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Extended solid solubility in ball-milled Al–Mg alloys

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Mixtures of elemental aluminium and magnesium powders corresponding to $Al_{70}Mg_{30}$ and $Al_{50}Mg_{50}$ compositions have been mechanically alloyed. After milling, an extended solid solubility of magnesium in aluminium upto 18 at% in the case of $Al_{70}Mg_{30}$ and 45 at% for $Al_{50}Mg_{50}$ was observed. These materials typically nanostructural (grain size 2–10 nm) transform into equilibrium structure upon heating. The stability of these materials was investigated using thermal analysis.

1. Introduction

In the search for alloys with high strength-to-weight ratio, Al–Mg alloys are very promising. In recent years, there has been great interest in studying alloys with metastable structures which can be better tailored to fulfil a broad set of requirements. Amongst these materials, supersaturated alloys can exhibit high ductility, good corrosion resistance and a broad single-phase homogeneity range. Supersaturated and amorphous alloys have been traditionally prepared by rapid quenching from the melt. In the case of Al–Mg alloys, about 37 at % solid solubility can be achieved using the rapid solidification method [1]. Recently, a mechanical alloying method has been employed for synthesis of supersaturated and amorphous alloys. Mechanical alloying was initially discovered by Benjamin [2]. Since that time many industrial laboratories have used this technique for processing advanced oxide-dispersion-strengthened superalloys.

While many new alloys have resulted from these development programmes, very little work on the fundamentals of mechanical alloying has been published. The present investigations of the formation of Al–Mg alloys by mechanical alloying were conducted for the purpose of providing a better understanding of this process.

In this work we present results of mechanically alloyed mixtures of aluminium and magnesium powders of nominal starting compositions of $Al_{70}Mg_{30}$ and $Al_{50}Mg_{50}$ (at %). For convenience, in the following discussion, the mechanically alloyed materials are referred to by their nominal starting compositions.

2. Experimental procedure

Ball milling has been carried out using an in-house-built ball mill with externally controlled ball movement [3]. The alloying process was performed using a planar-type ball mill that consists of a few hardened steel balls confined in a stainless-steel, horizontal type cell. The ball movement during the milling process is confined to the vertical plane by the cell walls and it is controlled by an external magnetic field. The intensity and direction of the field can be externally adjusted allowing the ball trajectories, impact energy and the shearing energy to be varied in a controlled manner. Using this milling device, different milling conditions can be selected. In this experiment, to prevent over welding, a moderate milling condition was used [3]. The milling was conducted in vacuum 10^{-3} torr (1 torr = 133.322 Pa). Appropriate amounts (70 Al–30 Mg and 50Al–50Mg at %) of elemental powders (about 150 μm in size and of 99.98% purity) were sealed under vacuum in a stainless steel mill together with hardened steel balls using the weight ratio of balls/powders of about 4. During milling a small amount of ball-milled powder was taken from mill and the structure was monitored by X-ray analysis. The X-ray diffraction patterns were obtained using a Philips diffractometer with CoK_{α} radiation. A computer-fitting program was used to deconvolute overlapping X-ray peaks, to determine the position and the full-width at half height of the various peaks.

Thermal analysis was carried out using a DSC-4 Perkin–Elmer microcalorimeter. A continuous heating mode with a heating rate of 80 °C min^{-1} was employed. Samples of 20 mg were sealed in aluminium containers and heated from 30–600 °C under flowing pure argon.

3. Results and discussion

3.1. $Al_{70}Mg_{30}$ alloy

The evolution of structural changes during milling is presented in Fig. 1. After 24 h milling, the X-ray pattern shows a full set of aluminium peaks and strongly reduced intensity of magnesium peaks. The unchanged aluminium peak positions indicate lack of solid solubility of magnesium in aluminium at this stage of milling. During the first phase of milling, mainly fracturing and strong deformation of metal particles is observed. An X-ray diffraction pattern

