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Amorphous formation processes of Al-20 mol % Cr alloys by mechanical grinding of equilibrium intermetallic compounds

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The amorphization of Al–20 mol % Cr alloys were investigated when different starting powders were mechanically ground using a vibration-mill. Mechanical grinding (MG) of two types of starting powders were examined: (1) single δ (Al–20 mol % Cr) phase powders and (2) a mixture of γ (Al–15 mol % Cr) and ε (Al–30 mol % Cr) phases powders. Amorphous Al–Cr alloys could not be obtained by MG of single intermetallic compound (δ phase) as the starting powders. But in the case of MG using the mixture of intermetallic compounds (γ and ε phases), some parts of the MG powders changed phase into an amorphous phase with a Cr content of about 30 mol % at the initial stage of the milling. On further milling, the formed amorphous phase reacted with residual crystalline γ phase (Al–15 mol % Cr) to produce an amorphous phase with a Cr content of 20 mol %. The former amorphous phase crystallized into the δ and ε phases, and the latter crystallized into an equilibrium δ phase by subsequent heat treatment.

1. Introduction

Mechanical alloying [1] and mechanical grinding [2] are methods of amorphization from the solid crystalline state. Many amorphous binary transition metal alloys have been formed by MA of a mixture of elemental crystalline powders or by MG of crystalline intermetallics.

Al–Cr alloys are one of the most typical metal-transition metal system. The amorphization of the Al–Cr system was achieved by the MG of rapidly solidified crystalline powders [3, 4]. Amorphous Al–Cr alloys were also produced by MA and a subsequent heat treatment using elemental crystalline Al and Cr as the starting powders [5].

In this paper, equilibrium intermetallic compounds γ, δ and ε phases have been prepared by MA of elemental Al and Cr and subsequent heat treatment. The amorphous formation process of Al–20 mol % Cr alloys was investigated by the MG using two types of starting powders: (1) single δ(Al–20 mol % Cr) phase powders and (2) a mixture of γ(Al–15 mol % Cr) and ε(Al–30 mol % Cr) phase powders which just corresponds to the composition of the δ phase. The MG Al–Cr powders were investigated by X-ray diffraction, transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDAX) and differential scanning calorimetry (DSC).

2. Experimental procedures

The equilibrium intermetallic compounds γ, δ and ε phases powders were prepared by MA of Al (nominal purity 99.9% and particle size 20 μm) and Cr (nominal purity 99.9% and particle size 62 μm) and subsequent heat treatment. The intermetallic compounds γ and ε phases powders were mixed to the composition of Al–20 mol % Cr. In this way, we prepared the Al–20 mol % Cr alloys by two different ways, namely (1) the single δ phase intermetallic compound powders and (2) the mixture of γ and ε phases powders.

The two types of powders were mechanically ground and alloyed with a vibration mill (Nisshin Giken: super misuni NEV-MA-8) in an argon atmosphere for various times. The sample-to-ball-weight ratio was kept to 1 : 57.

MG powders were characterized by a X-ray diffraction study using CoKα radiation at room temperature. Thermal properties were examined in an argon atmosphere with a DSC (Perkin Elmer : DSC-7 instrument) at a heating rate of 0.33 K sec^{-1}. TEM (Hitachi : H-8000 electron microscope) revealed the microstructure of the powders and its subsequent change during the heating stage which correspond to the DSC curve. The chemical compositions of the microstructure were determined by EDAX (Kevex : DELTA plus-3 analyser). The samples for TEM were made by slicing the powder embedded in resin using a diamond blade.

3. Results and discussion

3.1. Mechanical grinding of intermetallic compound δ phase powders

Fig. 1 shows X-ray diffraction patterns of samples after MG of the single δ phase powders. With increasing

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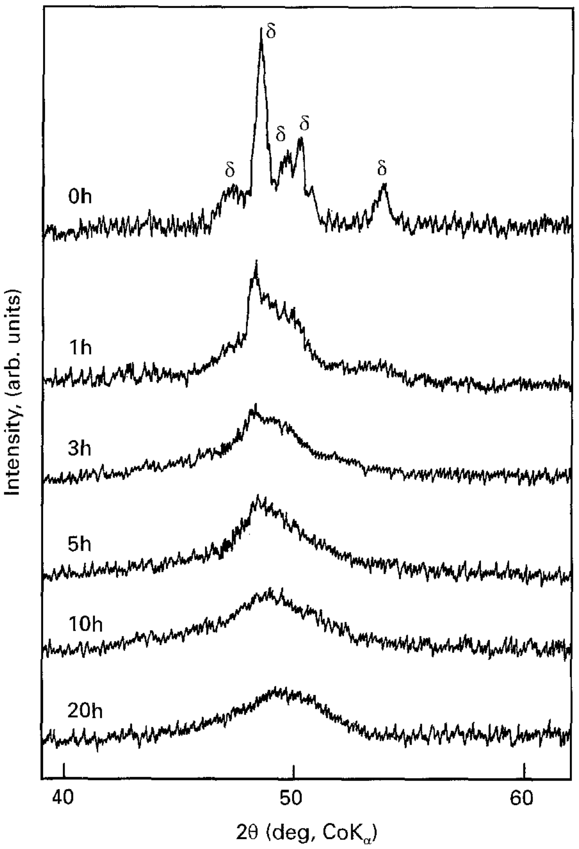

Figure 1 X-ray diffraction patterns of single δ phase samples vibration-milled for various times.

