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Mechanical alloying of Ni–Nb in different atmospheres

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Abstract

The formation of Ni–Nb alloys prepared by mechanical alloying (MA) in different atmospheric conditions was examined by X-ray diffraction. Ball milling of elemental Ni and Nb powders under an argon atmosphere for alloys with Nb contents up to 15 at.% forms a supersaturated solid solution on the base of Ni. Amorphous alloys are formed if the Nb content is more than 20 at.%. The interaction of metallic powders Ni and Nb was absent and a b.c.c. phase was formed for all compositions up to pure Nb, when MA of Ni–Nb powders was performed in the presence of water, alcohol or acetone in Ar and air atmospheres. This phase, identified as the interstitial phase of oxygen in niobium, has the lattice parameter $a = 3.390$ Å and an O content of about 34 at.%.

Keywords: Mechanical alloying; Nickel; Niobium

1. Introduction

Mechanical alloying (MA) as a high energy ball-milling technique can be used to synthesize alloys with controlled phase composition. In the course of an investigation of binary alloy systems prepared by MA from pure metallic powders the Ni–Nb system was examined. Many studies of the formation of Ni–Nb composite metal powder by MA have been devoted to the understanding of the mechanism of the crystalline-to-amorphous phase transition and a study of "amorphous" structure [1–5]. Koch et al. [1] reported the preparation of "amorphous" $Ni_{60}Nb_{40}$ from elemental niobium and nickel in a controlled environment. They stressed that the X-ray diffraction (XRD) patterns and crystallization behavior show strong similarities to those for amorphous liquid quenched $Ni_{60}Nb_{40}$. Schwarz and Koch [2] carried out similar experiments on $Ni_{32}Ti_{68}$ and $Ni_{45}Nb_{55}$; they studied the influence of the negative heat of mixing in the process of amorphization by MA. The structural changes of $Ni_{60}Nb_{40}$ produced by the MA was reported in [5]. Thus most MA studies are performed under stationary Ar or He atmosphere and for specific compositions. In this paper we report the formation of Ni–Nb alloys produced by MA in different milling conditions and discuss a region of amorphization for the Ni–Nb system as a whole.

2. Experimental procedure

The elemental powders of Ni (100 μm; purity, 99.99%) and Nb (100 μm; purity, 99.96%) were mixed to give the desired average compositions of Ni–Nb (5, 10, 15, 20, 25 and 50 at.% Nb). The MA was carried out in a vibrating frame grinder and a planetary ball-milling machine at ambient temperature under a purified argon atmosphere and in air. The milling time was determined as specific relative to a mass of a specimen. The ball-to-powder weight ratio was 20 to 1.

The interaction progress for the MA was followed by XRD with Cu Kα and Co Kα. The lattice parameter was determined from the peak corresponding to the (220) reflection for the f.c.c. structure of Ni. The error was $\Delta a = 1 \times 10^{-3}$ Å. The Scherrer equation was used for the definitions of a coherent domain size L [6]. The diffraction (111) line of Ni(Nb) solid solution was used. The peak breadth was calculated by means of the fourth-central-moment methods [7].

A thermal analysis was carried out using a Perkin–Elmer DSC-7 calorimeter. The heat effect was measured at a heating rate of 40 °C min^{-1} in the temperature range 100–725 °C, under flowing argon.

The distribution of powder particle sizes was determined with an Analysette-22 laser diffraction microanalyser.

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3. Results and discussion

It has been revealed that nickel dissolves up to 15 at.% Nb and forms a supersaturated solid solution in an argon atmosphere. The evolution of the α-Ni lattice parameter as a function of specific milling time is shown in Fig. 1. As can be seen, the lattice parameter increases for up to 25 h and the subsequent vibration treatment decreases the lattice parameter. A similar effect was observed after MA with a planetary ball mill for 200 min. According to [6], the atomic volumes of the solid solutions based on Ni lie on the straight line: $V_{at} = 10.99 + 0.057x$, where x is the atomic content of Nb. The maximal lattice parameter of the Ni(Nb) solid solution achieved $a = 3.578$ Å after vibration milling for 25 h. The maximum amounts of Nb at two compositions Ni–10at.%Nb and Ni–13at.%Nb calculated from the above formula correspond to 9.3–9.6 at.% Nb. However, XRD patterns do not fix the diffraction lines of the initial Nb phase. Therefore we suppose that saturation to an even greater degree is achieved, and the accumulation of vacancies during MA reduces the Ni lattice parameter. Annealing for 1 h at 1100 °C in vacuum results in the formation of an equilibrium solid solution ($a = 3.554$ Å). The coherent domain size L estimated from broadening of an α-Ni crystalline reflection decreases to about 100 Å after MA for 15 h in a vibrating frame grinder and does not change very much after subsequent MA. The value of L is plotted against milling time in Fig. 2.

The milling of Ni–Nb with more then 20 at.% Nb leads to amorphization. After vibration milling for 5 h and after planetary ball milling for 50 min in argon, only a single broad peak is observed (Fig. 3).

