ON THE MECHANICAL MILLING OF AlCuCo QUASICRYSTALLINE PHASE.

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ABSTRACT
In the present work, the $Al_{65}Cu_{15}Co_{20}$ alloy composition was processed by high-energy ball milled to systematically evaluate the phase transitions of the quasicrystalline prealloyed ingot. The quasicrystalline alloy was previously fabricated by conventional casting techniques. Subsequently, this alloy was milled for different times using an SPEX mixer mill. The microstructures were examined by high-resolution electron microscopy and the structural changes were also analyzed by X-ray diffraction patterns. The results indicate that the quasicrystalline alloy is stable after 5 h of milling, containing nano-quasicrystalline domains. However, the sample milled by 10 h shows a quasicrystal-to-amorphous phase transition. Subsequently, after 20 h of milling, the amorphous phase re-crystallizes to the B2 structure type.

Keywords: quasicrystal, HREM, FFT, phase transform.

MOLIENDA MECÁNICA DE LA FASE CUASICRISTALINA AlCuCo.

RESUMEN
En este trabajo, la aleación de composición $Al_{65}Cu_{15}Co_{20}$ fue sometida a molienda mecánica de alta energía para sistemáticamente evaluar las transiciones de fase del lingote prealeado cuasicristalino. La aleación cuasicristalina se fabricó previamente por colada convencional. Subsecuentemente, esta aleación fue molida por diferentes periodos de tiempo en un molino SPEX. La microestructura fue examinada mediante microscopia electrónica de alta resolución y los cambios estructurales fueron también analizados por de difracción de rayos-X. Los resultados indicaron la estabilidad de la fase decagonal hasta 5 h de molienda, conteniendo dominios nano-cuasicristalinos. Sin embargo, la muestra molida por 10 h mostró en primer lugar una transición de fase cuasicristal a fase amorfa, subsiguientemente, después de 20 h de molienda, la fase amorfa recristaliza a la fase cristalina tipo (B2).

Palabras clave: cuasicristal, HREM, TRF, transformación de fase.

INTRODUCTION

Since the discovery of Al-Cu-Co stable-decagonal (D) quasicrystalline phase [1], several investigations have been conducted to explore the phase stability. For example, it has been demonstrated that D-phase transforms to crystalline phases for different processing conditions, for example annealing temperature [2] and high-energy ball milling (HEBM) [3,4]. According to the phase equilibrium diagram the D-phase is stable up to at least 1000 ^{o}C [5]. Several alloy compositions indicates that the D-phase is formed by a peritectic reaction between the B2 phase and the liquid [5]. These investigations suggest that the B2 phase has an important role on the formation of the D-AlCuCo phase. On the other hand, HEBM is a simple and inexpensive technique for the synthesis of nanostructured materials [6]. In this technique, particles are subject to heavy deformation, cold work-hardening and subsequent fragmentation [6]. There are few works about the examination of the quasicrystal structure nature after prealloyed powders are subject to heavy deformation and particle fragmentation for different periods of milling time [4]. Quasicrystalline nanostructured materials could improve the physical properties at nano-scale regime. Therefore, in this work the D-AlCuCo quasicristalline phase has been mechanically milled to evaluate the structural and phase stability during different milling times. This investigation was conducted by X-ray diffraction (XRD), Scanning and

Transmission electron microscopy observations (SEM and TEM).

MATERIALS AND METHODS

The nominal composition of $Al_{65}Cu_{15}Co_{20}$ alloy was prepared by conventional casting of the elements in an induction furnace and solidified by cooling in air. High purity elements of Al, Co and Cu were used, (99% alfa-Aldrich Co.). The as-cast ingots were subject to high-energy ball milling in a vibratory ball mill (SPEX Mixer/Mill, 8000 M). The ball-to-powder weight ratio was 7 to 1. 75 HRc stainless steel vials and balls of 1.2 cm diameter were used. The milling times were 1, 2, 3, 4, 5, 10 and 20 hours. The structural and chemical characterization were carried out using X-ray diffraction (XRD) with Cu Kα radiation, transmission electron microscopy (TEM), Philips TECNAI F20 and scanning electron microscopy (SEM) JEOL 6400 with microanalyzer BRUKER XFlash 4010.

