

ALUMINUM ALLOYS

UDC 669.715'3'721'22:621.789

EFFECT OF CHEMICAL COMPOSITION ON THE STRENGTH OF ALLOYS OF THE Al–Cu–Mg–Ag SYSTEM AFTER HEATING AT 180–210°C

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The effect of the chemical composition, in particular, of alloying with silver (up to 0.6%) and of the Cu/Mg ratio (from 21.2 to 1.6) in alloys of the Al–(2.4–6.3)% Cu–(0.30–2.0)% Mg system on their mechanical properties is studied. Comparative analysis of the strength characteristics of alloys and of the kinetics of their overaging in tests of pressed semiproducts with a thickness of 10 mm in states *T* and *TI* and after additional heating at a temperature of 180–210°C is performed. Equations characterizing the softening due to the overaging are obtained, which make it possible to compare the properties of alloys under different modes of additional heating.

INTRODUCTION

Alloys of the Al–Cu–Mg–Ag system are discussed as a possible structural material for supersonic aircraft at operating temperatures of up to 200°C [1, 2]. The introduction of silver in an amount of about 0.5 wt.% (0.1 at.%) into heat-treatable alloys of the Al–Cu–Mg system with about 6 wt.% Cu and a high Cu/Mg ratio (about 15–20) changes the mechanism of formation of nuclei in artificial aging. Numerous studies have shown that joint alloying of alloy Al–(5–6)% Cu with magnesium and silver in an amount of 0.5 wt.% each changes the morphology of the θ' -phase segregated in artificial aging of alloys of the Al–Cu system. Instead of the formation of hardening segregations (plates) over planes $\{100\}_\alpha$ of the crystal lattice of aluminum, which is typical for the θ' -phase, fine hexagonal plate segregations oriented primarily over planes $\{111\}_\alpha$ appear [3–5].

After aging in a mode corresponding to the domain of maximum hardening, the composition of these segregations corresponds to the θ (CuAl₂)-phase, but they have a monatomic layer of magnesium and silver on their habitus plane [4, 5]. In most works these segregations are denoted as the “ Ω -phase” [1–5]. The crystal structure of the θ -phase is a slightly distorted tetragonal crystal structure of the θ -phase, but is commonly assumed to have an orthogonal elementary cell [6, 7]. Due to the similarity of crystal structure and the

same chemical composition as the θ -phase, the Ω -phase is also denoted $\{111\}\theta$ or $\theta_{\{111\}}$ [8].

A typical feature of the Ω -phase in an artificially aged state is slow thickening of the hardening segregations in the stage of coagulation aging that occurs in subsequent heating to up to 200°C (Fig. 1) [9]. It is assumed that this promotes high creep resistance in specimens of alloys of the Al–Cu–Mg–Ag system as compared to commercial high-temperature alloys of the Al–Cu–Mg system [2, 10]. The assump-

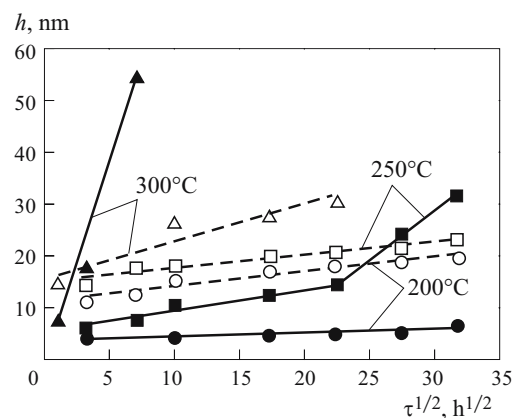


Fig. 1. Dependences of the thickness *h* of segregations of the Ω -phase in alloy Al–6.5% Cu–0.45% Mg–0.4% Ag–0.5% Mn–0.2% Zr (the solid lines) and of the θ' -phase in alloy Al–4% Cu (the dashed lines) on the duration of heating at 200, 250, and 300°C [9].

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TABLE 1. Chemical Composition of Alloys and Volume Fraction of the θ -Phase in the Structure

Alloy	Content of elements, wt.%								Cu/Mg	V_{θ} , vol.%	Grade of prototype alloy
	Cu	Mg	Ag	Mn	Ti	Zr	Fe	Ni			
1	6.3	0.30	–	0.60	0.15	–	0.03	0.01	21.2	2.6	D21
2	5.7	0.36	–	0.68	0.05	0.10	0.03	0.01	15.8	1.7	–
3	5.9	0.37	0.22	0.65	0.04	0.10	0.05	0.01	16.0	1.6	–
4	5.4	0.42	0.41	0.50	0.04	0.10	0.04	0.04	12.9	1.0	–
5	5.3	0.35	0.56	0.59	0.04	0.11	0.06	0.01	15.0	0.8	–
6	5.4	0.45	0.61	0.97	0.04	0.10	0.04	0.01	12.0	0.5	–
7	5.0	0.55	0.50	0.68	0.04	0.11	0.04	0.01	9.0	< 0.1	–
8	4.6	0.77	0.52	0.60	0.04	0.11	0.03	0.02	6.0	< 0.1	D1
9	4.0	1.35	0.54	0.60	0.05	0.10	0.03	0.01	3.0	< 0.1	D16
10	3.1	2.00	0.53	0.60	0.03	0.10	0.03	0.03	1.6	< 0.1	VD17
11	2.4	1.40	0.51	0.56	0.04	0.11	0.55	0.49	1.7	4.8*	AK4-1ch