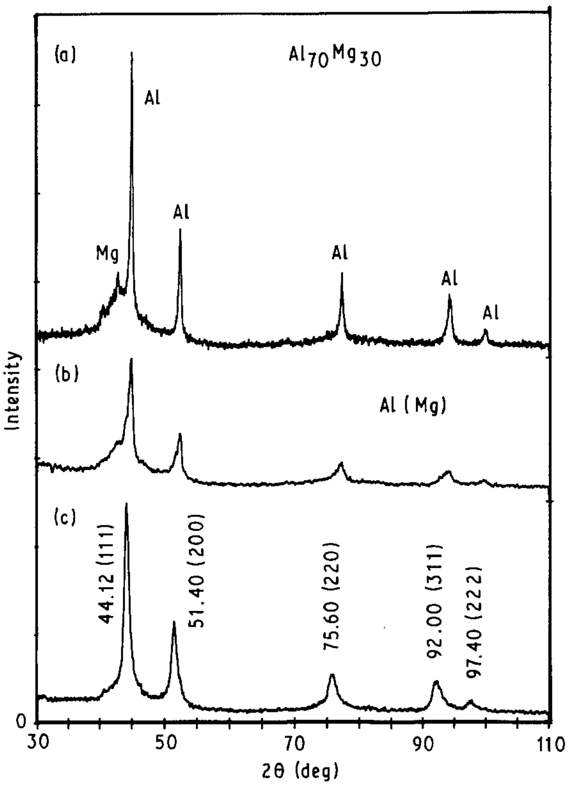

Figure 1 X-ray diffraction patterns of $Al_{70}Mg_{30}$ mixtures ball milled for (a) 24 h, (b) 48 h, or (c) 72 h.

taken from a sample milled for 48 h, shows broadened aluminium peaks at positions shifted towards smaller angles (Fig. 1b). The new peak positions indicate the existence of 7 at% Mg solubility in aluminium. Magnesium X-ray peaks are strongly broadened and less intense due to the strongly distorted structure. Following this stage of milling, significant alloying has occurred. Fig. 1c shows an X-ray pattern taken from sample milled for 72 h. The shift of the peak positions (marked in Fig. 1c) indicate an expansion of the aluminium lattice up to 0.4128 nm. This can be interpreted as an 18 at % solid solution of magnesium in aluminium [4].

Prolonged milling for up to 100 h gave results essentially similar to that following 72 h milling. One can conclude that the milling process (at this particular milling condition) is able to extend the solubility of magnesium in aluminium for the $Al_{70}Mg_{30}$ starting mixture up to a maximum of 18 at %. It is interesting to note that this is the equilibrium solid solubility at 450 °C [5].

Using the rapid quenching technique the maximum solid solubility that can be achieved in the Al–Mg system is 36.8 at% [1]. We were not able to extend the solid solubility in the $Al_{70}Mg_{30}$ composition over 18 at % using ball milling. This result may indicate that during mechanical alloying the solid solution is mainly created by locally rising temperature caused by colliding balls. The locally increased temperature during individual collision can reach 400 °C [5], this being close to the solidus temperature of the $Al_{70}Mg_{30}$ alloy. On the other hand, Al–Mg alloys exhibit a relatively small enthalpy of mixing (Fig. 2) [6, 7]. Such a small negative enthalpy of mixing as a thermodynamic driving force for a solid state reaction might not be sufficient to create a solid state reaction at room temperature, but it might be sufficient to create fast interdiffusion at a temperature close to the melting point. The details of this process cannot be fully described at this stage of research.

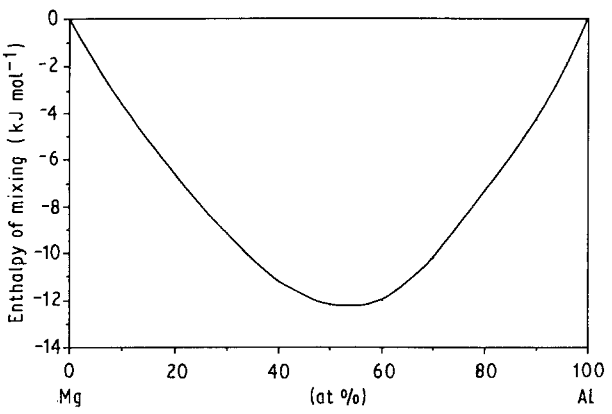

Figure 2. Negative enthalpies of mixing in the Al–Mg alloys calculated using the Miedema model [7, 8].

