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TEMPERATURE RANGES OF PHASE TRANSFORMATIONS AND MECHANICAL PROPERTIES OF ALLOYS OF THE Al – Cu – Mg – Ag SYSTEM WITH VARIOUS Cu/Mg RATIOS

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The effect of the content of silver in the amount of 0.6 wt.% and of the Cu/Mg ratio in the range of 1.6 – 15 on the temperature ranges of phase transformations and on the properties of alloys of the Al – Cu – Mg – Ag system is studied with the aim of amending heat treatment modes. Pressed strips with cross section 10 × 100 mm are studied after natural and artificial aging. The method of differential scanning calorimetry is used to determine the temperature ranges and thermal effects in solid-phase dissolution (segregation) of excess phases and melting of the structural components. Mechanical properties are determined at room and elevated temperatures and the microstructure over the cross section of the strips is studied.

INTRODUCTION

In the second half of the 20th century foreign scientists began intense studies of the influence of silver on the structure and mechanical properties of semiproducts from aluminum alloys with different alloying systems [1 – 4]. It was shown that the effect of silver on the properties of aluminum alloys bearing copper and magnesium is connected with the changes in the mechanism of decomposition of the solid solution in artificial aging. In alloys with about 5 – 6%[2] Cu and Cu/Mg = 15 – 20 the decomposition yields a new modification of the θ-phase ($CuAl_2$) known as the Ω-phase. The composition of the Ω-phase corresponds to that of the θ-phase, but its plates lie in plane {111} of the solid solution instead of planes {100}, which is typical for hardening segregations of the θ′-phase. The habitus plane of plates of the Ω-phase contain one to two atomic layers of silver and magnesium. Due to the high dispersity and enhanced thermal stability of segregations of the Ω-phase, Al – Cu – Mg alloys with silver additive have higher strength characteristics at room and elevated temperatures and exhibit maximum creep resistance in the temperature range of 100 – 150°C. These alloys are promising materials for new-generation supersonic passenger airplanes.

Al – Cu – Mg alloys with a lower Cu/Mg ratio, which occupy the $\alpha + S$ or $\alpha + \theta + S$ phase regions of the ternary phase diagram, also exhibit the effect of hardening due to alloying with silver because of the appearance of the Ω-phase instead of the θ′-phase and the presence of silver in the solid solution and in the *S*-phase.

Works devoted to a comparison of the properties of commercial aluminum alloys with silver additive and various Cu/Mg ratios, which are produced and studied under comparable conditions, are absent in the domestic literature. Foreign authors present data obtained in studies of similar semiproducts fabricated from a limited number of alloys or compare the properties of semiproducts of different kinds [1, 4]. This complicates consideration of the effect of silver alloying of alloys with different proportions of Cu to Mg on the mechanical properties of semiproducts the structure of which has been formed under identical conditions.

The aim of the present work consisted in studying the influence of silver and of the Cu/Mg ratio on the mechanical properties of similar semiproducts subjected to heat treatment under comparable conditions and on the temperature ranges of phase transformations. The data obtained were used for correcting the heat treatment conditions.

METHODS OF STUDY

The chemical composition of ingots 134 mm in diameter cast by the semicontinuous method is presented in Table 1. Composition *1* corresponds to commercial high-temperature aluminum alloy of grade D21 [5]. Composition *2* was used as the base one for subsequent silver alloying after analyzing

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[2] Here and below the content of elements is given in mass percent.

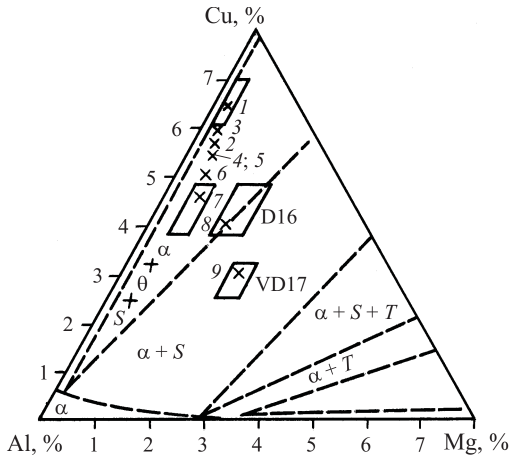

Fig. 1. Location of studied alloys in phase regions of the Al – Cu – Mg ternary phase diagram at 200°C. The numbers of the alloys are given at the symbols. The parallelograms denote regions corresponding to standard chemical compositions of alloys D21 (*1*), D1(*7*), D16 (*8*), and VD17 (*9*).

published data [4]. The alloy contains less copper than D21 and is additionally alloyed with zirconium at a reduced content of titanium. Alloys *3 – 5* differ from alloy *2* by additional amounts of silver ranging from 0.2 to 0.6%. In alloys *4 – 9* the Cu/Mg ratio is varied from 12.9 to 1.6 at a mean silver content of about 0.5%; the amount of copper and magnesium corresponds to that in domestic prototype alloys (Table 1). The location of the studied alloys relative to the phase regions of the ternary phase diagram [6] is presented in Fig. 1.