* Volume fraction of insoluble Al_9FeNi phase.

** Alloy 5 contains 0.10% V and 0.06% Mo in addition to the listed elements.

tion of high thermal stability of the Ω -phase, which is based on its slow thickening, is widely used in the literature. However, numerous examples show that the four-component alloys soften substantially in long-term heating due to coarsening of the structure as a result of growth of the ends of the plates of Ω -phase [11].

The degree of softening of an alloy due to long-term heating can be used as a characteristic for estimating the prospects of application of the alloy as a refractory material in structures with limited life subjected to heating during operation. Systematic studies of this aspect of alloys of the Al – Cu – Mg – Ag system have not been performed.

Below we present the results of a study of the effect of the main alloying elements in the content range typical for deformable aluminum alloys on the mechanical properties of the Al – Cu – Mg – Ag system with additives of transition metals.

The aim of the present work is to compare the kinetics of softening of alloys of the Al – Cu – Mg – Ag system in the range of coagulation aging at a temperature of 180 – 210°C for evaluating their thermal stability.

METHODS OF STUDY

The chemical composition of ingots 134 mm in diameter obtained by the method of semicontinuous casting is presented in Table 1. Composition 1 corresponds to commercial aluminum alloy of grade D21 [12]. Alloy 2 without silver contains Mn, Ti, and Zr transition metals that are typical components of commercial aluminum alloys.

In heat-treated semiproducts the transition metals form a dispersoid from fine (0.02 – 0.2 μ m) inclusions of aluminides of transition metals distributed in the solid solution [13]. These inclusions preserve their sizes in heat treatment

of the semiproducts, hinder the recrystallization, refine the grain structure, and promote elevation of the characteristics of high-temperature strength.

The other alloys differ in the content of silver, in the Cu/Mg ratio, and in the additives of transition alloys. Composition 11 contains 0.5 wt.% iron and 0.5 wt.% nickel, which form an insoluble high-temperature Al_9FeNi phase in the form of inclusions over 1 μ m thick. Such alloying is used in commercial refractory aluminum alloys of type AK4-1 [12]. In compositions 1 – 10 iron and nickel are admixtures. All the alloys also bear from 0.01 to 0.05 wt.% silicon admixtures.

The compositions of the tested alloys with a low Cu/Mg ratio are close to commercial deformable aluminum alloys of grades D1, D16, VD17, and AK4-1 in the content of copper and magnesium (Table 1). In accordance with the ternary phase diagram, hardening of these alloys due to artificial aging occurs through metastable modifications of stable θ ($CuAl_2$)- and S (Al_2CuMg)-phases, i.e., θ'' -, θ' - and S'' - and S' -phases depending on the used mode of artificial aging [12]. At a high content of magnesium, alloys of the Al – Cu – Mg system contain a $T(Al_6CuMg_4)$ phase. Alloying with silver affects the process of the decomposition of the solid solution and changes the proportion of the segregating hardening phases, which will be considered later. However, experimental data and their interpretation by different authors in the study of a sequence of structural transformations in the initial stages of decomposition of the solid solution differ. This concerns the formulation of structural differences in the observed modifications of hardening phases and the determination of the time boundary between the aging stages, in which these structural modifications occur. For this reason the used notation of metastable modifications of hard-

ening phases used here will be conventional to a certain degree in order to match the most frequently used terms.

Turned homogenized ingots with the compositions presented above were pressed at 450°C to obtain strips with a cross section of 10 × 100 mm. The strips were quenched in water after heating at 500°C for alloys 9 and 10 with high content of magnesium and copper and at 525°C for the other alloys. Then the strips were stretch flattened with residual strain of less than 1%.

In order to choose the duration of aging to the state of maximum hardening (state *TI*) the preforms for specimens from the strips were subjected to natural aging for more than one month and then to artificial aging at 190°C for from 4 to 24 h. This aging temperature is typical for deformable aluminum alloys of the Al–Cu–Mg system. Curves describing the variation of the properties of the specimens as a function of the aging time were used for determining the hold time required for ensuring maximum hardening in the aging. Specimens of each alloy aged to a maximum strength were subjected to overaging in the following modes: (1) 180°C for 72, 96, and 120 h; (2) 190°C for 16, 48, and 96 h; (3) 200°C for 16, 48, and 96 h; (4) 210°C for 8, 24, and 72 h. Specimens of all alloys aged artificially in the same mode were gathered into one batch.

