Superstructure in nano-crystalline $Al_{50}Cu_{28}Fe_{22}$ alloy

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Abstract

This work reports the formation of nano-crystalline $Al_{50}Cu_{28}Fe_{22}$ by high-energy milling. For obtaining the nano-crystalline material, the $Al_{50}Cu_{28}Fe_{22}$ alloy synthesized through slow cooling of the molten alloy was subjected to ball milling, which was carried out in attritor mill at 400rpm for 5h, 10h, 20h, 40h and 80h with a ball to powder ratio 40 : 1 in hexane medium. The x-ray diffraction observation of ball-milled samples revealed that the milling duration of 5h to 40hrs has led to the formation of nano-phase. The average crystallite size comprising the nano-phase has been found to be $\sim 17$nm. When the nano-crystalline alloy, $Al_{50}Cu_{28}Fe_{22}$ was vacuum annealed at a temperature of 500$^\circ$C for 5 to 20 hrs, new structural phases representing superstructures of the parent nano-crystalline phase were found. The superstructure have been found to correspond to simple cubic with $a = \sqrt{2}a_p$ and face central cubic with $a = 2a_p$ ($a_p$ = lattice parameter of parent nano-crystalline alloy). It has been proposed that the formation of different type of superstructure resulting due to different duration of ball milling followed by annealing is possibly governed by minimization of free energy of the disordered B2 phase.

Keywords: quasicrystal; nano-crystal; ball milling; superstructure; B2 phase
I. INTRODUCTION

Recently there has been a considerable scientific and technological interest in the formation of nano-crystalline/quasicrystalline phase in the Al – Cu – Fe alloys by mechanical milling [1]. Quasicrystals have many properties which make them interesting for industrial applications like light weight, large strength to weight ratio and high hardness with a low frictional coefficient [2]. Nanostructured material, which can be defined as a material with the crystallite size less than 100nm are synthesized by either bottom-up or top-down processes [3]. The bottom up approach starts with atoms, ions or molecules as building blocks and assembles nanoscale clusters or bulk material from them. The top down approach for processing of nanostructured materials starts with bulk solid and ends in obtaining a nano structured phase through special processing routes e.g. mechanical milling, re-solidification through chemical methods etc. Nano-phase materials have significantly different behaviour from their macroscopic counterparts because their sizes are smaller than the characteristic length scales of physical phenomena occurring in bulk materials [4]. The nanostructure materials are produced by using various methods, among which high-energy ball milling (BM) which is also known as mechanical milling (MM) has attracted much attention [5]. The advantages of high-energy ball milling for the synthesis of nano-structured materials are the formation of a more homogeneous product and good reproducibility [6]. The mechanical milling technique has been used to obtain amorphous alloys [7], high coercively permanent magnetic metallic compounds [8] and quasicrystals [9-10]. The formation of a quasicrystalline phase by BM/MM has been reported in a number of Al and Ti based systems [11]. Recently Mukhopadhyay et al [12] have studied the effect of mechanical milling on the stability of Al-rich, Al – Cu – Fe and Al – Cu – Co quasicrystalline alloys. They have reported that the icosahedral quasicrystalline phase in Al – Cu – Fe system undergoes transformation to a bcc (B2 type) crystalline phase as a result of ball milling [13]. In this case, B2 phase does not transform into any other crystalline/quasicrystalline phase during isothermal annealing at 850°C up to 20h. It has been concluded that the B2 phase is more stable than the icosahedral quasicrystalline phase at those compositions. It should be mentioned that Al-rich Al_{65}Cu_{20}Fe_{15} system is of significant interest due to the high temperature structural stability of icosahedral quasicrystalline phase. The available phase equilibria data indicate that the B2 phase is a major phase on the Al-deficient side of sto-
ichiometry [14]. The B2 structure can be understood in terms of ordering in a bcc lattice and converting it to be a simple cubic lattice. Therefore, unlike a bcc lattice, one type of atom occupies the body-centered position and another type occupies the cube corners in the ordered lattice. When the composition deviates from the stoichiometry, the compositional defects must be introduced to preserve the crystal structure. Its unit cell contains two different atoms located respectively at the vertex and at the center of the cube. It is one of the basic simple structures that can transform into more complex structures via twinning at the atomic level, termed as chemical twinning [15]. The B2 type phase is often present together with the quasicrystals and has fixed coherent orientation relationship with the latter [16-17]. The detailed investigation of the B2 phase is also important due to its practical applications [18-19]. Though quasicrystals have many curious properties, they are also extremely brittle, porous and composition-sensitive. It is therefore interesting to substitute them by approximant materials, particularly B2 based ones, which are more easily prepared and have similar performance characteristics [20]. The purpose of the present study is to investigate the influence of high-energy ball milling on the phase stability, crystallite size, lattice strain and lattice parameter of B2 phase formed in the pre-alloyed $Al_{50}Cu_{28}Fe_{22}$ sample. Present investigation clearly shows the evolution of ordered simple cubic phase ($a_{sc} = 4.12\,\text{Å}$) and as well as fcc ($a_{fcc} = 5.8\,\text{Å}$) $\tau_2$ phase after milling followed by annealing. The evolution of the nano-structure at different stages of ball milling has also been investigated.