The X-ray diffraction pattern taken after 72 h milling of the $Al_{70}Mg_{30}$ mixture exhibits an increased background radiation level near the strongest magnesium peak positions (Fig. 1c). With the $Al_{70}Mg_{30}$ starting alloy composition, the presence of 18 at % solid solution suggests that unreacted magnesium should be present. This phenomenon can be explained by assuming that the $Al_{70}Mg_{30}$ as-milled structure is of the nanocrystalline type [8]. This material is composed of nanometre-sized crystals (more likely solid solution crystals) distributed in a large volume of interfacial substance. In this case the very disordered interfacial region consists of excess magnesium and aluminium atoms. Owing to the featureless character of the interfacial region, the diffracted X-rays are weak and scattered, so in consequence makes magnesium poorly visible on the X-ray diffractograms. Furthermore, the crystal size can be estimated by applying the Scherrer formula [9]. This gives a crystal size of 10 nm, consistent with our interpretation of a possible nanocrystalline structure.

In order to characterize the stability of the supersaturated solid solution structure, the ball-milled material was annealed under vacuum at 400 °C for 2 h. The X-ray pattern taken from the annealed sample is presented in Fig. 3b. A fully equilibrium structure with aluminium and Al_3Mg_2 phases, is seen. This result indicates that during annealing, the interfacial region, which is composed of magnesium and aluminium atoms, undergoes fast transformation into an equilibrium structure.

3.2. $Al_{50}Mg_{50}$ alloy

Fig. 4 shows X-ray diffraction patterns which have been obtained after 24 h milling (Fig. 4a) and 76 h milling (Fig. 4b). The sample milled for 24 h exhibits overlapping magnesium peaks with visible aluminium peaks. The sample milled for 76 h gives an X-ray diffraction pattern which might be interpreted as an

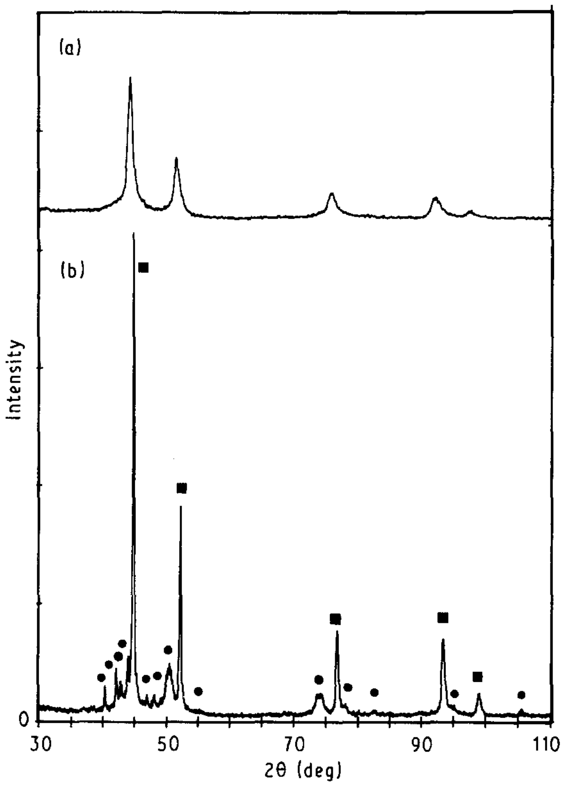

Figure 3 X-ray diffraction patterns of $Al_{70}Mg_{30}$, (a) as-milled, (b) annealed at 400 °C for 2 h. (■) Al, (●) Al_3Mg_2.

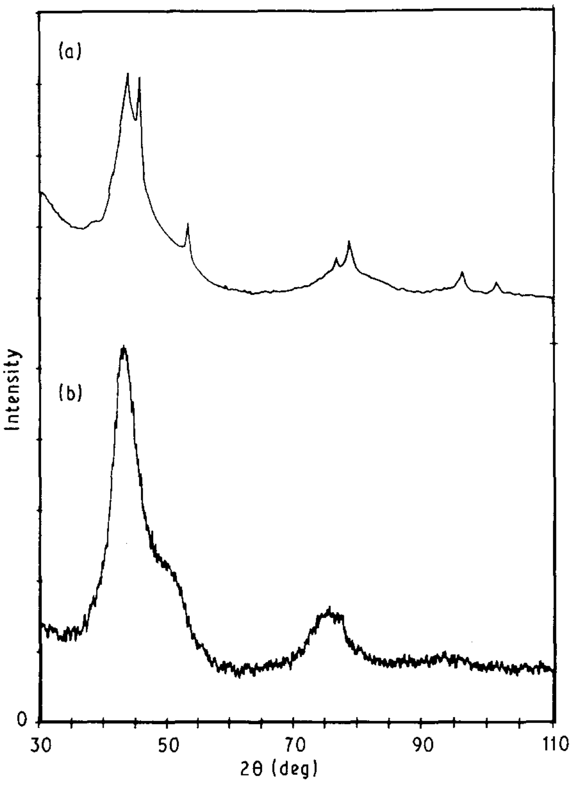

Figure 4 X-ray diffraction patterns of $Al_{50}Mg_{50}$ mixtures ball milled for (a) 24 h, and (b) 76 h.