Values of the strength characteristics (σ_r , $\sigma_{0.2}$) at room temperature obtained for every mode of overaging (T_i , τ_i) were used for computing regression equations of the kind

$$\log \sigma = b_0 + b_1/T - b_2 \log \tau, \quad (1)$$

where σ is the ultimate rupture strength σ_r or the yield strength $\sigma_{0.2}$ of the material (MPa) after heating for the time τ_i (h) at a temperature T_i (K) [14]. These equations describe satisfactorily the variation of the strength characteristics during overaging. The regression coefficients b_0 , b_1 , and b_2 in Eq. (1) were determined by the least squares method from 12 combinations of $\log \sigma_r$ (or $\log \sigma_{0.2}$), $1/T$, and $\log \tau$ obtained experimentally for the overaging modes used.

The mechanical characteristics (σ_r , $\sigma_{0.2}$, and δ) after all modes of aging were determined as the mean value of the results of tensile tests of two to three longitudinal specimens with functional part 5 mm in diameter and design length of 25 mm, which were performed at room temperature. Specimens in state *TI* were tested additionally at 175°C after heating and a hold of 20 min.

The electrical conductivity γ is an important characteristic of a material. It depends on the structure of the solid solution and changes in natural and artificial aging of aluminum alloys, and is therefore connected with changes in the strength characteristics [15]. We determined it for each state by the method of eddy currents using a VÉ-20N device with a set of standards on the milled surface of check specimens. The value of the electrical conductivity is related to the overaging parameters through the equation [16]

$$\log \gamma = b_0 - b_1/T + b_2 \log \tau. \quad (2)$$

In order to study the microstructure of the alloys we used light microscopy with magnification of up to × 500. The grain structure was studied after anode oxidizing of electrically polished longitudinal and transverse sections and then observed in polarized light. The presence of excess phases was determined after etching of the sections in 0.5% aqueous solution of hydrofluoric acid. Their volume content was determined by the linear method of quantitative metallographic analysis on longitudinal sections with secants oriented over the thickness of the strip.

RESULTS AND DISCUSSION

Microstructure of Pressed Strips

After the heat treatment (quenching and aging) the strips had a fibrous nonrecrystallized structure with long stretched grains and individual inclusions of excess phases that differed in the amount, shape, and post-etching color in alloys with different compositions. The structure of the alloys bearing over 0.5 wt.% copper primarily contained excess θ -phase, the individual inclusions of which did not dissolve in homogenization of the ingots and heating of the pressed preforms for quenching. The amount of the θ -phase increased with increase in the copper content in the alloy (Table 1).

Alloys with an elevated content of magnesium, which occupy the $\alpha + S + \theta$ and $\alpha + S$ domains of the ternary phase diagram, may have individual inclusions of undissolved S-phase. However, they are quite few (less than 0.1 vol.%); ditto for inclusions of undissolved phases with variable composition (AlFeMnCuSi) present in most alloys with a low content of iron and silicon admixtures. Alloy *II* with elevated content of Fe and Ni primarily contains an insoluble Al_9FeNi phase. The excess phases mentioned are typical for Al–Cu–Mg alloys with the compositions considered [12]. The presence of silver in an amount of about 0.1 at.% does not cause the appearance of new excess phases.

Since the strips have the same nonrecrystallized structure, the degree of recrystallization cannot be the reason behind the difference in the mechanical properties of the alloys, just like the variable content of coarse excess phases that harden the material but little. In this case the difference in the properties of the alloys should be connected with the formation of hardening segregations of a different type in the decomposition of the solid solution and with the fineness, which depends on the duration of the aging or on the overaging mode.

Mechanical Properties and Electrical Conductivity of the Alloys in States *T* and *TI*

The mechanical properties of the alloys in state *T* after one month of natural aging are presented in Table 2. It is known that alloys of the Al–Cu and Al–Cu–Mg system with a low content of magnesium harden poorly in natural aging and therefore are subjected to artificial aging [12]. It

TABLE 2. Mechanical Properties and Electrical Conductivity of Alloys at Room Temperature in State *T* (Natural Aging)