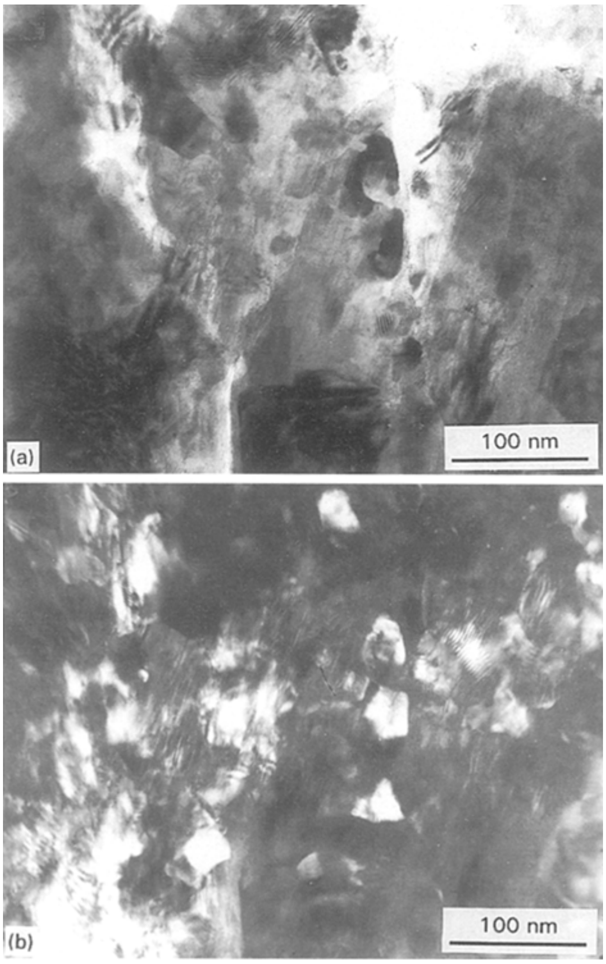

Figure 2 TEM images and electron diffraction patterns of single δ phase samples vibration-milled for 0 and 72 ks. (a) Bright-field image, 0 h (b) Dark-field image, 0 h (c) Electron diffraction pattern, 0 h (d) Bright-field image, 20 h (e) Dark-field image, 20 h (f) Electron diffraction pattern, 20 h.

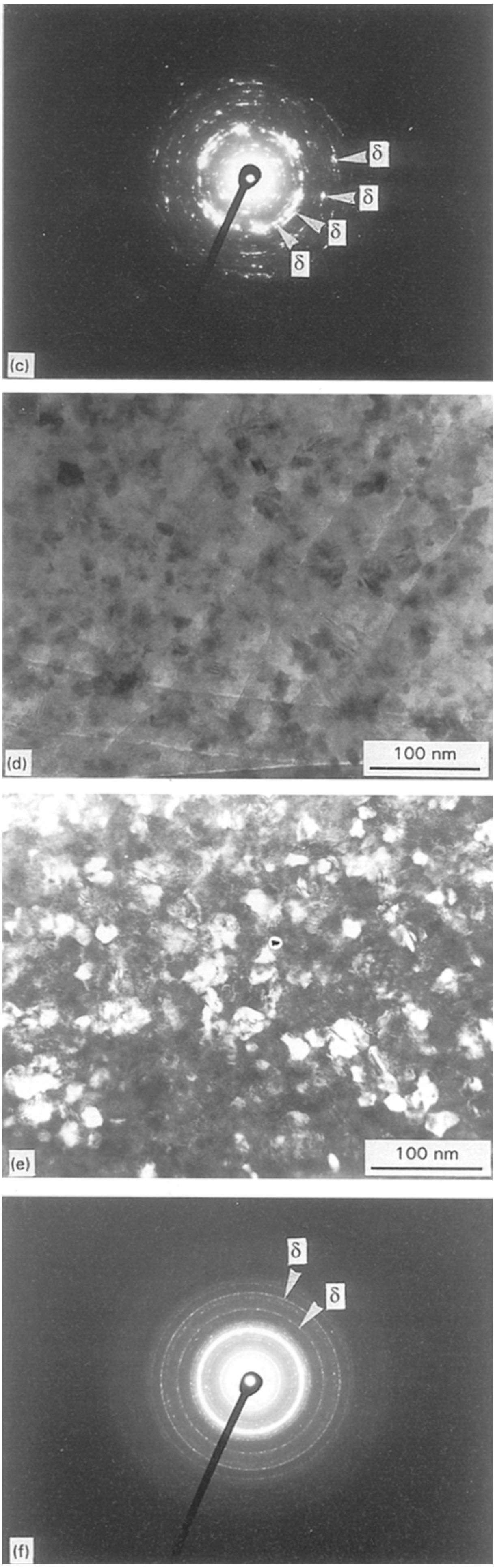

Fig. 2 (Continued)

