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Modeling the amorphous structure of mechanically alloyed amorphous $Ni_{30}Nb_{70}$ using anomalous wide-angle X-ray scattering and reverse Monte Carlo simulations

J.C. de Lima [a],*, A.S. Ferreira [b], R.S. de Biasi [c]

[a] Departamento de Física, Universidade Federal de Santa Catarina, Campus Universitário Trindade, S/N, C.P. 476, 88040-900 Florianópolis, Santa Catarina, Brazil
[b] Departamento de Engenharia Mecânica, Universidade Federal de Santa Catarina, Campus Universitário Trindade, S/N, C.P. 476, 88040-900 Florianópolis,Santa Catarina, Brazil
[c] Seção de Engenharia Mecânica e de Materiais, Instituto Militar de Engenharia, 22290-270 Rio de Janeiro, RJ, Brazil

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ABSTRACT

The atomic short range order of a mechanically alloyed amorphous $Ni_{30}Nb_{70}$ alloy (a-$Ni_{30}Nb_{70}$) was determined using two total structure factors $S(K)$ derived using anomalous wide angle X-ray scattering (AWAXS) measurements as input data for reverse Monte Carlo (RMC) simulations. The coordination numbers (N_{ij}) and interatomic distances (R_{ij}) for the first neighbors were obtained. The chemical short range order (CSRO) and the chemical medium range order (CMRO) of a-$Ni_{30}Nb_{70}$ were investigated using the Cowley-Warren parameter α_{CW}. The results suggest a preference for homopolar pairs or clusters in the first and second coordination shells. The angular distribution of bonds between first neighbor atoms is taken as evidence for the presence of distorted polyhedral units with triangular and square faces in the atomic structure of a-$Ni_{30}Nb_{70}$.

1. Introduction

Bulk metallic glasses (BMGs) based on the Ni-Nb system are functional and structural materials with unique properties [1–3]. For example, Ni-Nb alloys with high niobium content have low sulfidation rates, allowing their use in working environments contaminated by sulfur such as coal gasification systems, high temperature gas turbines, petrochemical units, and coal burning power plants [3].

The Ni-Nb system has been investigated using different techniques. Barbee et al. [4] reported the formation of amorphous Ni_xNb_{1-x}, with $30 \le x \le 80$ at.%, by vapor quenching; Enayati et al. [5], P.Y. Lee and C.C. Koch [6], F. Petzoldt [7], among others, reported the formation of amorphous Ni_xNb_{1-x}, with $20 \le x \le 80$ at.%, by mechanical alloying (MA).

MA is an efficient technique to synthesize nanostructured crystalline materials, amorphous alloys and metastable solid solutions [8–10]. This method has many advantages including processing at low temperatures, easy composition control, inexpensive equipment and the possibility of scaling up. Its disadvantage is contamination from the milling media and possibly by the milling atmosphere. MA has been used to produce commercially important alloys, in particular, those whose components have a very high melting point [11], replacing techniques based on fusion. For some systems, the use of MA increases the solubility limit of solid solutions [8]. It has been applied to mixtures composed of immiscible elements [8,12–14], allowing the formation of solid solutions that are unstable in equilibrium conditions, but the physical mechanisms involved are not well understood. For industrial applications, a better understanding of these mechanisms is required.

Recently, de Lima et al. [15] proposed a thermodynamic approach to describe the formation of intermetallic binary alloys by MA. This model assumes that during milling, nucleation and growth of new phases occur in the interfacial component of a composite powder at average temperatures of <373 K. From a thermodynamic point of view, the interfacial component is assumed to behave as an ideal solution. Thus, the Gibbs free energy and equilibrium volume equations can be used together with the excess Gibbs free energy for metals in nanometric form, to estimate the activation energy associated with diffusive processes responsible for grain growth, grain boundary migration, atomic migration, and nucleation of new phases. It has been observed that for activation energy (E_a) values around 0.03 eV, the final product of milling shows an amorphous structure; while for values around 0.06 eV, the final product shows a nanocrystalline structure. The details of this thermodynamic approach are described in Ref. [15] and will be not repeated here.

