INVESTIGATION OF THE PHASE EQUILIBRIA IN ALUMINUM ALLOYS CONTAINING LITHIUM

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The results are given of investigation of a number of aluminum systems containing lithium including Al−Li−Sc, Al−Li−Mg−Sc, Al−Li−Mg−Si, and Al−Li−Mg−Cu. On the basis of an analysis of the phase interactions obtained in these systems their general rules are considered.

Interest in aluminum−lithium alloys is the result of the possibility of obtaining materials with a unique combination of high elastic modulus and low density and also with an increased specific heat and good cryogenic properties [1]. Four basic systems on the basis of which production compositions of alloys have been developed may be distinguished: Al−Mg−Li (1420, 1421, 1423) [1, 2]; Al−Mg−Li−Cu (1430, 1440, 1450, 2091, 8090, 8091) [2, 3]; Al−Cu−Li (VAD 23, 2020) [1-3].

Information on the phase diagram of Al−Mg−Li−Cu is very limited [4, 5]. In Al−Mg−Li system alloys an increased silicon content is allowed. In addition, to improve the corrosion resistance and plasticity transition metals such as Zr, Mn, and Sc are added to these alloys [2].

This article presents the results of investigation of alloys of the Al−Li−Cu−Mg, Al−Li−Sc, Al−Li−Mg−Sc, and Al−Li−Mg−Si systems and considers the phase diagrams of these systems.*

The alloys were melted in corundum crucibles in an electric resistance furnace and cast in 20-mm diameter thin-walled copper permanent molds. As the result of the high chemical activity of magnesium and lithium, the alloys were melted under a layer of flux of 80% LiF + 20% LiCl. The lithium was added in pure form with a content of it in the alloy of more than 2.5% or in the composition of Al−3% Li alloy.† Silicon, zirconium, scandium, and copper were added in the form of Al−12% Si, Al−1% Zr, Al−2% Sc, and Al−48% Cu alloys. A99 aluminum (99.99% Al), MG96 magnesium (99.96% Mg), MOb copper (99.96% Cu), metallic lithium (99.8% Li), zirconium iodide (99.9% Zr), semiconductor silicon, and SkM-1 Scandium (99.986% Sc) were used as the charge materials.

In order to ease production of alloys in the equilibrium condition before long annealing the 20-mm high samples cut from the ingots were worked by upsetting by 50% on a hydraulic press with a force of 1600 kN. The temperature of heating of the samples was 300-400°C. Then the samples were sealed in evacuated quartz ampuls with a residual argon pressure of $0.5 \cdot 10^5$ Pa and annealed in an electric furnace for 200 h at 400°C for alloys of the Al−Cu−Li−Mg and Al−Li−Mg−Sc systems and at 430°C for alloys of the Al−Li−Mg−Si system.

The investigation of the microstructure was made on NU-2E and Reichert microscopes with magnifications up to 1500×. Kelle's etchant (2.5 ml HNO_3, 1.5 ml HCl, and 1 ml HF in 100 cm^3 of water), a 0.1% solution of HF in water, and a mixture of aqueous solutions of HF in water, and a mixture of aqueous solutions of 5% HCl, 5% HNO_3, and 5% HF in a ratio of 1:1:2 were used for etching of the specimens. Specimens of the series of alloys were electrolytically polished in an electrolyte of 100 ml H_2SO_4, 400 ml of H_3PO_4, 50 g of CrO_3, and 25 ml of H_2O. The electrolytic polishing temperature

*V. V. Kinzhibalo, I. G. Korol'kova, E. V. Muratova, A. A. Oreshkina, A. T. Tyvanchuk, and A. S. Fridman participated in studying the phase diagrams.

†Here and subsequently wt.% of the elements is given.

