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Stability of mechanically alloyed vacancy ordered phase in $Al_{70}Cu_{15}Ni_{15}$ alloy during annealing

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Abstract. A nano τ_3 vacancy-ordered phase in the Al-Cu-Ni alloy system has been synthesized with a composition close to $Al_{70}Cu_{15}Ni_{15}$ by mechanical alloying a mixture of elemental powder in a high-energy ball mill by varying milling time from 10 to 100 hours. The stability of nano-crystalline τ_3 vacancy-ordered phase has been studied under thermal annealing in vacuum as well as in air. The x-ray diffraction and transmission electron microscopy techniques were employed for characterization of the milled and annealed samples. The powder after 100 h of milling was found to contain mostly nano τ_3 phase with the partial ordering, and with crystallite sizes in the range of 10-20 nm along with a lattice strain of ~0.67 %. The milled powder, after annealing in vacuum at 700 ºC for 60 h, revealed the formation of a strain-free and ordered τ_3 phase with a crystallite size of 80 nm, indicating grain coarsening. It is interesting to note that the milled powder annealed in air at 700 ºC for 60 h showed the formation of $(Cu,Ni)Al_2O_4$ type spinel phase with the lattice parameter of 8.1 Å and the lattice strain as 0.52 %. The average grain size of spinel phase was found to be ~ 40 nm.

1. Introduction

In quasicrystal forming alloy systems, there always exist crystalline phases with the same or similar local structures as those of the quasicrystals. These crystalline phases are referred to as approximants and usually they are formed with large unit cells and complicated structures. The complex crystalline phases in metallic alloys including vacancy ordered phase often co-exist with quasicrystals or incommensurate crystal in many Al-based alloy systems [1]. The vacancy ordered phases (VOPs) being an interesting class of intermetallic phases comes under the broad category of structures with ordered defects [2]. It has been shown that the vacancy ordered phase can be considered as an approximant phase to one-dimensional as well as two-dimensional decagonal quasicrystals [3-5]. VOPs represent a class of structure where compositions and diffraction effects display a close relationship with the golden mean, τ (where, $\tau=1/2(\sqrt{5}+1)$. These structures can be described in terms of basic B2 (CsCl) type of cell with the ordering among transition metals and vacancy along the [111] direction. Dong et al. [6] have carried out extensive investigations on the occurrence of B2 phase, which resulted in the realization that the valence electron concentration of the B2 phase is similar to

that of a quasicrystal. The B2 phase and related VOPs were found to co-exist extensively with the quasicrystalline phases, particularly in Al-Cu-TM (Ni, Co, TM= transition metal) systems and they follow a well-defined orientation relationship [7-10]. VOPs and disordered B2 phases are of considerable interest for the understanding of the stability and transformation behavior of quasicrystalline phases during nonequilibrium processing [10-11]. The τ_3 VOP (Al_3Ni_2 type) exhibits rhombohedrally distorted B2 lattice (hexagonal). Thus it can be considered as a superstructure of B2 phase due to ordering among transition metal atoms and vacancy along [111] direction in the (111) layers. It has been suggested that Al-Cu-Ni system has an arrangement of vacant and filled sites in the truncated Fibonacci sequence along [111] quasiperiodic Fibonacci chain [11]. During complete disordering, the structure becomes bcc (i.e disordered B2). The τ_3 or any other higher order VOPs can be formed because of ordering among the vacancies and the transition metal atoms along [111] directions. This structural description using distorted bcc lattice is convenient for understanding the order-disorder transformation qualitatively.

In the last two decades, a class of materials with a nanometer-sized microstructure have been synthesized and studied for their useful properties and possibility for technological applications [12]. Nanocrystalline phases were found to exhibit size dependent properties, such as lower melting points, higher energy gaps, and stability of thermodynamically non-equilibrium structures [13-15]. In comparison to macro-scale phases, increased ductility and toughness of the brittle materials was observed [16]. Among various processing techniques, high energy ball milling processes have been widely used for producing the bulk nanocrystalline and amorphous materials in complex metallic alloy systems [17-19]. Mechanical alloying (MA) is now recognized as a versatile process for synthesizing nanocrystalline powders [20].

