

Amorphous Phase of the Alloy $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$

Luciano Nascimento

Materials Science and Physics Study Group / MSPSG-IPEA, CP: 58700-075, Patos-PB, Brazil

DOI: <https://doi.org/10.30609/jeti.v4i2.12425>

Abstract. The Co-Nb-B alloy was obtained by high-energy ball milling (HEBM) from the mixture of elemental powders in the composition $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$ (atomic percentage (at%)). The milling times were set at 0.1, 5, 10 and 15 hours and the powder mixture was processed in an attritor mill at 300 rpm. A process control agent (ACP) was used, namely: stearic acid, to the mixture in question in order to establish a balance between welding and fracture events during processing in a planetary mill, planetary mill Model: NQM2L Mill Pulverizer. 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.

Keywords: Milling Time. Amorphous Alloy $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$. Amorphous Phase.

1. Introduction

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 regular crystal structure (short-range ordering). Such a structural configuration ensures a unique combination of properties that cannot be attained in crystalline materials, such as high mechanical strength, corrosion/radiation resistance, and specific electric/magnetic properties. It explains ever growing interest in studies on the formation of amorphous structures and their crystallization, and on industrial-scale implementation of amorphous materials. However, the amorphous state is essentially metastable; it inherently possesses the possibility of transforming into more stable crystalline state. To study the kinetics of crystallization and thermal stability of amorphous alloys is very important for finding possible applications [1]. Amorphous complexions are of particular interest due to their ability to enhance diffusion and damage tolerance

mechanisms, because of the excess free volume present in these structures. Metallic glasses can be produced in several routes such as solid state reaction, mechanical alloying (MA), fast quenching, and etc. Compared to other conventional techniques, MA has an advantage that (a) amorphous alloys can be obtained at temperatures much below the crystallization temperature of its constituents and (b) structural changes may happen during the amorphization reaction. HEBM is a solid-state non-equilibrium process suitable for production of nanocrystalline or amorphous metallic alloys, intermetallic phases, stable and metastable metallic compounds, bulk metallic glasses, nanocrystalline reinforced amorphous alloys, and etc. More than 50 years after their discovery, many systems have demonstrated extraordinary abilities unattainable by other manufacturing methods [2-3].

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 ball milling (HEBM) 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]. The Process Control Agents (ACP) people work as a kind of lubricant, reducing cold welding between the particles of the sample powders. This welding occurs, primarily, due to the plastic deformations suffered by the sample elements during grinding. Thus, ACP's are generally organic materials and can be in the form of solids, liquids or gases. Generally, the most important ACP's are: Generally, the most important ACP's are Generally, the most important ACP's are Generally, the most important ACP's are stearic acid, hexane, methanol and ethanol. Most of these compounds decompose during the milling process and interact with the powder forming new compounds that are incorporated as inclusions and / or dispersoids inside of the particles. 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 is introduced into the particles.

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]. Among the common alloying elements (B, Si, P, Zr, Ni, Nb), metalloids are essential elements that substantially impact the properties of Fe-based amorphous alloys. 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 $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$ through the high-energy ball milling (HEBM) 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 ($\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$) and mechanically homogenized and the components were weighed on a precision scale, Micronal B4000 with a resolution of 10^{-2}g 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 20 mm, 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 $5 \cdot 10^{-2}$ 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. Stearic acid (Vetec) was used, which varied 1% of the nominal mass of the powder mixture in the stoichiometry of the amorphous alloy $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$. Stearic acid is known as a controlling agent of the grinding process (ACPs), whose main function is to prevent the grinding affected by the welding of the powder particles. For the identification of the phases of the amorphous $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$ alloy, a Shimadzu XRD 6000 diffractometer was used, using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). 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 SUPERSCAN SSX-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. For the identification of the phases of the amorphous $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$ alloy, a Shimadzu XRD 6000 diffractometer was used, using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). 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.

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 XRD patterns of the $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$ sample exhibit a broad diffuse peak (halo of diffraction), and there are no Bragg peaks (the crystal indicator), which proves the priority presence of an amorphous phase at 45° [12, 13].

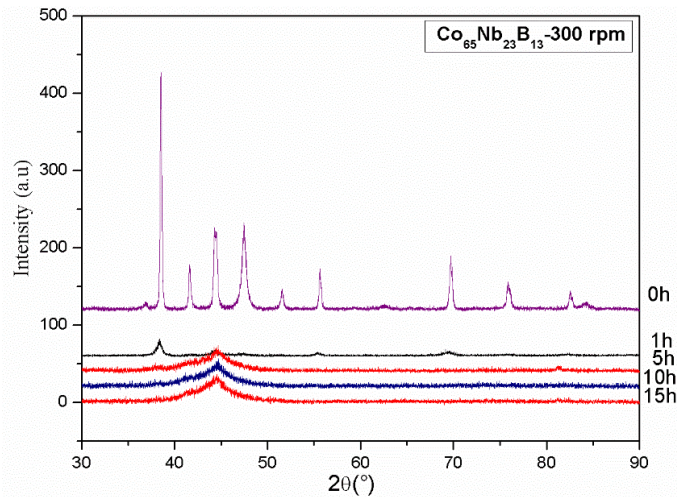


Figure 1. X-ray diffractograms (XRD) of alloy $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$ in the times (1, 5, 10 and 15 h).