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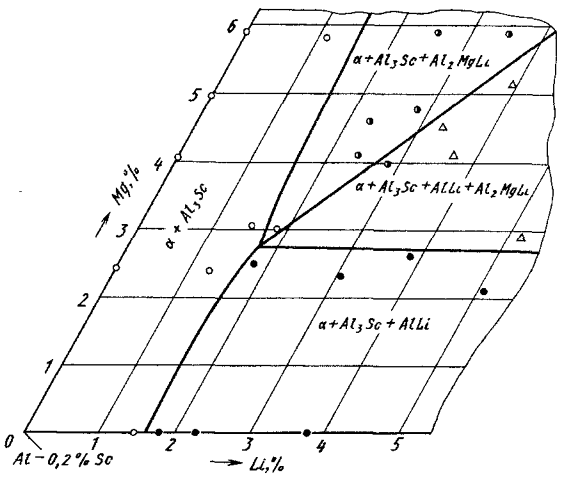

Fig. 1

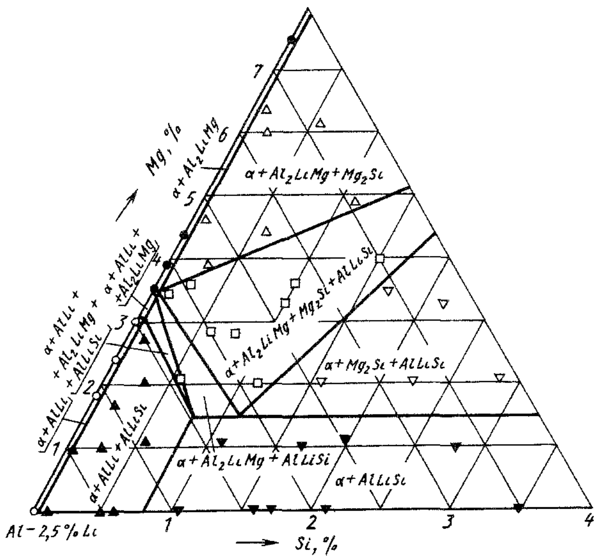

Fig. 2

Fig. 1. Section of the isothermal tetrahedron of the Al−Li−Mg−Sc system at 400°C.

Fig. 2. Section of the isothermal tetrahedron of the Al−Li−Mg−Si system at 430°C. Lithium content 2.5%.

was 70-90°C. A JEM-200A electron microscope was used to investigate the fine structure of the alloys. The foils were prepared by the electrolytic method in a 20% solution of perchloric acid in ethyl alcohol at −20°C with a voltage of U = 10 V.

The qualitative micro-x-ray spectral analysis was made on a JSM-U3 scanning electron microscope with a micro-x-ray spectral attachment and on a Spektrozond instrument.

Differential thermal analyses were made of specimens weighing from 30 mg to 10 g with use of a modernized PRT-1000 instrument in a flow of argon or under flux in a resistance furnace. The error in temperature measurement was no more than ±5°C.

The diffractograms of the specimens were recorded on a DRON-2.0 instrument in filtered K_α-radiation.

The investigations conducted made it possible to establish the phase compositions of alloys of the above systems, to determine the temperature and character of the nonvariant transformations, and to construct the polythermal and isothermal sections. The results of these investigations are given below.

The Al−Li−Sc System. Alloys of this system were investigated in the area of contents up to 5% Li and 3% Sc. Microstructural and x-ray diffraction analyses of alloys annealed at 450°C and thermal analysis showed the presence in equilibrium with the aluminum solid solution of two phases, Al_3Sc and AlLi. The AlLi phase corrodes in air and in an etchant of a mixture of aqueous 5% solutions of acids acquires a black color. Crystals of Al_3Sc phase are light gray. During thermal analysis they segregate along the height of the specimen. A nonvariant eutectic equilibrium occurring at ~595°C according to the reaction

$$L \rightleftarrows \alpha + Al_3Sc + AlLi \quad (1)$$

was established.

The Al−Li−Mg−Sc System. Alloys in the area of contents of up to 6% Mg and 5% Li with a constant scandium content of 0.2% were investigated. Microstructural and x-ray diffraction investigations made it possible to establish the presence of three phases, Al_3Sc, AlLi, and Al_2MgLi, in the structure of the alloys together with the aluminum solid solution. In the investigated area of contents of the elements no new ternary or quaternary phases were detected. All of the investigated alloys correspond to the phase areas $\alpha + Al_3Sc$, $\alpha + Al_3Sc + AlLi$, $\alpha + Al_3Sc + Al_2MgLi + AlLi$, and $\alpha + Al_3Sc + Al_2MgLi$. In the section of the isothermal tetrahedron there are boundaries between these areas at 400°C (Fig. 1).