amorphous structure, but careful analysis revealed characteristic asymmetry of the X-ray peaks towards higher angles. Also, a third broad peak within the region $2\theta = 80°–100°$ is visible. This complicated X-ray pattern is composed of several overlapped peaks. A numerical method (fitting program) was used to analyse this pattern and to obtain the positions and full-width a half height of the X-ray peaks. A Lorentz-type curve was found to be the best fit. The result of the deconvolution of the X-ray spectra is seen in Fig. 5. Positions of the separated peaks (marked in the figure) together with peak positions at higher angles, correspond to a structure composed of 40 at % solid solution of magnesium in aluminium. The grain size, determined using a peak broadening formula, was 2 nm.

Five samples milled separately, under the same conditions, for the same time, showed basically the same structure: solid solution Al(Mg) with variable solubility of magnesium from 36–45 at %. This result indicates that the end product of the ball-milling process, a homogeneous solid solution with an amount of unreacted aluminium and magnesium, seems to be highly dependent on the milling condition: for example, milling energy, type of ball movement, ball-to-powder weight ratio and local milling temperature.

During the milling process of $Al_{70}Mg_{30}$ and $Al_{50}Mg_{50}$ mixtures, the same milling conditions were maintained. It can be assumed that at the same milling conditions the locally increased temperature caused by colliding balls should be similar. Hence, in comparison with the $Al_{70}Mg_{30}$ composition, the higher solid solubility in the case of $Al_{50}Mg_{50}$ alloy cannot be explained as a result of the local overheating only, but as a result of a higher driving force for solid state reaction which is caused by an increased value of negative heat of mixing for this particular composition (Fig. 2).

In order to determine the stability of the ball-milled $Al_{50}Mg_{50}$ mixtures, the samples were continuously heated up to 600 °C. A typical DSC trace obtained at a heating rate of $80\,°C\,min^{-1}$ is shown in Fig. 6. Curve 1 reflects a phase transformation upon heating in the as-milled material. Curve 2 characterizes a second run of the sample previously heated to 600 °C and cooled to room temperature at a cooling rate of $320\,°C\,min^{-1}$. The following thermal effects have been detected: an exothermic broad effect with an onset temperature of 120 °C, a clearly visible intermediate exothermic peak at 340 °C, and another exothermic effect below the melting point. In order to

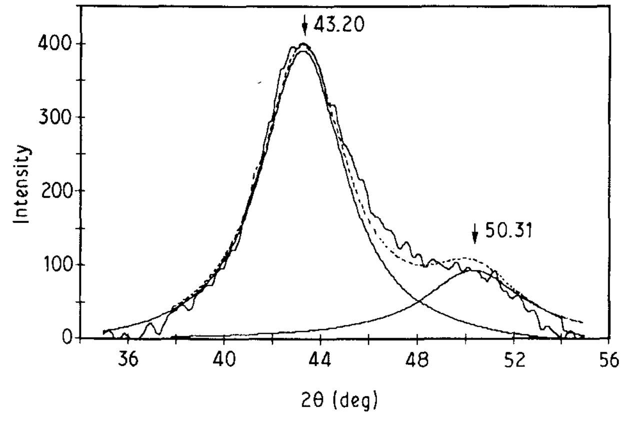

Figure 5 X-ray diffraction pattern of as-milled $Al_{50}Mg_{50}$. Deconvolution of overlapped X-ray peaks: (———) deconvoluted peaks, (– – –) sum of deconvoluted peaks.