RESULTS AND DISCUSSION

Figures 1 a,b show SEM-micrographs of the as-cast ingot. Both images show that the structure tends to growth along the <00001> direction, direction and can also be observed the quasicrystal quasicrystal (QC) facets (decaprisms). This morphology of as-cast specimen was frequently observed in the SEM analysis and has been commonly reported in different decagonal alloy systems [4, 7, 8]. Figures 2a,b correspond to the HRTEM images obtained from the as-cast specimen and its corresponding Fast Fourier Transform (FFT) pattern. Quasiperiodic arrangements from this alloy composition can be illustrated. The quasiperiodic structure including a five-fold zone axes is shown in figure 2a, however, the five-fold symmetry can be better observed through the FFT pattern. Many sharp spots located at perfect decagonal positions are indicated in the FFT pattern, which illustrate the characteristic decagonal symmetry of D-phase. Figure 2b show another decagonal phase orientation, the quasiperiodicity of the lattice can be appreciated along of semi-diagonal direction of their FFT. XRD patterns from the Al_{65}-Cu_{15}-Co_{20} alloy which has been obtained using conventional solidification in air are shown in Figure 3 (0 hrs). The coexistence of D and B2 phases can be observed. The crystalline phase has an intermetallic precursor based on AlCo, where Cu element is introduced into AlCo intermetallic lattice to form a solid solution B2-Al(Cu,Co)**.**

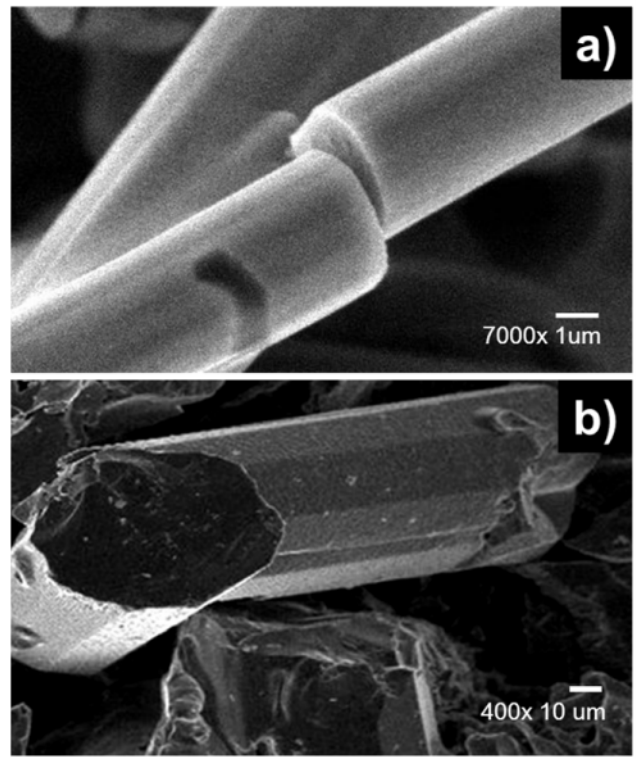

Fig. 1. (*a*) Micrograph of the as cast ingot where decaprisms characteristic of the decagonal phase can be observed, (b) micrograph of grains where the decagonal symmetry can be better appreciated.

Figures 3, also shows the XRD patterns of the samples milled different times 1, 2, 3, 4, 5, 10 and 20 h. Several structural changes occur during the milling process. For example, the most intense peaks of both phases (D and B2) tend to overlap. Therefore, the phase identification can be made based on lower intensities peaks, for example, with the first peak of D-phase (2 1 -1 2 1) as well as with the (211) cubic reflection. As milling time proceeds, the intensity of the XRD peaks was decreased,

while their width is increased suggesting finer crystal size and internal strain. After 5 h of ball milling D-phase remains stable (see (21-121) reflection). However, for 10 h of milling the diffraction peaks of the D-phase apparently disappeared. Finally, for 20 h of milling the X-ray diffraction pattern show peaks related with the B2-phase instead D-phase. In addition, the diffraction peaks of the B2 phase appear increased in intensity suggesting a re-crystallization process.