More recently, there have been studies on the formation of spinel phases from quasicrystalline materials in Al-Co-Ni and Al-Ni-Fe systems [21-22]. The synthesis of aluminum–transition metal nanocrystalline spinel has been investigated intensively in the recent years due to their unique potential applications [23-24]. The spinel structure is characterized by a simultaneous occupation of tetrahedral and octahedral positions by metallic cations in an FCC oxygen lattice. Aluminum based spinels constitute an important class of advanced ceramic materials with a wide variety of technological applications. The $CoAl_2O_4$, $NiAl_2O_4$ and, $CuAl_2O_4$, possess interesting electronic, magnetic and catalytic properties and are used in industry as ceramic pigments, coatings and catalysts [25-26]. The spinel materials can be prepared by many methods such as solid-state reaction, hydrothermal, alkoxide hydrolysis, sol-gel method and microwave-induced methods [27-28]. The most general method is the solid-state reaction, which involves the mixture of metal oxides followed by sintering at high temperature. Recently, the nanospinel materials have been synthesized by milling quasicrystalline precursor, followed by annealing [29]. It is not clear in any of the prior work whether true thermodynamic equilibrium of the spinel phases could be achieved.

Here we reported the stability of nano τ_3 vacancy-ordered phase formed by MA in the $Al_{70}Ni_{15}Cu_{15}$ alloy system in order to understand the microstructural evolution during annealing in vacuum and air. No other VOPs or QC were detected during the investigation. The $(Ni,Cu)Al_2O_4$ spinel phase with nano size microstructure was found to form during air annealing.

2. Experimental procedure

Powder mixture of 10 g containing 70 at% Al, 15 at% Cu and 15 at% Ni respectively were used in Szegvari Attritor Ball mill with a ball to powder ratio of 80: 1 and with a speed of 400 rpm. The attritor consists of a cylindrical stainless steel tank of inner diameter of 13 cm. Hardened steel balls of diameter of 6 mm were used. The milling operation was conducted for 10 to 100 hours in a hexane medium. Isothermal heat treatment of milled sample was carried out at 700 0C for 60 h in vacuum as well as in air. The mechanically milled and annealed samples were characterized by powder X ray diffraction (XRD), Philips PW 1710 diffractometer using CuKα radiation (λ=1.5418 Å). Transmission electron microscopy (TEM) was carried out in a Tecnai G20 at 200 kV electron microscope

employing imaging and diffraction modes. A chemical analysis using EDX attached with TEM exhibited that the contamination of Fe (0.6 wt %) in the alloy are within the acceptable limit and thus it can be negligible. The grain size and the lattice strain of the sample have been calculated from the integral width of the physical broadening profile. Cauchy and Gaussian components are obtained from the ratio of full width at half maximum intensity (2ω) and integral breadth (β). In a single line analysis the apparent crystallite size 'D' and strain 'e' can be related to Cauchy (βc) and Gaussian (βG) widths of the diffraction peak at the Bragg angle θ [30].

3. Results and Discussion

Figure 1 (a-c) shows the XRD patterns of elemental Al, Cu & Ni peaks as function of milling time, indicating gradual alloying and the evolution of τ_3 phases after 100 h of milling. There is no significant change during milling up to 50 h except peak shift and peak broadening (Fig.1 (b)). After 100 h of milling (Fig.1(c)), the peak corresponding to any pure elements cannot be identified, suggesting that a single phase has formed. It is difficult from the XRD patterns alone to ascertain whether disordered B2 (bcc) or disordered VOPs have formed, because the superlattice peaks corresponding to VOPs cannot be identified easily except in case of 100 h milling where the superlattice peak of (100) can be discerned. It is important to point out that (100) peak shown on the patterns (Fig.1c) confirms the existence of τ_3 phase as this peak cannot be indexed due to B2 phase though other peaks can be indexed based on the B2 phase.
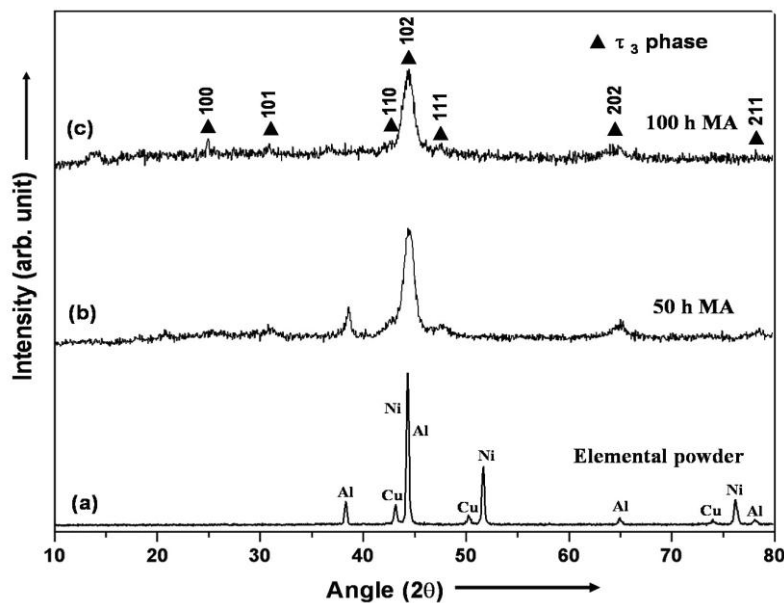

