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Formation and thermal stability of nanocrystalline Cu–Ti–Ni prepared by mechanical alloying

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Abstract

The formation and thermal stability of nanocrystalline $Cu_{70}Ti_{20}Ni_{10}$ powders by mechanical alloying have been studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). The composition (at.%) of the sample has been examined by energy dispersive X-ray analysis (EDX) attached to SEM. After milling, the material was found to have a disordered f.c.c. structure, with nanocrystalline grain sizes around 4.7 nm determined from the f.c.c. (111) diffraction peak. The DSC signal decreases monotonically with isothermal transformation owing to grain growth. The crystal grains do not grow by heating until the intermetallic $TiCu_3$ and NiTi phases nucleate at 450 °C.

Keywords: Mechanical alloying; Cu–Ti–Ni system; Nanocrystalline materials; Thermal stability

1. Introduction

The first definitive demonstration that structurally amorphous alloys can be prepared by mechanical alloying (MA) was reported by Koch et al. [1] for samples of $Ni_{60}Nb_{40}$. The technique of MA, usually made via ball milling, has been used extensively in recent years to synthesize non-equilibrium phases such as amorphous quasicrystalline and nanocrystalline materials [2–5].

Nanocrystalline materials exhibit quite different properties from both crystalline and amorphous materials [6], due to the structure in which extremely fine grains are separated by what some investigators have characterized as "gas-like" disordered grain boundaries [7]. Since the nanocrystalline structure is a non-equilibrium state and subject to grain growth by heating, the systematic study of stability of the structure is one of the most important topics with respect to its application. There have been a number of observations on the stability of nanophase materials against grain growth [8–12].

In this paper, we report on the formation and thermal stability of nanocrystalline $Cu_{70}Ti_{20}Ni_{10}$ produced by mechanical alloying.

2. Experimental procedure

Elemental Cu, Ti and Ni powders were blended to the composition 70 at.% Cu + 20 at.% Ti + 10 at.% Ni and then sealed in a cylindrical steel vessel in an argon gas atmosphere. Subsequent MA was carried out in a rotating ball mill (90 mm in diameter), with a ball-to-powder weight ratio of 15:1 and a revolving velocity of 250 rev min^{-1}. Steel balls of 20 mm diameter were used. The milling process was performed in alternating intervals of 10 min milling, followed by a pause of 10 min in order to keep the milling temperature relatively low, without substantial cooling of samples. The vessel was opened after 1, 3, 5, 10, 20 and 40 h of processing in an argon atmosphere, and small amounts of sample powder were taken out for XRD, DSC, SEM and TEM observation. The as-milled powders were annealed in evacuated quartz tubes to induce growth at several temperatures, ranging from 440 to 1000 °C for 600 s, and several annealing times were tried at 440 °C, ranging from 10 to 600 min. In the

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isothermal experiments, the samples were heated at a rate of 20 K min^{-1} up to a starting temperature of the DSC peak, and held until the signal was no longer measurable.

3. Results and discussion

Fig. 1 shows a series of XRD patterns of mechanically alloyed $Cu_{70}Ti_{20}Ni_{10}$ powders as a function of milling time t. As t increases, all the diffraction lines of the intact elements broaden in width and decrease in intensity. The peak broadening represents a reduction in the crystallite size and an inducement of strain in the milled samples. No XRD peaks of any compound were found, except for those associated with the elemental powders. The Ni peaks disappear after 10 h of MA, and the Ti peaks disappear after 20 h of MA. The XRD spectrum after 20 h of MA shows a disordered f.c.c. structure. No structural changes were observed upon further milling up to 100 h.

Fig. 2 shows the t-dependence of the crystallite size of the f.c.c. phase estimated by (111) peak. The crystallite size was estimated using Scherrer's formula [13] given by $D_{hkl} = k\lambda/\beta\cos\theta$, where D_{hkl} is the crystallite size estimated by a (hkl) line, k the Scherrer constant, β the half-width, λ the X-ray wavelength and θ the diffraction angle. The crystallite size decreases with t and reaches a steady state value of 4.7 nm after 20 h of milling. In addition, an estimate was made as to how the mechanical strain is stored during the MA process. From the half-widths of the Bragg peaks, the root mean square strain is calculated by applying Williamson and Hall's equation [14,15]. The (atomic) strain increases with t for $t < 20$ h.

