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Formation of amorphous Al–Cr alloys by mechanical alloying of elemental aluminium and chromium powders

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Mechanical alloying (MA) of elemental aluminium and chromium powders has been performed using a conventional ball-mill. The MA process produces composite metal powders and homogeneously alloyed powders. During continuous heating at the rate of 0.33 K sec^{-1} Al–15 at% Cr samples ball-milled for 800 and 1000 h showed two exothermal peaks. The first peak which appeared at the lower temperature corresponds to amorphization of the MA powders. It was confirmed by X-ray and transmission electron microscopy that the heat-treated powders, quenched from a temperature just above the first peak, were amorphous phase. Amorphous Al–Cr alloys were formed using elemental powders by MA and subsequent heat treatment.

1. Introduction

Mechanical alloying (MA) is one method of amorphization from the solid crystalline state [1], and many amorphous binary transition metal alloys have been produced by MA of crystalline elemental powders [2–9]. Milling leads to a composite of the two elemental components with a very fine microstructure. With further milling, the composite structure will be continuously refined until the internal structure can no longer be revealed by optical microscopy or scanning electron microscopy (SEM). The amorphization reaction occurs by interdiffusion at the boundaries of the two phases. In this respect the amorphization is similar to the amorphization of multilayered thin films during heating [10–12]. Amorphization by solid-state reaction with diffusion was first found in the reaction of hydrogen absorption [13]. The heating temperature must be below the crystallization temperature. In addition to the heat treatment, the driving forces for this amorphization are the large negative heat of mixing in the systems [5–7, 10] and the release of stored energy in the form of chemical disorder and lattice and point defects [5].

The first amorphization of the Al–Cr system by solid-state reaction was achieved by mechanical grinding (MG) of rapidly solidified crystalline powders [14]. The starting powders were mainly icosahedral quasicrystalline. The purpose of this work was to investigate whether amorphous Al–Cr alloys could be produced by MA and the subsequent heat treatment using elemental crystalline powders. The structure change was studied primarily by X-ray diffraction, transmission and scanning electron microscopy (TEM and SEM), as well as differential scanning calorimetry (DSC).

2. Experimental procedures

Aluminium powders (average particle size ~50 μm) and chromium powders (average particle size ~10 μm) were placed in a ball-milling pot of 120 mm i.d. The conventional ball-milling method was deliberately chosen in order to ensure a low-energy MA process. The advantage of such a low-energy MA process exists in the larger possibility of retaining the non-equilibrium structures formed by the mechanical energy. The temperature of a vial during MA process was about 360 K in this experiment. Milling was carried out in a stainless steel vial with 1000 stainless steel balls of 10 mm diameter, and at a rotation speed of 90 r.p.m. The sample to ball ratio was kept at 1/120 by weight. Powders were sealed in the pot in an argon atmosphere with 4 wt % methanol and ball-milled for various lengths of time.

MA powders were characterized by X-ray diffraction study using CuKα radiation at room temperature. Thermal properties were examined in an argon atmosphere with DSC (Du-pont 910), at a heating rate of 0.33 K sec^{-1}. Electron microscopy (SEM and TEM) revealed the microstructure of the powders and its subsequent change during the heating stage which corresponded to the DSC curve. Samples for TEM were made by slicing the powder embedded in resin using a sapphire blade.

3. Result and discussion

3.1. Process of alloying

The MA process consists of repeated mechanical mixing, cold welding, fracturing, and rewelding of ultrafine alloy powders [15]. Fig. 1 shows the typical process of successive dispersion of chromium particles into the aluminium matrix by ball-milling for Al–

