TEM Investigation of Precipitation in Al-Mn Alloys with Addition of Zr

Michaela Poková1,2, Miroslav Cieslar1, Jacques Lacaze2
1Charles University in Prague, Faculty of Mathematics and Physics, Ke Karlovu 5, 121 16, Prague 2, Czech Republic
2CIRIMAT, ENSIACET, 5 allée Emile Monso, BP44362, 31030 Toulouse cedex 4, France. pokova@karlov.mff.cuni.cz

Aluminium and its alloys belong to the most widely used metallic materials for industrial applications. One of the possible casting methods is twin-roll casting which produces sheets with high solid solution supersaturation. Decomposition of this supersaturated metal during heat treatment was studied in aluminium alloys from the AW-3003 series – one standard grade and the other modified by addition of zirconium. Characterization by differential thermal analysis and observations by electron microscopy revealed that precipitation of α-AlMnFeSi phase occurred in two steps around 360 and 450 °C in twin-roll cast sheets, firstly on subgrain boundaries and afterwards also within the grains. In cold-rolled sheets, precipitates formed directly within the grains. The zirconium addition shifts recrystallization to higher annealing temperatures in the cold-rolled Zr-containing alloy.

Keywords: Aluminium alloys, AW-3003, TEM, precipitation, α-AlMnFeSi

1 Introduction

Twin-roll casting is a form of economic production of alloys when a sheet of thickness of around 10 mm is cast with a high solidification rate. The initial microstructure of such materials exhibits high solid solution supersaturation and can suffer from macrosegregation in a form of central eutectic segregates and of microsegregation which scales with the dendrites arm spacing [1]. This process is applied to AW-3003 alloys which are basically low alloyed aluminium alloys of the Al-Fe-Mn-Si system. The semi-products are then cold-rolled to sheets 1 mm in thickness or less.

In the Al rich corner of the Al-Mn-Fe-Si system, two main phases besides (Al) and (Si) are in equilibrium: orthorhombic Al3(Si,Mn,Fe) and cubic or hexagonal α-AlMnFeSi (with stoichiometric composition usually between Al12(Mn,Fe)3Si and Al15(Mn,Fe)3Si3) [2-5]. If an aluminum alloy of the AW-3003 series is cooled rapidly during solidification, the resulting aluminium matrix is a solid solution supersaturated in Mn which then decomposes during heat treatment [6]. Dispersoids, which nucleate during annealing are mainly of α-AlMnFeSi phase. According to [7-9] the amount of α-phase dispersoids rises when the annealing temperature increases from 300°C up to 500°C and then their partial dissolution occurs at higher temperatures.

Thus, the temperature of isothermal annealing significantly influences the size and amount of precipitated particles [10]: at 400°C only a small number of precipitates is formed thanks to the low diffusion rate of Mn while the largest quantity of precipitates is formed when the annealing temperature is 450°C. With increasing annealing temperature, the precipitates tend to spheroidize and almost no precipitates are formed during annealing at 630°C.

Concerning technological applications of aluminium alloys, prevention of grain coarsening during high temperature treatment is required [11]. This can be achieved by appropriately chosen parameters of processing of the alloy: suitable distribution of second phase particles can provide desired properties. In this line of thoughts, small amount of zirconium added to aluminium alloys and appropriate thermo-mechanical treatment can lead to the formation of metastable Al3Zr precipitates with L12 structure with the diameter in the magnitude of 10 nm [12]. They pin moving grain boundaries, so they can increase recrystallization temperature and induce a fine grained structure [13-14].

In the present work we have focused on the evolution of the microstructure during annealing and the influence of cold-rolling and small zirconium addition on the distribution of the precipitates.
2 Experimental

Two materials based on a commercial aluminium alloy EN-AW 3003 were studied, one without and the other one with the addition of 0.16 wt.% Zr. The nominal composition of the AW 3003 series is 1.0 – 1.5 wt.% Mn, less than 0.7 wt.% Fe and 0.6 wt.% Si, 0.05 – 0.2 wt.% Cu and less than 0.2 wt.% Zn. Sheets with thickness about 10 mm were prepared by twin-roll casting in the industrial conditions. Afterwards they were cold-rolled (CR) in several steps to a thickness of around 1 mm.