Alloy	σ_r , MPa	$\sigma_{0.2}$, MPa	δ , %	γ , MS/m
1	450	300	14	17.5
2	490	325	17	18.3
3	485	330	17	18.3
4	515	340	20	17.5
5	500	335	17	16.5
6	500	335	14	16.8
7	500	350	15	16.9
8	505	320	17	16.8
9	550	360	15	16.5
10	515	335	17	16.6
11	465	310	13	17.1

can be seen from Table 2 that as a result of alloying with silver and zirconium at a somewhat elevated content of magnesium the strength characteristics of alloys 4 – 7 exceed somewhat those of alloys 1 and 2 that bear no silver. However, the maximum strength in state *T* occurs in alloy 9 with Cu/Mg = 3, which lies close to the quasi-binary α – *S* section in the phase diagram of the Al – Cu – Mg system. Such a ternary alloy is hardened due to clusters, segregations of GPB zones, and an *S''*-phase formed due to artificial aging [12, 17]. When this alloy is additionally alloyed with silver, the leading role of the GPB zones and intermediate phases is preserved, but they contain silver and segregate in a finer form [17]. If the composition of a ternary alloy lies in the depth of the $\alpha + S$ domain of the phase diagram at a lower Cu/Mg ratio, the strength characteristics decrease [12]. This law holds in the case of a silver additive too (alloys 9 – 11 in Table 2).

Alloys with a low Cu/Mg ratio in state *T* have a reduced conductivity due to the appearance of high structural distortions in the matrix under natural aging [15]. A decrease in γ also occurs in alloys 5 and 6 with an elevated content of transition metals.

Artificial aging at 190°C increases considerably the strength characteristics of the material with simultaneous growth in the conductivity and decrease in the ductility (elongation). For some alloys growth in the yield strength with decrease in the conductivity is accompanied by decrease in the ultimate rupture strength. For this reason, the range of maximum hardening for all the alloys was determined in terms of the attainment of maximum yield strength. The set of characteristics obtained for this state is presented in Table 3. Alloys with Cu/Mg > 6 attain maximum hardening after aging for 4 h; alloys with a low Cu/Mg ratio exhibit this property after aging for 8 h. Table 3 presents the presumed hardening phases in these alloys according to the reference data of [3 – 5, 18, 19]. It is assumed that in alloys with silver and a high magnesium content a metastable *T* phase (Al₆CuAgMg₄) appears in the initial stages of arti-

TABLE 3. Mechanical Properties and Electrical Conductivity of Alloys at Room Temperature in State *T/* in the Range of Maximum Hardening

Alloy	τ , * h	σ_r , MPa	$\sigma_{0.2}$, MPa	δ , %	γ , MS/m	Probable hardening phases
1	4	460	370	11	19.8	θ'
2	4	450	350	12	20.6	θ', S'
3	4	470	390	10	20.4	θ', Ω, S'
4	4	500	430	11	20.2	Ω, θ', S'
5	4	500	440	10	19.0	Ω, θ', S'
6	4	530	470	9	20.0	Ω, S', θ'
7	4	545	490	9	19.8	Ω, S', θ'
8	4	550	500	10	19.8	Ω, S', θ'
9	8	500	445	13	21.0	S', T
10	8	490	370	12	19.6	S', T
11	8	430	320	13	19.0	S'

* Duration of aging at 190°C.

cial aging and is replaced by an *S*-phase in long-term heating [3, 19].

Maximum strength characteristics are observed in alloys hardened by segregations of several types, with the Ω -phase playing the leading role [3]. Accordingly, alloys 7 and 8 with compositions corresponding to the middle part of the $\alpha + S + \theta$ phase domain of the ternary phase diagram exhibit maximum strength and the highest hardening in artificial aging. In these alloys the hardening should be ensured by Ω -, θ' - and S' -phases. The transition of the figurative point of alloys 10 and 11 into the middle of the $\alpha + S$ phase domain causes a decrease in the strength characteristics and in the degree of hardening in artificial aging.

Artificial aging causes regular growth in the electrical conductivity. Figure 2 presents typical curves of variation of properties in the process of artificial aging for some of the studied alloys. The highest rate of variation of the properties is observed in the stage of hardening aging. In the region of softening the properties change much more slowly.

Table 4 presents the mechanical properties in states *T/* determined at 175°C. Elevation of the test temperature decreases the strength characteristics without violating the proportion of their values at 20 and 175°C; the higher the strength value at room temperature the higher it is at 175°C. The yield strength decreases less than the ultimate rupture strength. Alloys 7 and 8 also have maximum strength characteristics at 175°C in short-term tests.