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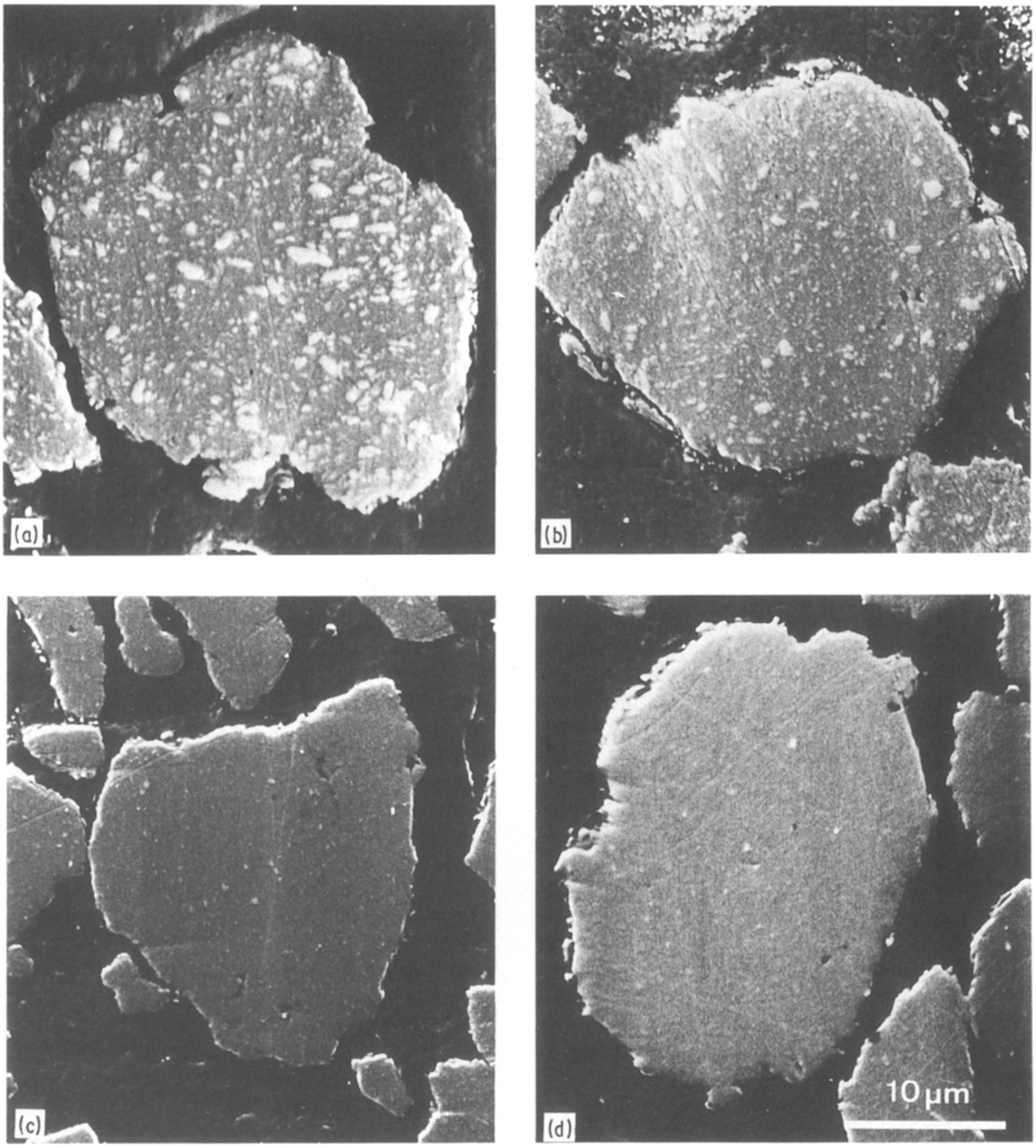


Figure 1 SEM images showing the typical process of successive dispersion of chromium particles into the aluminium matrix, after (a) 100 h, (b) 300 h, (c) 500 h and (d) 800 h.

15 at % Cr powders. As milling progresses, the chromium particles are further refined, as fracturing and cold welding of the powder particles continue. The reduction in the chromium particle size can be clearly seen in the SEM images as shown in Fig. 1: after ball-milling for 800 h, the chromium particles become sub-micrometre in size so that individual chromium particles cannot be identified by SEM (Fig. 1d).

Figs 2a and b show TEM images of a sliced sample ball-milled for 800 h. It is noticeable that very fine chromium particles are distributed in the amorphous matrix. After ball-milling for 1000 h, TEM images of the sample reveal locally no images of crystal grains as shown in Figs 2 c and d. The line patterns running left to right upwards are the wrinkles on the sample formed by the knife edge of the thin-slicing apparatus.

Quite similar results have been observed for Al–20 at % Cr powders.

3.2. MA of mixtures of elemental aluminium and chromium powders (Al–15 at % Cr)

Fig. 3 shows X-ray diffraction patterns of Al–15 at % Cr samples ball-milled for various lengths of time. The peak intensities of aluminium and chromium crystals decrease with increasing ball-milling time.