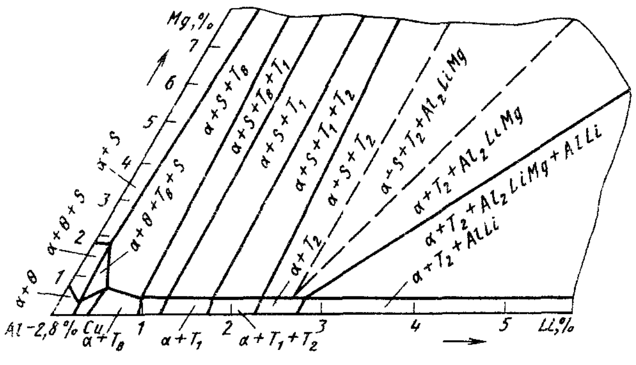

Fig. 3

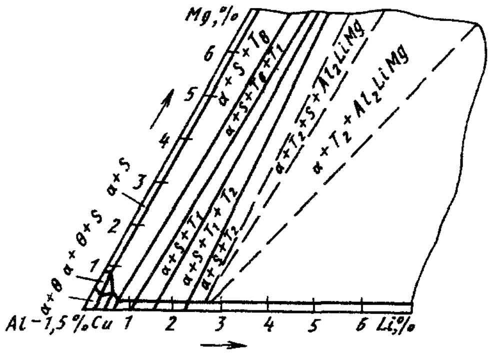

Fig. 4

Fig. 3. Section of the isothermal (400°C) tetrahedron of the Al−Li−Cu−Mg system with a constant 2.8% copper content.

Fig. 4. Section of the isothermal (400°C) tetrahedron of the Al−Li−Cu−Mg system with a constant 1.5% copper content.

The Al−Li−Mg−Li system. The section of the isothermal tetrahedron of the Al−Li−Mg−Si system at 430°C with a constant 2.5% lithium content, up to 7.5% Mg, and up to 2.5% Si was constructed (Fig. 2). The phases AlLi, Al_2MgLi, Mg_2Si, and AlLiSi (T) are found in equilibrium with the aluminum solid solution.

The Al−Li−Cu−Mg system. In contrast to the Al−Li−Sc, Al−Li−Mg−Sc, and Al−Li−Mg−Si systems which we first investigated there is some data on the Al−Li−Cu−Mg system in the literature. In [4] alloys of the quasiternary Al−Al_2CuMg(S)−Al_2CuLi (T_1) system were investigated by thermal and microstructural methods and fusibility curves of this system were drawn on the basis of data of three polythermal sections for 80, 70, and 50 at.% aluminum. However, production alloys are richer in aluminum than the alloys studied in [4]. In [5] alloys of the Al−Li−Cu−Mg system containing 2.0-2.7% Li, 0.5-2.8% Cu, and up to 1.5% Mg annealed in the 500-610°C range each 5°C were investigated by microstructural and x-ray diffraction methods. The temperatures of the solidus and solvus of the investigated alloys were determined and the mathematical relationships of these temperatures to alloy element contents were derived. In all of the investigated alloys one excess phase, which on the basis of x-ray analysis was identified as T_2 (Al_6CuLi_3), was observed.

An investigation made by us of Al−Li−Cu−Mg system alloys containing up to 6-7% Mg and 4% Li with a constant 3 and 1.5% copper content showed that the phase composition of the alloys is more complex than follows from [4, 5]. In the studied area of contents the phases T_B, T_1, and T_2 of the Al−Li−Cu system, Al_2LiMg of the Al−Li−Mg system, θ (Al_2Cu), S of the Al−Cu−Mg system, and AlLi of the Al−Li system are found in equilibrium with the aluminum solid solution. Identification of the phases was difficult as the result of their small size, small volume share, similar etchability, and form of the precipitate. On the basis of x-ray data the following phase equilibria were established:

$$\alpha \rightleftarrows S+T_B, \tag{2}$$

$$\alpha \rightleftarrows S+T_B+T_1, \tag{3}$$

$$\alpha \rightleftarrows S+T_2, \tag{4}$$

$$\alpha \rightleftarrows T_2+\mathrm{Al_2MgLi}, \tag{5}$$

$$\alpha \rightleftarrows S+T_1+T_2, \tag{6}$$

The presence in the alloys of θ and S (Al_2CuMg) phases was confirmed by micro-x-ray spectral analysis. The character of distribution of magnesium makes it possible to assume that there is some solution of it in T_1 and T_2 phases. Figures 3 and 4 show sections of the isothermal tetrahedra at 400°C drawn from a combination of data of various methods.