Overaging Kinetics at 180 – 210°C

In order to study the softening of alloys during overaging in a range of 180 – 210°C new preforms were aged to state *T/* in the mode mentioned above. The properties obtained for

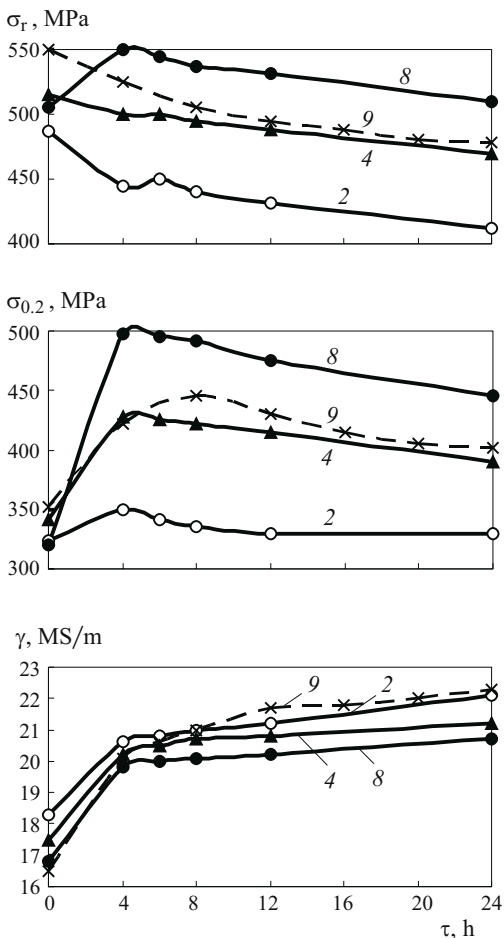


Fig. 2. Dependences of the properties of alloys on the duration of artificial aging at 190°C (the numbers at the curves correspond to the numbers of the alloys).

this batch of specimens in state *T1* corresponded on the whole to those presented in Table 3.

Growth in the temperature and in the time of overaging causes a decrease in the strength characteristics and an in-

TABLE 4. Mechanical Properties of Alloys in State *T1* at 175°C

Alloy	σ_r , MPa	$\sigma_{0.2}$, MPa	δ , %
1	365	330	16
2	355	305	17
3	365	335	17
4	390	370	19
5	380	365	19
6	425	420	15
7	445	435	14
8	445	435	19
9	370	345	18
10	365	320	19
11	345	285	16

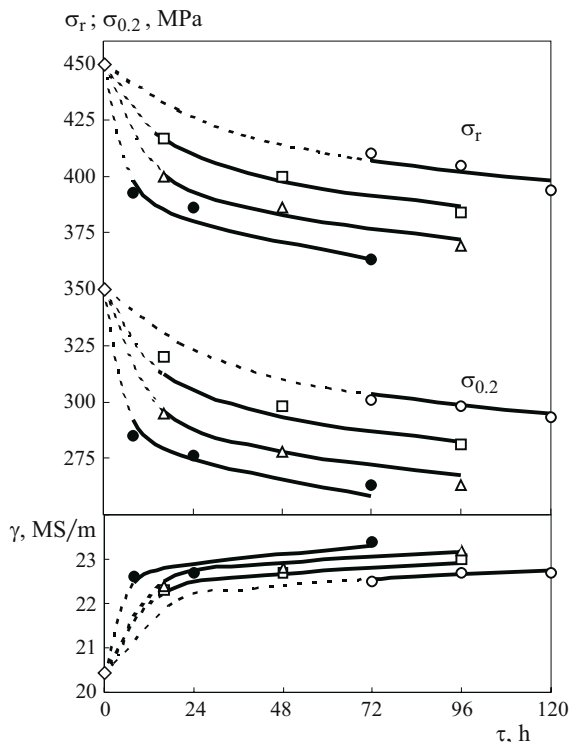


Fig. 3. Dependences of the properties of alloy 4 at room temperature on the time τ of overaging after heating at different temperatures (the symbols present experimental data; the lines present computed values): \circ) 180°C; \square) 190°C; \triangle) 200°C; \bullet) 210°C; \diamond) properties in the initial state *T1*.

crease in the electrical conductivity. This is shown in Fig. 3 for alloy 4 with a medium level of strength. Noticeable decrease in the strength characteristics occurs in all of the alloys, but the maximum absolute softening occurs in the alloys with maximum strength characteristics in state *T1*. The obtained sets of points (σ, T, τ) are describable by equations of kind (1). The coefficients b_0, b_1, b_2 of this equation for strength characteristics are presented in Table 5. The corresponding coefficients of equations of kind (2) for the electrical conductivity are presented in Table 6. In Eqs. (1) and (2) computed by the least squares method the coefficient R of correlation between the experimental and computed values of logarithms of σ_r and $\sigma_{0.2}$ or γ exceeds the critical value of $R_{0.05; 8} = 0.632$ at a significance level of 0.05 and 8 degrees of freedom (the number of tests minus the number of determined regression coefficients), which indicates the statistical significance of the equations obtained [20]. Figure 3 presents the curves of variation of properties computed from equations obtained for alloy 4 at the used heating temperatures. The maximum (for all the alloys) deviation of the individual experimental value of σ from the computed curve is observed for alloy 7 and amounts to 15 MPa at an average deviation of less than 6 MPa.