milling time, the peaks decrease in their intensities and become broader. Finally MG powders reveal a halo-like profile between $2\theta = 45°$ and $55°$. Fig. 2 shows TEM images of the single δ phase powders milled for 0 and 20 h. The δ grains are observed in Fig. 2. The δ grain size is about 31 nm. This value is similar to the value (about 34 nm) evaluated from the half width value of the δ diffraction peak by using the Scherrer formula [6]. The δ grains are finely dispersed in the sample milled for 20 h as shown in Fig. 2. The δ size is about 11 nm. It is confirmed from this TEM observation that the sample milled for 20 h is not an amorphous phase but nano-crystalline δ grains although they show a halo in the X-ray diffraction pattern. DSC curves of MG powders heated to 973 K are shown in Fig. 3. Both X-ray diffraction patterns and TEM images of the sample as-milled for 20 h and the heat treated sample are shown in Figs. 4 and 5. The diffraction peaks of sample heat treated to 973 K are a little sharper than that of the sample as-milled for 20 h as shown in Fig. 4, while the δ size hardly changes as shown in Fig. 5. Therefore the exothermal reaction as shown in Fig. 3 corresponds to the relaxation of the strain in powders introduced during MG.

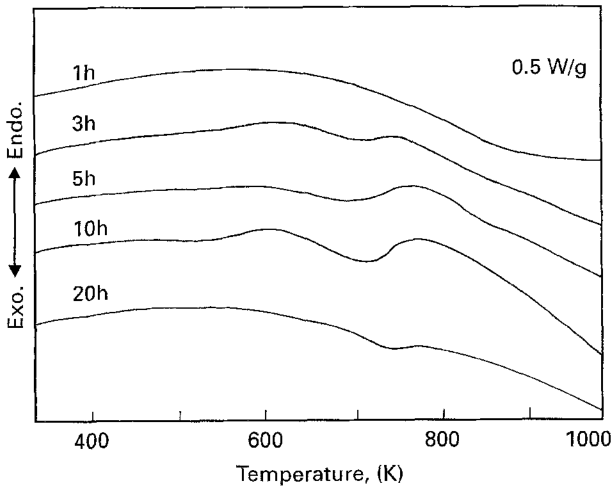

Figure 3 DSC curves of single δ phase samples vibration-milled for various times. The DSC curves are taken during continuous heating at a rate of 0.33 K sec^{-1}.

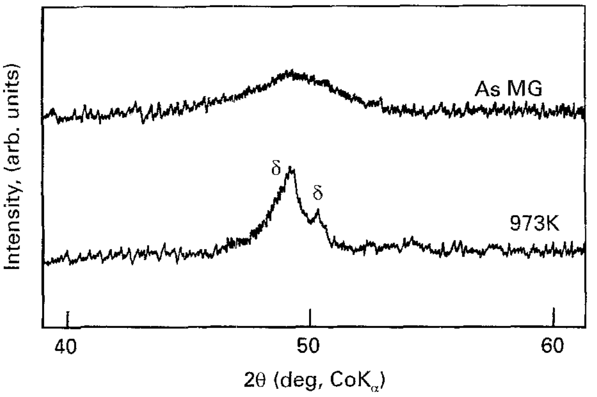

Figure 4 X-ray diffraction patterns of single δ phase samples vibration-milled for 20 h: as vibration-milled and quenched from each heating temperature corresponding to the DSC curve.

