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Influence of the degree of scandium supersaturation on the precipitation kinetics of rapidly solidified Al-Mg-Sc-Zr alloys

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ABSTRACT

In this work, we present for the first time detailed and quantitative precipitation kinetics of industry-scale belt-casted AlMg4Sc0.4Zr0.12 alloys. We investigate the age hardening behavior in a temperature range between 250 °C and 400 °C within 180 min as a function of the degree of scandium supersaturation prior to ageing. The hardness evolution is correlated to in-situ synchrotron X-ray diffraction measurements and the precipitate population is analyzed using high-resolution scanning transmission electron microscopy (HR-STEM) and energy filtered TEM in terms of precipitate size, volume fraction, and number density. Here we found that a greater solute Sc-content results in more pronounced age hardening and slightly faster $Al_3(Sc,Zr)$ precipitation kinetics. The precipitate size at a given temperature is not affected by the degree of Sc-supersaturation, while the number density showed a linear relation with the Sc-content in solution prior to ageing. In peak age condition, the $Al_3(Sc,Zr)$ volume fraction was close to the Al_3Sc equilibrium volume fraction of a binary Al-Sc alloy.

1. Introduction

Conventional AlMg alloys possess good work-hardenability, welding characteristics and corrosion resistance but only limited strength compared to age hardening high-strength Al-alloys such as AlCu [1]. In order to increase the specific strength of AlMg alloys while maintaining the beneficial materials properties, the balanced addition of small amounts of scandium and zirconium is considered as one of the most promising approaches [2], [3].

The dominant metallurgical system for AlMgScZr alloys with technically relevant chemical compositions [4], i.e. less than 6 wt.% Mg, 1 wt.% Sc and 0.5 wt.% Zr, is the Al-rich side of the binary system Al-Sc [5]. For an alloy that follows the Al-Sc system, the materials properties strongly depend on the presence and nature of the equilibrium phase Al_3Sc. When exceeding the eutectic composition of around 0.6 wt.% Sc, primary Al_3Sc phases are the first solid phases that form during solidification. It was shown that these phases serve as nucleation sites for Al-grains leading to considerable grain refinement but no substantial strengthening [6–12]. If Al_3Sc phases form as precipitates from a supersaturated solid solution, on the other hand, significant strengthening could be achieved [2], [7], [8], [13–15]. In a review paper by Røyset and Ryum [16], the average strengthening of AlMg alloys modified with Sc was quantified with around 60 MPa per 0.1 wt.% Sc which corresponds to the highest increment of strengthening per atom alloyed to Al. Moreover, in case of presence of these precipitates in a deformed microstructure, softening due to recrystallization was inhibited in a wide temperature range due to Zener pinning effect [17–22]. The strengthening effect from secondary Al_3Sc precipitates is, however, limited by the maximum solubility of Sc in Al of around 0.4 wt.% at the eutectic temperature of 660 °C. The addition of Mg and Zr to AlSc alloys further decreases the maximum Sc solubility as well as the Sc concentration at the eutectic point [11], [23]. Owing to this very limited solubility even at temperatures close to melting, a high degree of supersaturation in Sc is only achievable using direct chill casting processes with high solidification and cooling rates.

Various investigations [13], [15], [23–38], focused on the description of the precipitation behavior of Al_3Sc during ageing. It was found that precipitation followed classical nucleation and growth theory with significantly retarded coarsening due to long-

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term particle coherence. In addition, the thermal stability of Al_3Sc could be further improved by adding zirconium in a Sc:Zr weight-ratio of around 2:1. This results in full solubility of Zr in $Al_3(Sc_x,Zr_{1-x})$. Clouet et al. [24], for example, attributed the thermal stability of the precipitates to the heterogeneous composition of the phase revealing a Sc-rich core and a Zr-rich shell as a result of different diffusion coefficients. The initial stages of precipitation, however, were not significantly affected by Zr additions [13], [16], [39]. The picture is similar for the influence of Mg on the precipitation kinetics of Al_3Sc or $Al_3(Sc,Zr)$, respectively. It was reported [2], [40], that solid solution strengthening was superimposed to precipitation strengthening in direct proportion to the amount of Mg present in solution, whereas the formation of Al_3Sc or $Al_3(Sc,Zr)$ appeared to be unaltered by the presence of Mg [2], [41].

Most of the existing literature discussed here focuses on the fundamental description of the metallurgical phenomena occurring during precipitation of Al_3Sc or $Al_3(Sc,Zr)$ in high-purity binary or ternary lab-scale alloys. Many studies in fact were carried out to elaborate or validate mathematical models on nucleation, growth or coarsening kinetics using AlSc as a model system. Only few investigations [4], [12], [42], show results of alloys produced at a larger scale on industrial equipment and more practically relevant ageing temperatures and times. However, no details on the precipitation kinetics were presented there.

In this work, we study the precipitation kinetics of two rapidly solidified AlMg4Sc0.4Zr0.12 materials focusing on the influence of the degree of scandium supersaturation prior to ageing. We investigate the hardness evolution as a function of temperature in the first stages of precipitation, i.e. up to only a few hours of ageing, and correlate the results to in-situ synchrotron X-ray diffraction (XRD) measurements. The correlating $Al_3(Sc,Zr)$ precipitate evolution is studied by high-resolution scanning transmission electron microscopy (HR-STEM) and energy filtered transmission electron microscopy (EFTEM) in terms of mean radius, volume fraction, and number density.