In a previous paper [16], this thermodynamic approach was used to calculate the E_a values for the Ni-Nb system. The calculated E_a values are consistent with reports in the literature that amorphous Ni_xNb_{1-x} alloys,

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* Corresponding author.

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with $20 \leq x \leq 80$ at.%, can be formed by MA from binary Ni and Nb mixtures. The calculated E_a values are reported in Ref. [16] and will be not repeated here.

As mentioned above, there are many articles describing the production of amorphous Ni_xNb_{1-x} alloys by different techniques. However, there are very few articles describing the atomic structure of these alloys [16]. This can be due to the difficulty to obtain the partial structure factors $S_{ij}(K)$of amorphous materials, as will be seen later. In an effort to fill this gap, this article describes the determination of the local atomic structure of the amorphous alloy $Ni_{30}Nb_{70}$ (a-$Ni_{30}Nb_{70}$) produced by MA.

2. Theoretical summary

2.1. Thermodynamic considerations about the formation of a-$Ni_{30}Nb_{70}$ by MA

Mechanical alloying is a process that involves moderate pressures. The bulk modulus of Ni ($B_0 = 187.6$ GPa) is slightly larger than that of Nb ($B_0 = 173$ GPa) [17]. Therefore, the energy necessary to achieve plastic deformation of Ni crystals is slightly larger than the energy necessary to achieve plastic deformation of Nb crystals. During the initial stage of MA, plastic deformation of Ni and Nb crystals leads to the appearance of defective chemical bonds associated with angle and length changes, as well as other kinds of defects (vacancies, dislocations, grain boundaries, twins, etc.). This chemical disorder stores a sizable amount of energy.

Due to the fact that the plastic deformation is slightly smaller in Ni crystals, with increasing milling time, necks in the Ni particles arise and break, causing the comminution of Ni particles [18]. A similar process occurs in the Nb particles, but in a smaller scale due to a larger plastic deformation. In addition, free Ni and Nb atoms may also arise. Mezey and Giber [19] calculated the surface free energies of solid chemical elements from internal enthalpies of atomization; the reported values for Ni and Nb are $\gamma_o = 2.364$ Jm^{-2} and 2.983 Jm^{-2}, respectively, at room temperature. These values indicate that the diffusion of Nb particles and/or atoms is slightly faster than the diffusion of Ni particles and/or atoms. As the milling time is increased, Ni and Nb crystals are gradually covered by plastically deformed Nb crystals, forming a composite structure of the lamellar type, with small interlamellar spacing, and an interfacial component made of different kinds of defects. For the Nb-rich compositions, only the diffraction lines of deformed Nb crystals are observed, as shown in Fig. 1. This figure shows the convolution of the diffraction lines Nb (110) and Ni (111) after 20 h of milling. The X-ray diffraction (XRD) patterns for Ni and Nb crystals were simulated using the structural data given in the ICSD codes Nos. 41508 and 44380 [20], respectively. For further milling times, the interlamellar spacing decreases and defects are eliminated, mainly at the interfacial component, releasing the stored energy. The addition of these energies to the energy supplied by the balls becomes the driving force to promote diffusion of Nb atoms into the plastically deformed Ni crystals. According to Ref. [7], there is a maximum thermodynamic driving force $\Delta G \approx$-31 $kJmol^{-1}$ for the reaction $(c\text{—}Ni + c\text{—}Nb) \overset{MA}{\to} (a\text{—}Ni_xNb_{1-x})$. This diffusion occurs under moderate pressures and in limited areas (those that are in contact with the balls). Thus, the local concentration of Nb atoms in the plastically deformed Ni particles may vary, forming Ni_xNb_{1-x} alloys with different compositions.