II. EXPERIMENTAL DETAILS:

An alloy of composition $Al_{50}Cu_{28}Fe_{22}$ was prepared by melting the high purity $Al$, $Cu$ and $Fe$ metals in an 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 0.5 mm in size and placed in an attritor ball mill (Szegvari Attritor) with a ball to powder weight ratio of 40 : 1. The attritor has a cylindrical stainless steel tank of inner diameter 13cm and the angular speed of mill was maintained at 400 rpm. The milling operation was conducted from 5 to 80h using hexane as a process control agent. The powder obtained after 10h and 80h of milling were annealed isothermally at 500°C for 5 to 20h in the evacuated quartz capsules (with vacuum of $10^{-6}\,\text{torr}$). The milled and heat-treated powders were characterized by powder X-ray diffraction (XRD) using a Philips 1710
X-ray diffractometer with $CuK_\alpha$ 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. 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 ($2\omega$) and integral breadth ($\beta$) [21]. In a single line analysis the apparent crystallite size ‘D’ and strain ‘e’ can be related to Couchy ($\beta_c$) and Gaussian ($\beta_G$) widths of the diffraction peak at the Bragg angle:

$$D = \frac{\lambda}{\beta_c \cos \theta} \quad (2.1)$$

and

$$e = \frac{\beta_G}{4\tan \theta} \quad (2.2)$$

The constituent Couchy and Gaussian components can be given as

$$\beta_c = (a_0 + a_1 \psi + a_2 \psi^2) \beta \quad (2.3)$$

$$\beta_G = [b_0 + b_{1/2}(\psi - 2/\pi)^{1/2} + b_1 \psi + b_2 \psi^2)] \beta \quad (2.4)$$

where $a_0, a_1$ and $a_2$ are Couchy constants $b_0, b_{1/2}, b_1$ and $b_2$ are Gaussian constants and $\psi$ is $2\omega/\beta$ where $\beta$ is the integral breadth obtained from XRD peak. The value of Couchy and Gaussian constant have taken from the table of Langford [21]

$$a_0 = 2.0207, \quad a_1 = -0.4803, \quad a_2 = -1.7756$$

$$b_0 = 0.6420, \quad b_{1/2} = 1.4187, \quad b_1 = 2.2043, \quad b_2 = 1.8706$$

From these, we have calculated the crystallite size D and the lattice strain ‘e’ for the milled $Al_{50}Cu_{28}Fe_{22}$ powders.

III. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns for the $Al_{50}Cu_{28}Fe_{22}$ alloy obtained after various milling durations has been shown in figure 1. Curve (a) shows the B2 phase obtained from
the as-cast ingot material and curve (b), (c), (d), and (e) are the XRD patterns from the powder milled for 5h, 10h, 20h, 40h and 80h respectively. It can be seen from Fig.1 that the peak corresponding to the (110) profiles of the B2 phase becomes broader and the intensity gets reduced with increasing milling time. These two effects are mainly attributed to the increase of the internal lattice strain and reduction of the grain size. The evolution of the nano crystalline phase in $Al_{50}Cu_{28}Fe_{22}$ can be easily noticed from the increase in the broadening of x-ray diffraction lines (Fig.1) during different period of ball milling. It should be noted that the shift of the peaks towards lower $\theta$ angle side with the increase in milling time indicates the increase in lattice parameter. Intensity of (110) peak goes on decreasing with increasing milling time. After 80h of milling, a diffuse broad peak appears indicating the transformation of the B2 phase to an amorphous phase. (see Fig. 1e). XRD pattern clearly indicates that the initial sharp diffraction lines get considerably broadened after ball milling, suggesting that the nano-crystalline phase appears as a result of milling.