Figure1. X-ray diffraction patterns of elemental powder with composition $Al_{70}Ni_{15}Cu_{15}$ (a), as well as milled powder for different milling durations (b-c). The gradual evolution of τ3 phase can be noticed.

The (100) peak can certainly confirm the formation of τ_3 phase. However, the presence of B2 phase as a minor one cannot be ruled out. The intensity of the other superlattice peaks is expected to be too weak to be detected due to defects, strain and nanocrystallinity effects. However with the help of TEM investigation it has been confirmed that the nano τ_3 phase is a major phase in the milled sample. The peak positions and the corresponding lattice parameters (hexagonal, a=4.1050 Å, c= 4.9541 Å) of the milled samples are found to agree closely with JCPDS data of the Al_3Ni_2 type τ_3 phase (a=4.065 Å, c=4.906 Å) [31]. The increase in lattice parameters can be interpreted due to Cu atoms and nanocrystallinity effect. In the initial stages of milling, the formation of metastable disordered Al-Ni (Cu) solid solution (B2 type) and/or disordered VOP appears to form. In the final stage these phases accommodate residual pure aluminum and give rise to partially ordered τ_3 phase. It can be argued that the intensity ratio of (100) or (001) peaks with (102) peak (most intense peak) can be approximately correlated with the degree of superlattice ordering of the τ_3 phase. In the disordered condition this will

be zero and the structure could be related to partially ordered B2 phase. It should be emphasized that τ_3 phase can be considered as superstructure of B2 phase with an introduction of structural vacancy along [111]. The effect of the reduced size of the crystallites and lattice strain can be observed on the overall peak intensities and broadening, which is obvious after 100h of milling (Fig.1b). By analyzing the peak broadening, the grain size and lattice strain were found to vary continuously with milling time. In case of 100 h milling, the crystallite size and the lattice strain were found to be $\sim$ 10-20 nm and $\sim$ 0.675 % respectively.
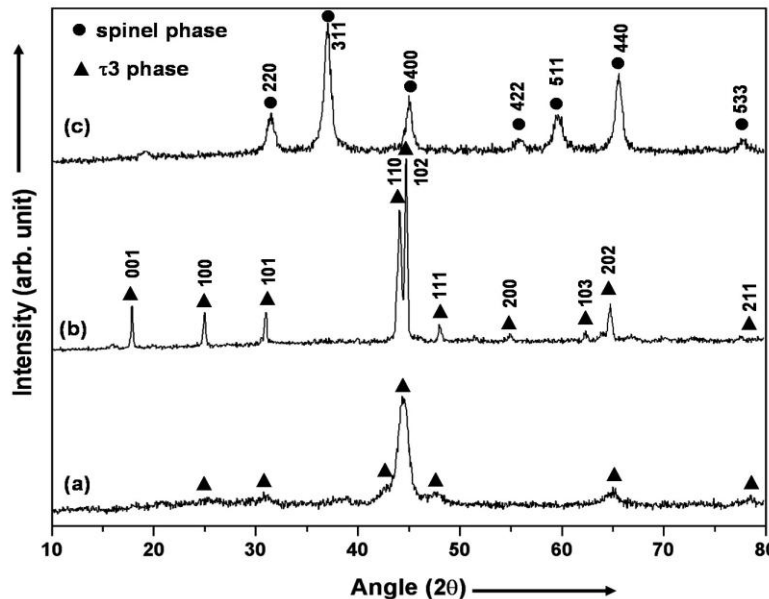

