

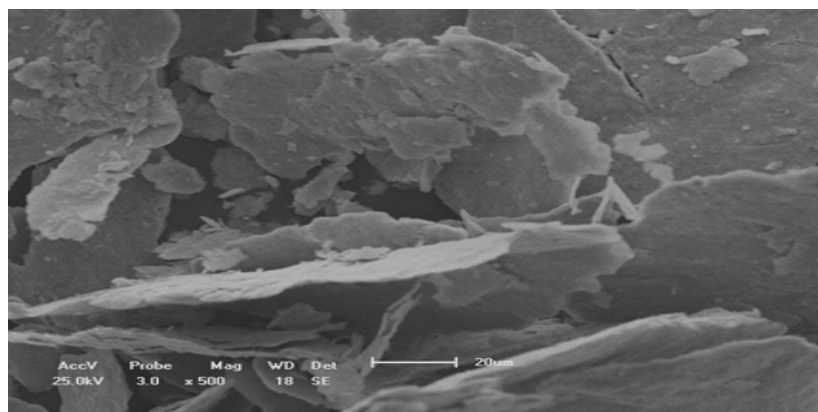
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Evolution of the Amorphous Phase of the Alloy $\text{Co}_{67}\text{Nb}_{25}\text{B}_{17}$

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The purpose of this work is to elaborate the amorphous alloy compound $\text{Co}_{67}\text{Nb}_{25}\text{B}_{17}$ from elementary powders using the planetary ball. The grinding of the amorphous $\text{Co}_{67}\text{Nb}_{25}\text{B}_{17}$ alloy was carried out for grinding times of 1, 5, 10 and 15 h. In 15 hours, the desired amorphous phase was obtained. The microstructural evolution was followed by the techniques of X-Ray Diffraction (XRD), Scanning Electron Microscopy and Energy Dispersion Spectroscopy (SEM / EDS). Experimental results show that the evolution of the amorphous phase was rapid at a speed of 300 rpm.

Graphical abstract



Keywords

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1. Introduction

Since the first amorphous alloy synthesized in the $\text{Au}_{75}\text{Si}_{25}$ system by rapid solidification, a wide variety of amorphous metal alloys have been developed over the next four decades [1]. Amorphous alloys or metallic glasses are a relatively new class of materials with a specific combination of technologically interesting properties. These materials are characterized by the absence of formation of a regular crystal structure, and thus have a structural configuration similar to that of frozen liquid, where the process of nucleation and growth of a crystalline phase have been kinetically supplanted. This structural configuration provides some properties that are frequently superior to those of crystalline materials, e.g., amorphous structure provides exceptional

properties such as high hardness, low friction coefficient, high corrosion and mechanical resistance to wear and excellent properties. Various physical, chemical, mechanical, thermal, electrical, magnetic properties are known (low magnetic loss, rapid flow reversal, high electrical resistivity and low acoustic loss) and biological (biomaterials) [2-3].

The amorphous or glassy state is thermodynamically unstable and is structurally susceptible to devitrification when heated above the crystallization temperature (T_x), or when subjected to prolonged isothermal treatments below T_x . The process of devitrification of certain alloys can be controlled to favor the formation of a nanocrystalline structure or to obtain only a small fraction of crystallized material, with

nanoparticles precipitated and incorporated into the residual amorphous phase. Various alloys that have such nanostructures or nanocrystals embedded in the matrix of an amorphous microstructure show better mechanical properties than those of alloys in the pure amorphous state. Thus, studies of controlled devitrification have attracted much interest in various research areas including physics, chemistry and materials science.

Amorphous alloys are a combination of disordered structures and interatomic metallic bond in a metastable thermodynamic state [4]. Amorphous alloys can be obtained through the High Energy Milling process (MAE) is a mechanochemical synthesis in which mixtures of powders of different metals or alloys are ground together to obtain a homogeneous alloy, through mass transfer [5]. By vibration or rotation, the spheres collide with the vessel walls resulting in a pressing of the powder with each impact, and in this way, the powder is repeatedly welded, fractured and resolved in an intense cyclic process of energy transfer that enables nanostructuring ground materials. During high energy, grinding, high deformation are introduced into the particles.