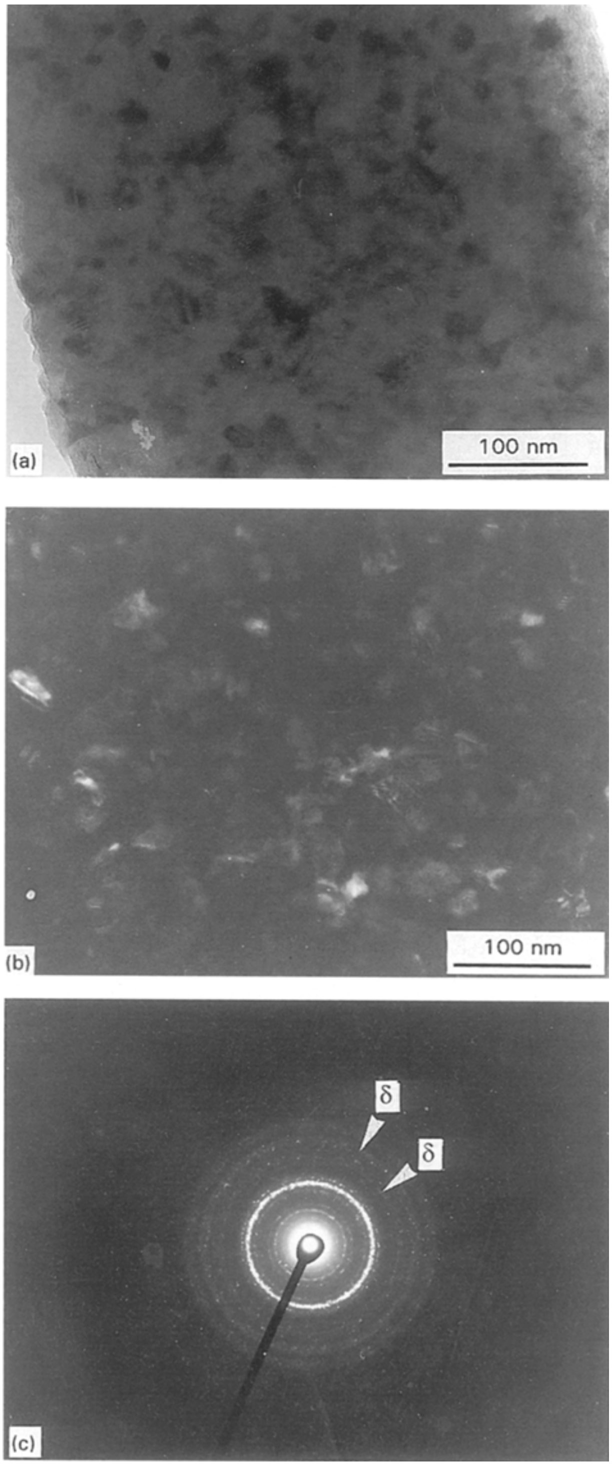

Figure 5 TEM images and electron diffraction pattern of heat treated sample vibration-milled for 20 h. (a) Bright-field image (b) Dark-field image (c) Electron diffraction pattern

3.2. Mechanical grinding of mixtures of the γ and ε phase powder

Fig. 6 shows the X-ray diffraction patterns of the mixtures of γ and ε phase powder vibration-milled for various times. With increasing milling time, the peak intensities decrease and a broad amorphous peak develops between $2\theta = 45°$ and $55°$. After 20 h milling, all the crystalline peaks have disappeared and only a broad peak is left. This tendency is almost the same as in case of MG of the single intermetallic δ phase.

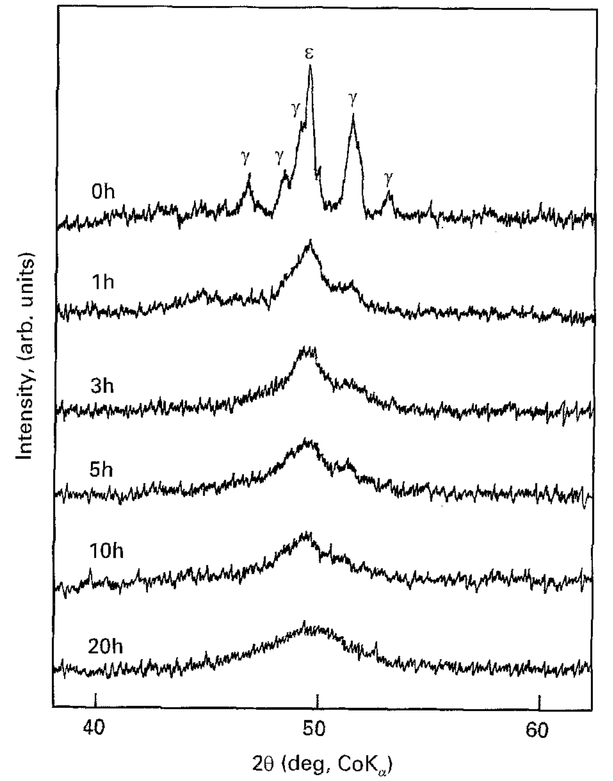

Figure 6 X-ray diffraction patterns of mixture of γ and ε powders vibration-milled for various times.

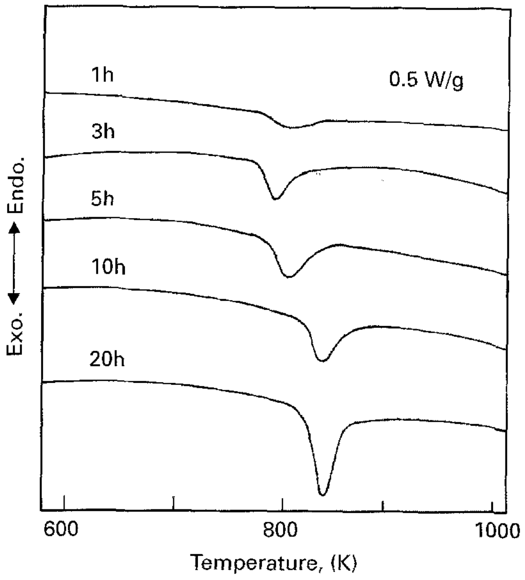

Figure 7 DSC curves of mixture of γ and ε powders vibration-milled for various times. The DSC curves are taken during continuous heating at a rate of 0.33 K sec^{-1}.

Fig. 7 shows DSC curves obtained during the continuous heating of the samples mechanically alloyed for various milling times at a rate of 0.33 K sec^{-1}. The exothermal peaks of the samples milled for 1, 3 and 5 h are lower than those of the samples milled for 10 and 20 h by about 50 K.

