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STUDIES ON THE STABILITY OF DECAGONAL PHASE IN $Al_{70}Ni_{24}Fe_6$ SYSTEM BY HIGH ENERGY BALL MILLING

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ABSTRACT

In the present investigation the decagonal quasicrystal phase has been synthesized in $Al_{70}Ni_{24}Fe_6$ system by melting the constituent pure metals and cooling it slowly in RF induction furnace. In order to study the structural and microstructural stability during ball milling, this material was employed for mechanical milling in an attritor ball mill for 1, 2, 4, 8 and 12h, in a hexane medium with a powder to ball ratio of 1:100. The milled powder was annealed in argon atmosphere for durations ranging from 1 to 20h at 500^{o}C. The as-cast alloy was found to consist of micron size decagonal phase along with Al_3Ni and $Al_{13}(Fe,Ni)_4$ type minority crystalline phases . The phase transformation from decagonal phase to a B2 crystalline phase has been observed. Powders milled for more than 8h contain predominantly a bcc phase. The crystallite size of the milled powder has been estimated to be around 14 nm. The crystallite size is found to decrease with increase in milling duration. Isothermal annealing treatment (12h mechanically milled powder at 500^{o}C) for 10h and 20h leads to the transformation of B2 phase to τ_3 type vacancy ordered phase.

Keywords: high energy ball milling, quasicrystal, decagonal phase, B2 phase, vacancy ordered phase.

1. INTRODUCTION

Ternary Al-based intermetallic alloys have been extensively studied in the last decade, due to their close relationship with the structure and properties of quasicrystals. It is well established that quasicrystals (QC) are a new class of intermetallic solids exhibiting forbidden rotational as well as quasiperiodic translational symmetry [1]. Ternary Al-Ni-Fe alloys are found to give rise to the formation of decagonal quasicrystal near the composition of $Al_{70}Ni_{15}Fe_{15}$ [2], with various degree of order in periodic and quasiperiodic planes. Recently the decomposition of the Al-Ni-Fe decagonal quasicrystalline phase has been studied in-situ and ex-situ employing transmission electron microscopy by Doldinger et al. [3]. In contrast to the known transformation modes of quasicrystals [nanodomain structures (NDS) and continuously transforming states (CTS) between quasicrystal and approximant], no long-range ordered transition state closely related to the quasicrystal have been observed by them during decomposition of Al-Ni-Fe decagonal phase.

Nanocrystalline solids, in which the grain size is in the nanometer range, can have technologically interesting properties and these can be produced in several ways, among the most common of which are high-pressure compaction of nanometer sized clusters, high energy ball milling etc. [4-5]. Ball milling is an effective technique for the preparation of nanocrystalline alloys. Milled products include amorphous, nanocrystalline and quasicrystalline phase, supersaturated solid solutions, reduced minerals high surface area catalysts and reactive

chemicals [6-7]. In recent years, phase transformation by ball milling has become a area of significant interest [8]. Recently Yadav et al. have studied the phase transformation of pre-alloyed Al-Cu-Fe icosahedral quasicrystalline materials during ball milling [9].

The aim of the present study is to synthesize a nano-phase microstructure by high-energy ball milling of the decagonal quasicrystalline phase (DQC) in Al-Ni-Fe system and to study the phase stability during milling and subsequent annealing. In course of this investigation it has been found that the pre-alloyed $Al_{70}Ni_{24}Fe_6$ material. containing a mixture of DQC and related crystalline [$Al_{13}(Fe\ Ni)_4$, Al_3Ni_2 and $Al_3Ni(Fe)$] phase were unstable during milling, transforming to nanocrystals of B2 phase.

