The effect of transition metals on the structure and hardening of Al-Mg-Si alloys after cold plastic deformation

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Abstract. The effects of equal-channel angular pressing (ECAP) and rotary swaging (RS) on the change in strength properties during aging at 170 °C of Al-Mg-Si alloys doped with Sc, Zr and Hf additions was studied. The methods of measuring hardness, electrical resistivity, testing mechanical properties, light and transmission electron microscopy were used. The higher hardening effect compared to the initial state was found in the alloys after ECAP than after RS, whereas the strength properties (tensile strength and yield strength) were higher for alloys subjected to RS than ECAP. Al-Mg-Si alloys with the combined additives of scandium with zirconium and scandium with hafnium showed practically the same values of hardness and strength properties at tensile testing during aging. The reason is in the identical nature of the decomposition of the supersaturated solid solution. It is determined by the sequence of precipitation of the strengthening phase Mg2Si and (Sc1x, Zr1x) Al3 and (Sc1x, Hf1x) Al3 dispersoids which impede the movement of dislocations both in alloys after deformation and after aging.

The strength characteristics of a wide range of metal materials can be significantly improved by using severe plastic deformation (SPD) in the processing of bulk metals and alloys at the expense of considerably refining the grain structure. For example, one of the methods of SPD, equal-channel angular pressing (ECAP), provides a material with ultrafine-grain structure [1]. However, despite the high level of strength, the successful use of such materials in industry also requires a sufficiently high ductility. It can be achieved by various heat treatments, which was shown by the example of Al – Mg – Si alloys in a number of works [2–4].

The strength properties of Al – Mg – Si alloys can be improved by such transition metals as Ti, V, Cr, Mn, Zr [5]. Additionally, these transition metals increase the recrystallization temperature of alloys. The effect of another rare earth element Sc on increasing the temperature of recrystallization is much tangible than any of the above-enumerated transition metal. In addition to an increase in the temperature of recrystallization, Sc contributes to higher hardening owing to the precipitation of ScAl3 hardening particles from the solid solution. Usually, Zr is added into the alloys combined with Sc.

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Zirconium dissolves in ScAl3, producing (Sc1-x, Zrₓ) Al₃ dispersoids. These dispersoids retain high dispersion thereby restraining the recrystallization and strengthening the aluminum matrix [6-8]. Zr additions simultaneously reduce the Sc content in alloys.

Al – Mg – Si alloys belong to dispersion hardening alloys with the Mg₂Si hardening phase, which in the first stage of aging appears as coherent particles of the β'' phase, then as the metastable phase β' and the stable phase of Mg₃Si [9]. Doping with transition metals, in particular, Sc and Zr, does not change the decomposition of the supersaturated solid solution, but gives an additional strengthening effect. A similar effect was observed by the addition of Hf introduced into the alloys together with scandium [7].

The influence of ECAP on the microstructure and hardening processes of Al-Mg-Si alloys, such as AA6082, AA6005, AA6063, was studied in a number of works [10-17]. Combining SPD and heat treatment in order to obtain a fine-grained structure with a high degree of supersaturation of the solid solution results in a significant increase in the hardness, strength, and ductility of these alloys.

In the present work, the effect of equal-channel angular pressing (ECAP) on the microstructure and strength properties of Al-Mg-Si alloys with combined (Sc + Zr) and (Sc + Hf) additions is investigated. In addition to ECAP, rotary swaging (RS) was used as industrial type of plastic deformation.

1. Experimental

The study was carried out on alloys made of high-purity materials, hereinafter, % is indicated by weight: Al of grade A99 (> 99.99%), Mg of grade Mg96 (> 99.96%), Si monocrystalline, semiconductor grade > 99.999%, Sc purity> 99.875%, Ti, Zr and Hf (iodide, 99.8% pure). The compositions of the alloys were close to the pseudobinary section of Al-Mg₃Si. The alloys were based on Al, the content of other elements was as follows: 0.75% Mg, 0.42% Si, 0.05% Ti and an additional 0.2% Sc and 0.15% Zr and Hf. Alloys were smelted in an electric resistance furnace in a graphite-chamotte crucible and cast at a temperature of ~720°C in a steel mold with a diameter of 25 mm and a height of 120 mm. 2 ingots of each composition were smelted. After casting and turning to a diameter of 20 mm, the ingots were first homogenized for 4 hours at a temperature of 480 °C, and then after heating at 525 °C for 2 hours quenched in water at room temperature. The ingots were subjected to rotary swaging to a diameter of 8 mm and ECAP at room temperature. ECAP was carried out along the Bc route, after each passage, turning the ingot around the longitudinal axis by 90 °; the angle of intersection of the channels was 120 °. After these treatments, the deformed samples were aged at a temperature of 170 °C during periods from 0.5 up to 16 hours.