Fig. 8 shows TEM images of samples milled for various times. From the bright field image as shown in Fig. 8a and the diffraction pattern as shown in Fig. 8c, the γ and ε particles coalesce in the sample milled for 1 h. In the bright field image of the sample milled for 3 h, moire patterns can be seen as shown in Fig. 8d.

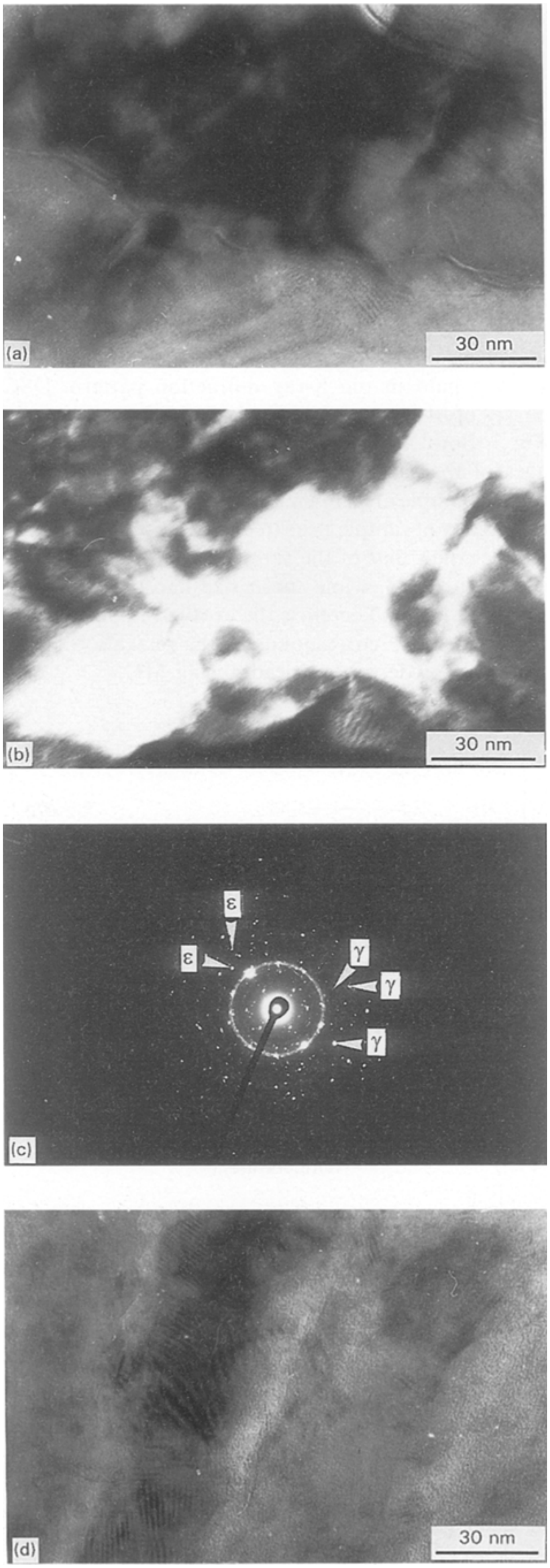

Figure 8 TEM images and electron diffraction patterns of mixture of γ and ε powders vibration-milled for various times. (a) Bright-field image, 1 h (b) Dark-field image, 1 h (c) Electron diffraction pattern, 1 h (d) Bright-field image, 3 h (e) Dark-field image, 3 h (f) Electron diffraction pattern, 3 h (g) Bright-field image, 10 h (h) Dark-field image, 10 h (i) Electron diffraction pattern, 10 h (j) Bright-field image, 20 h (k) Dark-field image, 20 h (l) Electron diffraction pattern, 20 h.