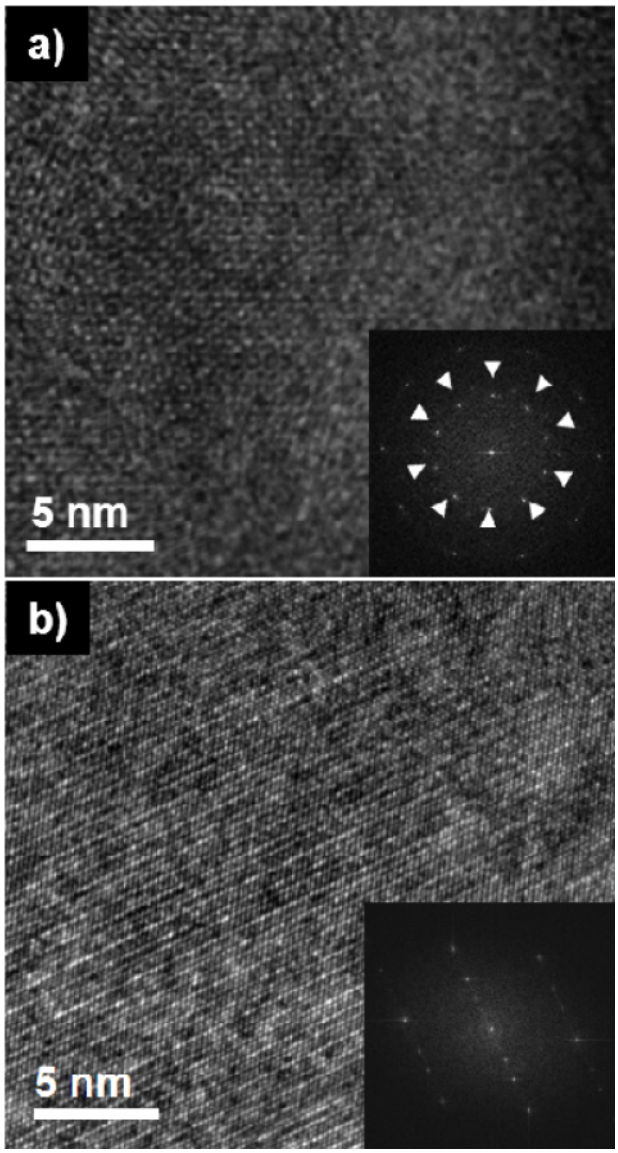

Fig. 2. HRTEM images show the quasi-crystalline phase to a high magnification, the corresponding FFT down shows the characteristic decagonal symmetry of D-phase.

These results indicate that with the increase of ball milling time the D-phase gradually disappears and the B2 crystalline phase grows. Previous research has been reported in different quasicrystalline alloys, that the mechanical milling induced direct transformation of the quasicrystalline phases to the cubic structure of B2-type [4, 9-11].

