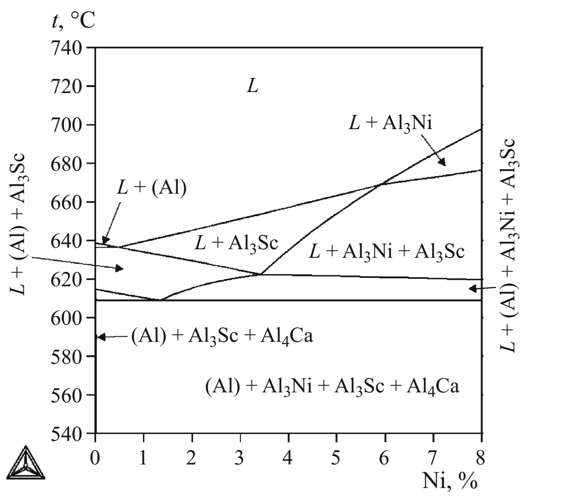

Fig. 2. Polythermal section of the Al – Ca – Ni – Sc system at 4% Ca and 0.3% Sc (designed with the help of Thermo-Calc).

(Al) + Al_4Ca (Fig. 3*b*). These eutectics have a quite fine structure, which can be determined under a high magnification impossible for optical microscopy. Primary crystals of phase Al_3Sc have not been detected in the structure of alloys *2* and *3*, which allows us to speak of complete dissolution of scandium in (Al).

The structure of alloy *4* agrees well with the computed results (Fig. 1*c*), because it contains colonies of two eutectics, i.e. a coarse (light) one and fine one (Fig. 4*a*). The fine eutectic seems to be a ternary one crystallized in the last turn. In alloy *5* we observe light primary crystals (Fig. 4*b*) with morphology corresponding to phase Al_3Ni [11]. In alloy *6* we detect primary crystals of two types, i.e., light compact ones and gray acicular ones (Fig. 4*c*), which cannot be explained by the simple structure of the Al – Ca – Ni diagram (Fig. 1*c*). It should be noted that all the quaternary alloys contained colonies of a fine eutectic.

Determination of the concentrations of all elements in individual particles and in eutectic colonies by the method of MXRSA allowed us to identify them. We analyzed at least three regions for each experimental alloy. The results obtained for alloy 6 (Fig. 5, Table 3) seem the most interesting. The composition of the acicular crystals (spectra *36 – 38*) corresponds to the expected phase Al_4Ca. On the other hand, by the data of [15] the light crystals (spectra *32 – 35*) belong to compound Al_9CaNi containing about 9 at.% Ca and about 9 at.% Ni. The less fine eutectic (spectra *42 – 44*) has composition close to a binary (Al) + Al_4Ca one (Fig. 1*b*), and the

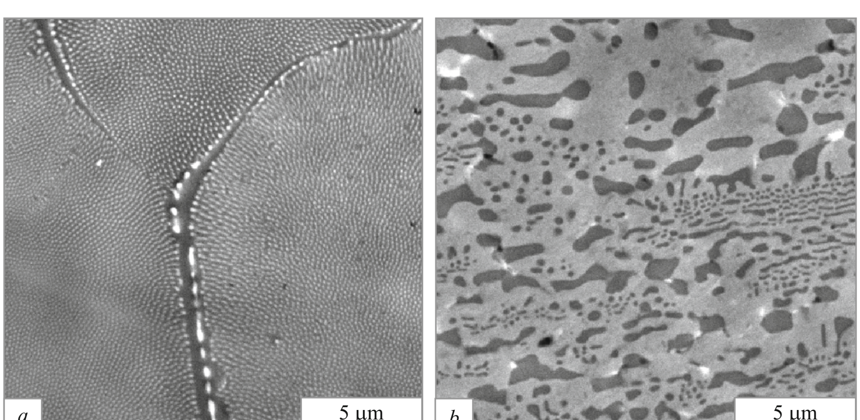

Fig. 3. Microstructures of cast alloys *2* (*a*) and *3* (*b*) based on binary eutectics.