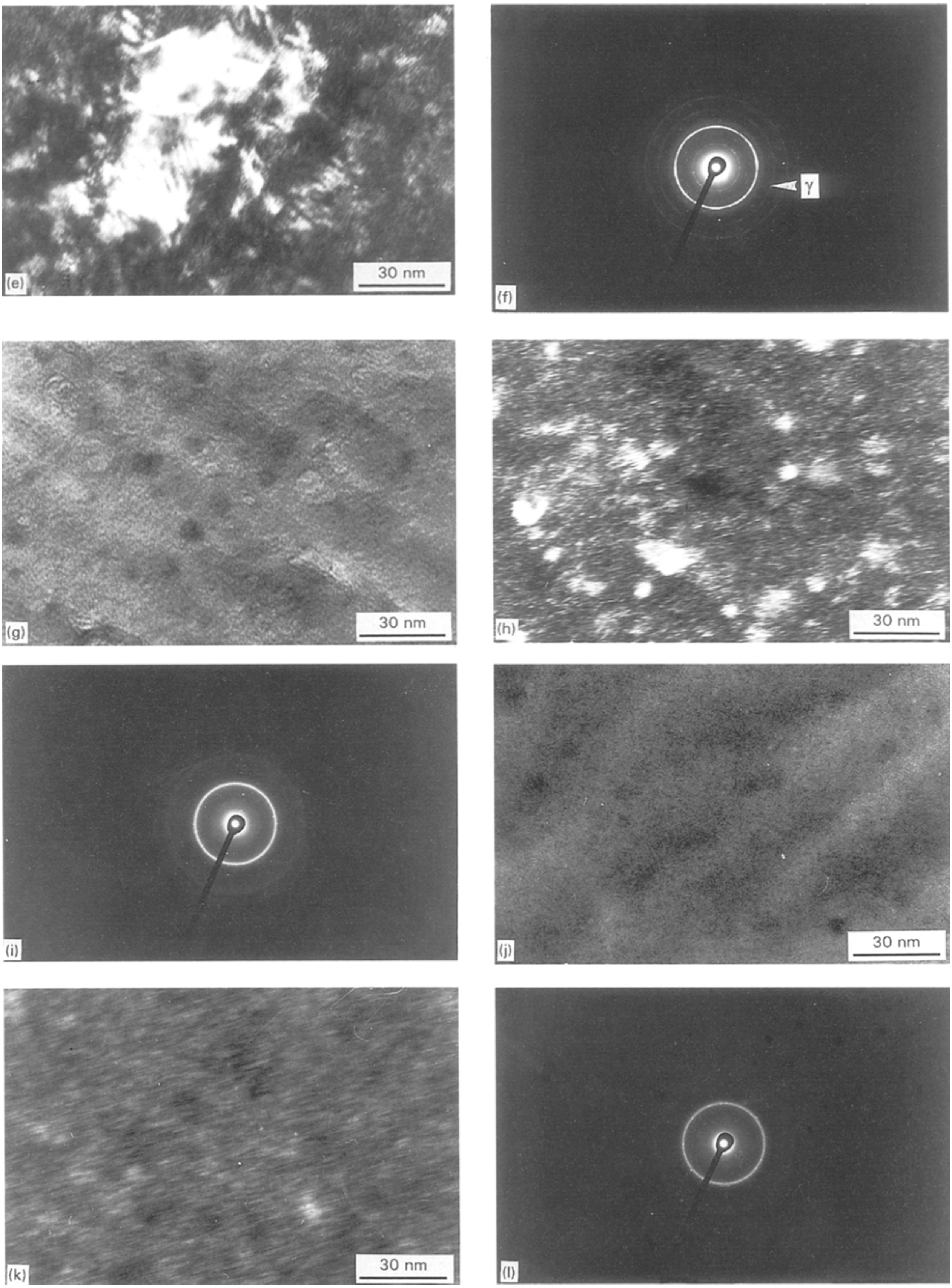

Figure 8 (continued)

From the calculation of the moire space these small particles are identified to be γ. As the milling time increases, the γ size decreases as shown in Fig. 8 and the powders become completely amorphous so that the γ phase can not be seen after milling for 20 h.

Fig. 9 shows the results of EDAX experiments for the composition of the amorphous phase. The Cr content of the amorphous phase formed by 3 and 5 h milling is about 30 mol %, and that of the amorphous phase formed by 10 and 20 h milling is about 20 mol %. The former is termed an ε-type amorphous

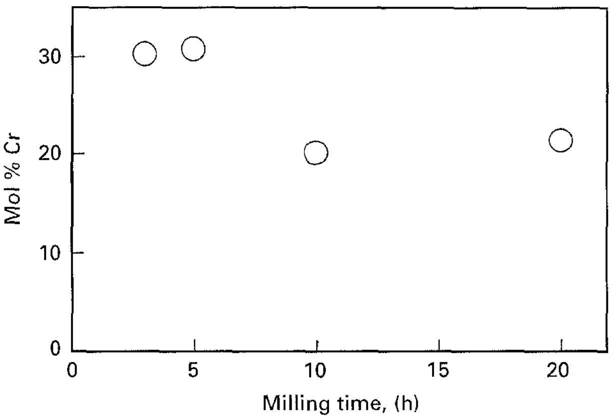

Figure 9 EDAX to determine the composition of the amorphous phase obtained by milling the mixture of γ and ε powders for various times.

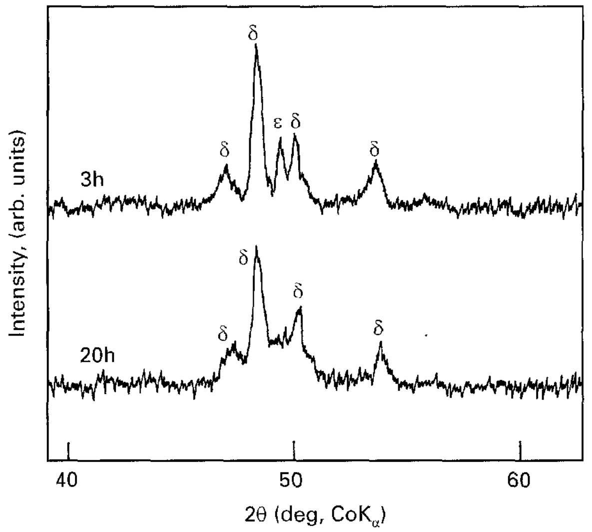

Figure 10 X-ray diffraction patterns of mixture of γ and ε powders vibration-milled for 3 and 20 h: quenched from a heating temperature of 973 K. The temperature corresponds to the DSC curves.

phase and the latter is termed a δ-type amorphous phase. Two different types of amorphous phase can be obtained from the same starting powders by MG as well as the case of MG using fully heat-treated atomized powders [4].