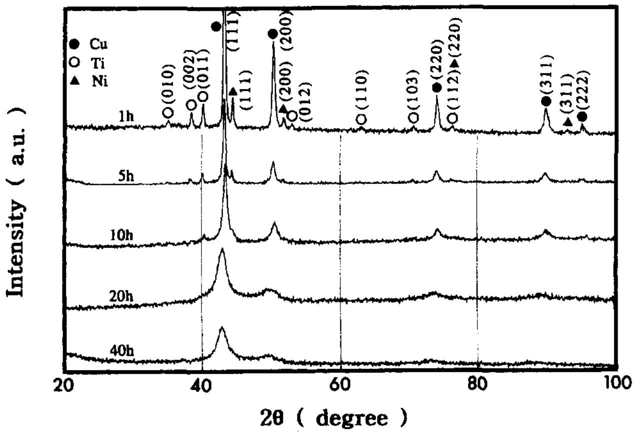

Fig. 1. XRD patterns of $Cu_{70}Ti_{20}Ni_{10}$ as a function of t.

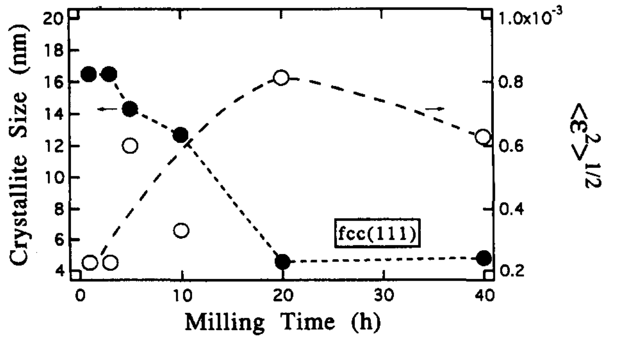

Fig. 2. Crystallite size and strain of mechanically alloyed $Cu_{70}Ti_{20}Ni_{10}$ as a function of t.

Fig. 3 shows the composition (at.%) as determined by EDX analysis. After 10 h of MA, the composition (at.%) is almost the same as that of the initial ratios of Cu, Ti and Ni powders. This result is similar to Fig. 1, showing the process of a disordered f.c.c. structure in XRD. Therefore it can be said that the variation of composition indicates the presence of a nanocrystallization process, which is also indicated by XRD and DSC.

The SEM technique was used to follow the changes in size and shape of mechanically alloyed powders at different stages of MA. The SEM images in Fig. 4 show the morphology of $Cu_{70}Ti_{20}Ni_{10}$ as a function of t. Evidently, the individual initial particles agglomerate to form composite particles of about 370 μm in diameter, which are blocky or plate-like in shape. The increase in t leads to disintegration of the agglomerated particles and smaller particle diameters. After 40 h of MA the particle size is much finer, about 50 μm in diameter, and more uniform in shape. The shape of the powder particles is irregular, with a blocky or angular morphology.

The DSC curve for alloy powder after 40 h of MA is shown in Fig. 5(a). The crystallization temperature T_x and peak temperature T_p at a heating rate of 20 K min^{-1} are 451 and 470 °C respectively. The acti-

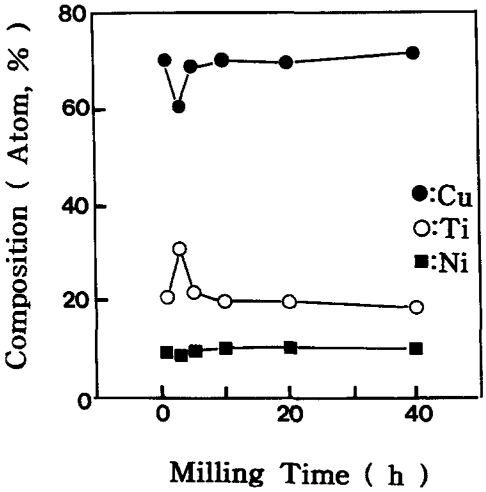

Fig. 3. Composition (at.%) of $Cu_{70}Ti_{20}Ni_{10}$ as a function of t.

