Study on the Formation of Nano Vacancy Ordered Phases by Mechanical Alloying

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Abstract

In the present investigation, the powder mixture of Al (70 at. %), Ni (15 at. %) and Cu (15 at. %) was mechanically milled in an attritor ball mill for 10, 20, 40, 60, 80 and 100 h in hexane medium at 400 rpm. The isothermal annealing of 100 h mechanically milled powder was done at 700 °C for 20, 40 and 60 h. The powders were characterized using X-ray diffraction, differential thermal analysis and transmission electron microscopy techniques. It was observed that mechanical alloying led to the formation of nano vacancy ordered (τ_3) phase after 80 h of milling. In the case of 100 h mechanical milling (MM) and subsequent annealing at 700 °C for 20, 40 and 60 h, powder exhibited the formation of ordered and perfect τ_3 phase with larger grain sizes. The phase formation and transformations in the above systems were discussed.

INTRODUCTION

Non-equilibrium processing technique such as mechanical milling/alloying (MM/MA) is being used recently to design the materials with the desirable microstructures suitable for technological applications [1–3]. This process has attracted the attention because of its potential in nanoscience and technology. It can provide the route for synthesizing bulk nanocrystalline and amorphous materials from immiscible systems and intermetallic compounds [4–5].

Ternary Al based alloys have been extensively studied recently for developing high temperature materials for industrial application [6]. In addition to the complex crystalline phases such as Laves phase, topologically closed phase and vacancy ordered phases, the quasicrystalline phases also appear in many systems. There are efforts to understand the origin of these complex metallic phases and their role for developing the advanced materials. It is found that many of the complex crystalline phases are related to quasicrystalline (QC) phases. For example, it was shown that the vacancy ordered phases, designated as τ phase can be considered as approximant phase to QC structures. The vacancy ordered phase, could be described in terms of basic B2 (CsCl) type of cell with ordering of vacancy along the [111] direction. The B2 (CsCl) superstructure being a common structure type in intermetallics contains two different types of atoms located on the vertex and center of a cubic unit cell. The series of stable vacancy ordered phases (VOPs) and its relation with one-dimensional quasiperiodicity was demonstrated by Chattopadhyay *et al.* [7]. The different t phases can be identified on the basis of the number of divisions made by Bragg peaks along [111] direction in the diffraction patterns. For example, τ_3 represents three times ordering along [111] direction of the basic CsCl unit cell and it is exhibited by three equal spacings in the diffraction pattern along [111] direction. VOPs in Al–TM (TM transition metal) system are a special class of structures wherein vacancies in the TM sublattice are ordered on the (111) planes [8]. Vacancy ordered phases (τ_3) in the Al–Cu–Ni system have arrangements of vacant and filled sites in the truncated Fibbonacci sequence along the [111] direction. These phases can be classified in terms of different sequence of ordering among Al atoms,

Cu/Ni atoms and vacancies along triad axis of the basic CsCl structure [9].

The aim of the present investigation was to synthesize nano vacancy ordered phase (VOP) by mechanical alloying of Al (70 at. %), Cu (15 at. %) and Ni (15 at. %) and to understand the microstructural and phase stability during subsequent annealing.

EXPERIMENTAL

Synthesis

Powder mixture of 10 g containing 70 at. % Al, 15 at. %, Cu and 15 at. % Ni was taken. These elemental powders were mechanically milled in Szegvari attritor ball mill with a ball to powder ratio of 80 : 1 (with total mass of balls being 800 g), under the speed of 400 rpm. The attritor had a cylindrical stainless steel tank of inner diameter 13 cm. Hardened steel balls 6 mm in diameter were used. The milling operation was conducted for up to 100 h in hexane medium. Isothermal heat treatments of 100 h milled powders were carried out at 700 °C for 10, 20 and 40 h.