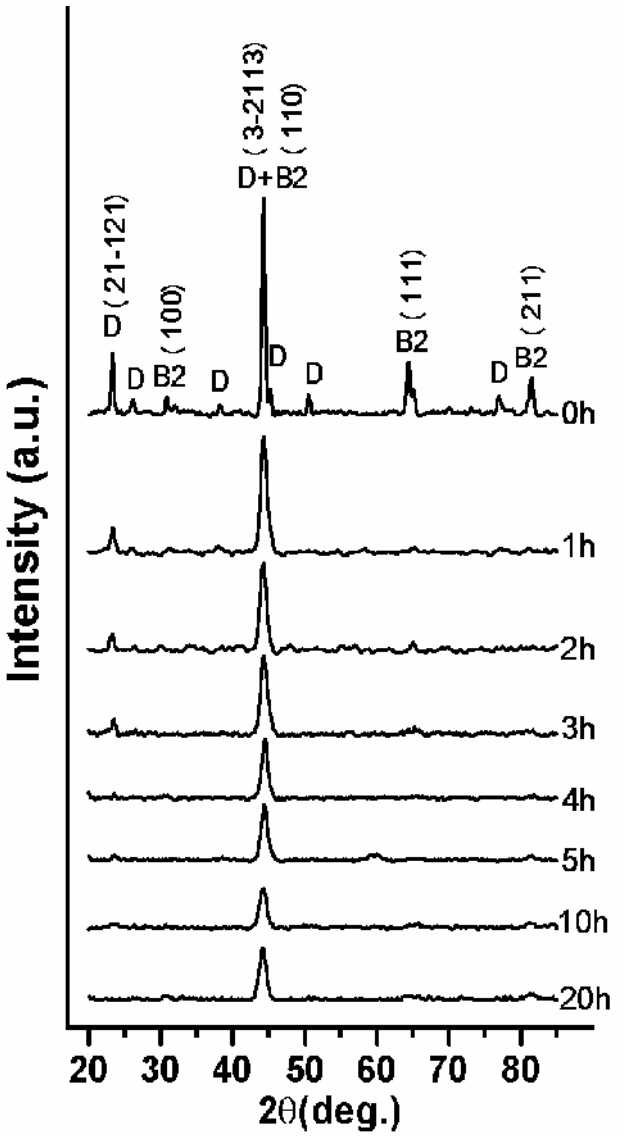

Fig. 3. XRD patterns of $Al_{65}Cu_{15}Co_{20}$ alloy as cast and samples milled for different times, the differences of the intensities in the peaks revel the evolution of structure as function of the time of milling.

EDS spectra obtained from quasicrystalline powders as a function of milling time are shown in Figure 4a-d. The obtained composition is closed to the nominal

composition of raw material. However, small quantities of oxygen element can be observed. The EDS-spectra show that the counts of oxygen increase with the increase of milling time**.** However, XRD patterns (figure 3) do not show any structural change. Therefore, this is clearly being attributed to superficial oxidation.

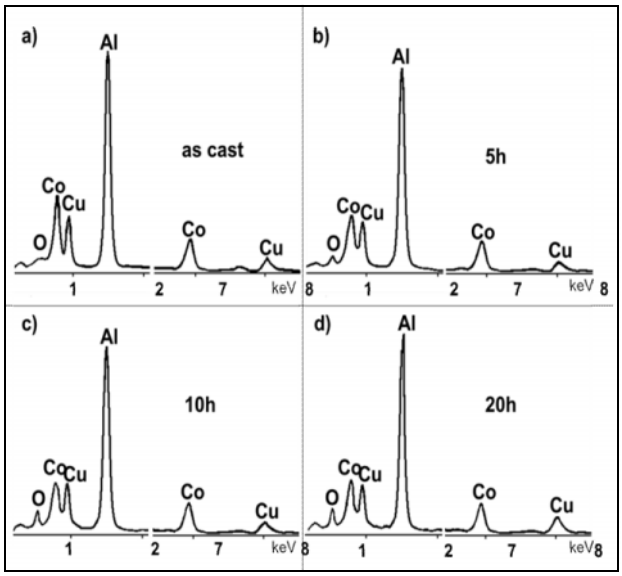

Fig. 4. EDS analysis spectra from the; a) as-cast sample and b) 5 h, c) 10 h and d) 20 h of milling times.

To complement the XRD analysis, HREM studies of the milled samples were carried out. Figures 5a-d show a series of HRTEM images and their FFT corresponding pattern from the adjoining regions of the powders milled for 5 h. Figure 5c show small regions with aperiodic arrangement. The Fast Fourier Transform (FFT) pattern exhibiting five-fold symmetry, and having all the characteristics due to the quasiperiodic structure. At this time of milling the presence of these quasicrystalline regions confirms the D-phase stability. These results are in agreement with the previous XRD results. Otherwise, regions with a poor quasicrystalline structure were frequently observed, suggesting that the D-phase tends to amorphization.

The D-phase is subject to constant breaking, welding and strain. This process induces structural defects which provokes the phase transition. For example, figure 5d correspond to the right side of the region illustrate in figure 5c. This image shows that the points of the outer circle in the FFT are missing. Only the internal points are present, which indicates that the quasicrystalline structure begins to lose the aperiodic arrangement.