The microstructure of the ingots was studied in the central zone (with respect to the thickness) after 1-h annealing at 360°C, which corresponded to a virtually nonhomogenized state, and after homogenizing by chosen regimes.

Turned homogenized ingots were pressed into strips with a cross section of 10 × 100 mm, which were hardened in water in chosen modes and subjected to stretch flattening with residual strain below 1%.

The structure and properties of the strips were studied in naturally aged states and after artificial aging of different durations at 190°C. The aging temperature of 190°C is typical for deformable aluminum alloys of the Al – Cu – Mg system.

In order to determine excess phases, specimens of cast or deformed material were subjected to etching in 0.5% aqueous solution of hydrofluoric acid, after which the qualitative structural parameters were determined by the method of linear metallographic analysis (the method of secants) at a magnification of × 485. For deformed alloys the measurement was performed on longitudinal specimens with secants oriented in the direction of the thickness of the strip. The volume fraction *V* of all the observed excess phases with inclusions over 0.5 μm in size and their thickness *m* were determined in middle layers of the thickness of a strip. The grain structure of the deformed material was determined by anode oxidation of electrically polished sections and in polarized light.

The temperature ranges and the values of thermal effects in solid-phase dissolution (segregation) of excess phases and in melting of structural components were determined by the method of differential scanning calorimetry (DSC) after heating specimens about 500 mg in mass in a DSC111 calorimeter to 20 – 600°C at a rate of 5 K/min.

The mechanical properties (σ_r, $\sigma_{0.2}$, δ) of the strips were determined from the results of tensile tests of longitudinal specimens with the diameter of the functional part equal to 5 mm and the design length 25 mm. The tests were performed at room temperature and at 175°C.

RESULTS AND DISCUSSION

The microstructure of the ingots in annealed (nonhomogenized) condition showed that they had a dendritic structure with excess phases lying over boundaries of dendrite cells. Their morphology and color after etching in 0.5% HF were typical for alloys of the Al – Cu – Mg system.

Alloys *1 – 6* with low content of magnesium primarily contained light inclusions of the θ-phase in degenerated

TABLE 1. Chemical Composition of Studied Alloys

Alloy	Content of elements, wt.%								Cu/Mg	Prototype alloy
	Cu	Mg	Ag	Mn	Zr	Ti	Fe	Si		
1	6.35	0.30	–	0.60	–	0.15	0.03	0.05	21.2	D21
2	5.70	0.36	–	0.68	0.10	0.05	0.03	0.04	15.8	–
3	5.90	0.37	0.22	0.65	0.10	0.04	0.05	0.01	16.0	–
4	5.40	0.42	0.41	0.50	0.10	0.04	0.04	0.02	12.9	–
5	5.40	0.45	0.61	0.97	0.10	0.04	0.04	0.01	12.0	–
6	5.00	0.55	0.50	0.68	0.11	0.04	0.04	0.02	9.0	–
7	4.60	0.77	0.52	0.60	0.11	0.04	0.03	0.01	6.0	D1
8	4.00	1.35	0.54	0.60	0.10	0.05	0.03	0.01	3.0	D16
9	3.10	2.00	0.53	0.60	0.10	0.03	0.03	0.01	1.6	VD17

$\alpha + \theta$ eutectic. Alloys *7* and *8* with enhanced magnesium content had additional dark inclusions of the *S*-phase (Al_2CuMg) in the composition of $\alpha + \theta + S$ eutectic. The structure of the ingot of alloy *9* primarily contained segregations of $\alpha + S$ eutectic. Inclusions of insoluble phases based of compounds of iron, silicon, and manganese with aluminum were also encountered in small amounts. The size of the dendrite cell (the middle chord) in ingots of different alloys varied from 25 to 35 μm. Metallographic analysis did not show the presence of any new phase due to the presence of silver in the alloys. However, this does not exclude the presence of a certain amount of silver in the composition of the observed excess phases.