Structural Characterization

The mechanically milled and annealed samples were subjected to structural characterization employing powder X-ray diffraction (XRD) using Philips PW 1710 diffractometer with CuK_α radiation (λ = 1.5418 Å). Differential thermal analysis (DTA) with heating rate of 10 °C /min was carried out. Thus prepared samples were studied by TEM using a Philips CM-12 electron microscope. The grain size and the lattice strain of the sample can be calculated from the integral width of the XRD peaks. Cauchy and Gaussian components can be obtained from the ratio of full width at half maximum intensity (2ω) and integral breadth (β) [10]. In a single line analysis the apparent crystallite size '*D*' and strain '*e*' can be related to Cauchy (β_C) and Gaussian (β_G) widths of the diffraction peak at the Bragg angle θ;

$$D = k\lambda/\beta_C \cos\theta \quad (1)$$

$$e = \beta_C/4 \tan\theta \quad (2)$$

The constituent Cauchy and Gaussian components can be given as

$$\beta_c = (a_0 + a_1\psi + a_2\psi 2)\beta$$

$$\beta_G = \_b_0 + b_{1/2}\_\psi\ 2\pi\_{1/2} + b_1\psi + b_2\psi 2\_\beta$$

where a_0, a_1 and a_2 are Cauchy constants, b_0, $b_{1/2}$, b_1 and b_2 are Gaussian constants, and $\psi = 2\omega/\beta$ where β is the integral breadth obtained from XRD peak. The values of Cauchy and Gaussian constant were taken from the Table of Langford [10]: a_0 = 2.0207, a_1 = 0.4803, a_2 = 1.7756; b_0 = 0.6420, $b_{1/2}$ = 1.4187, b_1 = 2.2043, b_2 = 1.8706.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of elemental powder showing Al, Cu and Ni peaks as well as the gradual evolution of τ_3 phase. Finally, after 80 and 100 h of milling, all the peaks corresponding to pure metals disappeared and instead broad peaks appeared (see Fig. 1, curves *5*, *6*). After milling for 60 h the phase formation was found to be completed and consequently the sample became τ_3 phase within 100 h of milling. It is clearly seen that, in course

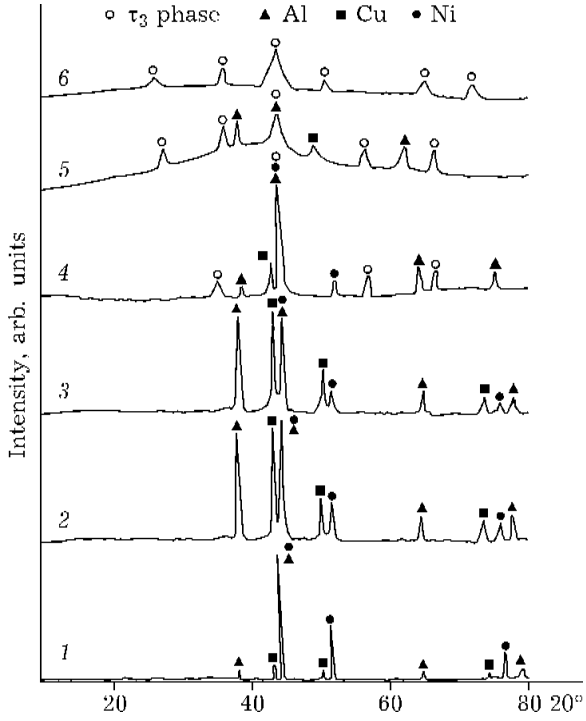

Fig. 1. XRD patterns for $Al_{70}Ni_{15}Cu_{15}$ elemental powder (*1*) as well as milled powders for different milling durations, demonstrating the gradual evolution of τ_3 phase, h: 10 (*2*), 20 (*3*), 40 (*4*), 60 (*5*), 100 (*6*).