The powder particles undergo cold welding to each other, especially if they are ductile, due to the great plastic deformation caused by the interaction between the grinding bodies in MAE. A process control agent - PCA (sometimes called a lubricant, surfactant or surfactant) is added along with the material load and grinding bodies during grinding to reduce the effects of cold welding. An PCA can be liquid, solid or gaseous. Most of the time, organic compounds are used as PCA, adsorbing on the surface of the particles, which reduces cold welding which leads to their agglomeration. A large number of substances are used as PCA in quantities typically between 1 and 5% by weight on the amount of powder to be processed. Stearic acid, hexane, methanol, ethanol and liquid N₂ are the substances commonly used as PCA in process MAE. It should be noted that there is no universal PCA. The quantity and type of PCA depends on: i) the ability to cold-weld the particles; ii) thermal stability of the compound and iii) amount of material to be processed. If the amount of PCA used is less than a certain critical value, there is a great tendency for the particle size to grow. If the quantity is larger, the particle size tends to decrease.

This are manifested by the presence of several crystalline defects, such as discrepancies, voids, stacking failure and an increase in the number of grain contours [6]. The presence of these defects, in addition to the refinement of the microstructure that reduces the diffusion distances and the increase in temperature during grinding, increases the diffusivity of the solute elements in the matrix, resulting in the production of powders with high sinterability compared to conventional grinding [7]. Many complex amorphous alloys with specific properties can be obtained by adding other elements to this system, such as Nb and various chemical compounds, which can be crystallized from the amorphous phase at specific temperatures [8]. Amorphous alloys based on Co, Fe, Nb, B and the amorphous Co-Nb-B type system are easily manufactured using solid-state reaction techniques and have good magnetic properties, thermal stability and high saturation magnetization, with high permeability, low coercivity and loss, which find their applications in the anti-theft security system, power electronics, telecommunications devices and automotive magnetism [9]. The amorphous alloys based on Fe-Si-B and Co-Nb-B have excellent soft magnetic properties [10]. Similarly, some alloys based on amorphous alloys and high volume amorphous alloys (BMGs) like Co-Nb-B consist of a covalent bond formed by a metalloid element

(B) and a transition metal element with a high modulus of elasticity (Co). In addition, since Nb and B have negative enthalpy of mixing with the constituent element in most Co [11]. In this work, the characterization of this amorphous alloy of the type Co₆₇Nb₂₅B₁₇ through the high energy grinding process was studied. The characterization study was (XRD) X-Ray Diffraction, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS).

2. Material and Methods

The powders of the elements Cobalt, Niobium and Boron, according to their granulometry (100-mesh sieve), having a purity of 99.99% each of the elements, Cobalt and Boron powders were obtained commercially from Aldrich Chemical Company. The Niobium powder was donated by CBMM - Companhia Brasileira de Metalurgia e Mineração. According to the manufacturer, niobium with an average diameter of 100 μm was obtained by hydration, followed by grinding and subsequent dehydration. Elementary powders were weighed in proportions appropriate to the composition (Co₆₇Nb₂₅B₁₇) and mechanically homogenized and the components were weighed on a precision scale, Micronal B4000 with a resolution of 10⁻²g to obtain the nominal compositions. The elemental powders were weighed in proportion, in the determined ball/powder ratio it was 20:1, thus indicating the total weight of the sample, 25g, as well as the weight of the chrome steel spheres, with three different sizes (6 spheres of 20mm, 4 spheres of 15 mm and 6 spheres of 10 mm), making a total of 225 g of spheres, using a planetary type mill. The collections were made at intervals of 1, 5, 10 and 15 hours of processing. This material was placed in a high hardness steel jar, which was sealed to obtain a vacuum of 5·10⁻² mbar, preventing possible contamination of powders. The jar with the mixture of powders was then placed in a planetary mill, planetary mill Model: NQM2L Mill Pulverizer where it was initially ground for 5h, with a rotation of 300 rpm. The rest of the container volume was used a process control agent - PCA, filled with cyclohexane (C₆H₁₂), which was added together with the material load and grinding bodies during grinding to reduce the effects of cold welding, with the objective of eliminating the oxidation of the powders during the grinding process. Cyclohexane was not used when the powders were just mixed. The nature and quantity of PCA used during grinding determine the final particle size and distribution of the powder, as well as the grinding efficiency. For the identification of the phases of the amorphous Co₆₇Nb₂₅B₁₇ alloy, a Shimadzu XRD 6000 diffractometer was used, using CuK_α radiation (λ = 1.54056 Å). The measurements were taken for a wide range of diffraction angles (2θ) ranging from 0° to 180° with an angular pitch of 0.05° and with counting time per point equal to 4 s. The SEM / EDS analysis was performed with a SHIMADZU SUPERSKAN SSSX-550 with an acceleration voltage of 0.5 to 30kV with a 10V step, after the sample was coated with a thin layer of gold deposited in a vacuum, in order to improve image contrast.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns (XRD) of the ground powders as a function of the grinding time. The verification of a halo of diffraction indicates the priority presence of an amorphous phase at 45° [12]. In the diffractograms, two crystalline phases and the amorphous phase were identified, according to the processing conditions.