The interaction of metallic powders was absent if MA was carried out in water, alcohol or acetone, and hydrogen was generated. The XRD pattern indicates a b.c.c. Nb-based phase (Fig. 4). This phase has a lattice parameter $a = 3.390$ Å. During vibration or planetary ball milling, the amount of b.c.c. phase increases, while the amount of crystalline Nb phase decreases. Ni does not take part in this process, as during this period the peak positions for nickel remain constant. After vibration ball milling for 5–10 h or planetary ball milling for 20 min for all compositions of alloys (5, 10, 15, 20, 50, 65 and 100 at.% Nb), niobium transforms

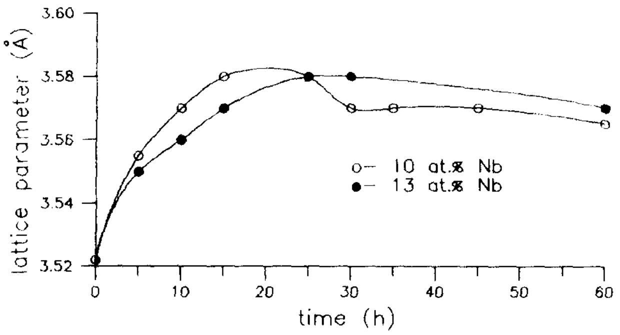

Fig. 1. Lattice parameter of Ni as a function of milling time for Ni and Nb powders after vibration ball milling in an argon atmosphere.

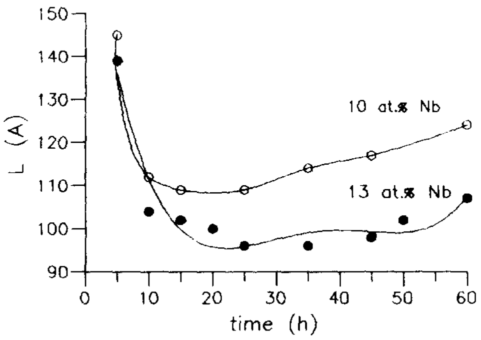

Fig. 2. Coherent domen size of α-Ni as a function of milling time after vibration ball milling Ni and Nb powders in an argon atmosphere.

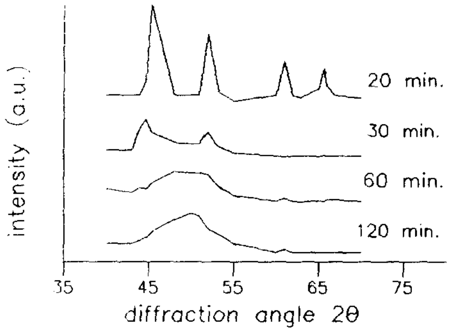

Fig. 3. XRD patterns of planetary-milled Ni–Nb powder blends (50 at.% Nb) in air (a.u., arbitrary units).

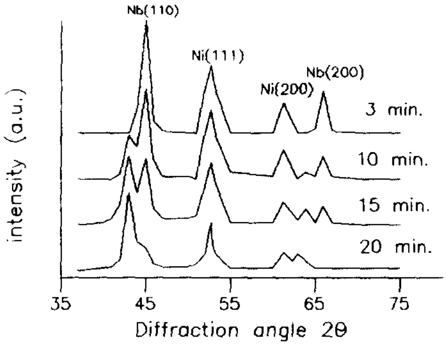

Fig. 4. XRD patterns of planetary-milled Ni–Nb powder blends (50 at.% Nb) in alcohol (air) (a.u., arbitrary units).

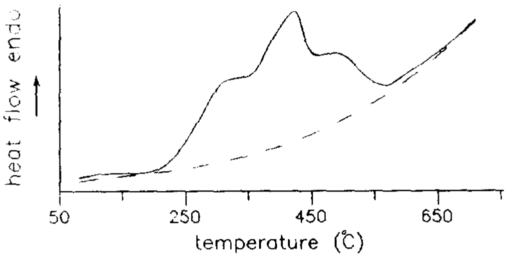

Fig. 5. DSC curve (40 °C $\min^{-1}$) of the b.c.c. phase after milling pure Nb in alcohol (air).

completely to the b.c.c. phase with a particle size of 2 μm. This phase was identified as an interstitial phase of oxygen in an Nb matrix. This is quite possible, because the atomic radius R_{Nb} of niobium is 1.43 Å, the radius r_{oct} of an octahedral interstitial hole is 0.59 Å and the atomic radius oxygen R_O is 0.60 Å) [8]. This phase has a constant composition, because the lattice parameter does not depend on the milling time and alloy composition. The extrapolation of the lattice parameter of the Nb–O solid solution as a function of oxygen content [9] gives the composition Nb–34at.%O. Probably this phase is a metastable suboxide NbO_x [10].

Behaviour of the b.c.c. phase prepared from pure Nb, was studied by calorimetric measurement. Three endothermic effects were found in the differential scanning calorimetry (DSC) curves (Fig. 5). Probably, it is associated with the formation of the oxide phases. After an anneal of the b.c.c. phase in vacuum the XRD pattern contains the diffraction lines for the NbO and NbO_2 phases. In accordance with the Nb–O phase diagram [11], even more than 34 at.% O is necessary for the formation of these two oxide phases. This is possible owing to the adsorption of oxygen at the specimen surface during MA. Chemical investigation of the b.c.c. phase will be the subject of further work.

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