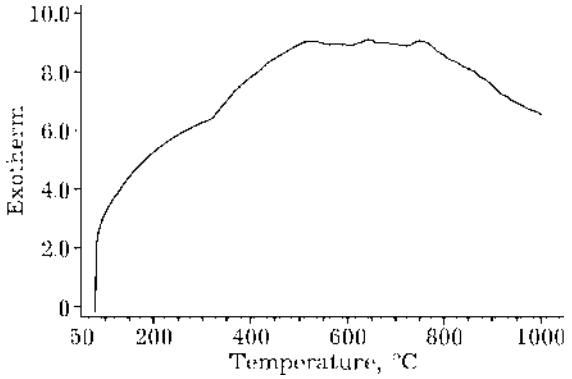

Fig. 2. DTA curve of the 100 h MM powders showing the broad exothermic peak suggesting the release of stored energy in the powder induced during milling. No phase transition can be seen.

of milling, the peak intensities are changing and broadening, suggesting that the solid solution among the elements and a large amount of defects are being introduced into the samples. The relative peak intensities of the final milled samples are found to be close to that of standard τ_3 phase as reported in JCPDS file [11], indicating that there is no texture induced into the samples during milling. By analyzing the peak broadening, the grain size and lattice strain were determined. The calculated crystallite size is found to be ~12 nm and the lattice strain to be ~0.675 % in case of 100 h MM powders. This confirms that by this milling technique we are able to obtain the nano VOP phase containing some defects causing the disordering in structure and leading to the peak broadening. The strain energy appears to be high from the estimated lattice strain (0.675 %) and this stored strain energy induced during milling can be found to release during DTA and annealing treatment.

Figure 2 shows the result of DTA investigation of 100 h MM powder. A broad hump in the DTA curve is seen which may correspond to annealing the defects in the system and thus the energy is released. It reaches a maximum at around 600 °C. No other sharp exothermic/ endothermic peaks corresponding to any phase transformation are observed. From this one can qualitatively understand the amount of energy released during the treatment.

Figures 3 show XRD patterns obtained from 100 h MM and subsequently annealed at 700 °C for 20, 40 and 60 h respectively. In all the cases the peak broadening is found to be reduced compared with that in the as-milled condition (see Fig. 3, curve *1*). This can be attributed to strain relaxation along with domain coarsening and perfect ordering. Figure 3, curve *4* was indexed using τ_3 structure with a = 8.7 Å which is the superstructure of B2 phase. It is interesting to note that the formation of vacancy ordered τ_3 phase due to mechanical milling seems to be possible in Al–Cu–Ni alloys system, even though the milling technique is known to introduce disordering among the atoms.

This formation of τ_3 phases was also monitored through rigorous transmission electron microscopic investigation by obtaining selected area diffraction patterns and microstructural features at different stages. The initial milling (10–20 h) of the starting powder mixture produces a lamellar (or layered) microstructure. It can be seen that the lamellar structure initiated from the edge of the Al powder. Further plastic deformation of these lamellae and diffusion of atoms between

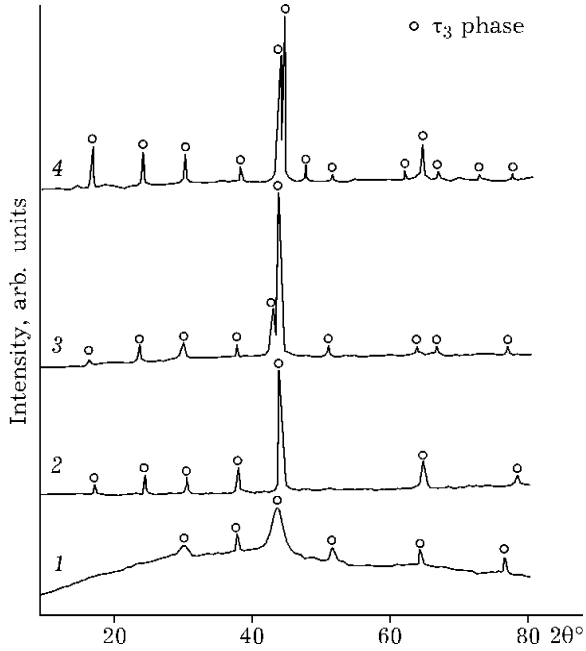

Fig. 3. XRD patterns from 100 h MM (*1*) and after annealing at 700 °C for 20 (*2*), 40 (*3*), 60 h (*4*). In all the cases the peak broadening is found to be reduced compared to that in the as-milled condition. This can be attributed to strain relaxation, grain coarsening and increase in degree of ordering.

