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STRUCTURE, PROPERTIES AND APPLICATION OF ALLOYS OF THE Al – Mg – Si – (Cu) SYSTEM

N. I. Kolobnev,¹ L. B. Ber,¹ L. B. Khokhlatova,¹ and D. K. Ryabov¹

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A brief review of the reports of ICAA12 devoted to high-technology weldable alloys of the Al – Si – Mg system is presented.

Key words: alloys of the Al – Si – Mg system, phase transformations, intercrystalline corrosion, mechanical properties.

The largest part of reports (74) delivered at ICAA12 was devoted to results of studies of alloys of the Al – Mg – Si – (Cu) system. The interest in this system is explainable by the good combination of strength and corrosion properties of the alloys, high ductility and weldability.

From the end of the 20th century alloys of this series have been used actively in the automotive industry as substitutes for the traditional steels, which lowers substantially the weight of automobiles. The alloys are also used widely in the building industry, shipbuilding and electrical technology. Alloys with an additive of 0.5 – 1.1% Cu (AA6013, AA6056, 1370) possess an enhanced strength level suitable for aircraft. The volume of the production of these alloys in many countries exceeds that of heat-hardenable aluminum alloys of other systems.

Plenary report [1] presents the latest achievements in the determination of the atomic structure of hardening segregations in alloys of the Al – Mg – Si system with additives of Cu, Ag and Ge. The quality of modern transmission electron microscopes (TEM), the use of a recently developed method of quantitative analysis and high-speed computers makes it possible to solve the task of investigation of hardening segregations in these alloys at a new level.

In addition to traditional methods of phase analysis (x-ray diffraction analysis, conventional light and dark-background transmission electron microscopy (TEM) in combination with microdiffraction) the authors of [1] use advanced methods of research including high-resolution transmission electron microscopy (HRTEM) together with energy-dispersive x-ray spectroscopy (EDXS), circular scanning of dark-background images (CSDBI), and three-dimensional atom-probe tomography (3DAPT).

Segregations of β'' - and β' -phases have several modifications with close crystal structures and are denoted differently in the works of adherents of different schools, i.e., phases L , S , C and $U1$, $U2$ and B' , respectively.

The generally accepted sequence of phase transformations in the process of decomposition of supersaturated solid solution (SSS) of hardened alloys of the Al – Mg – Si system can now be presented as follows:

SSS – clusters – GP zones – β'' – β' , $U1$, $U2$, B' – $\beta(\text{Mg}_2\text{Si})$, Si .

In the case of copper-bearing alloys the sequence of phase transformations is

SSS – clusters – GP zones – β'' , L , S , C – Q' – $Q(\text{Al}_5\text{Cu}_2\text{Mg}_4\text{Si}_6)$.

It is known that the maximum hardness of alloys of the Al – Mg – Si system is provided by formation of hardening segregations of a β'' -phase.

At first the method of 3DAPT in combination with HRTEM was used to establish that the Mg/Si ratio (in atomic fractions) is 5/6, i.e., the β'' -phase has formula Mg_5Si_6 . The latest experimental data obtained by these methods with matching the intensity of the microdiffraction reflections to the design model by the method of least squares and minimization of the free energy of the system with allowance for the close packing of atoms of different sorts have shown that the most accurate composition of segregations of the β'' -phase is described by formula $\text{Mg}_5\text{Al}_2\text{Si}_4$. Such results explain the known fact that the maximum strength of alloys of the Al – Mg – Si system corresponds to Mg/Si ~ 1 rather than to Mg/Si = 2.

Substitution of some silicon atoms by aluminum atoms gives a considerable gain the free energy. Figure 1 presents

¹ All-Russia Research Institute of Aircraft Materials (FGUP “VIAM”), Moscow, Russia (e-mail: olanko@bk.ru).