The crystalline phases were indexed by JCPDS standards, with a solid solution rich in Cobalt, isomorphous of the structure HCP63/mmc of pure cobalt, and the other rich in Niobium, isomorphous of the structure CCC (Im-3m) of pure Niobium. We also observe the crystallographic directions through the X-ray diffraction that occurs in the scattering directions that satisfy Bragg's Law with the three most intense lines of each of the crystalline phases, being, therefore, the peaks for Co: (110), (100), (002) and (101) with HC structure and for Nb: (110), (200), (200) and (211) with CCC structure, which are comprised in the angular range of $37^\circ < 2\theta < 57^\circ$.

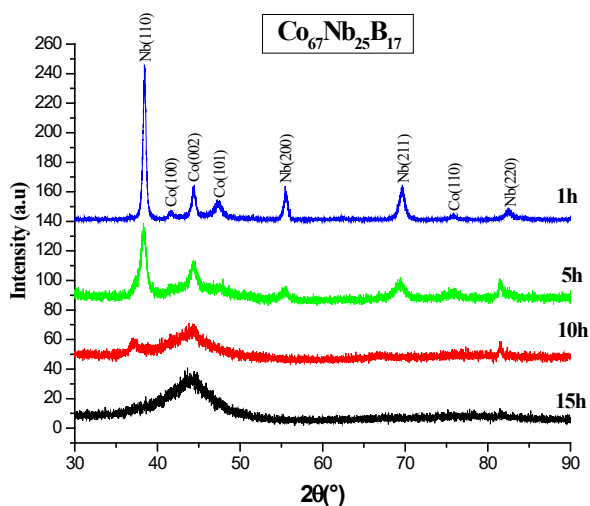


Fig. 1. X-ray diffractograms (XRD) of alloy $\text{Co}_{67}\text{Nb}_{25}\text{B}_{17}$ in the times (1, 5, 10 and 15 h).

After 1 hour of grinding, it was observed that all peaks of pure Cobalt decreased dramatically in contrast to the initial mixture, and after 5 h of grinding, most of the peaks of pure Co had disappeared and the intensities of the Nb peaks decreased dramatically in intensity.

The last two x-ray diffraction patterns shown in the diffractograms correspond to the alloys of the $\text{Co}_{67}\text{Nb}_{25}\text{B}_{17}$ powders after 10-15 h of treatment by high energy grinding. The powders were amorphous for the time range between 10 and 15 h and for grinding conditions with 2 and 3 ball sizes and speed 300 rpm. However, for the sample ground at a speed of 300 rpm (high energy level), the appearance of the amorphous phase and the addition of the phases rich in Co and Nb were abrupt and stabilized in 15 hours of grinding and with the appearance of the amorphous phase desirable, indicating that the solid state would be complete at that moment.

An additional solid-state reaction process allows Boron to diffuse into Co-Nb, forming amorphous Co-Nb-B. Figure 2, respectively, shows the powder of the amorphous alloy $\text{Co}_{67}\text{Nb}_{25}\text{B}_{17}$, the result of the electron micrograph of the sample obtained by Scanning Electron Microscopy with thin layers of lamellar particles in the shape of highly porous irregular plates.

The sizes of lamellar particles rich in oxides obtained through powders are below $20\mu\text{m}$. The influence of B, on the growth dynamics of the amorphous phase and the addition of the niobium and cobalt-rich phases has a direct influence on the refining of the microstructure [13]. The emergence of fractions of the amorphous phase in the early stages of high energy or planetary ball mills is linked to the complexation of B with the rich phases of Cobalt and Niobium in intermetallic

solution, it is clearly seen when ground at 300 rpm in 15 hours in the SEM micrographs in very thin lamellar format. The Boron content has a great influence on the initial moments of grinding as an amorphizing agent, making it practically harmless for longer grinding times. The emergence of fractions of the amorphous phase in the early stages of high-energy grinding and its evolution is directly proportional to the decrease in the rich phases of cobalt and niobium complexed with Boron that amorphizes the structure, which can be seen in the analysis X-ray diffraction and SEM micrograph. Figure 3 shows, EDS spectrum of the amorphous alloy $\text{Co}_{67}\text{Nb}_{25}\text{B}_{17}$, concentrations of Cobalt, Niobium and Boron with the small amount of Oxygen that allows the formation of oxides on its surface and the presence of coupled B for borate compound emergences.