2. EXPERIMENTAL DETAILS

The alloy of composition $Al_{70}Ni_{24}Fe_6$ was prepared by melting the high purity Al, Ni and Fe metals in RF induction furnace, in the presence of dry argon atmosphere. The ingot formed was re-melted several times to ensure better homogeneity. The as-cast ingot was crushed to particles less than 0.5mm in size and placed in an attritor ball mill (Szegvari Attritor) with a ball to powder weight ratio of 100:1. The powder obtained after 12 h of milling were annealed isothermally at 500^{o}C for 10 to 40h in the evacuated quartz capsules (with vacuum of 10^{-6} torr). The milled and heat-treated powders were characterized by powder X-ray diffraction (XRD) using a Philips 1710 W X-ray diffractometer with CuKα radiation. The effective crystallite size and relative strain of mechanically milled powders as well as heat-treated products were calculated based on line broadening of XRD peaks [10]. The use of the Voigt function for the analysis of the integral breadths of broadened X-ray diffraction line profiles forms the basis of a rapid and powerful single line method of crystallite-size and strain determination. In this case the constituent Couchy and Gaussian components can be 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 Couchy (β_c) and Gaussian (β_G) widths of the diffraction peak at the Bragg angle θ ;

$$D = \lambda / \beta_c \cos\theta \qquad \text{(i)}$$

and

$$e = \beta_G / 4 \tan\theta \qquad \text{(ii)}$$

The constituent Couchy and Gassian 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 & a_2 are Couchy constants, b_0, $b_{1/2}$, b_1& b_2 are Gassian constants and $\psi = 2\omega/\beta$ where β is the integral breadth obtained from XRD peak. The value of Couchy and Gassian constant have taken from the table of Langford [11]

$a_0 = 2.0207$, $a_1 = -0.4803$, $a_2 = -1.7756$
$b_0 = 0.6420$, $b_{1/2} = 1.4187$, $b_1 = -2.2043$, $b_2 = 1.8706$

From these, we have calculated the crystallite size D and the lattice strain "e" for the milled powder. Scanning electron microscopy using Philips XL-20, transmission electron microscopy (TEM) studies using a Philips CM-12 operating at 100kV were carried out in order to confirm the crystallite sizes and the structure of the phases evolved during milling and subsequent annealing.

3. RESULTS AND DISCUSSION

The scanning electron micrographs shown in fig. 1(a) reveal the growth morphology of the decagonal phase found in as solidified ingot where elongated rods, can be observed. It has been reported that the decagonal phase grows along the cylindrical axis (tenfold direction) parallel to the five-fold axis of the icosahedral phase [12]. The structure obtained after 12h milling time, with agglomerated powder particles of the order of (m in size, is shown in figure 1(b). Each agglomerate contains tightly packed reactants. The surface of 12h milled powder particles is definitely smoother than the surface of the as cast alloys. The composition of as cast alloy and milled powder, which was analyzed by energy dispersive X-ray spectra shown in Fig. 2. It was found that the composition of the milled powder is close to the nominal composition. The contamination during milling due to balls was not identified. The amount of oxygen assessed from the peak in energy dispersive X-ray spectra was negligible and this perhaps can be related to surface oxide layer rather than to bulk. The peak corresponding to carbon has been observed in energy dispersive X-ray spectra, indicating contamination from hexane, which was used as milling medium.

In order to investigate the formation, growth behaviour and homogeneity of the as cast as well as milled sample, X-ray powder diffraction patterns of all the samples were obtained. Figure 3(a) show X-ray powder diffraction (XRD) patterns obtained from the as cast alloy indicating the presence of decagonal Al2Ni, Al13 (Fe Ni) and B2 phase.

It was suggested by Ma et al. [12] that decagonal quasicrystals have some structural similarity with several well-known stable crystalline structures, for example Al13Fe4, Al3Ni and B2 phase. All the three crystalline neighbors of the decagonal phase can exist above and below the temperature of the decagonal phase formation. Fig. 3(b-d) shows the XRD patterns from various milled specimens. The broadening increases with milling time (1- 4h) as intensity gets reduced. These two effects are mainly attributed to increase of the internal lattice strain and reduction of the crystallite size. The observation after milling from 8h to 12h in fig. 3(e-f) suggests the transformation from the DQC to the B2 phase. The evaluation of the nano-crystalline B2 phase after 12 h of milling can be easily noticed from the increase in the broadening of XRD peaks (Fig. 3) during different period of milling. It should be noted that the center of the broad peak shifts towards the position of (110) peak (fig. 3f) suggesting that complete transformation to the B2 phase has taken place. The calculated crystallite size (d) from XRD as a function of milling time shows a rapid decrease up to 16 nm with milling time of 12 h.