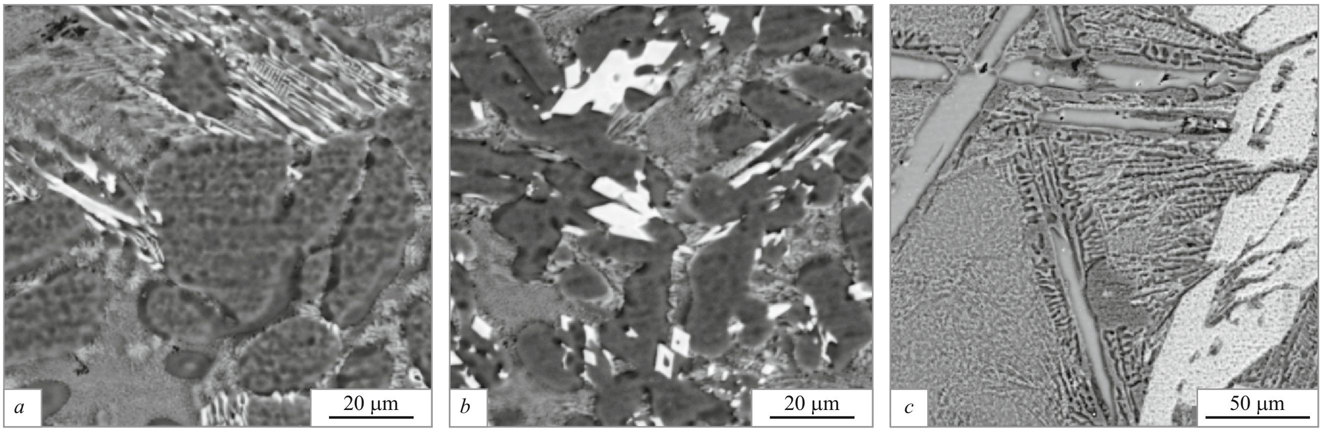

Fig. 4. Microstructures of cast alloys of the Al – Ca – Ni – Sc system: *a*) alloy *4*; *b*) alloy *5*; *c*) alloy *6*.

finer eutectic (spectra *39 – 41*) most probably matches a ternary (Al) + Al_4Ca + Al_8NiCa one. It should be noted that the concentration of scandium in the eutectics is close to its content in the alloy. At the same time, its concentration in the primary crystals is obviously lower. We have not detected primary crystals of Al_3Sc in any of the alloys studied, which does not agree with the computed polythermal section (Fig. 2). This mismatch may be explained by the influence of the conditions of nonequilibrium crystallization, which results to this or that degree in a shift of phase boundaries. The results of the MXRSA also confirm the identification of primary crystals of phase Al_3Ni in alloy *5*. Note that the composition of the fine eutectic in alloys *4* and *5* is about the same as in alloy *6* (Table 3). It may be assumed with a high probability that in all the quaternary alloys it is represented by a ternary eutectic (Al) + Al_3Ca + Al_9NiCa.

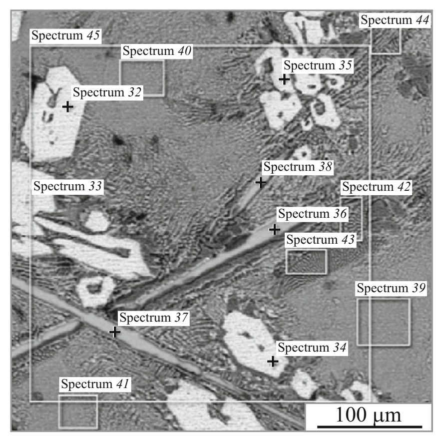

Fig. 5. Analyzed regions of the cast structure of alloy *6* (Table 3).

To estimate the precipitation hardening of the experimental alloys we analyzed the curves describing the dependence of their hardness on the annealing temperature. It can be seen from Fig. 6 that maximum hardness is attained in all the

TABLE 3. Results of Quantitative Analysis of the Composition of Individual Particles and Structural Components in Cast Alloy 6 (Fig. 5)