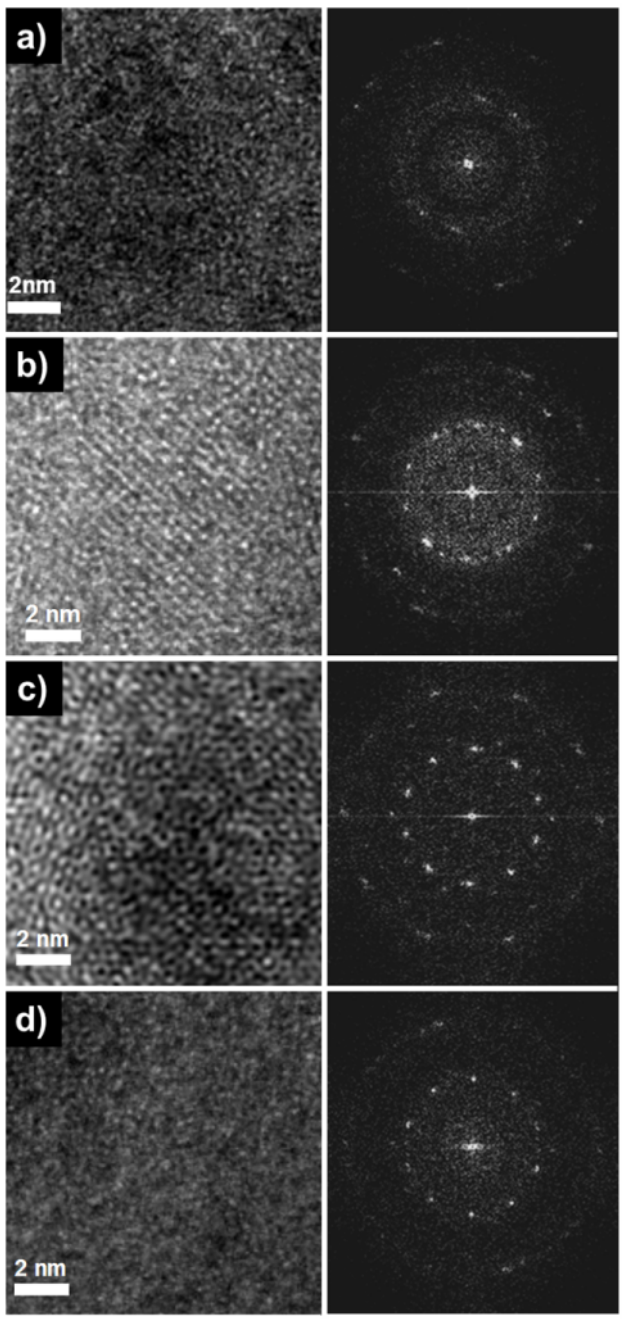

Fig. 5. HRTEM images show several quasicrystalline regions of the powders after 5 h of milling.

The same happens in figure 5b; the points on the outer circle are poor defined. Finally, in the figure 5a, can be note that the intensity of the rings almost entirely been lost, suggesting that the D-phase transforms to an amorphous phase. These results can explain why during TEM observations amorphous regions were commonly observed.

On the other hand, the ball-milling induced points and planar defects for example, figure 5c show high density of vacancies in the structure. As the milling time increases, the number of defects increases at the point where the material almost entirely loses the quasicrystalline arrangement, as a consequence of this the structure tends to amorphization. The D-phase subjected to constant breaking, welding and microstrain of the grains due to the mechanical milling; induce structural defects accumulating the milling energy which it is necessary for inducing the phase transition [9, 11].

Nanocristalline regions of sample milled for 20h are shown in figure 6a, b and c. The measurement of interplanar distances correspond to [110] reflection of the B2 cubic structure of Al(Cu,Co). As indicated from its corresponding FFT the images are oriented approximately along [111] and [100] zone axis (Figs 6a and b). Additionally in the same images, brightness spots are observed which can be associated to the minor presence of points defects. Thus, these HREM results confirm the presence of well-defined crystalline arrays. In addition, figure 6c shows amorphous regions around the crystalline phase observed for 20 h of milling.

Figure 7 illustrate a DSC-graph for different times of milling. An exothermic peak can clearly be seen. As previously observed from XRD and HREM results, this exothermic peak can be attributed to the crystallization of the B2-phase. The crystallization process is more evident when the crystal size decreases. It has been commented that during the milling time the inducing energy of the milled system seem to be more restructuring in a cubic crystal under B2 structure type [4, 12].

The presence of an amorphous phase observed here during the ball-milling of D-phase is explained since is formed from a reversible peritectic reaction [3] in which an amorphous phase is involved. Possibly, this is the reason for which the quasicrystalline phase transforms to an amorphous phase and subsequently this phase transforms to a crystalline phase. These results suggest that the B2-phase is structurally related to the formation and decomposition of D-phase.