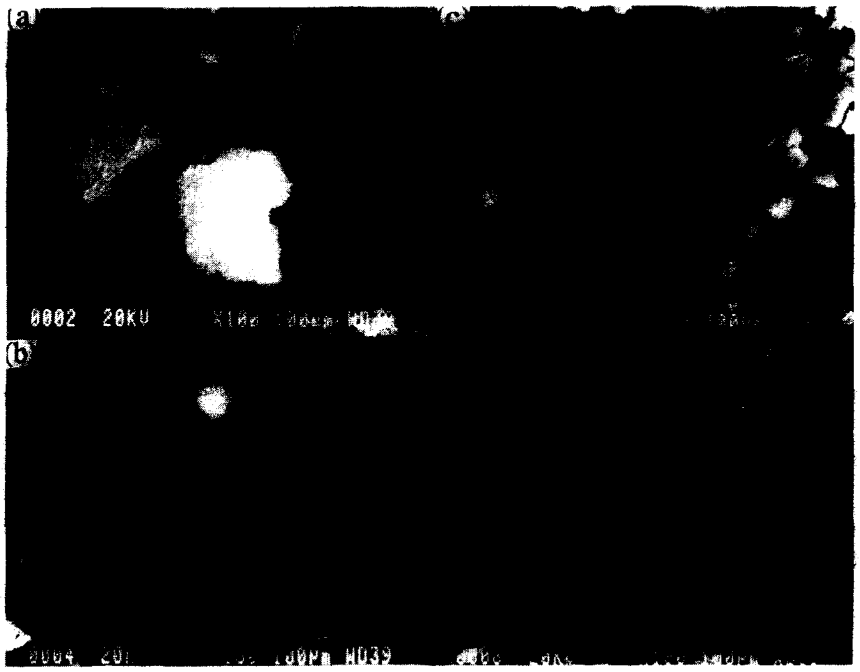

Fig. 4. SEM images for $Cu_{70}Ti_{20}Ni_{10}$ after different t: (a) 1 h, (b) 10 h, (c) 20 h and (d) 40 h.

vation energy is estimated to be 242.7 mJ mg^{-1}, using the Kissinger equation [16]. Chen and Spaepen [17] have proposed a calorimetric test to distinguish between amorphous and nanocrystalline samples. In the isothermal experiments, the samples were heated at 20 K min^{-1} to a starting temperature of the DSC peak ((a) 393, (b) 403 and (c) 413 °C), and held until the signal was no longer measurable. As shown in Fig. 5(b), the signals decay monotonically, demonstrating unambiguously that the transformation process is a grain growth type. The integration of the exothermic peak with respect to a baseline from $t_{I_{p2}}$ to t_f, after the isothermal starting point I_{p2}, is estimated to be 162.5, 159.5 and 155.0 mJ mg^{-1} for 393, 403 and 413 °C respectively. The difference between these values and $\Delta H = 164.0$ mJ mg^{-1} measured in the scanning experiment is due to grain growth during heating. In particular, a small rising peak is observable at the isothermal start point I_{p1}. This may be due to the effect of a small amount of amorphous material included in the nanocrystalline material. This phenomenon may be a general characteristic of nanophase materials produced by MA. The values of the small exothermic peaks (a) and (c) are estimated to be 8.5 and 2.1 mJ mg^{-1} respectively.

Fig. 6 shows a series of XRD patterns of mechanically alloyed powders obtained by quenching samples which were isochronally annealed at several temperatures for 600 s. The intensities of the XRD peaks associated with the f.c.c. structure increase sharply with increasing annealing temperature, while the line-width decreases, suggesting that grain growth