To study the effect of annealing on the ball milled powders, the sample milled for 12 h was subjected to annealing for various time periods. Fig. 4(b-d) shows the XRD pattern obtained after 12 h of milling followed by annealing at 500oC for 10, 20 and 40 h annealed samples. Fig. 4(d) have been indexed using (3 structure with a=8.7Å which is the superstructure of B2 phase. The formation of superstructure due to ball milling and subsequent annealing has been observed for the first time in Al-Ni-Fe alloys system.

The transformation in Al-Ni-Fe system from DQC to B2 phase was also monitored through transmission electron microscopic investigation. Fig. 5(a-c) shows several zone axis diffraction patterns of the decagonal Al70Ni24Fe6 alloy. The diffraction patterns of the decagonal phase typified by its 10 fold, D as P type patterns are shown in Fig. 5(a-c). The superstructure (3 phases has been observed in 12 h BM and 40 h annealed sample, which is closely related to the CsCl-type structure [13]. Alternatively (3 phase can be present as a vacancy ordered CsCl-type where each third transition metal atom along one of four <111> direction is found to be missing.

4. CONCLUSION

On the basis of our present investigation regarding the transformation behaviour of $Al_{70}Ni_{24}Fe_6$ quasicrystalline alloy during mechanical milling and subsequent annealing, the following conclusions can be drawn:

- The decagonal quasicrystalline phase in $Al_{70}Ni_{24}Fe_6$ is unstable under high-energy ball milling.
- It has been found that the high-energy ball milling of $Al_{70}Ni_{24}Fe_6$ results in the formation of a nanocrsytalline B2 phase.
- Lattice strain has been found to increase with increase in milling time
- A curious type of transformation of B2 (a=2.9Å) phase into ordered $\tau 3$ (a=8.7Å) has been observed in 12h ball milled sample after isothermal heat treatment of 500^{o}C for 40 hrs.

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FIGURES

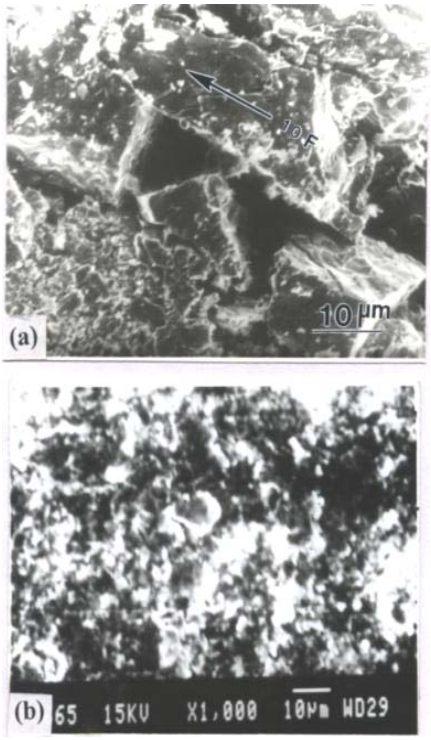

Fig. 1 Scanning electron Micrographs of (a) as-cast $Al_{70}Ni_{24}Fe_6$ alloy showing decagonal phase , (b) the powder particles obtained after 12 h of milling .

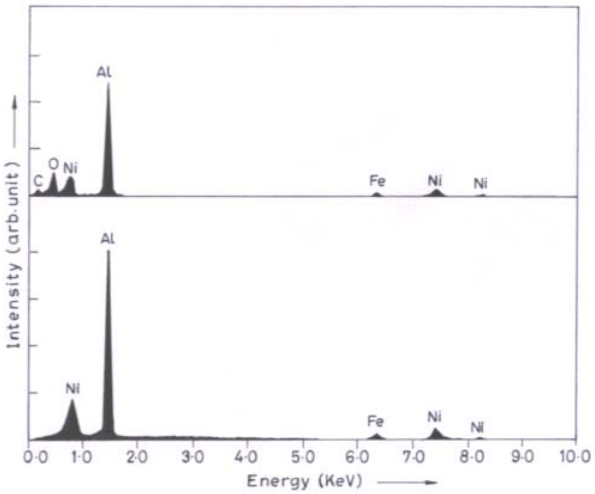

Fig.2 Energy-dispersive spectrum of (a) the as cast $Al_{70}Ni_{24}Fe_6$ alloy, (b)powder milled for 12 h ,showing O and C peaks ,indicating some amount of the contamination of the powder