Spectrum	Content of elements, wt.%				Phase (structural component)
	Al	Ca	Sc	Ni	
32	69.61	12.17	0.05	18.17	Al_9NiCa (primary)
33	69.00	12.44	0.10	18.46	Al_9NiCa (primary)
34	69.17	12.13	0.06	18.64	Al_9NiCa (primary)
35	70.21	11.88	0.08	17.82	Al_9NiCa (primary)
36	72.66	26.93	0.16	0.25	Al_4Ca (primary)
37	72.59	26.91	0.16	0.35	Al_4Ca (primary)
38	72.51	26.96	0.11	0.42	Al_4Ca (primary)
39	88.87	7.10	0.44	3.59	(Al) + Al_4Ca + Al_9NiCa (eutectic)
40	89.49	6.98	0.33	3.20	(Al) + Al_4Ca + Al_9NiCa (eutectic)
41	89.15	7.07	0.31	3.47	(Al) + Al_4Ca + Al_9NiCa (eutectic)
42	91.57	6.85	0.44	1.13	(Al) + Al_4Ca (eutectic)
43	92.24	6.84	0.24	0.68	(Al) + Al_4Ca (eutectic)
44	90.62	8.01	0.27	1.10	(Al) + Al_4Ca (eutectic)

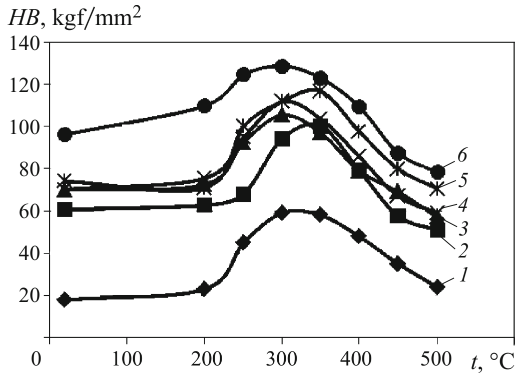

Fig. 6. Hardness of alloys of the Al – Ca – Ni – Sc system containing 0.3% Sc as a function of the annealing temperature (stage heating).

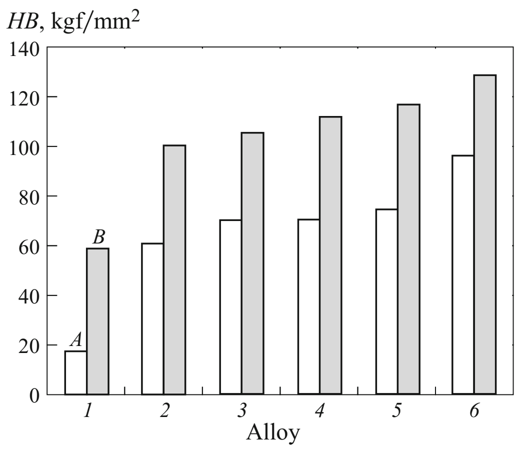

Fig. 7. Effects of hardening of alloys *1* – *6* of the Al – Ca – Ni – Sc system containing 0.3% Sc: *A*) cast condition; *B*) after annealing for maximum hardness.

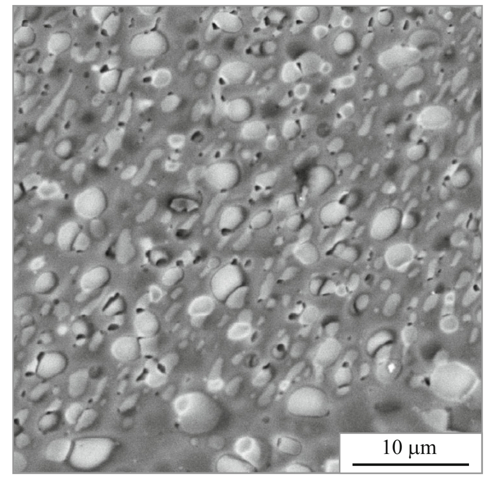

Fig. 8. Microstructure of alloy *6* after heat treatment by regime S600 involving stage heating to 600°C.