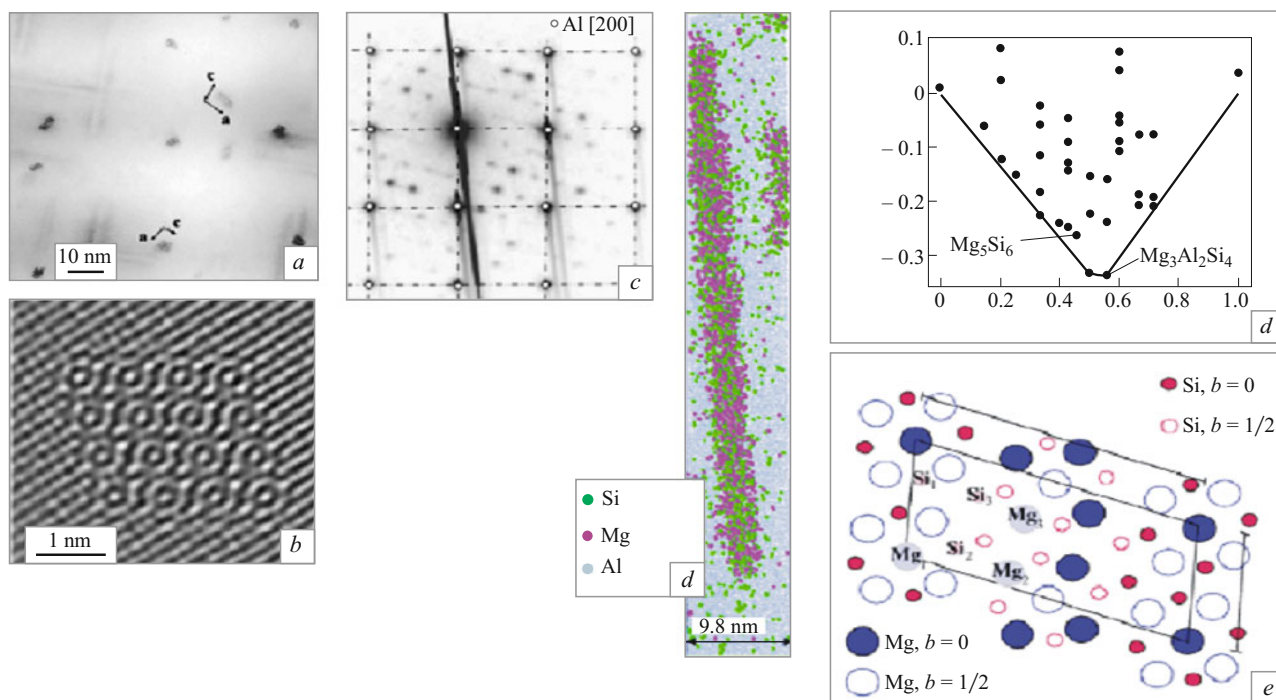


Fig. 1. Examples of determination of the crystal structure and chemical composition of segregations of β'' -phase in alloys of the Al – Mg – Si system by different methods: *a, b*) electron microscopy with medium-resolution TEM; *c*) microdiffraction; *d*) three-dimensional atom probe tomography; *e*) minimization of free energy; *f*) plotting a structural model of arrangement of atoms in the lattice of the phase.

the results of a study of the crystal lattice of the β'' -phase by the methods mentioned.

Computations have shown that substitution of some silicon atoms by atoms of aluminum gives a considerable gain in the free energy; substitution of atoms at positions Si3 is more favorable than substitution at positions Si1 and Si2. Silicon atoms at positions Si1 and Si2 form a spatial net with strong energy bonds, whereas at position Si3 they take places between the nodes of this net.

It is shown in Fig. 2 that the crystal lattices of hardening phases of type β' can be plotted on the basis of very close and somewhat distorted lattices of silicon atoms with an almost hexagonal cell, where the silicon atoms are located over close-packed directions oSi . In addition, the authors determine the lattice parameters of the segregated phases and find coincidences between the lattice parameter c of phases β' , U_2 , and B' and parameter a of the aluminum matrix.

Reports of Australian researchers [2 – 5] present results of HRTEM and 3DAPT studies of the crystal structure of hardening segregations in Al – Mg – Si alloys with excess silicon and in model and commercial alloys with a copper additive after natural aging of different duration and subsequent artificial aging. These data are compared to measured values of strength and ductility.

The products of decomposition of SSS are classified according to their sizes and morphology into (*I*) segregations (over 500 atoms), (*II*) about equiaxed coherent zones

(167 – 500 atoms), and (*III*) clusters (less than 167 atoms). The clusters are divided into three kinds according to their chemical composition, i.e., (*1*) with dominance of Mg atoms, (*2*) with dominance of Si atoms, and (*3*) (Mg + Si) clusters with $Mg/Si \geq 1$. The contribution of each of the decomposition products into the hardening is estimated for the case of their direct formation during low-temperature aging (LTA). The effect of clusters and zones formed as a result of LTA on the hardening after high-temperature aging (HTA) that corresponds to attainment of maximum strength is determined. These studies allow the authors to explain the known fact of negative influence of natural aging on the strength after artificial aging of the alloys of the system studied.