The materials were first subjected to differential thermal analysis (DTA) with a SETARAM SETSYS 16/18 equipment with the heating rate 5 K/min. The samples for DTA were cylinders with diameter 4 mm and length 5 mm with the mass of around 25 mg. According to the DTA records, temperatures for further investigation were chosen as 300, 400, 500 and 620 °C for as-cast sheets, and 280, 380, 500 and 620 °C for cold-rolled ones. Specimens were annealed in the air furnace to selected temperatures with the same heating rate as the one used during DTA and subsequently quenched into cold water. Afterwards they were observed in the transmission electron microscope (TEM) JEOL JEM 2000FX at 200 kV and in the scanning electron microscope (SEM) LEO 435VP equipped with energy-dispersive X-ray analyser.

3 Results

3.1 Differential thermal analysis

The DTA records shown in figure 1 reveal several exothermic peaks in all materials. As-cast materials (label Al for standard AW-3003 and Al+Zr for AW-3003 Zr modified grade) exhibit one small peak with maximum around 360°C and a main peak at 450°C. The relative amplitude of the main peak is higher for the material with zirconium. In cold-rolled materials the main peak occurs at 430°C while the thermal arrests at lower temperatures are much less well defined. Temperatures of the onsets and ends of the peaks were chosen for observations of precipitation processes in TEM and SEM: 300, 400, 500 and 620 °C for as-cast sheets; 280, 380, 500 and 620 °C for cold-rolled sheets, respectively.

3.2 Scanning electron microscopy

SEM examinations show that after casting primary particles are clustered in eutectic colonies at grain boundaries (Figure 2). Near the sheets surface they are often lined up in the casting direction. After annealing new precipitates, much smaller than the primary particles, are present in both materials. Apparent is their alignment at subgrain boundaries.

EDS analyses show that primary particles in Zr-free alloy contain (besides aluminium) also manganese, iron and silicon. The silicon content is slightly higher than the contents of Mn and Fe, which are comparable. In the Zr-bearing alloy silicon is dominant, too, but manganese prevails over iron in the primary particles composition. This composition corresponds to the α–AlMnFeSi phase.

3.3 Transmission electron microscopy

Observations in TEM revealed that twin-roll cast materials consist of an (Al) matrix with minor phase particles in eutectic colonies. In the cold-rolled sheets, subgrains are elongated in the rolling direction due to the deformation and a high density of dislocations was observed (Figures 3a and 3b).

After annealing with the heating rate of 5 K/min to 300 °C (Figures 3c and 3d) slight spheroidization of primary particles occurs and during further heating to 400 °C first precipitates of α–phase form. In the Zr-free alloy they can be found mainly at subgrain boundaries while in the Zr-bearing alloy precipitates formed not only on subgrain boundaries but also within the subgrains in random clusters (Figure 4).

Concerning the cold-rolled sheets, first α–phase precipitates are observed in both alloys after heating to 380 °C. However, they are rather smaller and more uniformly distributed within the subgrains in Zr alloy as compared to cold-rolled material without Zr.

In all alloys annealed to 500 °C high density of secondary particles is present. In non-deformed sheets the precipitates not only decorate subgrain boundaries but their dense population is observed also inside the subgrains. In cold-rolled materials new small particles with average diameter of around 30 nm precipitated next to those that nucleated at lower temperatures and coarsened during further annealing to approximately 80 nm (Figure 5). The size of precipitates is comparable in both alloys, with and without zirconium. Recrystallization has already started in cold-rolled material without Zr at this temperature and in some parts of the foils small subgrains are replaced by grains with larger diameter.