Fig. 4 shows DSC curves obtained during continuous heating at a rate of 0.33 K sec^{-1} for various lengths of ball-milling time. The exothermal peaks of the samples ball-milled for 50, 100 and 200 h appear at about 870 K, and it is confirmed by X-ray diffraction analysis that the reacion corresponds to the formation of an equilibrium γ-phase [16]. The peak temperature

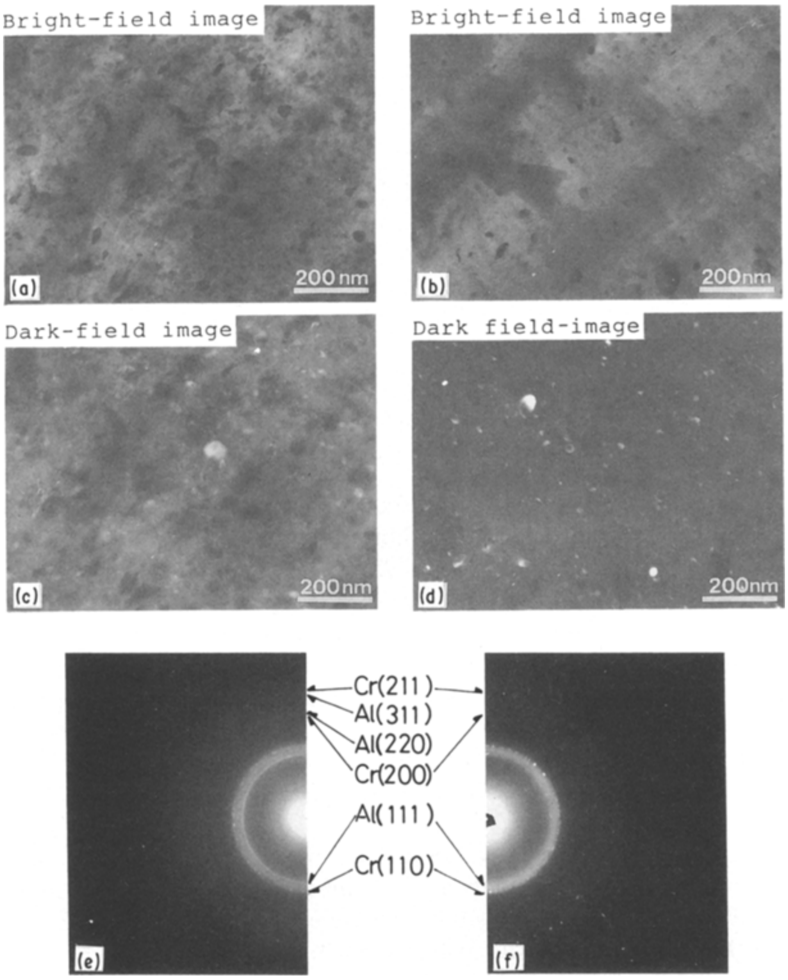


Figure 2 TEM images (a to d) and electron diffraction patterns (e and f) of Al–15 at % Cr samples ball-milled for (a, c, e) 800 and (b, d, f) 1000 h.

shifts to the lower one as the ball-milling time increases. The samples ball-milled for 200, 300 and 500 h have a relatively sharp exothermal peak at about 660 K. This also corresponds to the formation of an equilibrium γ-phase, and this temperature is about the same for γ formation in the case of mechanical grinding (MG) of rapidly solidified Al–15 at % Cr alloy powders [14]. These different temperatures for γ formation may be caused by the difference of the diffusion process. A higher temperature is necessary to form γ-phase for mixtures of elemental powders. However, a longer ball-milling time produces ultrafine structure and defect concentration in the powder, and lowers the temperature necessary for γ formation.

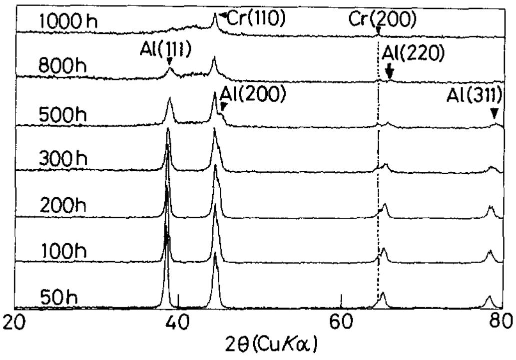


Figure 3 X-ray diffraction patterns of Al–15 at % Cr samples ball-milled for various lengths of time.