Figure 2. XRD patterns obtained from 100h MM (a), after annealing in vacuum (b) and in air (c) at 700 °C for 60h respectively. In case of vacuum annealing the peak broadening is found to be reduced compared to that in the as-milled condition, where as in case of air annealing the $(Ni,Cu)Al_2O_4$ spinel phase has been observed.

Figure 2 (a-c), show XRD patterns obtained from 100 h milling followed by annealing at 700 °C for 60 h in vacuum as well as air respectively. In case of vacuum annealing, the peak broadening was found to reduce after annealing (Fig.2 (b)). The sharpness and intensity of the peaks were improved significantly. This can be attributed to the ordering, annihilation of defects, strain relaxation, and grain coarsening. The degree of superlattice ordering which is found to enhance can be estimated from the ratio of the (100) or (001) peak with (102) peak. All the peaks in the diffraction patters were indexed according to the Al_3Ni_2 structure type. The splitting of (110) peak of B2 phase into (110) and (102) peaks of τ_3 phase is an indicative that the phase transformation towards ordered structures has taken place. It can be concluded that the partially ordered τ_3 phase obtained after milling gave rise to a perfect and long range ordered τ_3 phase after 60 h of annealing. It is known that the high-energy ball milling technique introduces defects, disordering and reduction of grain size, and thereby destabilizes the ordered phase. However in the present case, it is interesting to note that the vacancy ordered phase has been formed even after MA of 100 h. The mechanical energy imparted during milling could not completely destroy the ordering between the vacancy and Cu/Ni atoms. It can be stated that τ_3 is more stable than B2 phase in this composition during milling though the disordered B2 phase can be considered as the parent phase from which τ_3 phase can be obtained as a superstructure due to the ordering of vacancy. The XRD pattern of 100 h mechanically milled and air annealed sample for 60h at 700 °C shows the formation of $(Ni,Cu)Al_2O_4$ spinel phase. The XRD pattern (Fig. 2(c)) shows the peaks corresponding to the spinel structure with the lattice parameter (FCC, a=8.15±0.04 Å). From these results, it is obvious that high rate of oxygen diffusion through the nano-VOP phases has lead to the formation of spinel structures since the kinetics depends on the particle size and activated surface.

TEM study revealed many interesting features of microstructural evolution in the milled and annealed samples. Fig 3(a) displays the bright field image obtained from the powder particle after 100 h of milling. The equiaxed nanocrystalline grains can be observed clearly in the microstructure. The grains

are found to have sizes ranging from 10 to 20 nm. The corresponding SAD pattern (Fig.3 (b)) was indexed based on τ_3 phase.
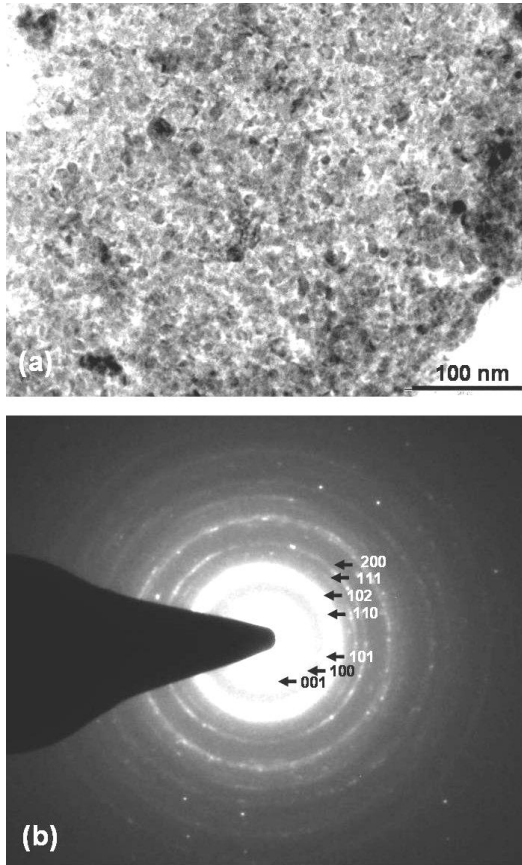