Samples were investigated by methods of measuring hardness and resistivity, testing of mechanical properties and TEM analysis. Hardness was measured according to the Brinell method by indenting a steel ball with a diameter of 2.5 mm under a load of 62.5 kg on an IT-5010-01M testing machine with an electronic reading system. The electrical resistivity was measured using a BSZ-010-2 microohmmeter on cylindrical samples with a diameter of 6 mm and a working region length of 27.5 mm. Transmission electron microscopy was performed on a JEM-2100 microscope at an accelerating voltage of 200 kV. Thin foils for observations were ground to a thickness of about 150 μm with abrasive paper with final thinning and obtaining foils with holes by ion bombardment. The mechanical properties were determined by tensile tests on specimens cut in the longitudinal direction with a diameter of 3 mm on an Instron-3382 machine with a tensile speed of ~ 1 mm/s.

2. Results and Discussion

The values of the hardness and electrical resistivity of Al-Mg2Si alloys with Sc, Zr and Hf additions after ECAP vs periods of aging at 170°C, are shown in figure 1.
The dependence of hardness (a) and electrical resistivity (b) of alloys 1-3 after ECAP vs the aging time at 170°C: 1 - Al-Mg$_2$Si, 2 - Al-Mg$_2$Si (Sc+Zr), 3 - Al-Mg$_2$Si (Sc+Hf).

Figure 1.

The highest values of hardness for all alloys were achieved almost in the first hours of aging (0.5-1h), then the hardness began to decrease, that was especially noticeably in an alloy without transition metals (1) after 2 hours of aging. Moreover, the hardness of alloys doped with (Sc + Zr) and (Sc + Hf) additions was almost the same. The values of electrical resistivity gradually decreased with increasing aging time up to 8 hours, and then remained practically unchanged. According to the changes in the electrical resistance, the decomposition of the solid solution at 170°C in the alloys subjected to ECAP ended after 8 hours of aging, although the hardness continued to decrease probably due to the coagulation of particles of the precipitated phases.

The change in hardness and electrical resistivity of alloys subjected to RS before aging is shown in figure 2.

The dependence of hardness (a) and electrical resistivity (b) of alloys 1-3 after cold RS vs aging time at 170°C: 1 - Al-Mg$_2$Si, 2 - Al-Mg$_2$Si (Sc+Zr), 3 - Al-Mg$_2$Si (Sc+Hf).

Figure 2.

As in the case of alloys subjected to ECAP, alloys containing no transition metals had lower hardness values (1), and the hardness values of alloys with Sc + Zr were close to the hardness values of alloys with (Sc + Hf). The highest hardness was achieved after 1 hour of aging, and a sharp drop in hardness was observed after 4 hours in alloys with transition metals and after 2 hours in alloys without transition metals. The most noticeable decrease in electrical resistivity occurred after 2 hours of aging, then its fall rate slowed down, and after 8 hours of aging remained at a constant level. A continuing decrease in hardness after reaching a constant value of electrical resistivity can be associated with the coagulation of the hardening phases released from the solid solution.

The hardness and electrical resistivity for alloys without deformation after quenching are presented at the figure 3. During the process of aging, a smooth increase in hardness and a decrease in electrical
resistivity were observed. After the 16 hours of aging the alloys deformed by RS or ECAP nearly softened, while the undeformed alloys reached maximum hardening. This process was observed up to the 50 hours of aging, however, the strength level was much lower (~ 200 - 230 MPa), compared with the strength of the alloys after quenching, deformation and aging for 1-2 hours.

Figure 3. The dependence of hardness (a) and electrical resistivity (b) of quenched alloys 1-3 vs the aging time at 170°C: 1 - Al-Mg$_2$Si, 2 - Al-Mg$_2$Si (Sc+Zr), 3 - Al-Mg$_2$Si (Sc+Hf).

The difference in the behavior of the alloys was determined by the fine structure formed in the process of deformation and aging. The structure of the quenched alloy (2) after 16 hours of aging at maximum hardness consisted of dislocation loops and networks of high density dislocations and tiny particles $\beta''$ in the form of needles (figure 4 (a, b)). Also, a large number of small inclusions of (Sc$_{1-x}$Zr$_x$)Al$_3$ dispersoids surrounded by elastic strains in the form of two dark crescents were observed in the structure. After 50 hours of aging a metastable $\beta'$ phase in the form of rods appeared in the alloy structure (figure 4 (c)). In the photomicrography of the Al-Mg$_2$Si (Sc+Zr) alloy sample after RS the simultaneous precipitation of $\beta''$ and $\beta'$ phases, as well as dispersoids (Sc$_{1-x}$Zr$_x$)Al$_3$ (figure 4d-f) were observed. $\beta''$ particles are clearly visible in the photo in a dark field (figure 4 (e)) in the form of thin needles up to 30 nm in length. $\beta'$ particles in the form of 50–100 nm rods are shown in figure 4 (d), and the point precipitates of dispersoids (Sc$_{1-x}$Zr$_x$)Al$_3$ about 40-50 nm in size in figure 4 (d - f).