X-ray diffraction patterns of samples continuously heat treated to 973 K after milling for 3 and 20 h are shown in Fig. 10. The exothermal peak at about 770 K corresponds to a change in the amorphous phase to the δ and ε phases. The peak observed at about 850 K corresponds to a change in the amorphous phase to an equilibrium δ phase. The apparent activation energy for crystallization from the δ-type amorphous phase is about 240 kJ mol^{-1}. An ε-type amorphous phase is produced at the initial stage. As the milling progresses further, pre-existing γ particles and the ε-type amorphous phase are mixed uniformly to produce a δ-type amorphous phase.

3.3 Amorphous formation process of Al–20 mol % Cr alloys

An amorphous alloy powder is not obtained by the MG of the single δ phase (Al–20 mol % Cr) powders but by the MG of the mixtures of equilibrium γ (Al–15 mol % Cr) and ε (Al–30 mol % Cr) intermetallic compound powder or by the MG of as-atomized powders or fully heat-treated powders of Al–20 mol % Cr alloys as has been reported previously [4]. A free-energy diagram of the Al–Cr system has been calculated for a temperature of 300 K [7–9]. Fig. 11 shows that the free energy of the mixtures of γ and ε powders for an average composition of δ is located at G^0. An increase in free energy is required in order to form an amorphous phase from the intermetallic compounds. Brimhall *et al.* [10] have suggested that for intermetallic compounds with narrow ranges of homogeneity, a slight deviation beyond the stoichiometric concentration results in a large rise in the free energy. As material transfer occurs between the γ and ε phases during MG, the compositions of the two compounds will be shifted towards the average δ phase. The compound will now have off-stoichiometric compositions and the free energies will rise, to values, for example, represented by G^1 and G^2. The free energy of the mixture of off-stoichiometric intermetallics will then be G^3, which is larger than that of the corresponding amorphous alloy at G^4. Thus $\Delta G = G^3 - G^4$ could act as the driving force for amorphization. Consequently an amorphous phase can be obtained in the case of MG using of the mixtures of γ and ε powders. The mechanical attrition raises the free energy of crystals by the generation of (1) point defects, (2) lattice defects and (3) chemical disorder. In the case of MG using the single δ phase powders, the free energy of the δ phase powders is raised by (1) and (2), but the amorphization does not occur. While in the case of MG using the mixtures of γ and ε powders, an amorphous phase can be obtained because of raising the free energy by (3). Therefore in the Al–Cr alloys the amorphization occurs due to raising the free energy not by (1) and (2), but by (3).

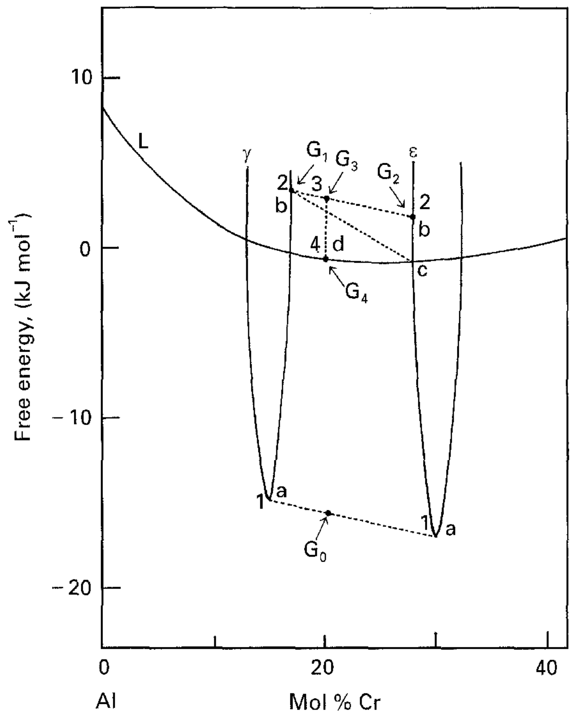

Figure 11 Free energy diagram for the binary Al–Cr system.