To study the effect of annealing on the MM powders, the samples milled for 10 hrs and 80hrs were subjected to annealing for various time periods. Fig. 2 (a), (b),(c) and (d) show the XRD pattern obtained after 10h of ball milling followed by annealing at $500^\circ C$ for 0h, 5h, 10h and 20h respectively. The XRD patterns corresponding to 10h and 20h, the annealed samples (Fig.2 (b,c)) have been indexed using simple a cubic structure with $a_{sc} = 4.1\text{Å}$. The most interesting feature to be noted is that these samples show cubic structure, which is a superstructure of the B2 phase. The lattice parameters of the superstructure phase and B2 phase are interrelated as $a_{sc} = \sqrt{2}a_p$, where $a_p$ is the lattice parameter of the B2 phase which is a parent phase. The formation of the superstructure due to the ball milling and subsequent annealing has been observed for the first time in $Al – Cu – Fe$ alloy. We propose a structural model for this new superstructure of B2 phase. Fig. 3 shows the structural model of superstructure with lattice parameter $\sqrt{2}a$ times of B2 phase ($a_p = 2.911\text{Å}$), which is obtained from the powder after ball milling for 10 h and subsequent annealing at $500^\circ C$ for 20h. Figure 3(a) shows two-dimensional model of superstructure, which clearly indicates that the face diagonal of a cube is playing a key role for the formation of the superstructure of B2 phase. The three dimensional model (fig. 3(b)) clearly depicts the unit cell of the superstructure of the B2 phase. The edge of the unit cell is the diagonal of a cube face ($\sqrt{2}a_p = 4.18\text{Å}$). The lattice parameter of the superstructure phase, which is calculated from the model, exactly matches with the lattice parameter obtained from XRD.
of 10h ball milled and 20h-annealed powders.

Fig. 4 (a) (b) (c) and (d) show the XRD patterns corresponding to 80h ball milled $Al_{50}Cu_{28}Fe_{22}$ powders annealed at 500$^0C$ for 0, 5, 10 and 20h respectively. In the case of 20h annealing, the sample has been cooled slowly to avoid the quenching effects and detect any transformation during cooling. Unlike the sample milled for 10h and annealed at 500$^0C$ for 10/20h, the XRD pattern shown in fig.4 (d) could be indexed only in terms of a fcc structure with $a = 5.84\AA$. However, the lattice parameter of this fcc phase is also related to B2 phase as $a_{fcc} = 2a_p$. The evolution of $\tau 2$ phases in 80h ball milled and 20h annealed powder can easily be explained by the structural model shown in Fig.5. We propose two-dimensional geometrical model as outlined for the formation of $\tau 2$ phases from the present B2 phase. Figure 5(b) shows the relationship between quasicrystalline and related crystalline ($\tau 2$) phases. The model is based on the concept of a polytope and an eight dimensional root lattice. Its basic atomic cluster forms a cuboctahedron with 12 vertices formed by intersection of three perpendicular squares with edge length of $\sqrt{2}a$. This polyhedron is transformed into an icosahedron when the squares are changed into rectangles with edge length ratio of $\tau : 1$. The properties of the eight dimensional root lattice give foundation to the possibility of mapping a quasicrystalline structure on a crystalline structure. The proposed geometrical model can be applied also to the polymorphic bcc-fcc transformation.

IV. CONCLUSIONS

On the basis of our present investigation it may be conclude that, the formation of the nano B2 phase starts after 5h of milling and gets completed after 40h of milling. Beyond 40h of milling the amorphous phase starts forming and the sample shows the coexistence of nano-crystalline and amorphous phases. After 80h of milling nano B2 phase transforms to amorphous phase completely. The $Al_{50}Cu_{28}Fe_{22}$ samples ball milled for 10h and 80h and annealed subsequently at 500$^0C$ for 20h, transform to the simple cubic ($a_{sc} = \sqrt{2}a_p$) and the fcc ($a_{fcc} = 2a_p$) phases respectively.

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FIG. 1: X-ray diffraction patterns of as-cast powder (a), Ball-milled powder after various milling times 5h (b), 10h (c), 20h (d), 40h (e) and 80h (h).

FIG. 2: XRD patterns obtained from the powder after Ball milling for 10h (a) and subsequent annealing at 500°C for 5h (b), 10h (c) and 20h (d).

FIG. 3: The Structural model of the simple cubic superstructure with $a_{sc} = \sqrt{2}a_p$ of B2 phase, obtained from the powder after ball milling for 10 h and subsequent annealing at 500°C for 20h.

FIG. 4: The XRD pattern obtained from the powder after ball milling for 80 h, (a) and subsequent annealing at 500°C for 5 h (b), 10 h (c) and 20 h (d). The curve (d) indicates fcc superstructure with $a_{fcc} = 2a_p$ of B2 phase ($a_p = 2.92\text{Å}$).

FIG. 5: The Structural model of the fcc superstructure with $a_{fcc} = 2a_p$ of B2 phase, obtained from the powder after ball milling for 80 h and subsequent annealing at 500°C for 20 h.
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