The Influence of Zirconium and Silicon Additions on the Microstructure and Hardening of AI–2% Mn Sheet Alloys

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Abstract

The structure and mechanical properties of ingots and rolled sheets of Al–Mn–Zr–Si alloys containing 2% Mn, 0–4% Si, and 0–1% Zr (wt.%) have been studied. Small addition of silicon substantially accelerates the strengthening of Al-Zr alloys, which is associated with the formation of the metastable Al₃Zr phase during annealing. Rolling of foundry ingots with 0.5% Zr and 0.2% Si, followed by annealing at 400 °C, makes it possible to obtain the strength values that are much higher than those achievable for AA3003-type commercial alloys (UTS - 240 MPa instead of 150 MPa).

1. Introduction

Wrought aluminum alloys of the AA3003 type with Mn addition are characterized by the optimum combination of technological properties (deformability, weldability) and corrosion resistance [1–2]. However, their strength properties are low (UTS < 200 MPa), though exceeding the level achievable for Al–Fe–Si alloys (1XXX series and AA8111 type) [2-4]. This disadvantage restricts the application of these alloys considering a higher strength can be generated by using Al–Mg–Si alloys of the 6XXX series, which retain some advantages of wrought AA3003 alloys. However, the strengthening in alloys of the Al–Mg–Si system is achieved after heat treatment (for example T6) including quenching in water, which requires special equipment for many kinds of wrought products. Moreover, these alloys can be used only at a temperature not higher than 200°C; otherwise the strengthening effect associated with secondary precipitates of metastable modifications of the Mg₂Si phase (β' and β'') disappears.

On the other hand, it is known that the substantial precipitation-hardening effect can be obtained by adding small (0.2–0.3%) amounts of Sc [5]. In this case, the strengthening due to the formation of Al₃Sc dispersoids (Ll₂) is achieved by annealing at 250–350°C after casting. Unfortunately, scandium is extremely expensive and, therefore, its wide application in commercial aluminum alloys seems to be not realistic. A similar effect can also be obtained if Zr addition (0.5-0.8%) is used in place of Sc, because the metastable modification of the Al₃Zr phase, which precipitates from the supersaturated aluminum solid solution, is isomorphic to the stable Al₃Sc phase [6-8].

Since silicon has a substantial effect (along with iron, the role of which requires special consideration) on the phase composition of Al–Mn alloys, we have used alloys of the Al–Mn–Zr–Si system for the present investigation. In contrast to zirconium, which does not form any phases with manganese, silicon may form an $AI_{15}Mn_2Si_3$ compound, in particular, in the form of secondary precipitates instead of the binary AI_6Mn aluminide. Moreover, according to [9], a small addition of Si has a positive effect on the morphology of AI_3Zr dispersoid particles.

Based on the above consideration, we specify the following tasks:

1. To study the effect of Zr and Si on the structure and mechanical properties of Al-2 wt.%Mn alloy;

2. To study the possibility of developing new wrought Zr-containing aluminum alloys, which would be superior to commercial AA3003-type alloys in strength and comparable with them in other properties.

2. Experimental Methods

For the purposes of the present investigation, we chose Al–Mn–Si–Zr alloys containing 2 % Mn, 0–1% Zr, and 0–4% Si (Figure 1). Alloys were prepared from 99.95% aluminum, 99.99% silicon, and master alloys (Al–10% Mn and Al–3.5% Zr) in an electrical resistance furnace using graphite-chamotte crucibles. Alloy preparation and pouring temperature was about 900 °C (above liquidus for alloys containing up to 0.8% Zr) to obtain the maximal zirconium concentration in the aluminum solid solution - (Al) after solidification [6-8]. The studies were carried out on ingots (15 x 30 x 180 mm) obtained by casting using graphite molds at a cooling rate of about 10 K/s. Ingots were heat-treated at 400–600°C in a muffle electrical furnace, with an acuracy of ~3 K. Ingots were rolled on a laboratory mill in 12 runs with a starting temperature of 300°C followed by subsequent runs without heating. The thickness of resulting sheets was ~2 mm, which corresponded to \approx 87% reduction.