Natural aging is shown to be accompanied by growth in the volume fraction of extended decomposition products and in the strength of Al – Mg – Si alloys. In state T6 (maximum hardening) the strength of the alloys decreases upon increase in the duration of the natural aging before artificial aging, decrease in the volume fraction of elongated decomposition products (≥ 225 atoms), and growth in the volume fraction of fine aggregates (4 – 75 atoms). In state T6 the strength is provided by combination of equiaxed GP zones and acicular segregations of β' -phase. As a result of artificial aging after natural one, the clusters with dominance of Mg atoms dissolve for the most part. The clusters with dominance of Si atoms and (Mg + Si) clusters with $Mg/Si \geq 1$ are inherited

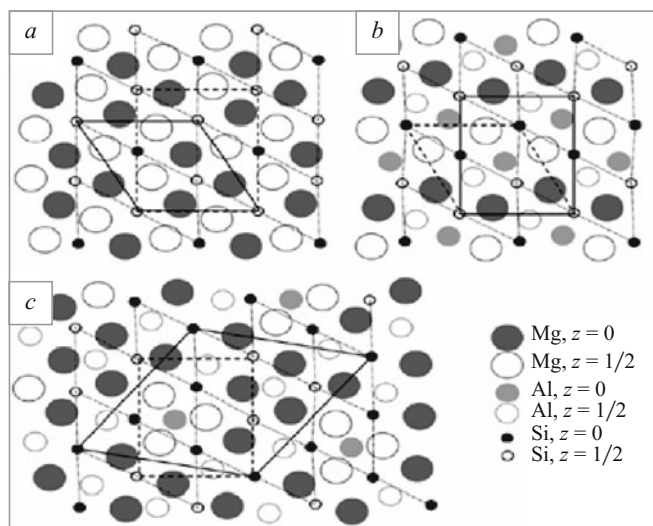


Fig. 2. Schemes of arrangement of atoms in crystal lattices of phases (axis $\langle 100 \rangle$ of the aluminum lattice with parameter $a = 0.405 \text{ nm}$ goes vertically): a) β' -phase; b) phase U2; c) phase B' .

and form more extended decomposition products. The GP zones precede the formation of segregations of β'' -phase.

Japan produces over 4 million tons of aluminum and its alloys a year, and the per capita consumption of aluminum in this country is the highest in the world. Beginning with the 1970s Japanese producers have persistently studied the crystal structure of decomposition products in alloys of the Al–Mg–Si–(Cu) system using various high-resolution methods (HTTEM, 3DAPT, etc.).

Eight reports on the topic were presented by Japanese scientists at the conference. Among them we should distinguish work [6] devoted to the action of an additive of 0.5 wt.% Ag on formation of the structure of segregations of β' -phase in alloy Al–1.0 wt.% Mg_2Si . The authors show that silver atoms concentrate at the angles of crystal cells of the β' -phase partially substituting silicon atoms and changing the symmetry of the lattice. The segregations of the β' -phase are fragmented. Silver atoms enrich the β –Al-matrix interphase and partially substitute aluminum atoms in the fcc solid solution.

The authors of [7, 8] have studied the effect of deformation on the structure and strength of sheets from Al–Si–Mg alloys in several states, namely, after 1-h artificial aging at 170°C (a cycle of painting of articles), quenching and natural aging, and aging for maximum strength at 100 and 180°C. In the first case an optimum strength has been attained at deformation with $\varepsilon = 3\%$. According to the data of TEM, the matrix contains uniformly distributed segregations of a β'' -phase. Growth in the strain ε suppresses the development of segregations in the matrix and initiates formation of coarse segregations of a β' -phase on dislocations. In the naturally and artificially aged conditions the test pieces are stretched with up to $\varepsilon = 10$. Studying the interac-

tion between the dislocations and the products of decomposition at 100°C (Mg + Si clusters) and 180°C (segregations of β' -phase) the authors show by DSC and TEM that under the natural aging the dislocations cut the clusters, while under the artificial aging the dislocations are fixed by segregations of the β' -phase.