In order to amend the temperature of homogenization of ingots with different compositions, the temperature at which the annealed material began to melt was determined by the method of DSC. The DSC curves obtained in heating of alloys *1*, *3*, *5*, *7*, and *9* differing in the contents of silver, copper, and magnesium are compared in Fig. 2*a* for the temperature range of dissolution of stable phases and beginning of melting of the eutectic and of the solid solution. It should be noted that in all the alloys the solid-phase dissolution of high-temperature phases does not end before the beginning of melting of the most fusible eutectics during heating in a calorimeter at a rate of 5 K/min. This follows from the presence of endothermic effect *I* on the DSC curve (Fig. 2*a*), which precedes endothermic effect *II* due to melting of the eutectic. The initial melting temperature of the alloys is presented in Table 2. It is virtually independent of the studied content of silver (0.6%) in the alloys and decreases with growth in the concentration of magnesium.

In alloys *1*, *3*, and *5* with low magnesium content the binary $\alpha + \theta$ eutectic melts at a relatively high and little changing temperature. In alloy *7* heated in the calorimeter the *S*-phase dissolves, and the binary $\alpha + \theta$ eutectic melts at a lower temperature than in alloys *1*, *3*, and *5*. In alloy *9* the nonequilibrium eutectic $\alpha + S$ melts at the lowest temperature. In this connection, the ingots of alloys *1* – *6* were homogenized at 520°C, and the ingots of alloys *7* – *9* were homogenized at 490°C.

Excess inclusions of the θ-phase are preserved in homogenized alloys *1*, *3*, and *5*. The DSC curves of the alloys have a peak due to an endothermic effect of melting of the $\alpha + \theta$ eutectic occurring at a higher temperature than in a nonhomogenized condition (Fig. 2*b*). The size of the thermal effect due to melting decreases substantially, and the preceding effect due to solid phase dissolution virtually disappears. In alloy *7* the presence of a low thermal effect at 529°C indicates preservation of a certain amount of $\alpha + \theta$ eutectic in the structure of the ingot. In alloy *9* homogenization causes full dissolution of the eutectic and disappearance of the *S*-phase. The corresponding peak on the DSC curve is absent (Fig. 2*b*). Thus, the majority of the studied alloys in the homogenized state bear a certain amount of undissolved inclusions of the θ-phase.

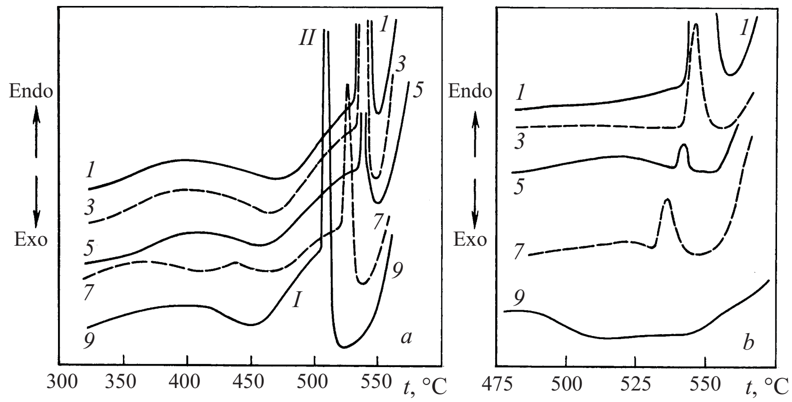

Fig. 2. DSC curves due to heating of cast alloys in nonhomogenized (*a*) and homogenized (*b*) conditions in the range of high temperatures (the figures at the curves correspond to the numbers of the alloys): *I*, *II*) endothermic effects in solid-phase dissolution and in melting of the low-melting eutectic respectively.

These data explain the chosen temperature of heating of pressed strips for hardening, i.e., 500°C for alloys *8* and *9* with high content of magnesium and 525°C for the rest of the alloys. The duration of the heating is 40 min.

A study of the structure of strips in a hardened and artificially aged state has shown that they have a nonrecrystallized structure with extended fibrous grains and a large-crystal rim, which is the largest in alloy D21 (the thickness over the broad face of the strip is 0.8 mm) and is absent or very narrow (0.1 mm) in zirconium-alloyed alloys.