Due to the annealing to 620 °C (Figure 6) the average size of α–phase precipitates increases in all materials from 60 nm at 500 °C to 150 nm, though this augmentation is more apparent in non-deformed states. The shape of the particles nucleated during heat treatment depends on the deformation: in cold-rolled sheets the precipitates...
are mainly spherical while their shape is more complex in non-deformed materials – they often appear as polygonal plates (Figure 5b). Both cold-rolled alloys are fully recrystallized after annealing at this temperature.

According to EDS analysis the content of manganese and silicon in all precipitates is comparable and much higher than the iron content.

**Fig. 2** Clusters of primary particles at grain boundaries after twin-roll casting (a) and primary particles (PP) with smaller precipitates (prec.) at subgrain boundaries after annealing to 620 °C (b) in Zr-free alloy

**Fig. 3** Microstructure after twin-roll casting with primary particles (a) and with subgrains and dislocations after cold-rolling (b). As-cast (c) and cold-rolled (d) alloys after annealing to 300 °C

**Fig. 4** First α-phase precipitates (prec.) on subgrain boundaries in Zr-free alloy (a) and in the bulk of Zr alloy (b). Cold-rolled materials with precipitates within the grains (c, d). Annealing to 400 °C or 380 °C, respectively
4 Discussion

After casting the microstructure of studied alloys is inhomogeneous with so-called primary particles clustered in eutectic colonies and high contents of Mn and Si supersaturated in the (Al) solid solution. Composition of primary particles corresponds to cubic and hexagonal α-AlMnFeSi phase with silicon content higher than iron and manganese [4, 15]. During heat treatment further manganese incorporates into these particles [8] which results in their spheroidization.

Differential thermal analysis records revealed temperature intervals of solid solution decomposition in all studied alloys. In the as-cast sheets the first exothermic peak occurs between 300 and 400 °C and is more pronounced in alloy without Zr, where the precipitates nucleate preferentially at subgrain boundaries. In the Zr-bearing alloy, some of the new particles form also inhomogeneously in clusters within the grains. A second stage of precipitation takes place in the temperature range 400-500 °C and new precipitates nucleate in the whole volume of the material, not only at the subgrain boundaries. Similar two-step precipitation has been already observed and monitored by resistivity measurement in Al-Mn alloys without addition of Zr [16]. Further annealing at higher temperature leads to partial dissolution of smaller precipitates and coarsening of the remaining ones.

Precipitation in cold-rolled sheets takes place directly within the subgrains. The most intense precipitation according to DTA occurs between 360 and 500 °C in the Zr-free alloy and 390 and 500 °C in the Zr containing alloy, respectively. At 620 °C the precipitates can be divided into two groups: coarsened particles with average diameter of around 120 nm, and smaller ones about 40 nm which precipitated at higher temperatures.

Thanks to the low solubility of iron in aluminium [17], most of Fe atoms are incorporated in the primary particles after casting. Solubilities of silicon and manganese are much higher and relatively significant amounts of Si and Mn atoms are dissolved in the aluminum matrix. Thus during decomposition of solid solution at elevated temperatures, precipitates are composed mainly of Mn and Si and contain nearly no Fe.

Concerning Al3Zr precipitates, certainly because of the high heating rate no such particles have been detected in the alloy with addition of zirconium. This is in
accordance with observation of Nes et al. [18], who estimated a critical heating rate 5 K/min, above which Al<sub>2</sub>Zr do not precipitate in the strip cast AlMnZr alloys. It has also been shown that cold-rolling of twin-roll cast aluminium AW-3003 alloys may have negative influence on Al<sub>2</sub>Zr precipitation [19]. However, recrystallization of the deformed substructure is shifted to higher temperature in the zirconium alloy; this effect can be attributed to clusters of zirconium atoms, which pin moving grain boundaries and thus retard recrystallization [20-21], but are under detection limit of conventional transmission electron microscope.