Several reports of Japanese researchers [9–11] are devoted to optimization of the chemical composition of alloys with respect to the total content of the main alloying elements, the Mg/Si proportion, and the additional alloying with Cu and Ag.

It is shown in [9] (Australia) that a reduced content of magnesium and silicon in alloys 6060/6063 affects positively the rate of compaction. At the same time, growth in the total content of magnesium and silicon transfers a low-strength alloy to the group of medium-strength alloys. When the silicon content exceeds that of magnesium the strengthening effect is higher.

In [10] alloy Al–0.3% Mg–0.5% Si is enriched with a low (0.5–0.8%) content of copper to raise its hardness additionally upon artificial aging at 180°C. However, if the alloy has to serve for a long time (4300 h) at 90°C (for example, in an automobile radiator) it is inexpedient to introduce copper, because in both cases the levels of the yield strength are close. The results of DSC and TEM reflect different actions of copper additive on formation of β'' -phase at 90 and 180°C.

Reports [11, 12] consider the effect of Cu, Ag, and Au additives in alloy Al–0.6% Mg–0.35% Si and of Cr, Co, Mn, and Ni additives in alloy 1.06% Mg_2Si on their hardening in the aging process. In alloy Al–0.6% Mg–0.35% Si the highest effect at the aging temperature of 150°C is provided by additives of Cu and Cu + Ag. In aging at 300°C maximum hardening is attained in an alloy with Cu + Ag + Au due to the higher density of the segregations. In the 1.06% Mg_2Si alloy with an additive of Ni and Co aging at 200°C yields maximum hardness also at a high density of segregations of the hardening phases. In the alloys with Mn and Cr the formation of dispersoids with Si lowers the concentration of Si in the solid solution and the density of the segregations of the hardening phases in the artificially aged state.

Most 6XXX alloys of the Al–Mg–Si–Cu system have an elevated quenching sensitivity affecting their mechanical and corrosive properties. The authors of [13] (Australia) have shown that the main factor influencing the strength of the alloys is the density of the dispersoids determined by the temperature and time of the heating for solution annealing. When the quenching is performed with lowering of the cooling rate, the dispersoids become centers of nucleation of coarse nonhardening Mg–Si particles, and zone free of segregation of hardening phases appear in the metal. This leads to lowering of the concentration of Mg and Si phases in the solid solution and, as a consequence, to a reduced level of strength and hardness of the alloy.

Some reports of Japanese researchers are devoted to the task of raising the efficiency and widening the range of application of aluminum alloys. For example, [14] shows the efficiency of rapid high-frequency induction heating for heat treatment, which makes it possible to lower the duration of the heating and the consumption of power in the production of pressed bars from alloy 6061 with required mechanical properties.

The authors of [15] state that one of the main causes of limited use of aluminum alloys in automotive articles is the insufficient adaptability to deep drawing due to the specific texture of cubic orientation in aluminum sheets. It is shown that asymmetric warm rolling produces shear strain in aluminum sheets. A texture with an enhanced shear component forms over the thickness of the sheet and resembles the recrystallization texture of low-carbon steels. The texture is reserved even after recrystallization annealing and the reduction ratio is increased.

The problem of formation of an ultrafine-grain structure as a method of raising the strength of alloys is considered in [16, 17]. [16] is devoted to the use of severe plastic deformation (SPD) in rolling of alloys 6063 and 5052 in a special rolling mill with calibration rolls. The deformation produces shear strain over the thickness of the sheet. This raises not only the strength but also the elongation due to formation of a subgrain structure and uniform distribution of dispersed nanosize particles. The authors of [17] apply multiple angular pressing to alloy 6082 at 270 and 350°C in initial, annealed, and aged conditions. They obtain a homogeneous ultrafine grain structure with high dislocation density. About 27% of the grains have large-angle boundaries. However, the structure remains stable only for 5 min of heating at 270°C.

Several reports are devoted to formation of grain structure in the process of pressure treatment and heat treatment of alloys 6XXX [18 – 20].

Sheets from alloy 6111 of the Al – Mg – Si – Cu system are used to study the effect of segregations due to natural aging (T4), overaging (OA), and strong overaging (SOA) on the processes of retrogression and recrystallization that occur after cold rolling during annealing at 325 and 445°C [18]. For states T and OA after the annealing the fraction of recrystallization and softening is 0.3 – 0.5. In state SAO the structure is completely recrystallized at maximum softening, which is explainable by the occurrence of retrogression, coarsening of segregated particles, presence of segregation-free zones, and duration of the annealing.