The structure of alloys was examined by the methods of optical, scanning electron and transmission electron microscopy (using a Neophot-30, JSM-35CF, and JEM-2000EX instruments, respectively), and also electron microprobe analysis (JSM-35CF) hereafter referred to as OM, SEM, TEM, and EMPA. Polished sections of specimens were prepared by electropolishing in a chlorine-alcohol electrolyte and were additionally oxidized to reveal the structure of grains in the optical microscope. Specimens (foils) for transmission electron microscopy were prepared in a chlorine-alcohol electrolyte. Electron-microscopic studies were conducted at an accelerating voltage of 120 kV.

Conventional methods were used to measure the hardness of specimens (Brinell hardness - <u>HB</u> on ingots and Vickers hardness -<u>HV</u> on sheets). Plane specimens of 10 x 160 mm in size were cut from sheets, which were then separated into three 20-mm zones for tensile tests (at a strain rate of 4 mm/min). Elongation was calculated in the zone of failure. The typical deviations from average values of mechanical properties given in Table 1 were: 10 MPa (UTS), 2% (EI), and 3HV.

3. Experimental Results and Discussions

Analysis of binary and ternary phase diagrams [1] and other known data pertaining to the selected system was done for preliminary assessment of the possible phase composition and the main characteristics of the microstructure of Al–Mn–Si–Zr alloys in the aluminum

corner of the diagram. This analysis show that the only Al₃Zr, Al₆Mn, and Al₁₅Mn₂Si₃ phases can solidify primarily as well as (Al). Since the primary crystals of these phases should not be present in the desired structure, we chose Al–2% Mn as a base composition, because at such concentration Mn almost completely enters in (Al) in casting, as was confirmed by the SEM and EPMA data. On the other hand, in order to obtain the best strength properties, it is desirable to have in the as-cast (Al) not only the maximum content of Mn, but also Zr and Si with the aim to obtain in the subsequent annealing the largest amount of secondary precipitates, in particular, Al₃Zr and Al₁₅Mn₂Si₃. If the lack of primary crystals of the Al₃Zr phase in the as-cast condition means the complete presence of Zr in (Al), then Si, along with its dissolution in (Al), can solidify in the form of free silicon-(Si), as well as can enter in the composition of eutectic inclusions of the Al₁₅Mn₂Si₃ phase.



Figure 1: Boundary of primary crystals of AI_3Zr phase in the Al-Mn-Zr-Si system at 2% Mn (a) and microstructure of typical alloys (as-cast, SEM): 1% Zr (b); 1% Zr, 2% Si (c); 0.75% Zr, 0.5% Si (d).

Figure 1a shows the compositions of the experimental alloys and the phase boundary in the Al-2% Mn-Si-Zr section in the as-cast state. As follows from this figure, there are no primary crystals of zirconium aluminide in silicon-free alloys containing up to 0.75% Zr. They are present in small amounts only in the alloy with 1% Zr (Figure 1b). Silicon reduces the maximum solubility of Zr in (AI), changing the morphology of AI₃Zr crystals to needles (Figure 1c). However, this reduction largely manifests itself at small Si concentrations (up to $\sim 1\%$); at higher Si concentrations, the observed effect of Si is insignificant. In particular, the primary crystals of the Al₃Zr phase in alloys with 4% Si and 0.5% Zr were not found. The results also imply that Zr does not affect substantially the boundary of appearance of the eutectic silicon, which lies in the concentration range 0.2-0.3%. At higher Si content (in allov), the structure contains eutectic inclusions of the Al₁₅Mn₂Si₃ and (Si) phases (Figure 1d). In this case, the Mn concentration in (AI) decreases and the content of Si in (AI) increases. Analysis of the kinetic HB curves shows that Si addition (beginning from 0.2%) substantially accelerates the process of precipitation hardening. Comparison of silicon-free alloys shows that hardening in the alloy with 0.75% Zr is higher than in the alloy with 0.5% Zr (Figure 2a). However, an increased Zr concentration leads to the formation of regions with cellular decomposition [8], which is less desirable than the uniformly distributed spherical Al₃Zr particles. The regions of cellular decomposition were not found in an Al–2% Mn-0.5% Zr-0.2% Si alloy, which is probably caused by the action of two factors: a decreased Zr concentration and the presence of small amounts of Si [9]. As follows from Figure 2a, Zr addition does not lead to substantial solid solution hardening. The main