The regression coefficients b_1 and b_2 presented in Table 5 determine quantitatively the effect of process factors on the

TABLE 5. Coefficients b_0, b_1, b_2 of Eq. (1)

Alloy	X	b_0	b_1	b_2	R
1	σ_r	1.8064	412.77	0.04324	0.944
	$\sigma_{0.2}$	1.3320	604.03	0.07105	0.961
2	σ_r	1.8895	361.40	0.04182	0.977
	$\sigma_{0.2}$	1.4551	512.80	0.05663	0.969
3	σ_r	1.7218	452.97	0.04883	0.993
	$\sigma_{0.2}$	0.7674	878.81	0.10022	0.991
4	σ_r	1.6837	489.58	0.05748	0.988
	$\sigma_{0.2}$	1.0432	756.07	0.09066	0.990
5	σ_r	1.8901	388.12	0.04819	0.989
	$\sigma_{0.2}$	1.1937	692.37	0.07758	0.991
6	σ_r	1.8153	438.70	0.04735	0.979
	$\sigma_{0.2}$	0.9913	815.97	0.09661	0.967
7	σ_r	1.3537	673.98	0.07246	0.994
	$\sigma_{0.2}$	0.4289	1105.45	0.12814	0.991
8	σ_r	1.6162	533.56	0.07014	0.965
	$\sigma_{0.2}$	0.8157	901.86	0.12629	0.978
9	σ_r	1.5491	547.13	0.05799	0.977
	$\sigma_{0.2}$	0.6061	964.99	0.10222	0.983
10	σ_r	2.0565	298.01	0.03301	0.960
	$\sigma_{0.2}$	1.5037	525.79	0.06001	0.973
11	σ_r	2.0832	254.85	0.02755	0.980
	$\sigma_{0.2}$	1.6046	441.41	0.04312	0.952

values of strength characteristics and their decrease in overaging. The higher these coefficients are, the greater the decrease in the strength characteristics upon elevation of the heating temperature or growth in the hold time. Comparing the coefficients b_1 and b_2 in Table 5, we see that the yield strength is a more sensitive characteristic and decreases by a greater value than the ultimate rupture strength; the values of b_1 and b_2 for $\sigma_{0.2}$ are always higher than for σ_r . The equations for alloys 7 and 8, the maximum hardening of which is ensured by a mixture of hardening phases with leading Ω -phase, have the highest values of the coefficients.

The correlation dependence of the strength at room temperature on the corresponding coefficient b_1 or b_2 for all the alloys is presented in Fig. 4. This dependence reflects the existence of a rule common for all the alloys, i.e., growth in the strength in state Tl accelerates the softening during heating. Simultaneously with the strength characteristics high-strength alloys exhibit rapid growth in the electrical conductivity during overaging, which is also a sign of accelerated structural transformations in the alloys.

Thus, the Al – Cu – Mg – Ag alloys possessing the highest strength exhibit the fastest softening in heating in a temperature range of 180 – 210°C.

If we compare the softening of alloy 2 without silver with that of alloys 4 – 6 with silver additives at a low content

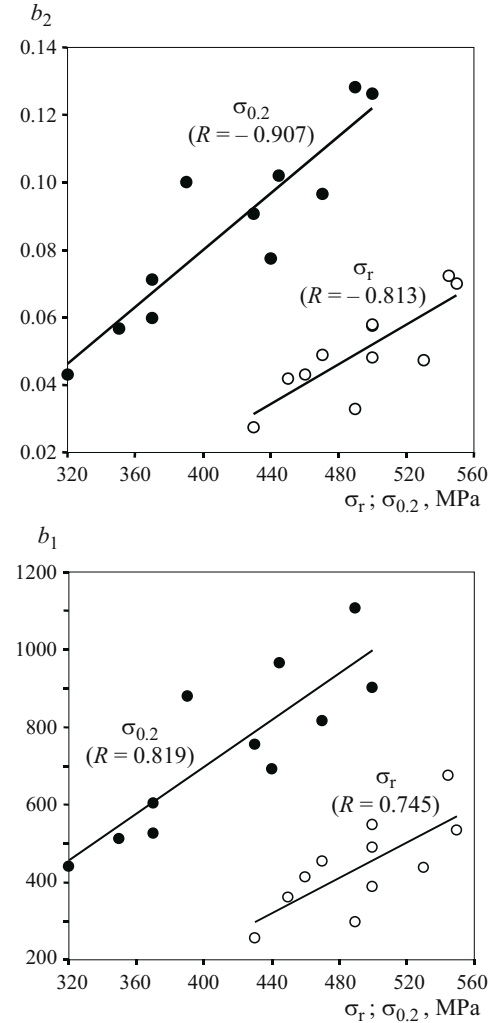


Fig. 4. Relation between strength characteristics of alloys in state Tl at room temperature and coefficients b_1, b_2 of Eq. (1). R is the coefficient of correlation between b and σ . $|R_{0.05; 9}| = 0.602$.