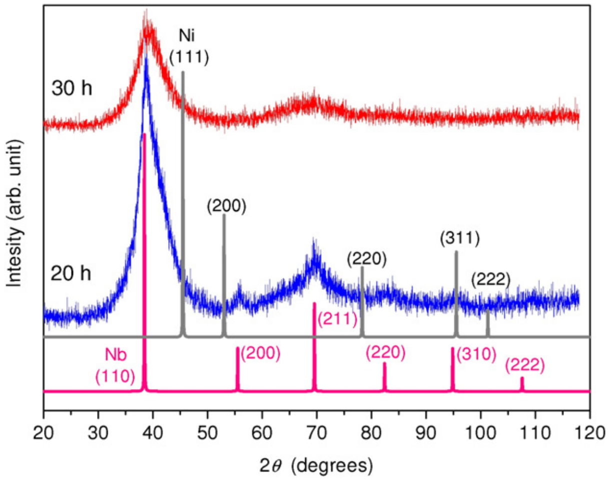

Fig. 1. Measured scattered intensity of a $Ni_{30}Nb_{70}$ mixture for two milling times. The simulated XRD patterns of elemental Ni and Nb powders are also shown. The Cu $K\alpha$ radiation was used.

During the final stage of MA, the lamellae become extremely narrow and the local concentration of Ni particles, Ni and Nb atoms in the plastically deformed Nb structure tends toward the starting composition, becoming a very homogeneous composite powder. At this stage, the individual constituents forming the composite structure are no longer optically identifiable. From the structural point of view, this composite powder is formed by crystallites of nanometric dimensions (2–100 nm) surrounded by defect centers. The number of atoms in both crystallites and defect centers is similar [21]. Thus, nanocrystalline and/or amorphous phases with the starting composition can be formed as well from the Ni and Nb atoms that remain unreacted, as shown in Fig. 1 after 30 h of milling.

More than a decade ago, we proposed a thermodynamic approach to study the formation of binary alloys by MA, starting from blended crystalline elemental metal powders [15]. In this approach, we assume that the mixture of interfacial components, which is formed by defect centers, of the elements in the ultrafine composite powder can be treated as an ideal solution, although it is a solid system, and that the solid state reaction in MA begins in this mixture. In order to promote nucleation and growth of new phases, activation energy must be supplied. As it was mentioned previously, this energy comes mainly from the mechanical energy of the balls, from elimination of defect centers, and from phase transformations. In order to be able to apply this thermodynamic approach to estimate the activation energy E_a necessary to start atomic migration, we assumed the entropy of sublimation of a gas as the cutoff value for the entropy of the ideal solution. This assumption overestimates the entropy of the ideal solution, but that does not change the general conclusions about the formation of alloys by MA. Ideal solutions for which the calculated activation energy values are smaller than 0.030 eV/at. lead to formation of amorphous alloys, while solutions with larger activation energy values yield nanocrystallites or solid solutions. The latter have the largest activation values. The details of this thermodynamic approach are described in Ref. [15] and will be not repeated here.

This thermodynamic approach was applied to the Ni-Nb system and the calculated activation energy E_a values are reported in Ref. [16] and will be not repeated here. The values show that amorphous alloys with nominal compositions up to 80 at.% of niobium can be produced. These predictions seem to be corroborated by the diffractograms shown in Fig. 1 as well as by the results reported by other researchers [4–7].

2.2. Description of the structure of amorphous alloys

The structure of an amorphous alloy with Ncomponents is described by $N(N+1)/2$ partial pair correlation functions $G_{ij}(R)$, which are the Fourier transformation of the same number of the partial structure factors $S_{ij}(K)$. The total structure factor $S(K)$is a weighted sum of $S_{ij}(K)$ and can be derived from the X-ray and/or neutron scattering measurements.

In order to determine the three $S_{ij}(K)$factors for an amorphous binary alloy, at least three independent $S(K)$factors are necessary. However, there are several difficulties to obtain independent $S(K)$ factors, such as