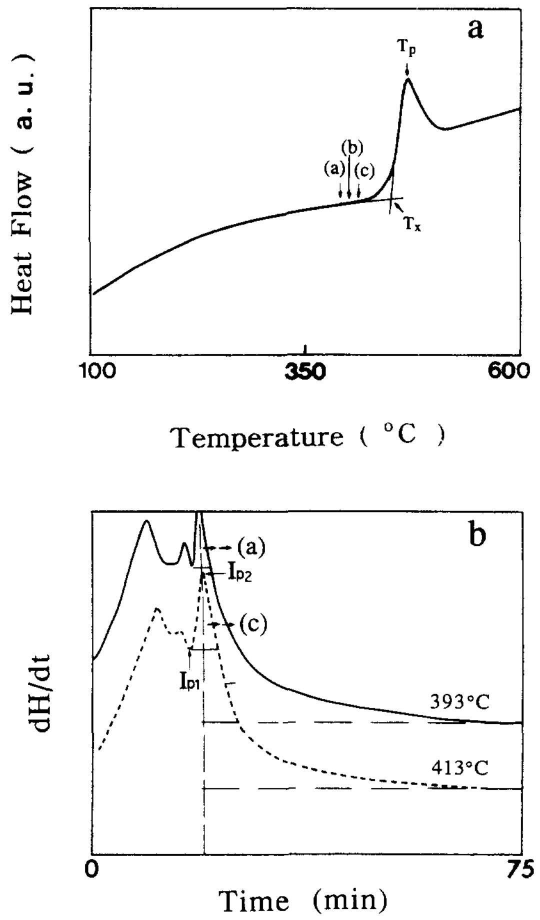

Fig. 5. (a) DSC thermogram of $Cu_{70}Ti_{20}Ni_{10}$ at a heating rate of 20 K min^{-1}. (b) Isothermal calorimetry traces at two temperatures for $Cu_{70}Ti_{20}Ni_{10}$.

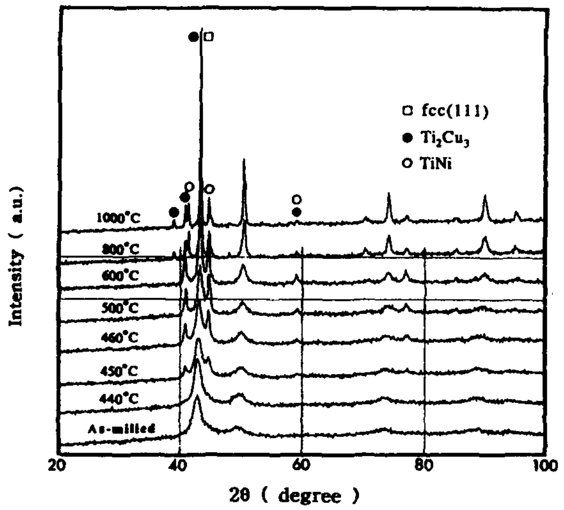

Fig. 6. XRD patterns of mechanically alloyed $Cu_{70}Ti_{20}Ni_{10}$ after heating at 40 K min^{-1} to the indicated temperatures.

takes place. Above 450 °C, peaks allotted to Ti_2Cu_3 and TiNi are observed and strain relaxation also takes place (changes of grain size and strain by heating are shown in Figs. 8(a) and 8(b)). The grain sizes determined from the final f.c.c. (111), (200) and (220) diffraction peaks after annealing at 1000 °C are estimated to be about 10.7, 9.8 and 10.3 nm respectively.

Fig. 7 shows the XRD patterns after annealing at (a)

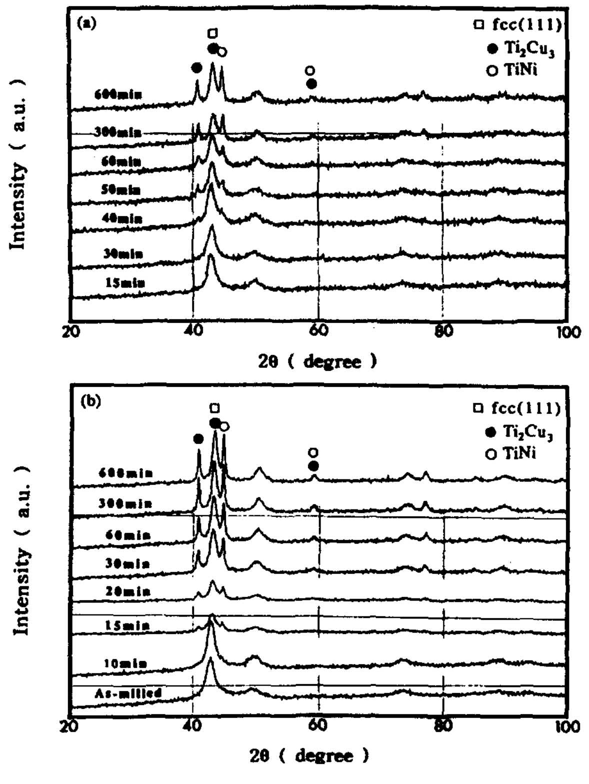

Fig. 7. XRD patterns of mechanically alloyed $Cu_{70}Ti_{20}Ni_{10}$ after heating at 40 K min^{-1} to the indicated times.