effect is associated with Al₃Zr dispersoids, the quantity of which increases up to the limit of solubility in the as-cast state. The influence of Si (Figure 2b) is determined by the four factors: (1) solid solution hardening in the as-cast state, which is determined by the Si concentration in (Al); (2) the distribution of Si between (Al) and Al₁₅Mn₂Si₃ and (Si) eutectic particles; (3) the formation of secondary precipitates of Al₁₅Mn₂Si₃ and (Si) in annealing; (4) the effect on the morphology of Al₃Zr dispersoids. As can be seen from Figure 2b, the increase of Si content in alloy leads to certain reduction of hardening effect, which is probably due to the decrease of Si concentration in (Al). As a consequence, the increase in the hardness of an Al–2% Mn–4% Si–0.5% Zr alloy caused by annealing is lower than that in an Al–2% Mn–0.2% Si–0.5% Zr alloy. Taking into account the absence of the nonequilibrium eutectic in the alloy with 0.2% Si (this factor affects on resistance to formation of hot cracks in ingots and in fusion welding), we chose this concentration for further investigation.



Figure 2: Hardness (HB) of the Al–2%Mn–Zr–Si alloys versus concentration of Zr (a) and Si (b): F– as-cast, T– annealing at 400 °C for 6 hours.

At the second stage, a comparative analysis was done of the structure and mechanical properties of sheets made of four alloys (Table 1). This allowed us to reveal the effect of Si and Zr. Alloys with Zr (nos. 1–2) were studied in the four states: TX1, TX2, TX3, and TX4. Zirconium-free alloys (nos. 3–4) were investigated only in the TX1 and TX3 states. All the sheets were of sufficiently high quality: no macro- and microdefects were found in them.

Analysis of ultimate strength (UTS) and hardness of alloys 1 and 2 shows (Table 1) that the positive effect of small addition of Si, which was revealed in ingots (Figure 2b), is also retained in sheets (in all the four states). It should be noted that the behavior of these two alloys is approximately identical. Preliminary annealing of ingots (which is aging, in essence) increases UTS and HV values after rolling. In this case, two hardening effects, precipitation and deformation, are added up; therefore TX2 alloys have a higher strength than TX1. The effect of subsequent annealing of sheets on UTS and HV depends on the ingot state. In particular, the TX3 state demonstrates for both alloys a small change in UTS and HV and an increase in elongation (EI) compared to the TX1 state. This is predominantly related to the competitive effect of two processes: formation of Al₃Zr dispersoids (hardening) and softening processes (removal of strain hardening). On the other hand, comparing mechanical properties in the TX2 and TX4 states shows that annealing of sheets with already present Al₃Zr particles leads to a certain softening. Since all the four alloys acquire an unrecrystallized structure after annealing at 400 °C, this softening may be related to recovery processes.