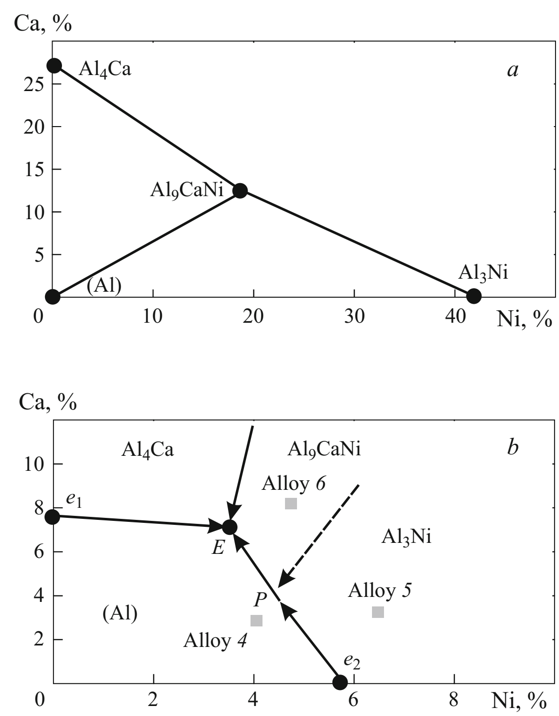

Fig. 9. Predicted constitution of the Al – Ca – Ni phase diagram in the region of the aluminum angle: *a*) phase regions in solid condition; *b*) projection of the liquidus surface.

alloys at 300 – 350°C (Table 2, regimes S300 and S350). The difference in the absolute hardening is relatively low (i.e., it does not differ from that of standard alloy *1*), which can be seen in Fig. 7. This means that (1) virtually the entire scandium has entered (Al) under crystallization and (2) it has precipitated during annealing in the form of nanoparticles of phase Al_3Sc (Ll_2). This means that nickel and calcium, both jointly and individually, do not affect negatively the hardening due to the scandium additive.

Starting with 500°C, annealing changes the structure of the eutectics; the aluminides are first fragmented and then coarsened. It can be seen that the finest eutectic in the structure of alloy *6* annealed by regime S600 (Table 2) contains particles of two kinds (light and gray) in addition to (Al) (Fig. 8). This means that such a eutectic is a three-phase one. The results of the MXRSA prove the identification of phases Al_4Ca and Al_9NiCA.

Generalization of the computational and experimental results allows us to determine the structure of the phase diagram of the Al – Ca – Ni system in the region of the aluminum angle. Specifically, we should expect there two three-phase systems, i.e., (Al) + Al_4Ca + Al_9NiCa and (Al) + Al_8NiCa + Al_3Ni (Fig. 9*a*), which corresponds to the variant given in [15]. The composition of the ternary eutectic and the structures of the experimental alloys allow us to describe the kind of the liquidus surface of this ternary system, as it is shown in Fig. 9*b*. With allowance for the structures of other ternary systems in the region of the aluminum angle [11, 12] we may expect existence of two nonvariant reactions, i.e., a eutectic reaction $L \rightarrow$ (Al) + Al_3Ca + Al_8NiCa (point E) and a peritectic reaction L + $Al_3Ni \rightarrow$ (Al) + Al_9NiCa (point P). It should also be noted that in accordance with the results obtained scandium should not form phases other than Al_3Sc in the quaternary system studied.

We may speak of a principal possibility of creation of castable aluminum alloys on the base of an (Al) + Al_4Ca + Al_9NiCa eutectic. Such alloys should combine high casting properties (due to the narrow range of crystallization) with the possibility of hardening due to annealing at 300 – 350°C (i.e., without quenching). It should also be noted that the computed total volume fraction of the particles of Al_4Ca and Al_9NiCa in the ternary eutectic is about 33 vol.%, which exceeds considerably the content of silicon particles in silumins. For this reason, we may expect a noticeable growth in the properties obeying the rule of additivity in multiphase systems (for example, the coefficient of thermal expansion and the modulus of elasticity). The high fineness of the eutectics also promises high mechanical properties, which requires, however, an experimental verification.

CONCLUSIONS

1. We have studied the phase composition of aluminum alloys of the Al – Ca – Ni – Sc system with the help of computational and experimental methods. We established that the aluminum solid solution may be in equilibrium not only with the phases of the binary systems (Al_4Ca, Al_3Sc and Al_3Ni) but also with the ternary Al_9NiCa compound.

2. Maximum hardening due to precipitation of nanoparticles of phase Al_3Sc is attained in all the alloys studied after annealing at 300 – 350°C. Starting with 500°C the morphology of the eutectics changes; the aluminides are first fragmented and then coarsened.

3. We have shown the principle possibility of creation of castable aluminum alloys on the basis of a (Al) + Al_4Ca + Al_9NiCa eutectic. We expect that such alloys should combine high casting properties with the possibility of hardening without quenching.

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