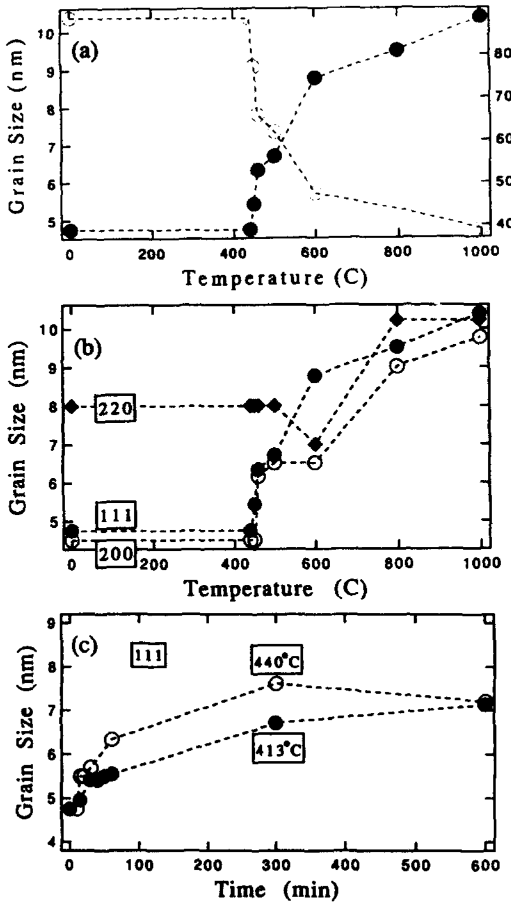

Fig. 8. Grain size and strain of mechanically alloyed $Cu_{70}Ti_{20}Ni_{10}$ after heating at 40 K min^{-1} to the indicated temperatures and times.

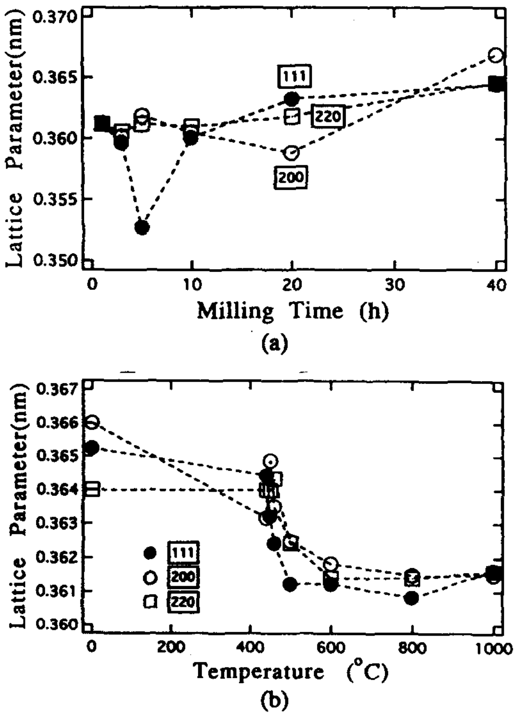

Fig. 9. Lattice parameters of mechanically alloyed $Cu_{70}Ti_{20}Ni_{10}$ after heating at 40 K min^{-1} to the indicated *t* and temperatures.

413 °C and (b) 440 °C for different times of mechanically alloyed powders. The peaks of Ti_2Cu_3 and TiNi are observed after 40 min at 413 °C and 15 min at 440 °C respectively. The peaks of Ti_2Cu_3 (014), (006) and TiNi (111) can be seen after 600 s at 800 °C (Fig. 6), however, they cannot be found after 600 min at 413 and 440 °C (Fig. 7). After annealing the grain size changes as a function of annealing time; these changes are estimated from the (111)-f.c.c. diffraction peak as shown in Fig. 8(c). The grain sizes determined from the final (111)-f.c.c. diffraction peaks are estimated to be about 7.2 nm, for 600 min, at 413 and 440 °C.

The change in lattice parameters with t is shown in Fig. 9(a). The lattice parameter for f.c.c. (111) decreases quickly after 5 h of milling, which results in a decrease of the nearest neighbor distance, which then increases and reaches a constant value after 20 h of milling. After 20 h of MA the lattice parameter calculated from the f.c.c. (111) peak is 0.3632 nm, which is slightly larger than the 0.3615 nm quoted for pure copper, suggesting that the other atoms are incorporated in the Cu matrix [11]. The lattice parameters of the heated powder decrease sharply when the annealing temperature is higher than 450 °C, reaching the value of pure Cu (0.3615 nm).

