Microstructural Aspects of Rapidly Solidified Al–Mg Alloys

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Microstructural aspects of rapidly solidified Al–10–60 at%Mg ribbons prepared by the single roller method were examined by X-ray diffraction analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The lattice parameter of the aluminum rich phase increases with magnesium content up to 35 at% indicating the extended solid solubility, whereas the maximum equilibrium solubility is equal to 18.9 at% at 723 K (eutectic temperature). As-quenched ribbons (20–34.3 at%Mg) comprised supersaturated solid solution, α, and a new metastable phase, X. 42 at%Mg ribbons consisted of the X phase only and 60 at%Mg ribbons were single phase of equilibrium y.

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I. Introduction

Al–Mg alloys are known for their good ductility, satisfactory work-hardening characteristics, and excellent corrosion resistance and weldability. A lot of experimental works have been accumulated in their practical uses. However, detailed studies on the microstructures(1)–(5) formed during rapid solidification and the subsequent phase change(6)(7) have been rather limited.

According to the Al–Mg equilibrium diagram, the maximum solid solubility of magnesium in aluminum is 18.9 at%(8) at the eutectic temperature, 723 K. The eutectic comprises the solid solution and the intermediate phase β, usually given the formula Mg2Al3, having a complex FCC structure, space group Fd3m (O7h) with $a=2.824$ nm and approximately 1168 atoms in the unit cell(9)(10).

It is well established that rapid solidification of melts can lead to the production of metastable phases(11)–(13). These metastable phases include supersaturated solid solutions, crystalline intermediate phases. This paper illustrates and analyses the variety of microstructures obtainable by a single roller method.

Microstructures of Al–Mg alloys in a wide composition range from 0 to 60 at%Mg have been investigated by means of X-ray diffraction analysis, electron microscopy and calorimetry.

II. Experimental

Al–Mg alloys with compositions in the range of 0 to 60 at%Mg, using 99.99% aluminum and high purity magnesium, were melted in an argon atmosphere in an alumina crucible and solidified by chill casting. From the master alloys, ribbon samples typically 3 mm in width and 50 μm in thickness were prepared using a single roller method in an argon atmosphere. The amount of melted alloys per run was about 3 g and the surface speed of the roller was about 42 m/s.

The X-ray diffraction study was carried out using CoKα radiation at room temperature. Simultaneous measurements of diffraction peaks from powdered high purity silicon were used as the standard. The thermal properties were examined in an argon atmosphere with a differential scanning calorimeter (DSC), Du-pont 910, at a heating rate of 0.33 K/s. Microstructural study was performed in a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The TEM sample was prepared by electrolytically thinning ribbons in a solution of 10% perchloric acid and 90% ethyl alcohol at 273 K.

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III. Results and Discussion

1. Lattice parameter of aluminum rich phase

Figure 1 shows the changes in lattice parameter versus initial magnesium content. King's relationship \(^{(14)}\) calculated from the data in solid solution is also shown as the reference. The lattice parameter of aluminum rich phase increases with magnesium content up to about 35 at% indicating the extended solid solubility, whereas the maximum equilibrium solubility is equal to 18.9 at\(^{\circ}\) at 723 K (eutectic temperature), but decreases again for much higher magnesium content. As seen in Fig. 2 the separation between the liquidus and the \(T_0\) temperature \(^{(15)}\) of the liquid and \(\alpha\) phases is not so large. The undercooling prior to solidification may exceed the \(T_0\) curve for magnesium contents of less than 35 at%.

2. X-ray diffraction analysis

X-ray diffraction patterns obtained from the ribbons (10, 20, 30, 34.3, 42 and 60 at\%Mg), prepared by the single roller method, are shown in Fig. 3. The peak of the aluminum phase shifts to a lower angle with increasing magnesium content in 10 - 34.3 at\%Mg ribbons. In 34.3 at\%Mg ribbons, high and low super-saturated \(\alpha\) (s.s.\(\alpha\)) and equilibrium \(\beta\) can be recognized clearly. Table 1 shows analysis of the X-ray diffraction pattern obtained from rapidly solidified Al-42 at\%Mg alloy. X-ray analysis shows no existence of aluminum phase for 42 at\%Mg ribbon and the extra lines are not matched with the \(d\)-values \(^{(9)}\) of \(\beta\). One of the diffraction peaks from an unknown phase, \(X\), appears at about 42.4° in 20, 30, 34.3 and 42 at\%Mg ribbons. This unknown phase will be discussed in the section of TEM. In 60 at\%Mg, the diffraction patterns are not significantly different in the as-solidified condition and annealing up to 700 K. The \(\varepsilon\) phase shown in Fig. 2 is not found in this study.

The solidification rate may be varied by controlling the surface speed of the wheel. Figure 4 shows X-ray diffraction patterns at the different surface speeds of about 27 m/s, 42 m/s and 61 m/s. The higher surface speed results in a higher solidification rate, but 42 m/s was employed to obtain good shaped ribbons in this study.