Figure 3. (a) Bright field images from 100h milled powder and (b) corresponding diffraction pattern showing a spotty ring pattern corresponding to the τ3 phase.
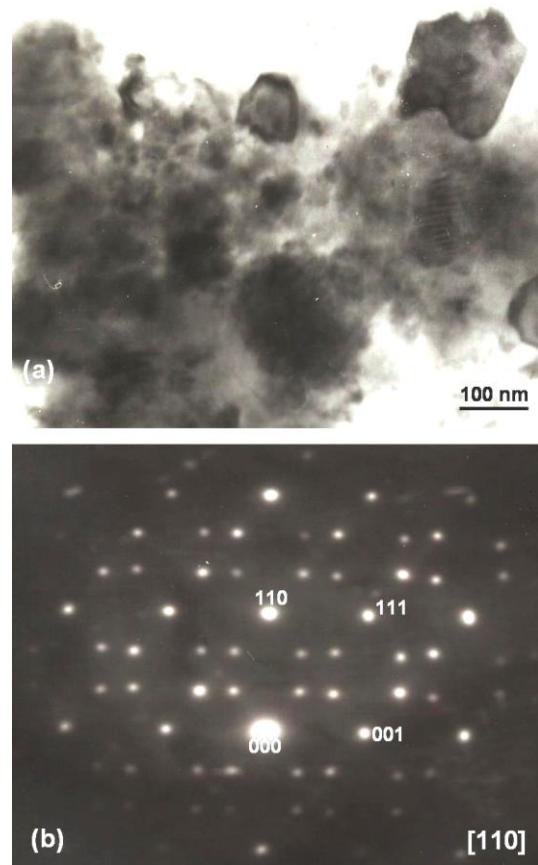
Figure 4. (a) The bright field image showing the microstructure of powder subjected to 100h milling followed by vacuum annealing at 700 °C for 60h, (b) corresponding diffraction patterns. The indexing of the diffraction spots reveals the presence of τ3 phase of [110] zone axis.

The lattice parameters obtained are consistent with that obtained from XRD patterns. The TEM evidence suggests that the τ3 phase is a major phase during milling. The existence of B2 phase could not be established in the milled samples. Figs. 4 (a) shows the microstructures of coarser grains of τ3 phase obtained from the powder sample subjected to 100 h milling followed by annealing at 700 °C for 60 h. The corresponding diffraction patterns along various zone axis can be indexed based on τ3 phase Fig. 4(b) showing the fundamental and superlattice spots (weak intensity). The indexing of the fundamental spots have been shown based on the B2 structure (a=2.94 Å) for clear distinction between superlattice and fundamental spots. In Fig.4 (b) the diffraction spot (111) is clearly divided into three equal spacing, confirming the structure to be τ3 phase. The spot 1/3 (111) is a superlattice peak and equivalent to (001) of τ3 phase. It is clear that perfectly ordered τ3 phase has formed after annealing as the diffraction pattern does not show any kind of diffuse scattering. In addition to the ordering the grain coarsening was found to be significant grains have grown from sizes of 10-20 nm to ~80-100 nm. The bright field microstructures of 100 h MM and air annealed sample at 700 °C for 60 h are shown in Fig. 5 (a). The average particle size appears to be consistent with data obtained from XRD. It is clearly visible that grains are having size ranging in between 40-80 nm. The corresponding