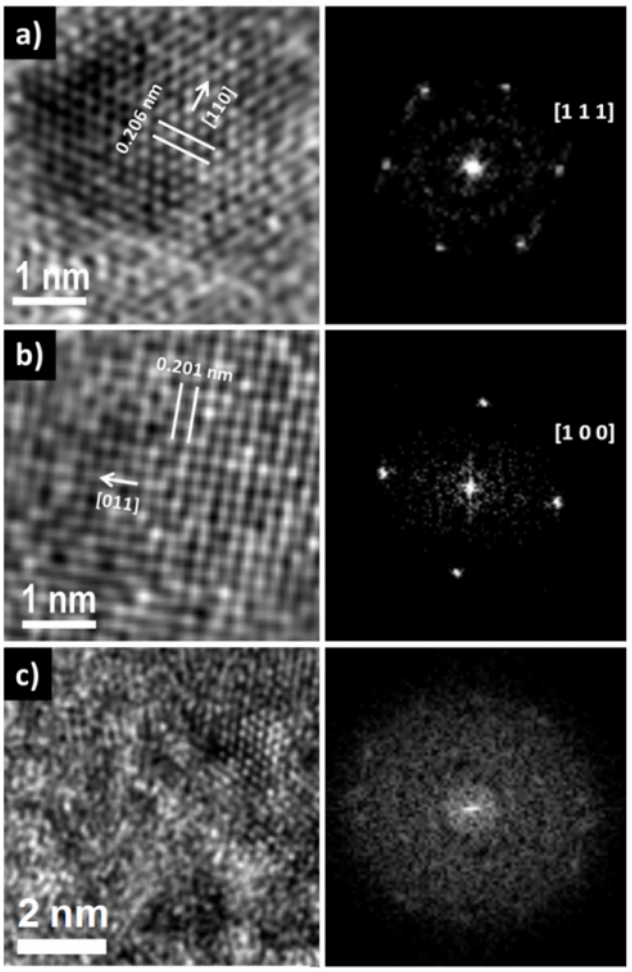

Fig. 6. HRTEM images from the powder sample milled for 20 h, a) and b) show periodic lattice fringes corresponding to the B2 phase, and respectively the fringes corresponding to the (110) and (011) sets of planes, c) amorphous regions around the crystalline phase.

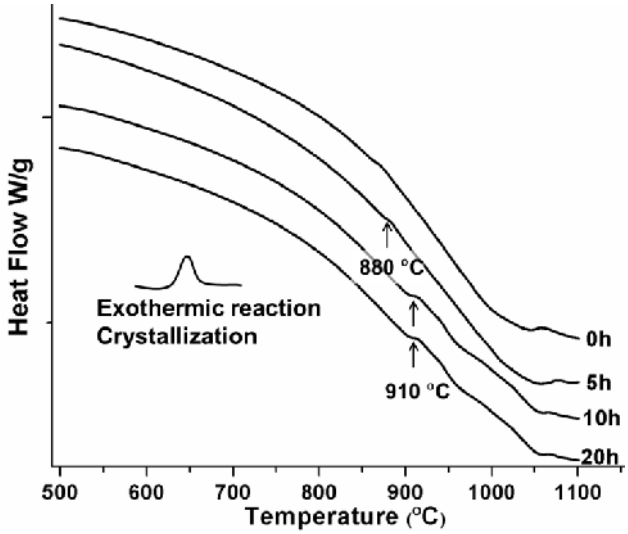

Fig. 7. DSC-graph for different times of milling, points of crystallization can be seen at 880 °C for 5h of milling, and 910 °C for 10 and 20h of milling.

CONCLUSIONS

After the XRD and TEM experimental results from the milled sample of $Al_{65}Cu_{15}Co_{20}$ alloy composition we can conclude that the D-phase is stable to 5h of milling, containing nano-quasicrysitalline domains. The sample milled for 10 h indicated that the D-phase transform to an amorphous state, which recrystallized to B2 structure for after 20 h of milling. Then, these results suggest that during mechanical milling the quasiperiodic arrangement collapses, transforming first to an amorphous phase and subsequently, a recrystallization process of the Al(Co,Cu) B2 type occurs.

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