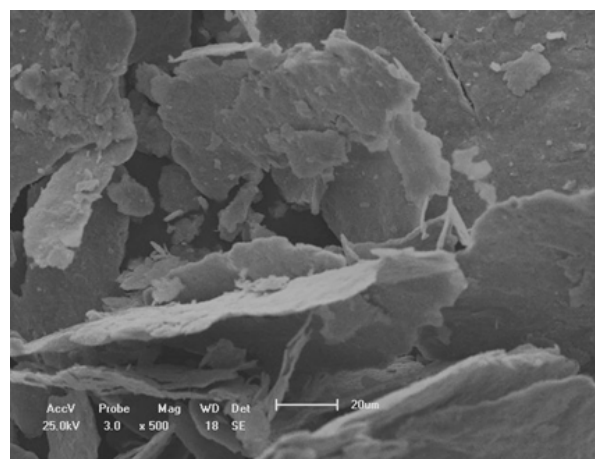


Fig. 2. SEM electron micrograph of the amorphous alloy $\text{Co}_{67}\text{Nb}_{25}\text{B}_{17}$ in lamellar format.

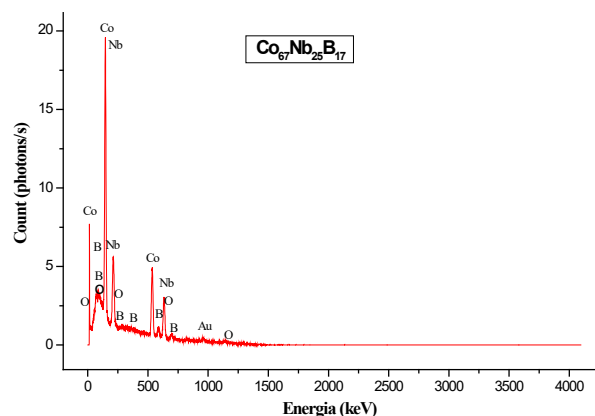


Figure 3. EDS spectrum of the amorphous alloy $\text{Co}_{67}\text{Nb}_{25}\text{B}_{17}$.

Boron can be combined with both metallic and non-metallic elements to form covalent compounds, since in no case does it give rise to ionic states, cations (positively charged ions) or anions (negatively charged ions). Due to the fact, the amorphous alloys are complexed with vitreous actresses based on boron oxide has been investigated for potential applications.

A wide variety of structural units make up the glass network formed by boron-based glass, favoring the acceptance of a wide range of rare earth doping agents or transition metals to obtain amorphous alloys. The oxygen complex is complexed with Co, Nb and B, which allows the peritectic reaction of solid state with amorphous phase rich in metallic and intermetallic oxide [14]. However, some

amorphous and glass-forming alloys form glassy-crystal or glassy-quasicrystal composites, which in some cases possess better properties than the single-phase alloys. On heating, these alloys exhibit different phase transformation behavior. In binary crystalline alloys peritectic reactions involving a liquid and a solid phase upon the completion yield a single solid phase. It is an alloy peritectoid reaction involves two solid phases producing another solid. The product solid phase forms at the interface between the two reactants, which is a diffusion barrier and generally causes such reactions to proceed much more slowly than eutectic or eutectoid transformations. In ternary and multicomponent alloys, binary peritectic reactions (like binary eutectics) may take place in a temperature interval. Some reactions in ternary alloys in which a liquid phase and a solid phase react to form two new phases are what are called quasi-peritectives that appear in amorphous alloy obtained by rapid solidification.

4. Conclusions

- In XRD diffractograms, it is possible to verify a much defined diffraction halo that indicates the priority presence of an amorphous phase in 45° of the Co₆₇Nb₂₅B₁₇ amorphous alloy.
- SEM analysis shows the morphology of the formation of thin layers of lamellar particles in the shape of plates and irregular high porosity due to the amorphization process of the alloy in the amorphous phase.
- The influence of B, on the growth dynamics of the amorphous phase and the addition of the niobium and cobalt-rich phases has a direct influence on the refining of the microstructure at a speed of 300 rpm, revealing the amorphous phase with lamellar particles of 20µm in size.
- In EDS it shows higher concentrations of Co and Nb, complexing with O and B; B being the amorphizing agent.

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