Fig. 10 shows the TEM bright-field images of the powders together with their corresponding selected area electron diffraction patterns (a) in the as-milled state, in the annealed states at (b) 600 °C, (c) 800 °C and (d) 1000 °C, and (e) in the annealed state at 440 °C for 600 min. Fig. 6(a) clearly shows an abundance of disordered f.c.c. grains with a crystallite size of about 5 nm, which agrees well with the value of about 4.7 nm estimated from the X-ray diffraction measurement. The corresponding diffraction pattern shows continuous rings due to the random orientation of adjacent crystals. The grain size of powders heated at the indicated temperatures agrees roughly with the calculated value.

4. Conclusions

We have produced nanocrystalline $Cu_{70}Ti_{20}Ni_{10}$ alloy powders with a crystallite size of about 4.7 nm by mechanical alloying. In the isothermal experiments,

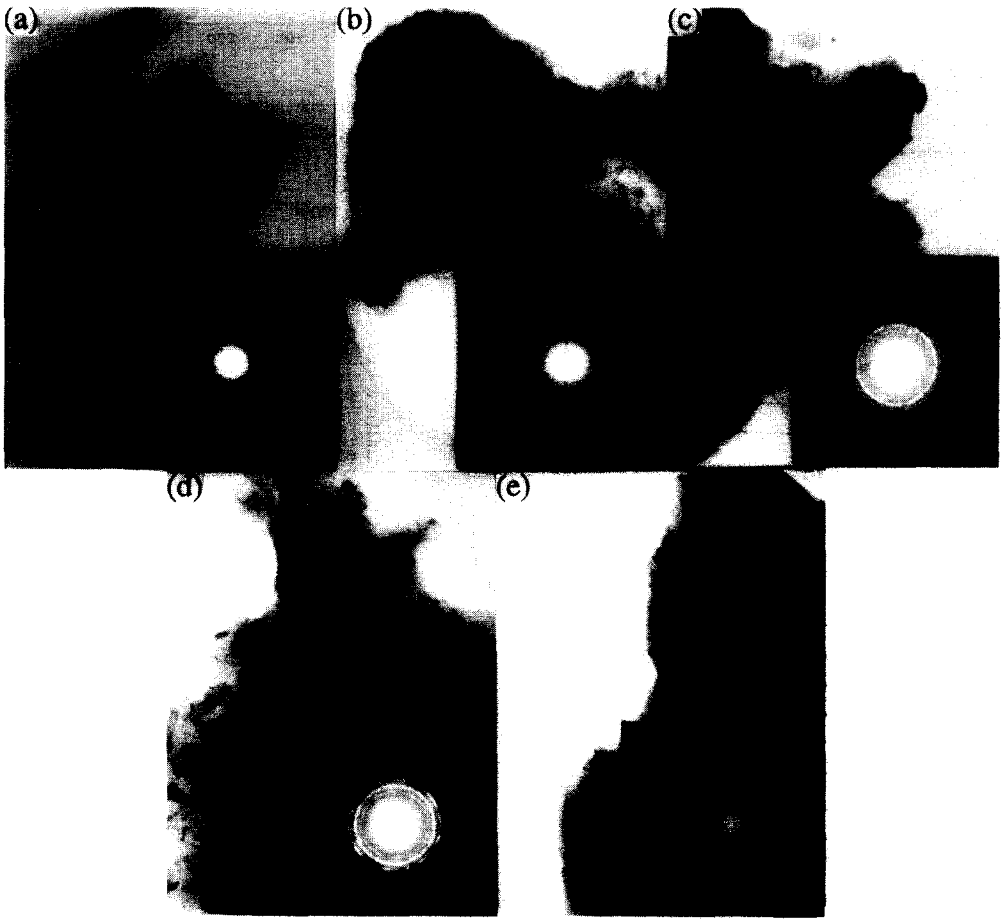

Fig. 10. Bright-field TEM images and selected electron diffraction patterns of powders that were (a) as-milled, annealed at (b) 600, (c) 800 and (d) 1000 °C, (e) annealed at 440 °C for 600 min.

the signals decay monotonically, demonstrating that the transformation process is a grain growth type. In particular, a small rising peak I_{p1} at the isothermal start point may be due to the effect of a small amount of amorphous material included in the nanocrystalline material and may be a general characteristic of nanophase materials produced by MA.

Peaks from Ti_2Cu_3 and TiNi are observed in samples heated to temperatures above 450°C and strain relaxation was found to occur. Thus the appearance of Ti_2Cu_3 and TiNi and grain growth take place at the same time. The lattice parameters of the heated powders decreased when the annealing temperature was increased above 450 °C, finally reaching the value of pure Cu (0.3615 nm).

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