5 Conclusion

In the present work decomposition of supersaturated solid solution of two twin-roll cast aluminium alloys was studied. The precipitation of α-AlMnFeSi phase particles was divided into two main stages: formation of precipitates around 350 °C at preferential nucleation sites - subgrain boundaries and subsequently above 450 °C in the whole volume of aluminium matrix. In sheets that were cold-rolled prior to annealing, precipitation occurred directly inside the subgrains; however, two sizes of precipitates can be distinguished after annealing up to 620 °C.

The recrystallization resistance was higher in the alloy with zirconium addition although due to the high heating rate no Al<sub>2</sub>Zr precipitates were detected.

Acknowledgment

This work was financially supported by a project of The Czech Science Foundation GAČR P107-12-0921. M. P. would also like to acknowledge support of student grants SVV-2012-265303 and GAUK 92210 and a scholarship from the French embassy.

References:


Fatigue resistance of dual phase steels in presence of microstructural inhomogeneities

Gejza Rosenberg1, L'uboš Juhár2
1) Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic, grosenberg@imr.saske.sk
2) Unit GM for Research USSE, U. S. Steel Košice, s. r. o, Vstupný areál US Steel Košice, 044 54 Košice, Slovak Republic

In the work, there are noted experimental results aimed at determination of influence of initial microstructure of the steel S355, that was exposed to different temperatures of intercritical annealing, on its resistance against cyclic loading by number of cycles needed to fracture the samples, loaded by stress amplitude σ = 500 MPa. Intercritical annealing at temperature ranging 740-840°C was carried out on a bar with the same thickness as the steel sheet in received state (B=9mm). Fatigue tests were realized on 1,2mm thick specimen cut from subsurface and middle area of initial thickness of the plate, where a banding structure occurred, thickness ~1,5 mm in the received state. It was discovered, that samples with microstructural banding have higher fatigue resistance independently on temperature of intercritical annealing.

Keywords: dual phase steel, microstructural banding, tensile properties, fatigue resistance

1 Introduction

Most of the literature about dual-phase steels deals with balance between strength and ductility. However, other properties are also important in dependence to area they would be used in. As almost all car components are exposed to cyclic loading, besides formability, fatigue properties belong to the most important [1]. The local stress concentration caused by mechanical or metallurgical defects such as carbides, non-metallic inclusions or grain boundaries is considered to be the most important factor that influences fatigue resistance [2]. Previous works dealing with fatigue strength mentioned raising effect of inclusions along with increase in strength as well as the fact that under certain conditions their effect can be the determining factor that controls fatigue strength of steels [3, 4]. At steels with very high tensile strength, initiation of fatigue cracks from defects or structural heterogeneities in the subsurface zones of a material is not an unique case [5, 6]. However, in case of presence of residual stress, initiation of fracture from subsurface zones can occur even in steels with strength lower than 1000 MPa [7].

Except for the stress concentrator, fatigue limits of the steel are influenced also by type of strengthening mechanism. It was discovered in the work [8], that the steels strengthened by increase in volume fraction of pearlite had the worst fatigue properties of all monitored steels. Also other authors [2] observed relatively poor fatigue resistance at mixed microstructures. Therefore, it is not surprising that dual phase steels do not always show sufficient fatigue properties [9] and values of ratio fatigue limit to tensile strength equals to σf/TS = 0,37 instead of commonly achieved σf/TS = -0,5 [1, 10].

The microstructure of dual-phase steels influences fatigue properties significantly, although the effect of individual structural properties is not clear [10-14] . In the work [10] at the steel AISI 1008 the ratio σf/TS ranged from 0,37 to 0,56 in dependence to volume fractions of martensite (VFM) and morphology of its elimination, at the steel AISI 1015 it ranged from 0,38 to 0,51. The highest σf had the samples with VFM = 46 % from the steel AISI 1008 and samples with VFM = 67 % from the steel AISI 1015. The samples with VFM=26% from the steel AISI1008 and with VFM=53% from the steel AISI1015 had the lowest σf values. Significant