Figure 4. TEM structure of Al-Mg$_2$Si+(Sc+Zr) alloy after quenching and aging at 170°C after 16 h (a, b) and 50 h (c) and after rotary swaging (d-f)
It should be noted that during the aging process after quenching, the phases appear in accordance with the established sequence $\beta'' \rightarrow \beta' \rightarrow \beta$ [9]. However, after quenching and cold deformation (RS and ECAP), the phases $\beta''$ and $\beta'$ appear simultaneously.

![Figure 5. TEM structure of alloy 3-Al-Mg$_2$Si+(Sc+Hf) after RS (a, b) and ECAP (c, d)](image)

In contrast to alloy 2 with additives (Sc + Zr), no precipitation of $\beta''$ particles was observed in the structure of alloy 3 with additives (Sc + Hf) after RS (figure 5). Only the precipitations of the $\beta'$ phase and particles (Sc$_{1-x}$Hf$_x$)$_3$Al$_3$ (figure 5 (a, b)) were visible. In the dark field, the point precipitates of the dispersoids (Sc$_{1-x}$Hf$_x$)$_3$Al$_3$ were observed (figure 5 (b)). After ECAP, the structure of alloy 3 was similar to that after rotary swaging (figure 5 (c, d)). In figure 5 (d) the precipitation of the $\beta'$ phase in a dark field on an enlarged scale and the absence of needle particles $\beta''$ are clearly seen.

The hardness and electrical resistivity of the alloys subjected to hardening of ECAP and RS have similar behavior. Hardness during aging at 170°C showed a continuous decrease after reaching a maximum at 16 hours of aging, and we can assume its further decrease. On the other hand, the drop in electrical resistivity practically stopped after 8 hours of aging that is the evidence of the completion of the decomposition process at the used temperature. The alloy hardness after ECAP is higher than after rotary swaging. The reason is in a stronger distortion of the crystal lattice. It should be noted that the hardness values of alloys containing (Sc + Zr) and (Sc + Hf) additions are almost the same. The aging time 1-2 hours was chosen to determine the mechanical properties for both alloys after ECAP and after RS corresponding to with a maximum in hardness dependences during aging at 170°C. The electrical resistivity in this aging time interval for alloys after RS has not yet begun to decrease, whereas for alloys after ECAP, the electrical resistivity decreased immediately after beginning of exposure at 170°C, since not only the decomposition of the solid solution took place, but also the removal of high stress obtained in the process of ECAP. The results of mechanical properties of samples after ECAP and RS with aging at 170°C for 2 hours are shown in figure 6.
Figure 6. Mechanical properties of Al-Mg-Si alloys with additives (Sc + Zr) (2) and (Sc + Hf) (3) after RS and ECAP and aging at 170 °C for 2 hours

One can see that the ultimate tensile strength and yield strengths of the alloy without transition metals (1) after ECAP and aging are lower than the similar properties of alloys with transition metals (2, 3), for example, for alloy (3) with (Sc + Hf) by 15 and 34 MPa, respectively. The ultimate tensile strength and yield strengths of alloys after RS and aging are higher than after ECAP, both for alloys with and without transition metals. The ultimate tensile strength and yield strengths of alloy with (Sc + Hf) (3) after rotary swaging are higher than similar properties after ECAP by 23 and 12 MPa, and without transition metals by 12 and 42 MPa, respectively. The relative elongation of alloys with transition metals is about 10%, compared with 7-9% for alloys without transition metals.

The analysis of the mechanical properties showed that the ultimate tensile strength and yield strengths of the alloys after RS were higher than after ECAP, while hardness was higher after ECAP. This may be due to the evolution of the microstructure during ECAP and RS, with a higher dislocation density during ECAP compared with RS and a significant effect of texture after cold deformation on mechanical properties.

3. Conclusions
1. The effect of cold plastic deformation by ECAP and RS methods and subsequent aging at 170°C on the strength properties of Al-Mg2Si alloys doped with (Sc + Zr) and (Sc + Hf) was studied. The greatest hardening of the alloys was achieved after 2 hours of aging for all studied alloys, regardless of the presence or absence of transition metals. However, the strength properties of alloys doped with transition metals are higher than that of unalloyed.
2. It has been shown that the hardness of Al-Mg2Si alloys, both unalloyed and alloyed with transition metals, is higher by 40-60 MPa when ECAP is used as a deformation, compared with RS. At the same time the ultimate tensile strength is higher for alloys after RS than after ECAP by ~ 12 (unalloyed) and ~ 23 MPa (alloyed) correspondingly.
3. It was found that Al-Mg2Si alloys with the combined additions of scandium with zirconium and scandium with hafnium showed the same behavior of the hardness and resistivity during aging and almost the same values of strength properties during tensile testing.

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