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 $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$ 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 $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$ in the times (0, 1, 5, 10 and 15 h), the result of the electron micrograph of the sample obtained by Scanning Electron Microscopy with a morphology with small, well-faceted irregular crystals and very homogeneous particle sizes.

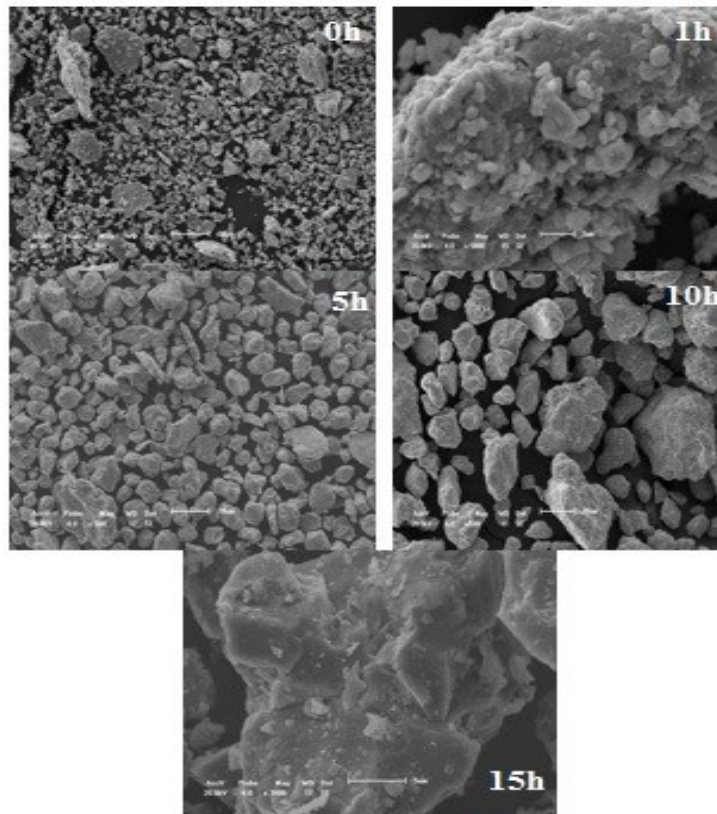


Figure 2. SEM electron micrograph of the amorphous alloy $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$ in the times (0,1, 5, 10 and 15 h).

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 [14].

The emergence of fractions of the amorphous phase in the early stages of high energy grinding 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.

Figure 3 shows, EDS spectrum of the amorphous alloy $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$, 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.

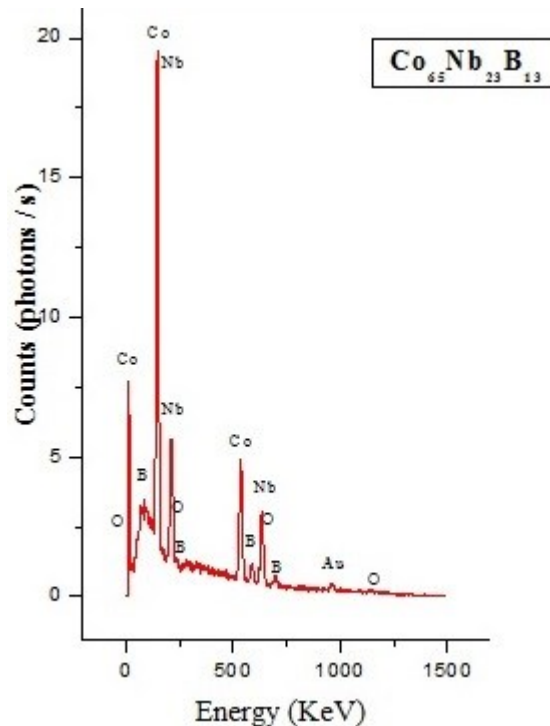


Figure 3. EDS spectrum of the amorphous alloy $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$.

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 peritetic reaction of solid state with amorphous phase rich in metallic and intermetallic oxide [15].

4. Conclusion

- 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 $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$ 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 of the amorphous alloy $\text{Co}_{65}\text{Nb}_{23}\text{B}_{13}$;

- 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.

5. Acknowledgment

The author thanks CNPq and CBMM - Companhia Brasileira de Metalurgia e Mineração.

6. Bibliography

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