The results of quantitative metallographic analysis of the structure of pressed strips are presented in Table 2. Due to the low content of the iron admixture the structure of the

TABLE 2. Initial Temperature of Thermal Effects of Melting (t_e) and Characteristics of the Microstructure of Tested Alloys

Alloy	Temperature t_e, °C, of semiproducts			V, vol.%	m, μm
	Ingot		Pressed strip	Pressed strip	
	annealing	homogenizing annealing	state T	state T	
1	533	543	537	2.6	3.0
2	–	–	–	1.7	2.8
3	534	543	–	1.6	2.9
4	–	–	537	1.0	2.6
5	532	540	536	0.5	3.0
6	–	–	–	< 0.1	–
7	522	529	524	< 0.1	–
8	–	–	–	< 0.1	–
9	506	–	510	< 0.1	–

Notations: *V* is the volume content of all observed excess phases with inclusions over 0.5 μm in size; *m* is their average thickness.

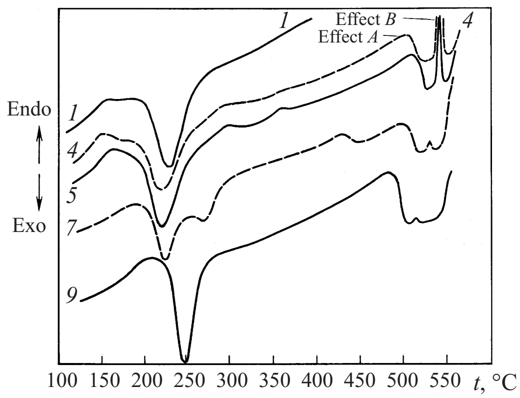

Fig. 3. DSC curves due to heating of deformed alloys in the hardened and naturally aged condition T (the figures at the curves correspond to the numbers of the alloys).

strips in the heat-treated state contains a very small amount of insoluble phases of variable composition like AlFeMnCuSi. The *S*-phase dissolves virtually fully during heating for hardening, and therefore the structure of the alloys with over 5% copper bears inclusions of the θ-phase. The higher the copper content above the 5% level, the more excess θ-phase in the structure; the amount of the θ-phase may vary from 0.5 to 2.6 vol.%. However, the mean thickness of inclusions of this phase changes little.

The properties of the strips after one month of natural aging (state T) are presented in Table 3. Alloys of the Al – Cu system with low content of magnesium are used primarily in an artificially aged state. Therefore, the properties in state T are auxiliary for them. Only for alloys of the Al – Cu – Mg system with elevated content of magnesium like D1 and D16, which harden substantially due to artificial aging and are used in this state, do the properties in state T characterize their operating capacity. It follows from Table 3 that alloying of D21 (alloy *1*) with silver and zirconium at somewhat elevated magnesium content and reduced content of copper and titanium (alloy *4*) increases the strength in artificial aging; σ_r rises by 65 MPa and $\sigma_{0.2}$ rises by 40 MPa.

TABLE 3. Mechanical Properties of Tested Alloys in State T at 20°C (pressed strips)

Alloy	σ_r, MPa	$\sigma_{0.2}$, MPa	δ, %
1	450	300	14
2	485	325	17
3	485	330	17
4	515	340	20
5	500	315	14
6	500	350	15
7	505	320	17
8	550	360	15
9	515	335	17

The strip from alloy *8* with Cu/Mg = 3, which corresponds to the content of copper and magnesium of alloy D16, has the highest strength characteristics after natural aging. It is known that this alloy exhibits maximum effect of natural aging [6, 7].

DSC curves obtained in heating of specimens cut from pressed strips in state T are compared in Fig. 3. Alloys *1*, *4*, and *5* have a weak endothermic effect on the DSC curves in the range of 150 – 170°C due to the dissolution of zones formed in natural aging of the alloys. The elevation of the content of magnesium in alloys *7* and *9* shifts the temperature range of this effect towards higher temperatures. Right after this effect we observe a considerable exothermic effect due to the decomposition of the solid solution and segregation of different modifications of θ′ (θ)- and S' (S)-phases; in the alloys with silver, the Ω-phase segregates too. The presence of silver in alloys *4* and *5* decreases somewhat the temperature range of the manifestation of this effect as compared to the similar range for alloy *1*. Alloy *7* exhibits a double exothermic effect due to the decomposition of the solid solution. The first peak is close in the temperature range to the effect of segregation of the θ-phase in alloy *1* and, evidently, of the Ω-phase in alloys *4* and *5*. The second, lower, effect should be ascribed to the appearance of the corresponding modifications of the *S*-phase at a content of 0.77% Mg in the alloy. Alloy *9* bearing 2% Mg lies in the ($\alpha + S$)-phase region of the ternary phase diagram, and therefore has one exothermic affect due to segregation of the *S*-phase in the higher temperature range than the effect of formation of the θ- and Ω-phases.