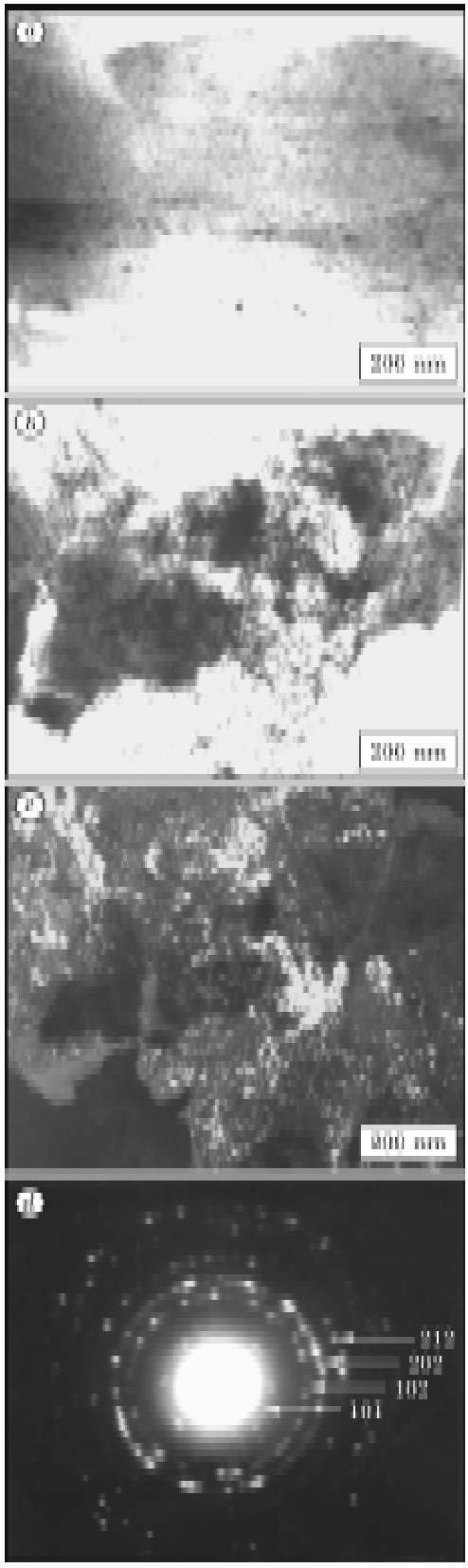

Fig. 4. Bright field TEM image of 60 (*a*) and 100 h MM sample (*b*); corresponding dark field image (*c*) and diffraction pattern (*d*). The rings observed in the diffraction patterns can be indexed due to τ_3 phase.

lamellar took place with increasing milling time. This lamellae microstructure gradually disappeared and a nanocrystalline microstructure evolved (as shown in Fig. 4, *a*–*c*). The bright and dark field TEM images clearly show the evolution of fine grains having sizes ranging from 10 to 20 nm (see Fig. 4, *b*, *c*), which agrees with the data, obtained from XRD patterns. The SAD pattern in Fig. 4, *d* was indexed due to τ_3 phase with the same lattice parameter that was obtained from XRD patterns. It is pertinent to point out that the τ_3 phase was designated as an approximant phase of decagonal quasicrystal by Dong *et al.* [12]. It is also interesting to note that the B2 phase is not stable in this system during milling. However, in the present milling experiments τ_3 phase was found to be a dominant phase,