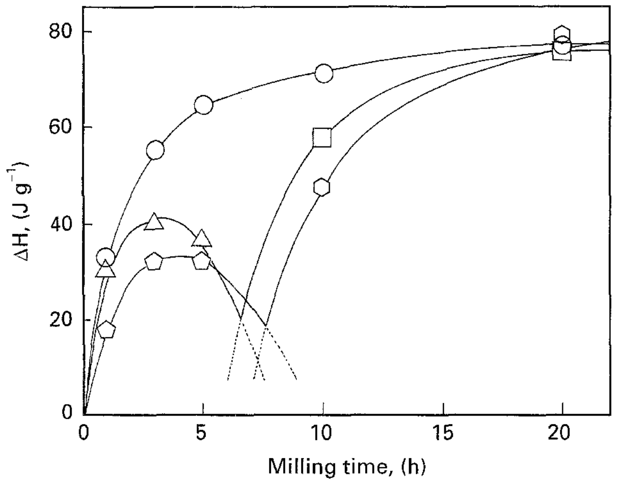

Figure 12 Total heat output of exothermal peaks in DSC curves for various times. ○ : As atomized powders, △: ε type heat treated powder, □ δ-type heat treated powder, ⌂ Mixture of γ and ε powders ε type. ⬠ mixture of γ and ε powder δ type.

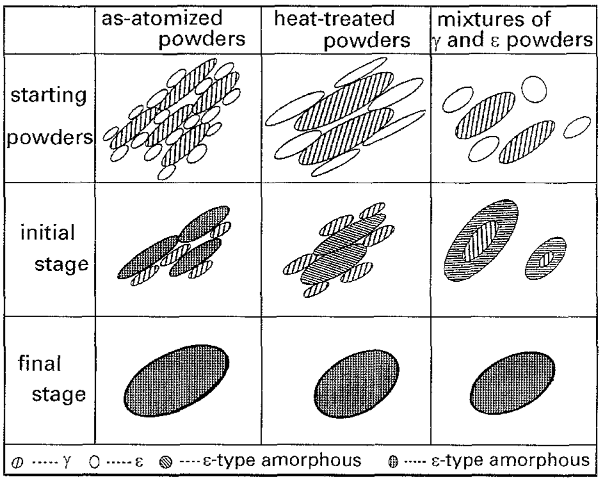

Figure 13 Schematically amorphous formation in the cases when as-atomized powders, heat-treated powders and mixture of γ and ε powders are used as starting powders.

Fig. 12 shows the total heat of crystallization of the samples from which a volume fraction of the formed amorphous phase can be estimated. For the amorphization of the intermetallic compounds, they have to be energized by milling to the amorphous state. So, the starting powders in the higher energy state can be easily energized to the amorphous state. If the three kinds of starting powders consisting of γ and ε phase are compared in their energy states, the hierarchy from highest energy state is (1) as-atomized Al–20 mol % Cr powders, (2) fully heat-treated atomized powders [4] and (3) mixtures of equilibrium γ and ε powders. The hierarchy corresponds fairly well to the amorphization speed by milling.

In the case of MG using as-atomized powders, a δ-type amorphous phase is produced directly. In the cases of MG using heat-treated powders or the mixture of γ and ε powders, an ε-type amorphous phase is produced at the initial stage. As the milling progresses further, pre-existing γ particles and the ε-type amorphous phase are mixed uniformly to produce the δ-type amorphous phase. In the case of MG using as-atomized powders, it is easy to mix γ and ε uniformly because they are previously finely mixed by rapid solidification. Therefore the amorphous formation using as-atomized powders can explain the process 1 → 2 → 3 → 4 as shown in Fig. 11. While in the cases of MG using heat-treated powders, it becomes a little harder to mix them uniformly because γ and ε grains grow by heat treatment. Furthermore, in the case of MG using the mixtures of γ and ε powders, it is very hard to mix γ and ε particles. In such cases, the amorphous formation can explain the process a → b → c → d. It is assumed that only an ε phase occurs in amorphization because the crystal structure or the hardness of the ε phase is different from that of the γ phase.

Fig. 13 shows schematically amorphous formation in the cases when as-atomized powders, heat-treated powders and mixtures of γ and ε powders were used as starting powders. The crystallization temperature of the ε-type amorphous phase obtained from heat-treated powders is higher than that of the ε-type amorphous phase obtained from the mixtures of γ and ε powders. This is the reason why structures around each ε-type amorphous phase are different as shown in Fig. 13, and why different impurity levels exist in the respective samples.

4. Conclusions

Two types of powders: (1) single δ(Al–20 mol % Cr) phase powders and (2) the mixtures of γ(Al–15 mol % Cr) and ε (Al–30 mol % Cr) phases powders were mechanically ground by the use of a vibration-mill.

In the case of MG using the single δ phase powders, an amorphous phase could not be produced. While in the case of MG using the mixtures of γ and ε powders, the amorphization of mixtures of intermetallics occurred so as to cause a steep rise in the free energy of the line compounds as material transfer moved their compositions off-stoichiometry. But in comparison with MG using as-atomized powders or fully heat-treated powders, the amorphization of the mixtures of γ and ε powders occurred more slowly because they were thermodynamically the most stable.

At the initial stage of the milling, some parts of the MG powders changed phase into an ε-type amorphous phase with a Cr content of about 30 mol %. On milling further, the ε-type amorphous phase reacted with the residual crystalline γ phase (Al–15 mol % Cr) to form a δ-type amorphous phase with a Cr content of about 20 mol %. At the continuous heating stage, the former changed into δ and ε phases at about 810 K while the latter changed into an equilibrium δ phase at about 850 K.

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