of magnesium (the hardening occurs primarily due to the Ω -phase), we see that the alloys with silver soften more rapidly. However, under specific conditions of overaging the sil-

TABLE 6. Coefficients b_0, b_1, b_2 of Eq. (2)

Alloy	b_0	b_1	b_2	R
1	1.6013	144.417	0.01908	0.914
2	1.5489	102.604	0.01662	0.954
3	1.6471	156.013	0.02032	0.988
4	1.6063	143.481	0.02100	0.989
5	1.5804	142.184	0.01750	0.973
6	1.5955	141.537	0.01880	0.967
7	1.7158	201.449	0.02555	0.982
8	1.6363	161.965	0.02717	0.946
9	1.6454	148.983	0.02417	0.940
10	1.4911	77.960	0.01149	0.898
11	1.4626	68.0195	0.01007	0.930

TABLE 7. Strength Characteristics of Alloys after Long-Term Heating (initial state $T1$)

Alloy	σ_r , MPa	$\sigma_{0.2}$, MPa	σ_r , MPa	$\sigma_{0.2}$, MPa	σ_r , MPa	$\sigma_{0.2}$, MPa	σ_r , MPa	$\sigma_{0.2}$, MPa
	180°C, 120 h		190°C, 96 h		200°C, 96 h		175°C, 1000 h (design values)	
1	420	325	415	310	392	295	400	295
2	395	296	385	280	370	265	370	270
3	420	315	400	300	380	260	385	270
4	450	340	425	315	400	285	400	290
5	450	370	425	335	415	320	410	320
6	480	390	470	370	450	340	450	335
7	495	405	465	360	425	320	440	325
8	440	350	420	315	405	300	395	280
9	430	330	410	305	390	280	395	285
10	450	350	440	340	415	315	420	315
11	390	305	380	305	365	280	370	290

ver-bearing alloys maintain their superiority with respect to the strength characteristics relative to the alloys without silver. It can be seen from Table 7 that the majority of alloys with silver have higher strength characteristics after long-term heating than alloy 2 without silver. Alloys 6 and 7 preserve the maximum strength despite their higher softening in coagulation aging. Alloy 8 has the highest strength in the initial state but loses its leading position due to the faster softening after long-term heating.

Tensile tests of specimens at room temperature after long-term heating have shown that the strength characteristics of the alloys decrease with respect to the initial condition due to coagulation of the hardening phases. These values of the strength characteristics are often called “restored strength” [14, 21]. The coefficients of equation (1) presented in Table 5 allow us to compute the restored strength after heating for several thousand hours [14]. Table 7 presents results of such computations for 1000-h heating at 175°C. They are close to the data obtained after 96-h heating at 200°C and reflect the same laws of variation of properties as mentioned above.

We can study the changes that occur in the structure of the solid solution in overaging using the curves describing the electrical conductivity. As an example, we present in Fig. 3 the curves for alloy 4. These changes satisfy Eq. (2), the coefficients of which are presented in Table 6. The coefficients have maximum values for alloys 7–9 where the structural changes cause a decrease in the strength characteristics.

Thus, silver additives in alloys of the Al–Cu–Mg system do not eliminate the strong softening in the range of 180–200°C, in which the thickness of the segregations of the Ω -phase is stable, and even increase the absolute value of the softening.

Thermal Activation Analysis of the Process of Coagulation Aging in Alloys with Different Compositions

The laws described by Eq. (1) are based on thermally activated processes of structural changes that occur in the coagulation of particles of the hardening phases. For this reason, the data obtained above can be used for determining the activation energy in the considered stage of overaging in different alloys for comparing it with the activation energy of diffusion of the main alloying components in aluminum, which is responsible for the temperature dependence of the process of coagulation of the hardening phases [22]. This energy was computed with allowance for fact that the rate of the reaction ν for many thermally activated processes depends on the temperature (T , K) in accordance with the Arrhenius equation [23]

$$\nu = \nu_0 \exp\left(-\frac{Q}{RT}\right), \quad (3)$$

where Q is the activation energy of the process, which determines the value of the change in the reaction rate upon a change in the temperature, kJ/mole, and $R = 8.31$ J/(mole · K) is the universal gas constant.

For the softening process in question its average rate in a specific interval of variation of the strength can be represented as $\nu = \Delta\sigma/\Delta\tau$, where $\Delta\sigma$ is the change in the yield strength and $\Delta\tau$ is the duration of the heating in which the softening occurs.