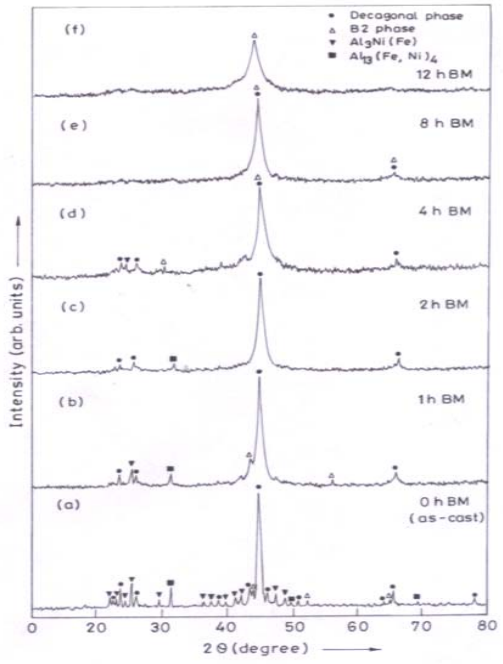

Fig.3 X-ray diffraction patterns of as cast powder (curve (a)), ball milled powde (Curve (b-f). Curve f shows the diffraction patterns obtained from the milled sample for 12 h duration, which shows the existence of nano- B2 phase .

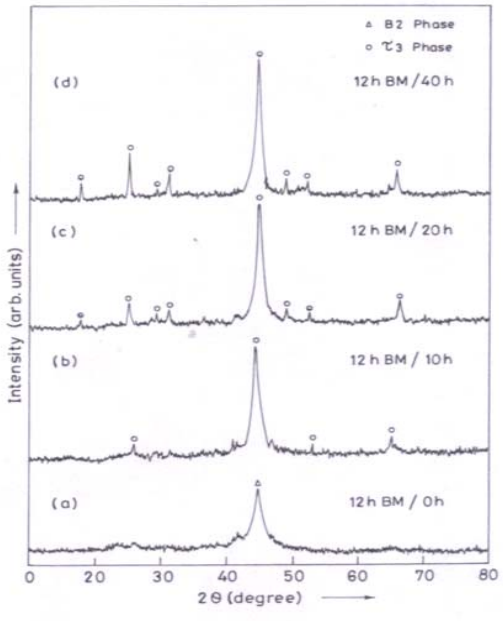

Fig.4 X-ray diffraction patterns obtained from the powder after ball milling For 12 h (Curve a) and subsequent annealing at 500 ° C for 10 – 40 h (Curve b-d). Curve d indicate τ3 (a =8.7 Å) phase

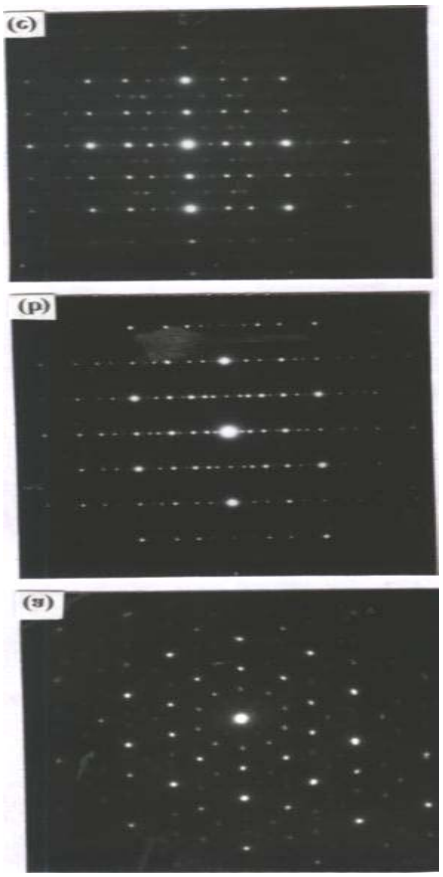

Fig. 5 Electron diffraction patterns of $Al_{70}Ni_{24}Fe_6$ corresponding to decagonal phase (a) taken with the incident beam parallel to the ten fold axis (b) two fold zone axis D type and (C) two fold zone axis of P type.