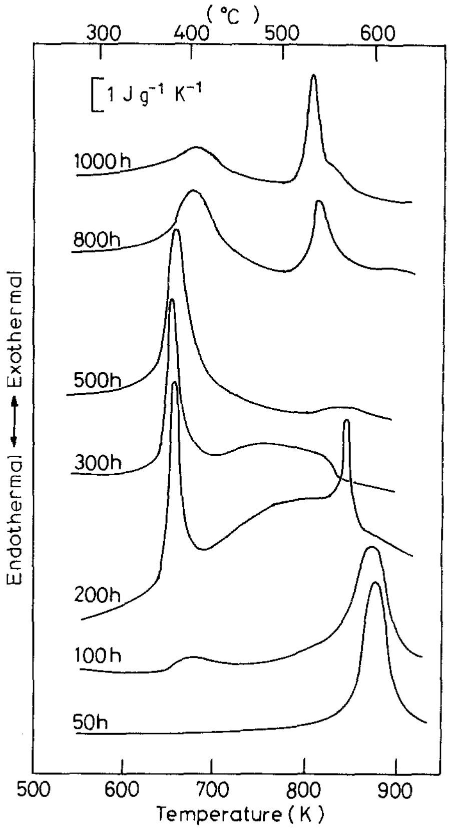


Figure 4 DSC curves of Al–15 at % samples ball-milled for various lengths of time. The DSC curves were taken during continuous heating at a rate of $0.33\,\mathrm{K\,sec^{-1}}$.

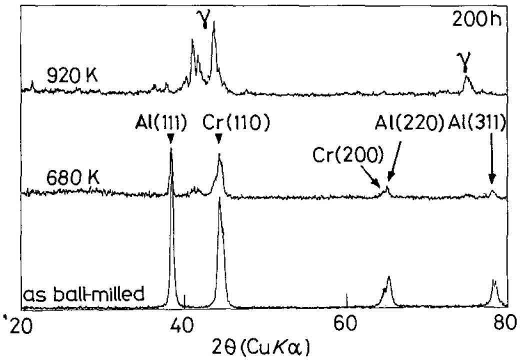


Figure 5 X-ray diffraction patterns of Al–15 at % Cr samples ball-milled for 200 h: as-milled and quenched from each heating temperature. The temperature corresponds to the DSC curve.

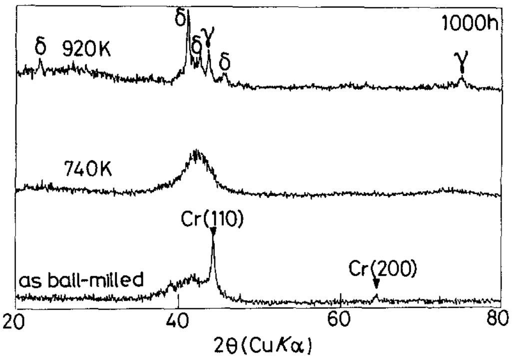


Figure 6 X-ray diffraction patterns of Al–15 at % Cr samples ball-milled for 1000 h: as-milled and quenched from each temperature. The temperature corresponds to the DSC curve.

X-ray diffraction patterns of samples as milled for 200 h and heat-treated samples are shown in Fig. 5. Just after the first peak temperature (680 K), it is noticed that the formation of γ-phase is in progress and crystalline aluminium and chromium remain in the sample. An equilibrium phase, γ, is only observed after heating to 920 K.

The samples ball-milled for 800 and 1000 h have two exothermal peaks. A broad peak observed at about 700 K corresponds to the amorphization of mechanically alloyed powders. The second peak observed at about 810 K corresponds to the change of amorphous phase into equilibrium phases γ and δ.

Fig. 6 shows X-ray diffraction patterns of samples as-milled for 1000 h and heat-treated samples. After the first peak temperature, all the crystalline peaks have disappeared; only a broad peak is left, indicating amorphization is complete to the resolution of X-ray diffraction. Equilibrium phases γ and δ are observed after heating to 920 K, and the γ formation temperature from the amorphous phase is lower than that from the mixture of the elemental powders.