We assume that the change in the yield strength $\Delta\sigma_{0.2}$ is constant for all the alloys. The value of $\sigma_{0.2}$ varies from 320 to 300 MPa; this range is present on the softening curves of all the alloys. Equations of kind (1) and the data of Table 5 can be used for computing the duration of overaging τ_1 and τ_2 at each temperature, which is required for attaining these values of the yield strength, and then obtaining the values of $\Delta\tau = \tau_2 - \tau_1$ and ν for each alloy.

The results of computations of the average rate of softening for the given conditions are presented in Table 8. In the range of $\sigma_{0.2}$ considered the alloys exhibit different rates of softening at the same temperature due to the special features of the occurrence of structural transformations in the given alloy and due to the occurrence of the range $\sigma_{0.2}$ in different stages of softening with respect to the initial strength level. In all the cases the dependences of $\log \nu$ on $1/T$ in accordance with Eq. (3) are straight lines, the slope of which is determined by the quantity $Q \log e/R$. It can be seen from Table 8 that in alloys 1–7 with a high Cu/Mg ratio (21.2–9.0) the activation energy of the softening process is close and varies within 158–172 kJ/mole independently of the presence of silver in the alloys. Variation of the content of silver in alloys 8–11 with low Cu/Mg ratio causes considerable fluctuations of the quantity Q . The cause of these fluctuations has to be determined.

TABLE 8. Average Rates ν of Softening of Alloys at Different Overaging Temperatures and Activation Energy Q

Alloy	ν , MPa/h, for temperatures, K				$\frac{Q \log e}{R}$	Q , kJ/mole
	453	463	473	483		
1	0.0750	0.1907	0.4662	1.0989	8447.5	162
2	0.3361	0.9050	2.3529	5.8582	8998.3	172
3	0.2121	0.5556	1.3986	3.3898	8721.9	167
4	0.1003	0.2503	0.6006	1.3937	8280.7	158
5	0.0246	0.0656	0.1677	0.4118	8864.8	170
6	0.0223	0.0563	0.1369	0.3210	8394.9	161
7	0.0441	0.1136	0.2813	0.6714	8571.2	164
8	0.1232	0.2695	0.5714	1.1765	7101.7	136
9	0.1243	0.3508	0.9456	2.4480	9377.2	179
10	0.0230	0.0602	0.1513	0.3654	8703.7	167
11	0.1117	0.3429	1.0081	2.8289	10,172.0	195

The values of the activation energy computed for the studied alloys $Q > 160$ kJ/mole coincide with the activation energy of the process in similar alloys without silver obtained in [24], i.e., $Q = 162 - 202$ kJ/mole. The values of the activation energy of the diffusion of the main alloying components in aluminum known from the literature are much lower. For example, [21] gives $Q_{Cu} = 133$ kJ/mole, $Q_{Mg} = 123.5$ kJ/mole, and $Q_{Ag} = 118.6$ kJ/mole. In [26] the respective values are somewhat different but close, i.e., $Q_{Cu} = 136.1$ kJ/mole and $Q_{Mg} = 130.4$ kJ/mole. The authors of [27] note that the growth of segregations of the Ω -phase is controlled by the diffusion in the solid solution with activation energy $Q = 136$ kJ/mole.

Thus, the temperature dependence of the rate of the softening process in overaging does not correspond with respect to the activation energy to the process of diffusion of the main alloying components in aluminum. Only in alloy 8 does the activation energy of these two processes coincide. This means that the effect of the temperature on the softening that occurs in overaging is manifested not only through the variation of the rate of diffusion processes in the solid solution.

CONCLUSIONS

1. The strength characteristics of alloys of the Al – Cu – Mg system in the studied range of copper and magnesium contents increase due to silver additives in an amount of about 0.5 wt.% and attain maximum values in state TI at Cu/Mg ratio of 6 – 9, which corresponds to the middle part of the $\alpha + S + \theta$ domain of the ternary phase diagram.

2. For all the alloys studied, growth in the temperature within 180 – 210°C and increase in the duration of the overaging cause a decrease in the strength characteristics in accordance with the softening equation $\log \sigma = b_0 + b_1/T -$

$b_2 \log \tau$; the highest softening is observed in silver-alloyed alloys with maximum strength in state TI .

3. The alloys with maximum strength in state TI at room temperature preserve maximum strength at the test temperature of 175°C too. However, after long-term heating the proportion of the strength characteristics of different alloys changes and should be determined from experimental data or by computation from the softening equations.

4. The activation energy of the softening process does not depend on the content of silver and varies from 158 to 172 kJ/mole for alloys with Cu/Mg ratio ranging from 21 to 9, which exceeds the activation energy of diffusion of the main alloying components in aluminum by a factor of 1.2.

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