Growth in the heating temperature above 300°C leads to the appearance of an endothermic effect due to dissolution of hardening phases. In alloys *1*, *4*, and *5* the most considerable effect corresponds to dissolution of particles of the θ-phase segregated in the preceding heating (effect *A* in Fig. 3). The next endothermic effect *B* connected with melting of the equilibrium α + θ eutectic occurs in alloys *1*, *4*, and *5* at the same temperature but differs in the value (height of the peak). This agrees with the volume content of the excess phase determined by metallographic analysis (Table 2).

Alloy *7* exhibits two endothermic effects due to dissolution of hardening segregations of *S*- and θ (Ω)-phases with maximum heat absorption at 427 and 498°C and a small peak of an endothermic effect due to melting of the eutectic, which corresponds to the peak in Fig. 2*b*. It is obvious that the effect with maximum at 427°C should be associated with dissolution of the hardening segregations of the *S*-phase. According to the Al – Cu – Mg phase diagram these segregations for the studied alloys appear later in the $\alpha + \theta + S$ region and dissolve earlier (with respect to the temperature) than the θ-phase. This conclusion follows from an analysis of vertical sections of the phase diagram [7].

The *S*-phase dissolves in alloy *9* at a higher temperature than in alloy *7* but at a lower temperature than the dissolution of the θ-phase in alloy *7*. In the specimen of alloy *9* in state T used for plotting DSC curves we detected a very small effect due to melting of the $\alpha + S$ eutectic, which is absent in Fig. 2*b* in a homogenized state. This can be connected with the presence of specific chemical and structural inhomogeneity in semiproducts obtained under commercial conditions.

The kinetics of artificial aging was studied at 190°C and in heating for up to 24 h. The results of a calorimetric study of the decomposition of the solid solution show that for alloys *1* – *7* with relatively low magnesium content this temperature of artificial aging lies closer to the temperature range of the decomposition of the solid solution established in dynamic heating than in alloys with high magnesium content.

This can be responsible for what is known in practice as more rapid phase decomposition in alloys with high Cu/Mg ratio. According to the curves describing the variation of properties of the studied alloys with increase in the time of artificial aging, maximum strength is attained in alloys with low magnesium content after aging for 4 – 6 h and in alloys with elevated magnesium content after aging for 8 – 12 h.

Table 4 presents the mechanical properties of alloys in the range of maximum hardening. Growth in the content of silver to 0.61% increases the strength characteristics at room temperature, i.e., σ_r by 80 MPa and $\sigma_{0.2}$ by 115 MPa (compare alloys *5* and *2*). It can be seen from Table 4 and Fig. 4 that the highest strength characteristics are observed in silver-alloyed compositions *6* and *7* with somewhat reduced content of Mg at Cu/Mg = 9 – 6. These compositions lie in the middle of the $\alpha + \theta + S$ region of the ternary phase diagram. It should be noted that in alloys with silver the segregations of θ′-, Ω-, and S'-phases produce a hardening effect [1 – 3]. In alloys *8* and *9* the maximum strength parameters attainable by artificial aging decrease upon transition to the $\alpha + S$ phase region.

DSC curves obtained in heating of specimens of alloy *7* in different states in the calorimeter are compared in Fig. 5. Aging for 4 h causes full segregation of the θ (Ω)-phase, which follows from the absence of the lower-temperature effect due to its formation. However, the exothermic effect due to segregation of the *S*-phase with maximum at 263°C is preserved. Even aging at 190°C for 24 h is insufficient for removing this effect, i.e., for full segregation of the *S*-phase. Since a hold at 190°C for 24 h causes substantial softening of the material (the yield strength decreases from 495 to 445 MPa), it is clear that the region of maximum strength properties corresponds to different degrees of segregation of θ (Ω)- and *S*-phases and their different dispersity. Decomposition with segregation of the θ (Ω)-phase occurs fully, whereas decomposition with segregation of the *S*-phase occurs only partially. The maximum strength corresponds to an optimum combination of the amount of inclusions of segregated phases and of their sizes.