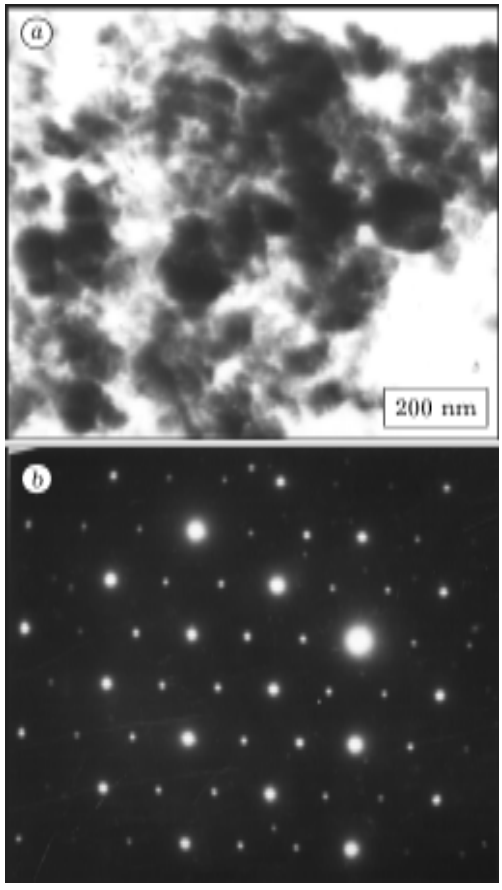

Fig. 5. TEM bright field image of 100 h MM and annealed at 700 °C for 60 h (*a*); the corresponding single crystal diffraction pattern of [110] zone axis (of pseudo cubic structure) clearly reveals the characteristic τ_3 phase (*b*) .

whereas after subsequent annealing treatment single τ_3 ($Al_3(NiCu)_2$) phase has formed (Fig. 5). The grain size appears to increase compared to that in as-milled sample. The single crystal diffraction pattern can be indexed due to τ_3 phase (see Fig. 5, *b*). The τ_3 phase is characterized by vacancy ordering in a B2 (CsCl) lattice. The vacancy sites are ordered along [111] direction of B2 pseudo cell dividing it into three periods; eventually the transformed cell is distorted rhombohedral. This can also be described by a hexagonal cell. It is known that in Al–Cu binary neither B2 nor τ_3 phase is stable unlike Al–Ni binary alloys, which could be due to the different electronic effect of Cu compared to that of Ni and other transition metal elements. As the composition of the present phase is close to the τ_3 (Al_3Ni_2 type), there is a less chance of formation of B2 phase, though the τ_3 is understood to be a superstructure of B2 phase. It can be understood that the excess Al can be accommodated in the form of defects or minor loss due to oxidation, which is unavoidable during milling. It is clear from the present investigation that we could synthesize nano and disordered τ_3 phase initially, and during subsequent annealing the more ordered and perfect form of τ_3 phase can be obtained. The grain coarsening can also be observed. But it will be possible to determine the annealing treatment where the strain relaxation and annihilation of the defects will be possible without much grain coarsening. Attempts are underway to understand the ordering among the Al/Ni/Cu atoms because it appears that this ordering could be related to the disordering among the metallic atoms and not among the vacancy and the metallic atoms. Otherwise we would have got other kind of disordered structures. But in the milled powder we have obtained τ_3 phase, which indicates that the vacancy is somewhat already ordered in the structure.

CONCLUSIONS

The formation of nano τ_3 vacancy ordered phase in the alloy system, Al–Ni–Cu was established by mechanical alloying of the elemental powder. The nano grain size was estimated to be around 10–20 nm in the milled sample. There is considerable amount of disordering; as a result, many reflections are not visible. The observed reflections are also broadened due to disordering, size and strain effect. However, after annealing at 700 °C the degree of ordering can be enhanced as the peaks are sharp and many more reflections are discerned. The crystallite size was found to increase and the strain was relaxed completely. The formation of disordered nano τ_3 phase appears to be related to the defects induced during the milling.

Acknowledgements

The authors would like to thank Prof. G. V. S. Sastry, Dr. R. K. Mandal and Dr. M. A. Shaz for many stimulating discussions. The financial support from Ministry of Non-Conventional Energy Sources, New Delhi, India is gratefully acknowledged. T. P. Yadav acknowledges CSIR for a Senior Research Fellowship, during which the work was completed.

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