2. Experimental

2.1. Material

The investigated material was an AlMg4Sc0.4Zr0.12 alloy casted to an 8 mm thick, 280 mm wide, and 30 m long belt using a continuous belt-casting technology. We have demonstrated that this alloy shows precipitation hardening upon ageing [12] and hot deformation [43] as well as resistance to static recrystallization due to Zener pinning from secondary precipitates [22].

Using a simple image analysis approach [12] we have shown that despite the rapid solidification process only 0.12 wt.% Sc of nominal 0.4 wt.% Sc was in solution in the as-cast (AC) state. The remaining 0.28 wt.% Sc was bound in primary and eutectic $Al_3(Sc,Zr)$ phases. To increase the amount of Sc in solution, a part of the material was rapidly remelted and solidified using a process similar to electron beam welding. This electron-beam re-solidification (EBRS) was performed using an acceleration voltage of 150 kV, a beam current of 10 mA, and a feed rate of 10 mm/s. In this condition, 0.39 wt.% Sc was in solution due to the high process temperatures and rapid solidification and cooling rates of up to 10^5 Ks^{-1} [44] compared to 10^{-1}–10^2 Ks^{-1} [45] for different casting processes. These results were verified by HRTEM energy dispersive X-ray spectroscopy (EDS) analyses of the $Al_3(Sc,Zr)$-free matrix, revealing a content of solute Sc of 0.15 wt.% in AC and 0.35 wt.% in EBRS condition. The chemical compositions and Sc-contents in solution for the two materials conditions are summarized in Table 1.

2.2. Methods

The samples in AC and EBRS conditions were heated in a furnace to 250 °C, 325 °C, and 400 °C with a heating rate of 1 °C/s and annealed for 180 min at these temperatures. A total of 12 samples was aged per condition and temperature. The individual samples were removed after different ageing times to measure the hardness.

To analyze the presence, formation or dissolution of different phases during the entire heating cycle, we performed in-situ synchrotron XRD measurements at the Austrian SAXS beamline at Elettra Sincrotrone Trieste [46] during the annealing treatment at 400 °C. The beamline was set-up to use monochromatic X-rays with a wavelength of 0.154 nm. X-ray patterns were recorded with a Pilatus 100 k pixel detector (Dectris, Switzerland). The angular scale of the patterns spanned the range between 30° and 53° and was calibrated with LaB_6 powder. The 70–100 μm thick samples were placed in a custom made sample support for transmission measurements, which was mounted on a DHS 1100 heating stage (Anton Paar). This arrangement allowed to capture XRD patterns every 10 s using the same temperature cycle as for the furnace annealing. To evaluate the intensity of the XRD peaks, the $Al_3(Sc,Zr)$ peak height was determined by fitting a Lorentzian peak with a linear background to the data for the given time step.

STEM and EFTEM investigations were carried out for the samples aged at 325 °C and 400 °C for 180 min. The samples annealed at 250 °C could not be analyzed quantitatively due to the very small precipitate size. Investigations were carried out on a Cs-probe corrected FEI Titan^3 60–300 kV equipped with a Super-X EDX detector (FEI) and a GIF Quantum energy filter (Gatan), operated at 300 kV and a FEI Tecnai F20 operated at 200 kV, equipped with a Gatan Tridiem post column imaging filter. STEM high-angle annular dark-field (HAADF) high resolution images were acquired at the Titan showing the heavier atoms Sc and Zr brighter than the Al matrix. To verify whether the elements in question were contained in the precipitates, simultaneous X-ray and electron energy-loss spectroscopy (EELS) acquisitions were performed. EFTEM investigations were carried out at the Tecnai F20. The filtering energy was set such to deliver highest contrast for further size analysis of the precipitates. This was reached at an energy of 40 eV with a slit width of 10 eV, generating bright precipitates in a dark matrix, similar to [22]. The EFTEM measurement data were used to calculate the precipitate radius assuming spherical particles. Based on the radius and sample thickness we calculated the precipitate volume and total measurement volume to quantify the precipitate volume fraction. The precipitate number density was finally evaluated by dividing the number of precipitates by the respective measurement volume.

For the TEM investigations all samples were prepared as follows: A thin foil with a thickness of about 500 μm and a diameter of 3 mm was cut from the bulk sample using a diamond wire saw and an ultrasonic disk cutter. After dimpling and polishing the sample, an Ar-ion milling step under 4 kV at an angle of 4° at the top and 6° at the bottom was carried out until a hole with electron transparent edges appeared. The investigations then were carried out at specimen thicknesses of about 0.5 times the inelastic mean free path.

3. Results

3.1. Hardness evolution

Fig. 1 shows the hardness evolution for different degrees of Sc-supersaturation and ageing temperatures. Before ageing, the hardness values for AC and EBRS conditions were almost identical, revealing values of 66 HV0.1 for AC and 65 HV0.1 for EBRS with