3. Scanning electron microscopy

Figure 5 shows SEM images of the cross-sections of 10 and 30 at\%Mg ribbons. SEM...
The images in upper side and wheel side planes of Al-Mg ribbons are shown in Fig. 6. The highest cooling and solidification rates occur at the wheel side. This leads to very small crystallites in this region and the largest amount of dissolved alloying element. Near the wheel surface, thermal gradient is perpendicular to the wheel surface and it forms columnar grain in the direction of the wheel surface normal. The heat flow condition may
Fig. 5 SEM images of the cross-sections of 10 and 30 at% Mg ribbons.

Fig. 6 SEM images in upper side and wheel side planes of Al-Mg ribbons.
Fig. 7 TEM images of 10, 20 and 30 at\%Mg ribbons.
Al-34.3 at% Mg

Fig. 8 TEM images of a 34.3 at% Mg ribbon showing the typical areas consisting of mainly s.s. α (a), equilibrium β (b), and metastable X (c) and (d). (c’) and (d’) are high magnification of (c) and (d).
Fig. 9  A bright field image and dark field images of a fan-shaped crystal in a 34.3 at% Mg ribbon.
Fig. 10 A bright field image and a dark field image of a 42 at\%Mg ribbon.

Al–42 at\%Mg
be disturbed as the solidification front moves away from the ribbon bottom surface and it caused to an irregular structure. As solidification proceeds from the wheel side, solidification will start from the upper side too.

4. Transmission electron microscopy

TEM study reveals the microstructural aspects of the ribbon. Figure 7 shows TEM images of 10, 20 and 30 at% Mg ribbons prepared by the single roller method. 10 at% Mg ribbons are a single phase where all the solute magnesium dissolved in the aluminium matrix. 20 at% Mg ribbon shows small precipitates at grain boundaries. From the X-ray study and electron diffraction analysis, it is confirmed that these precipitates are a new metastable phase, X, formed during rapid solidification. 30 at% Mg ribbons comprise s.s. $\alpha$ and X.

Figure 8 is TEM images of a 34.3 at% Mg ribbon showing the typical areas consisting of mainly s.s. $\alpha$ (a), equilibrium $\beta$ (b), and the metastable X (c) and (d). X in 30 at% Mg ribbons and (c) makes a network with $\alpha$, and that in (d) makes a radiating fan with $\alpha$. Figure 9 shows a fan shaped crystal. The crystal is characterized by the radiating branches which stem from the center core. Dark field images show that X has the same orientation locally but different in the fan shaped crystal.

Figure 10 for a 42 at% Mg ribbon shows a bright field image and a dark field image taken using an arrowed diffraction spot. It may be concluded that the ribbon is the single phase, X, by the X-ray study and electron diffraction analysis.

The X phase appears in the composition range from 20 at% Mg to 42 at% Mg and has different shapes depending on solute content. Figure 11 shows a TEM image of a 60 at% Mg ribbon. Massive grains are equilibrium $\gamma$ only.

5. A new metastable phase, X

A new metastable phase, X, formed during solidification was observed in the range of 20 to 42 at% Mg. The observed d-space and intensities of the reflections did not correspond to any equilibrium and metastable phase reported. Precise electron diffraction analysis partly threw light on the structure of X. Figure 12 shows selected area diffraction patterns from $\beta$ and X. The schemes show the differences between the two phases in the distance ratio of the diffraction spots. The distance of the diffraction spots in these phases is different with a constant ratio as shown schematically in this figure. Diffraction spots from X do not correspond to the double diffraction of $\beta$ and also the R phase reported by Murray(15). $\beta$ is a complex FCC structure, space group Fd3m ($O_h$) with $a=2.824$ nm and approximately 1168 atoms in the unit cell. This is characterized by
Fig. 12 Selected area diffraction patterns from $\beta$ and X. Series of (a), (b), (c) and (d) show 3-fold, 2-fold, 2-fold and 4-fold symmetry respectively. In these phases, the distance of the diffraction spots is different with a constant ratio as shown schematically in this figure.
the presence of 672 icosahedral subunits in the unit cell\(^9\). X is quite similar to \(\beta\). Main difference in these phases is the distance ratio of the diffraction spots. The 10 intense diffraction spots of the [110] zone lie on a ring (such as 880, 777 and 3311) in \(\beta\), and the intensity of the 10 spots in enhanced than the others in X. At continuous heating stage (0.33 K/s), X decomposed into \(\beta\) (start at 540 K, end at 580 K) with an exothermal peak (at 560 K).

IV. Summary

Microstructural aspects of rapidly solidified Al–Mg alloys, with compositions in the range of 0 to 60 at\%Mg, prepared by single roller method have been investigated. The main results are summarized as follows:

1. The lattice parameter of aluminum increased with increasing magnesium content up to about 35 at%.

2. As–quenched ribbons (20–34.3 at\% Mg) comprised supersaturated solid solution, \(\alpha\), and a new metastable phase, X. 42 at\% Mg ribbons were consisted of X phase only and 60 at\%Mg ribbons were a single phase of equilibrium \(\gamma\).

3. A new metastable phase, X, was observed in the range of 20 to 42 at\%Mg and had different shapes depending on the solute magnesium content.

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