TEM studies were performed to characterize the microstructure of the amorphous phase formed by heat treatment. Fig. 7 shows TEM images and an electron diffraction pattern of an Al–15 at % Cr sample ball-milled for 1000 h and heated to 740 K. Both bright- and dark-field images show a typical amorphous structure and the diffraction pattern exhibits only a broad diffused ring typical of an amorphous structure. The line patterns in this figure are again caused by the slicing apparatus.

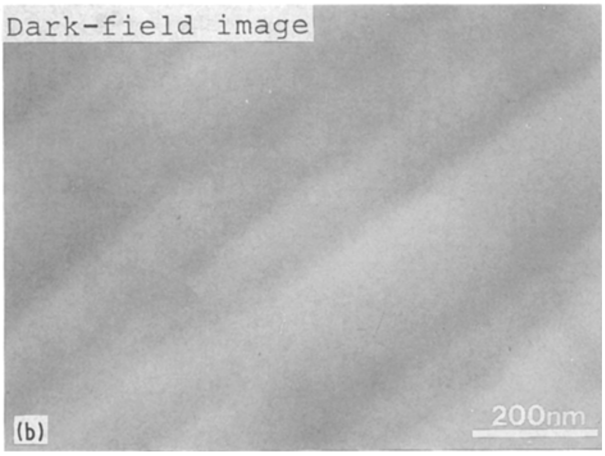
3.3. MA of mixtures of elemental aluminium and chromium powders (Al–20 at % Cr)

Fig. 8 shows X-ray diffraction patterns of Al–20 at % Cr samples after various lengths of ball-milling time. With increasing ball-milling time, the Bragg reflections of the elements become only slightly broader and their intensities decrease continuously.

Fig. 9 shows DSC curves obtained during continuous heating at a rate of 0.33 K sec^{-1} for various lengths of ball-milling time. The samples ball-milled for 50 and 100 h have a small exothermal peak at the lower temperature which corresponds to γ formation.

Bright-field image

Dark-field image



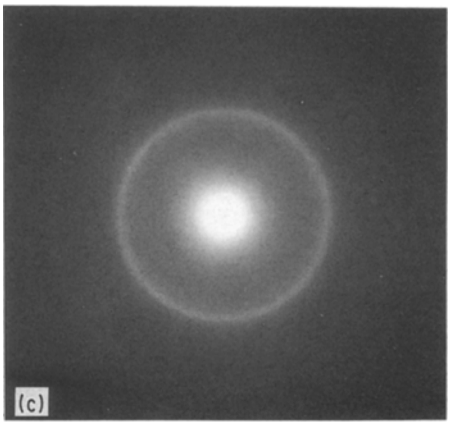


Figure 7 TEM images (a, b) and electron diffraction pattern (c) of an amorphous Al–15 at % Cr sample. The sample was ball-milled for 1000 h and heated to 740 K just after the first peak shown in Fig. 4

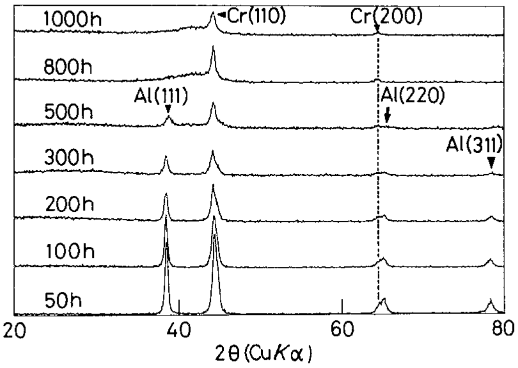


Figure 8 X-ray diffraction patterns of Al–20 at % Cr samples ball-milled for various lengths of time.

At about 870 K mixtures of elemental powders make γ-phase. However, this γ-phase co-exists with crystalline chromium phase. After full annealing, an equilibrium δ-phase has been formed from γ and chromium phases. The sample ball-milled for 300 h has a sharp exothermal peak at about 660 K. It corresponds to the γ formation as described in Section 3.2 and crystalline chromium still remains in the sample. γ- and chromium phases form δ-phase at about 850 K.

X-ray diffraction patterns of samples as-milled for 500 h and heat-treated samples are shown in Fig. 10. After the first peak temperature (770 K), a diffused amorphous-like peak and a crystalline chromium peak are observed. The second peak corresponds to the formation of δ-phase from both phases.