Sheets with 1-mm thickness from technically pure aluminum after severe plastic deformation by rolling and subsequent annealing exhibit an ultrafine-grained structure, the formation of which is describable by the term “crushing of gains” [19]. In the deformation process neighbor slip regions with boundaries described as “geometrically necessary boundaries (GNBs) become off-oriented. The off-orientation of these regions increases upon growth in the plastic strain. In addition, the dislocations have a tendency to form low-energy configurations, the boundaries of which are called

“identical dislocation boundaries” (IDBs). The microstructure of the ultrafine grains obtained is close to a strain-induced one with elongated boundaries and a great number of dislocations and sub-boundaries, though the elongated ultrafine grains have higher off-orientation. The changes occurring in the structure in the annealing process may be called “continuous recrystallization” that is accompanied by recovery of the elongated ultrafine grains.

A study of the dependence of the grain size on the pressing parameters (the rate, the temperature, and the degree of strain) in direct pressing of alloy 6082 in a press that makes it possible to harden the bars right after the pressing, has shown that the thickness of the grains is independent of the temperature and rate of the pressing but depends on the equivalent plastic strain [20].

Reports [21, 22] are devoted to the effect of hydrogen on the results of fatigue tests of test pieces of alloys 6061 as compared to alloy 7075 and alloys of the 6XXX series. In the early stages of the fatigue tests the alloy is charged with hydrogen from the atmosphere. The concentration of hydrogen during testing decreases in proportion to the number of cycles. In alloy 7075 hydrogen charging is the highest. It is shown that hydrogen localizes at excess particles of phase AlFeSi in alloy 6061 and of phase Al₇Cu₂Fe in alloy 7075, which is responsible for formation of regions of brittle intergrain fracture. Introduction of copper into alloys of series 6XXX lowers their susceptibility to hydrogen charging in the process of fatigue tests. The alloys contain no embrittled regions.

Alloys of series 6XXX belong to the corrosion-resistant group, but segregation of secondary phases [β (Mg₂Si) and Q (Al₁₄Si₇Mg₈Cu₂)] can lead to the appearance of intercrystalline corrosion (IC). Studies of the kinetics of the IC and pitting corrosion of alloy 6111 in underaged, aged for maximum strength, and overaged conditions have shown that the degree of corrosion damage increases with growth in the hardening [23]. The copper-enriched phases on grain boundaries behave as cathodes and create microscopic galvanic couples with the adjacent zones with reduced content of Cu and Si, which intensifies the IC. In the stage of overaging the susceptibility of the alloy to IC and the degree of the hardening decrease. The test pieces after aging are cooled in air, though there are data that water cooling increases the corrosion resistance.

Work [24] concerns plates from domestic alloy 1370 of the Al – Mg – Si – Cu system. It is shown that low-temperature thermomechanical treatment and multistage aging can provide effective decrease in the susceptibility of the alloy to intercrystalline corrosion and growth in the strength properties. After the use of cold rolling or tensile deformation between the quenching and the three-stage aging of plates with a thickness of 12 – 20 mm the depth of the IC does not exceed 0.1 mm and the rupture strength σ_r attains 425 – 440 MPa. Stage aging by mode T78 of alloy 6056 with a close composition decreases σ_r to 365 MPa and removes the

susceptibility to intercrystalline corrosion in the presence of pitting with a depth of 0.16 mm.

CONCLUSIONS

Aluminum alloys of the Al–Mg–Si and Al–Mg–Si–Cu system are used widely in the automotive industry, railroad transport, instrument making, and the building industry due to the combination of corrosion resistance, strength, and ductility. The ample research of these alloys is devoted to the laws of the action of their composition including the Mg/Si proportion and microadditives of transition alloys on the structure, phase composition and properties. Active interest is attracted to the causes of the appearance of intercrystalline corrosion in alloys of the systems and to the ways for raising their resistance to this kind of corrosion. Modern methods of study make it possible to determine not only the fine structure of the alloys but also the lattice parameters of the phases, and the distribution of the alloying elements. This allows the researchers to raise to a higher level of understanding of the dependence of the macroproperties of the alloys on their microstructure.

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