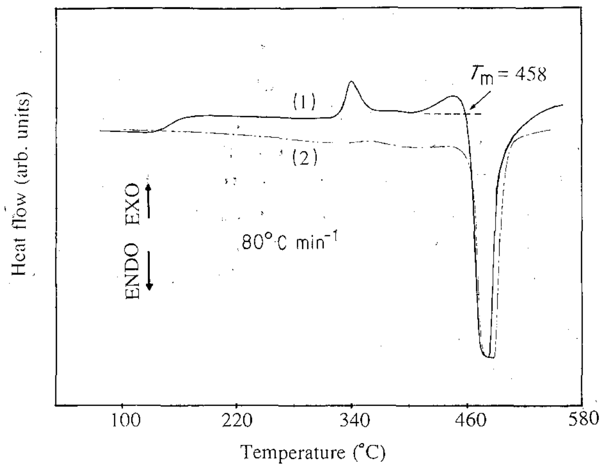

Figure 6 DSC traces of as-milled $Al_{50}Mg_{50}$.

determine the structural changes upon heating, one sample was heated up to 280 °C, just below the onset of the intermediate exothermic peak, and immediately cooled to room temperature at a cooling rate of 320 °C min^{-1}. The X-ray analysis revealed precipitation of the Al_2Mg_3 intermetallic phase (Fig. 7a) when the second sample was heated to 380 °C. An X-ray investigation showed the presence of Al_2Mg_3 and AlMg equilibrium phases. On the basis of these results one can conclude that the low-temperature exothermic event, below the intermediate exothermic peak, corresponds mainly to precipitation of the Al_2Mg_3 phase while the high-temperature exotherm, above the exothermic peak, corresponds to the precipitation of the AlMg phase. The exothermic intermediate peak might be a result of overlapping of those two effects or to rapid transformation of the interphase region. Although a contribution from the exothermal effects due to the internal stress relaxation cannot be excluded. The strong endothermic peak with onset temperature at 458 °C is associated with the melting of $Al_{50}Mg_{50}$ alloy. The melting temperature obtained from the DSC curve (458 °C) is close to equilibrium melting temperature (460 °C) of the $Al_{50}Mg_{50}$ [4].

5. Conclusions

The effect of milling on the alloying process of $Al_{70}Mg_{30}$ and $Al_{50}Mg_{50}$ mixtures of elemental aluminium and magnesium powders was investigated. It was found that ball milling extends the solid solubility of magnesium in aluminium up to 18 at % for $Al_{70}Mg_{30}$ and up to about 40 at % for $Al_{50}Mg_{50}$. The end-milling material shows typical nanometre-type structure with a grain size of 2 and 10 nm for $Al_{50}Mg_{50}$ and $Al_{70}Mg_{30}$, respectively. Upon heating, as-milled samples transform into the equilibrium structure.

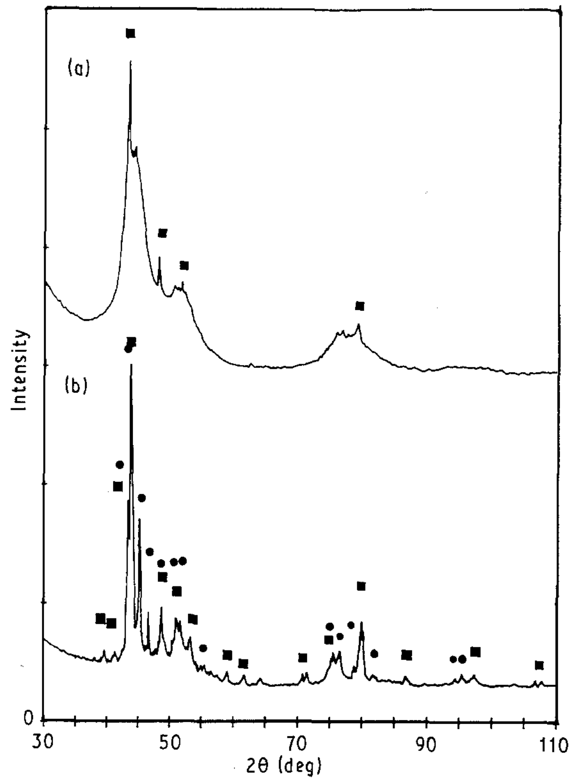

Figure 7 X-ray diffraction patterns of $Al_{50}Mg_{50}$ annealed in the DSC in the continuous heating mode (80 °C min^{-1}), up to (a) 280 °C and (b) 380 °C. (■) Al_2Mg_3, (●) AlMg.

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