Fig. 11 shows X-ray diffraction patterns of samples as-milled for 800 h and heat-treated samples. The sample ball-milled for 800 h consists of an amorphous-like phase and some chromium phase. Only after heating to 850 K, is an unknown phase, X, observed. This phase changes into an equilibrium phase, δ, with an exothermal peak at about 900 K.

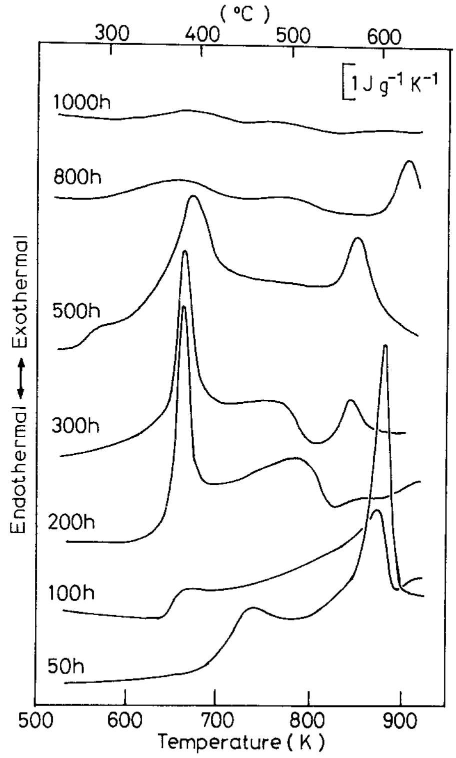


Figure 9 DSC curves of Al–20 at % Cr samples ball-milled for various lengths of time. The DSC curves were taken during continuous heating at the rate of 0.33 K sec^{-1}.

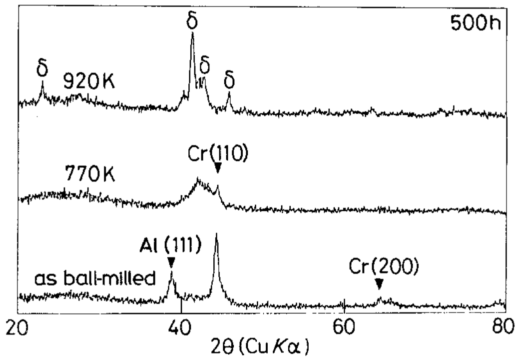


Figure 10 X-ray diffraction patterns of 20 at % Cr samples ball-milled for 500 h: as-milled and quenched from each heating temperature. The temperature corresponds to the DSC curve.

3.4. Extension of solid solubility

The lattice parameter of the aluminium-rich phase is shown in Fig. 12 as a function of ball-milling time. It decreases with increasing ball-milling time. The aluminium peak of X-ray diffraction patterns becomes diffuse as the ball-milling time increases. The extension of solid solubility is estimated by the use of King's relationship [17, 18] calculated from the data in solid solution. About 5 at % Cr is the maximum of the extended solid solubility, whereas the maximum equilibrium solid solubility is 0.37 at % Cr at 934 K [16].

3.5. Amorphization of MA powders by heat treatment

Heats of formation for solid alloys at 298 K from elemental aluminium and chromium solids are $-0.85\,\mathrm{kJ\,mol^{-1}}$ (γ-phase, 15.4 at % Cr) and $-0.98\,\mathrm{kJ\,mol^{-1}}$ (δ-phase, 20 at % Cr), respectively [19].

Only amorphous phase can be obtained by the heat treatment of Al–15 at % Cr MA powders as described in Section 3.2. Fig. 13 shows the DSC curve of an Al–15 at % Cr sample ball-milled for 1000 h. The sample is heated to 740 K after the first peak and quenched to room temperature. X-ray analysis (shown in Fig. 6) and TEM studies (shown in Fig. 7) show that the heat-treated powders, quenched from a temperature just above the first peak, are amorphous phase. When the sample is re-heated continuously at

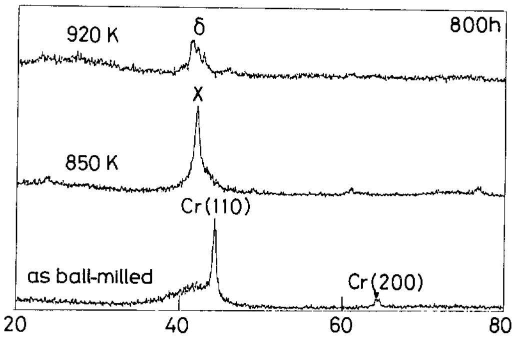


Figure 11 X-ray diffraction patterns of 20 at % Cr samples ball-milled for 800 h: as-milled and quenched from each heating temperature. The temperature corresponds to the DSC curve.