Nº	Alloy	State*	UTS, MPa	EI, %	HV
1	Al - 2 % Mn - 0.5 % Zr	TX1	200	6	69
		TX2	270	5	89
		TX3	200	13	71
		TX4	240	13	77
2	Al- 2 % Mn - 0.5 % Zr – 0.2 % Si	TX1	245	7	81
		TX2	280	6	97
		TX3	250	13	84
		TX4	245	16	91
3	Al - 2 % Mn	TX1	180	7	66
		TX3	145	18	54
4	Al - 2 % Mn - 0.2 % Si	TX1	220	8	77
		TX3	170	16	64

Table 1 Mechanical properties of the Al-Mn-Zr-Si sheet alloys system

* TX1 – rolling of as-cast ingots, TX2 – rolling of ingots subjected to annealing at 400° C for 6 h, TX3 – rolling of cast ingots and annealing of sheets at 400° C for 6 h, TX4 – rolling of ingots subjected to annealing at 400° C for 6 h and annealing of sheets at 400° C for 3 h.

As can be seen from Table 1, annealing of sheets increases plasticity and reduces the difference in UTS and HV values due to the different initial states of ingots, especially for alloy 2. Taking this fact into account the choice of the TX3 state seems to be guite evident. because the TX4 state is more complex and gives no advantages in mechanical properties. Moreover, plasticity in the as-cast state is higher, which should favor the technological efficiency in rolling. A higher stability of the structure in the annealed state compared to the cold-worked condition should also be taken into account. This is important for articles that must be subjected to heating. Comparison of the mechanical properties of alloys 3 and 4 shows that the positive effect of Si addition is revealed also in the absence of Zr: alloy 4 has a substantially higher strength and hardness than alloy 3, but plasticity is approximately the same in both alloys. However, alloys 3 and 4, in contrast to alloys 1 and 2, are softened after annealing in spite of the lack of noticeable recrystallization. It is in the TX3 state that advantages provided by combined addition of Zr and Si are most pronounced (Figure 3a): the strength of alloy 2 (250 MPa) is ~60% higher than the strength of the base alloy 3. An increase in the annealing temperature (up to 600 ^oC) is undesirable because it significantly decreases the hardness of all alloys.

In all the alloys (except TX1) we find Mn- and Zr-containing dispersoids, the size of which depends on the annealing temperature. In the TX2–TX4 states, the size of Mn-containing dispersoids is about 100–200 nm (Figure 3b), whereas Al₃Zr dispersoids are much smaller (~5 nm); their detection is difficult, because they are often located in dislocation clusters (Figure 3c). The regions showing a coarser cellular decomposition (typical of castings made from an Al–0.8 % Zr [7]) were not found. Sheets subjected to annealing at 400 °C are characterized by the polygonized structure with subgrains of about 0.5 μ m in size (Figure 3d).

The obtained data point to the possibility of substantial strengthening of AA3003-type aluminum alloys with Zr addition and optimized Si concentration. Further investigations aimed at designing new wrought low-alloyed aluminum alloys of wide purpose are therefore desirable.

Conclusions

1. The structure and mechanical properties of ingots of Al–Mn–Zr–Si alloys containing 2 wt.% Mn, 0–2% Si, and 0–1% Zr have been studied. The solubility of Zr in the aluminum solid solution in the as-cast state is shown to be no less than 0.5% at the Si content up to 4%. Small addition of Si (beginning from \approx 0.2%) substantially accelerates the hardening of Al-Zr alloys, which is related to the formation of the metastable Al₃Zr phase during annealing.

2. The effect of Zr and Si on the structure and mechanical properties of Al–2% Mn sheet alloys has been studied. It is shown that rolling of foundry ingots with subsequent annealing at 400°C makes it possible to reach much higher strength than that of AA3003-type commercial alloys (240 MPa instead of 150 MPa). This is due to the presence of Al₃Zr dispersoids that are formed during annealing and make it possible to retain the hardening in highly deformed sheets.



Figure 3: Effect of Zr and Si additions on the ultimate tensile strength (UTS) of an AI–2% Mn alloy in the TX1 (1) and TX3 (2) states (a) and TEM structure of a sheet alloy AI–2% Mn–0.2% Si–0.5% Zr alloy: (b), (c), (d)

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