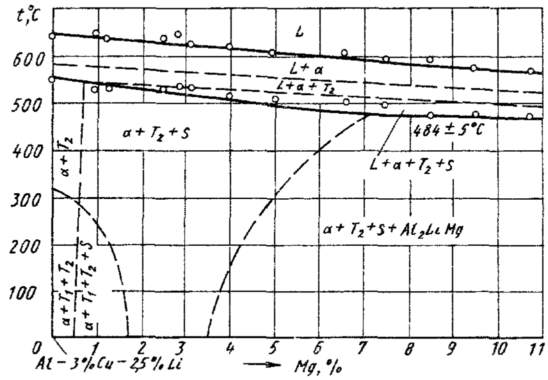

Fig. 5. Polythermal section of the Al−Li−Cu−Mg system with constant 3% copper and 2.5% lithium contents.

Both sections intersect five two-phase areas, $\alpha + \theta$, $\alpha + T_B$, $\alpha + T_1$, $\alpha + T_2$, and α + S; nine three-phase areas, $\alpha + \theta$ + S, $\alpha + \theta + T_B$, $\alpha + T_B + T_1$, $\alpha + T_1 + T_2$, $\alpha + T_2 + Al_2MgLi$, $\alpha + T_2$ + AlLi, $\alpha + S + T_B$, $\alpha + S + T_1$, and $\alpha + S + T_2$; and five four-phase areas, $\alpha + S + T_1 + T_2$, $\alpha + S + T_2 + Al_2MgLi$, $\alpha + T_2 + Al_2MgLi$, $\alpha + \theta + T_B$ + S, and $\alpha + S + T_B + T_1$. On the sections shown the boundaries of certain phase areas are conditionally designated by broken lines, which designate difficulty in identification of particles of phases in the alloys.

On the basis of the results of chemical, differential thermal, microstructural, and x-ray diffraction analyses two polythermal sections, one of which is shown in Fig. 5, were constructed. The section passing through the compositions of alloys with constant 3% copper and 2.5% lithium contents intersects the area of primary crystallization of the aluminum solid solution and also the plane of nonvariant equilibrium at 480°C. As the result of superimposition of thermal effects, thermal analysis did not make it possible to determine the phase areas within the range of crystallization and therefore the boundaries between them are conditionally designated with broken lines. The solidus lines are drawn on the basis of data obtained on the phase composition of alloys of this section in the annealed condition and taking into consideration data on the ternary Al−Li−Cu system. An analysis of the results obtained shows that alloying of Al−3% Cu−2.5% Li alloys with magnesium in the investigated range of contents leads to formation of ternary phases of S and Al_2MgLi and also to a reduction in the liquidus and solidus temperatures. At 484°C these phases participate in the nonvariant eutectic equilibrium

$$L \rightleftarrows \alpha + S + T_2 + Al_2MgLi. \quad (7)$$

In Al−Li−Cu−Mg system alloys the existence of four more nonvariant transformations is assumed:

$$L + T_B \rightleftarrows \alpha + S + \theta, \quad (8)$$

$$L \rightleftarrows \alpha + \theta + S + T_B, \quad (9)$$

$$L + T_2 \rightleftarrows \alpha + T_1 + S, \quad (10)$$

$$L + AlLi \rightleftarrows \alpha + T_2 + Al_2MgLi. \quad (11)$$

This assumption is based on the results of investigation of alloys of the section with constant 3% copper and 1% magnesium contents and also taking into consideration reference data on the ternary systems [7]. The complexity in construction of this section is related to the fact that it intersects a very large number of phase areas with narrow content ranges.

Therefore the investigations conducted showed that under equilibrium conditions a number of secondary phases the quantity and type of which depend upon the alloying system may form in the structure of production aluminum alloys.

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