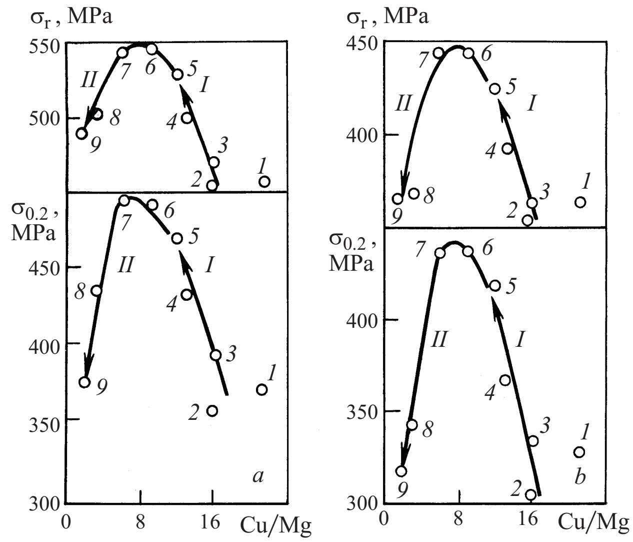

Fig. 4. Strength characteristics at room temperature (*a*) and at 175°C (*b*) for pressed strips from studied alloys with different Cu/Mg ratio in state T1 (the figures at the circles denote the numbers of the alloys): *I*) growth in the content of silver at close Cu/Mg ratios; *II*) decrease in the Cu/Mg ratios at close silver contents.

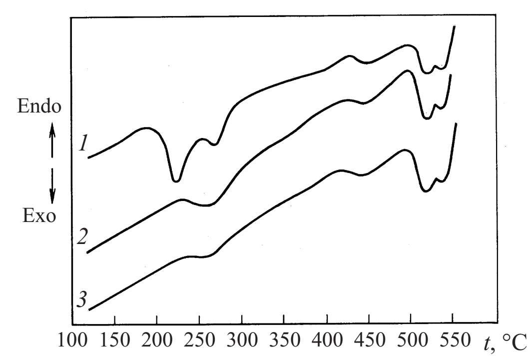

Fig. 5. DSC curves due to heating of deformed alloy *7* in different states: *1*) state T; *2*, *3*) state T1, aging for 4 h and 24 h, respectively.

TABLE 4. Mechanical Properties of Tested Alloys in State T1 (pressed strips) at 20 and 175°C in the Range of Maximum Hardening

Alloy	σ_r, MPa	$\sigma_{0.2}$, MPa	δ, %	σ_r, MPa	$\sigma_{0.2}$, MPa	δ, %
	20°C			175°C		
1	455	370	11	365	330	16
2	450	355	12	355	305	17
3	470	390	10	365	335	17
4	500	430	11	390	370	19
5	530	470	9	425	420	15
6	545	490	9	445	435	14
7	545	495	10	445	435	20
8	500	430	13	370	345	19
9	490	370	12	365	320	20

The results of the determination of the mechanical properties of pressed strips at 175°C under conditions of short-term tests (20-min heating) are presented in Table 4. The behavior of the dependences of the strength on the Cu/Mg ratio remains the same as at t_{test} = 20°C (Fig. 4*b*).

The results obtained show that alloying of the Al – Cu – Mg system with silver in an amount of about 0.5% promotes a substantial increase in the strength of semiproducts, especially if the Cu/Mg ratio is chosen appropriately. For pressed strips with nonrecrystallized structure the growth in the strength due to the addition of about 0.5% Ag is 150 and 100 MPa at room temperature and 130 and 90 MPa at 175°C for $\sigma_{0.2}$ and σ_r, respectively.

CONCLUSIONS

1. Addition of up to 0.6% silver into alloys of the Al – Cu – Mg system with high Cu/Mg ratio (about 16) increases considerably the strength of artificially aged pressed strips at room and elevated temperatures.

2. Alloys of the Al – Cu – Mg – Ag system bearing about 5% Cu, 0.6% Mg, and 0.5% Ag have maximum strength characteristics at room and elevated temperatures.

3. The established regular features of variation of the temperature ranges of structural transformations in alloys of the Al – Cu – Mg – Ag system with different amounts of alloying elements have been used for determining the conditions for heat treatment of ingots and pressed strips from alloys of this system.

4. It has been shown that the temperatures of homogenization and heating for hardening are independent of the silver concentration in an amount of up to 0.6% and are determined by the amounts of copper and magnesium.

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