selected area diffraction pattern (Fig. 5(b)) confirms the presence of spotty rings due to the (Ni,Cu)Al2O4 spinel phase with lattice parameter   8.1 Å of FCC lattice.
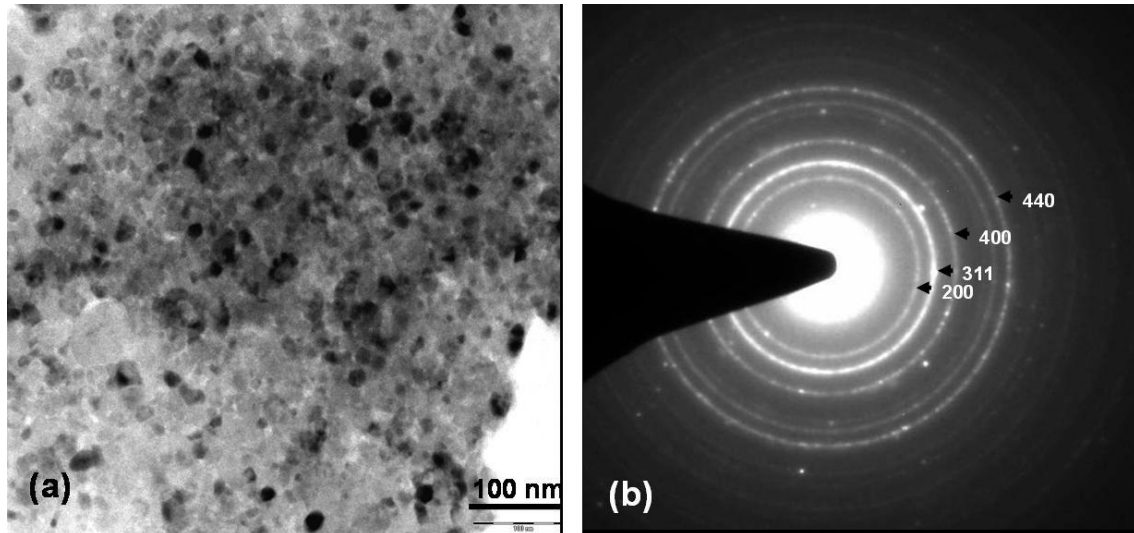

Figure 5. (a) Bright field images of powder sample after 100 h of milling and 60 h of annealing in air at 700 ºC, showing the aggregates of nano spinel of the order of 60-80 nm in size, (b) the corresponding diffraction ring pattern shows the formation of spinel phase.

In the present milling experiments τ_3 phases was found to be evolving after 100 h of milling. Earlier the formation of micron size grains of τ_3 phase by rapidly solidification in Al-Cu-Ni system have reported and it was found difficult to obtain the nanometric grain size [32]. The present study demonstrates that by high energy ball milling and controlled annealing nano τ_3 phase can be synthesized. It appears that the ordering tendency among the vacancy and the metallic atoms are so strong that the complete disordering cannot be achieved even after 100 h of milling. Furthermore, it will be worth studying the evolution of superlattice ordering as a function of further milling as well as annealing. The formation of spinel phase was possible due to profuse oxidation during air annealing. However the nanocrystalline phase has also played an important role for the formation of spinel as it has enhanced the oxidation kinetics. The nano VOP phase obtained after milling of the elemental powder has reduced the activation energy for the diffusion of oxygen atoms due to the strained and nanoscale microstructure. The oxidation reaction being exothermic in nature it generates heat, which further increases the rate of oxidation. This is very much similar to the process called as self propagating high temperature synthesis (SHS), reported for synthesizing spinels by solid state reactions [33-34]. Thus the mechanically activated powder surface along with the nano scale microstructures, and exothermic reaction, has caused the easy formation of nanospinel even at moderate annealing temperature. It is interesting to point out that the significant grain growth of the spinel has not taken place. This could be understood due to the fact that the phase transformation needs to be advanced by the restructuring of the resultant spinel phase. The micromechanisms of spinel phase formation as well as the evolution of nano VOPs phase requires further investigation.

4. Conclusions
In the present investigation formation of nano vacancy ordered phase in Al-Cu-Ni system by mechanical alloying of elemental powders has been achieved. The stability of nano VOPs has been studied under vacuum and air annealing. The ordering, strain relaxation and grain coarsening have been observed after annealing of the nano VOPs in vacuum at 700 °C for 60 h. The crystallite size of

the vacuum annealed nano $Al_{70}Cu_{15}Ni_{15}$ powder is found to be ~ 100 nm. It has been found, that for same annealing condition in air, a nano $(Ni,Cu)Al_2O_4$ spinel phase has formed. The minimum annealing temperature and time were found to be 700 °C and 60 h respectively.

Acknowledgement

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