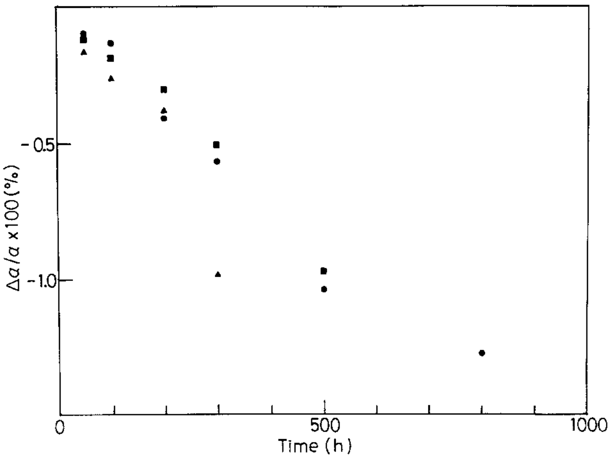


Figure 12 Lattice parameter of the aluminium-rich phase as a function of ball-milling time for (●) 15 at % Cr, (■) 20 at % Cr, (▲) 25 at % Cr.

the rate of 0.33 K sec^{-1}, it only shows an exothermal peak corresponding to crystallization into γ- and δ-phases because it is in the amorphous state at room temperature.

Activation energy for crystallization of the Al–15 at % Cr amorphous phase, which is prepared by 1000 h MA and heat treatment, is measured by the changes in the peak temperature due to the changes in heating rates (0.083, 0.17 and 0.33 K sec^{-1}). By the application of Kissinger's analysis [20], the apparent activation energy is determined to be 190 kJ mol^{-1}. This value and the crystallization temperature are lower than those of the Al–20 at % Cr amorphous phase produced by the mechanical grinding of rapidly solidified crystalline powders [14].

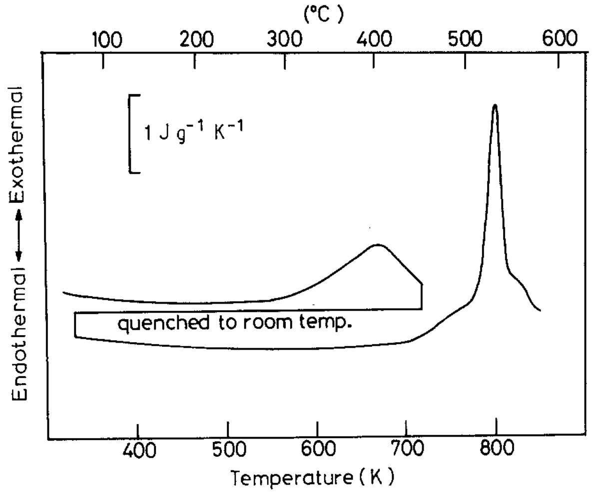


Figure 13 DSC curve of Al–15 at % Cr sample ball-milled for 1000 h. The sample was heated to 740 K for amorphization at a rate of 0.33 K sec^{-1} and quenched to room temperature, and then reheated for crystallization at the same rate.

4. Conclusions

Elemental powders of aluminium and chromium were mechanically alloyed by the use of conventional ball-milling. The chromium powder particles were broken into small pieces and dispersed in the aluminium matrix. In the later stages of ball-milling, both the particle size and the matrix crystal grain size became too small to be identified under the electron microscope.

During continuous heating at the rate of 0.33 K sec^{-1}, Al–15 at % Cr samples ball-milled for 800 and 1000 h showed two exothermal peaks. After the first peak temperature, all the crystalline peaks had disappeared, only a broad peak was left, indicating amorphization was complete to the resolution of X-ray diffraction. This was also confirmed by TEM studies. Amorphous Al–Cr alloys using elemental aluminium and chromium powders were formed by MA and subsequent heat treatment.

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