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Comparative study of NiW, NiMo and MoW prepared by mechanical alloying

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Abstract

The present work concern the amorphisation process induced by mechanical alloying in the NiW, NiMo and MoW systems. The alloys chosen combine a group of transition elements varying from very similar atomic radius and electronic valences (MoW) to different ones (NiW and NiMo). The three systems achieved an amorphous state after 50 h of milling. The mechanism of amorphisation proposed for NiW and NiMo was the combined effect of an excess concentration of the solute atoms entering into the structure of one of the elements and a critical concentration of defects. Continuous formation of an amorphous phase at the interface of the crystalline phase was observed during the process. MoW seems to amorphize by continuous reduction of grain size down to a critical value where the amorphisation takes place.

Keywords: Mechanical alloying; Amorphisation; Scanning and transmission electron microscopy; X-ray diffraction

1. Introduction

The NiW, NiMo and MoW are very important alloys for high temperature applications and as corrosion resistant materials and also have a great importance as nanoparticles for catalysis. Mechanical alloying (MA) is an alternative route for preparation of these alloys resulting in nanophase or amorphous materials after prolonged milling periods. Several requirements have been reported [1] to reach amorphisation by mechanical milling of transition–metal binary alloy systems: large negative heat of mixing, different atomic size (>10%) and fast diffusion of one element into the other. However, amorphisation in systems that do not meet these requirements have also been reported [2,3].

Amorphisation during mechanical alloying has been proposed to initiate by the formation of amorphous nuclei at the interfaces that grow by interdiffusion reaction under interfacial metaestable equilibrium [1] just as in a conventional solid-state amorphisation reaction. A classification of possible amorphisation reactions due to interdiffusion under metaestable equilibrium have been proposed by Weeber and Bakker [4] categorizing these in three types depending on the mechanisms involved and the characteristics of the diffraction patterns. Koch [5] proposed that the driving force for amorphisation of intermetallic compounds is either due to an excess in the solute content or due to the creation of a critical defect concentration.

The NiMo system obtained by mechanical alloying has been widely studied by several authors [3,6–9]. In general, amorphisation in this system is reported after 30–54 h depending on the method of milling and the composition used. The amorphisation mechanism has been proposed to occur by diffusion of Mo into the Ni and the creation of defects due to deformation during milling.

The Ni–W system obtained by MA has been less studied [2,10–12]. Aning et al. [2] reported that amorphisation of the Ni phase is attained when a critical W concentration is achieved through MA. Other studies in the NiW(Fe) system [10–12] show that amorphisation is reached even for high W contents.

For MoW no reports on MA have been found in the literature, as far as we know. This system is an isoelectronic alloy forming a complete solid solution for all the composition range.

In the present work, we study the amorphisation behavior of NiMo, NiW and MoW. These systems do not fulfill the conditions mention earlier for amorphisation. These systems do not have a large negative heat of mixing: −3 kJ mol for NiW [2], −11 kJ mol for NiMo [6] and although a small positive heat of mixing for MoW has been reported [13], our calculation applying Miedema model was −0.20 kJ mol. The atomic radii of the pure metals are 1.24 Å for Ni and 1.39 Å for Mo and 1.41 Å for W. These are small atomic radius differences and

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heats of mixing smaller than those typical of early-late transition metal systems that undergo amorphisation during mechanical alloying.

2. Experimental

Elemental high purity Ni, Mo, and W powders, analytical grade, with an average particle size of 2.2, 3 and <0.5 μm, respectively, were mixed in a proportion of 50% at to form the three binary systems (Ni–W, Ni–Mo and Mo–W) in a WAV turbule during 1 h and then mechanically alloyed in nitrogen atmosphere, using a SPEX 8000, for different milling periods: 5, 20 and 50 h, using vial and balls of stainless steel, and a ball-to-powder weight ratio (BPR) of 8:1. The characterization of powders was carried out by X-ray diffraction (XRD), scanning (SEM) and transmission electron microscopy (TEM). The X-ray diffractometer was a Siemens 5005 with Cu Kα radiation (Ni filter). The TEM observations were performed in a Philips CM10 at 80 keV and SEM observations were performed in a Philips XL-30 attached with an EDS system EDX4.

3. Results and discussion

Fig. 1 shows electron backscattered SEM images of the different systems NiMo, NiW and MoW, milled for 5 and 50 h. After 5 h of milling the formation of larger agglomerates are observed and as milling progresses the homogenizing process continues up to 50 h. EDS analysis shows some contamination with Fe from the vial with milling time. The contamination content varies from 3 at.% after 20 h to 8 at.% after 50 h of milling for all alloys. The NiMo and NiW behave very similar, however, for MoW particle size decreases, after only 5 h of milling, to smaller values than those reached for the other two systems and the agglomerates formed after 50 h are more uniform. Fig. 2 shows the XRD patterns for the different periods of milling. In these patterns only the main reflexions are shown: Ni (1 1 1), Mo (1 1 0) and W (1 1 0), in order to observe clearly the peak shifting and decrease in intensity as milling proceeds, indicating the reduction in grain size and loss of crystallinity. For Mo–W system the Mo (2 1 1) and W (2 1 1) reflexions are also show formation of the solid solution with milling.

TEM analysis of these materials shows the progression of amorphisation from the very early stages of milling (Figs. 3–5). For Ni–Mo after 5 h of milling the electron diffraction pattern consist of a strong diffuse halo overlapped with some crystalline spots corresponding to Ni(Mo) and Mo phases, indicating the beginning of amorphisation of some particles co-existing with crystalline ones. This is also observed in the bright field image showing some particles and the formation of an amorphous region at their interface (Fig. 3a). The XRD pattern for this milling period shows a decrease in intensity and broadening of Ni and Mo peaks, also peak shifting suggesting diffusion of one element into the other. After 20 h of milling the XRD pattern shows a small Mo peak and a much broadened Ni reflexion, indicating the progression of amorphisation. This is consistent with the electron microscopy analysis; Fig. 3b shows the bright field image of small particles coexisting with an amorphous type of structure. Also a very strong diffuse amorphous halo contribution overlapping a crystalline spotty ring is observed in the electron diffraction pattern. After 50 h of milling the material is almost completely amorphous. The XRD shows a continuous decrease in intensity and broadening of the Ni and Mo peaks with milling and the formation of a separate broad peak which does not correspond to Ni or Mo main reflexions, suggesting that the process of amorphisation fulfills the characteristics of type II mechanism according to Weeber and Bakker [4]. The amorphous phase seems to form after a critical density of lattice deformation is reached due to diffusion of certain amount of Mo, exceeding the solid solubility limit, into the fcc Ni lattice. The atomic radii are 1.39 Å for Mo and 1.24 Å for Ni, this implies that Mo distorts the Ni lattice when it enters into solution and when the amount of Mo exceeds certain amount over 30% amorphisation occurs as have been reported [7–9].

The NiW system shows decrease and broadening of the W and Ni peaks and the formation of a solid solution Ni(W) after 5 h. The behavior is very similar to the NiMo system. After 20 h the Ni peak almost disappears and after 50 h an amorphous phase

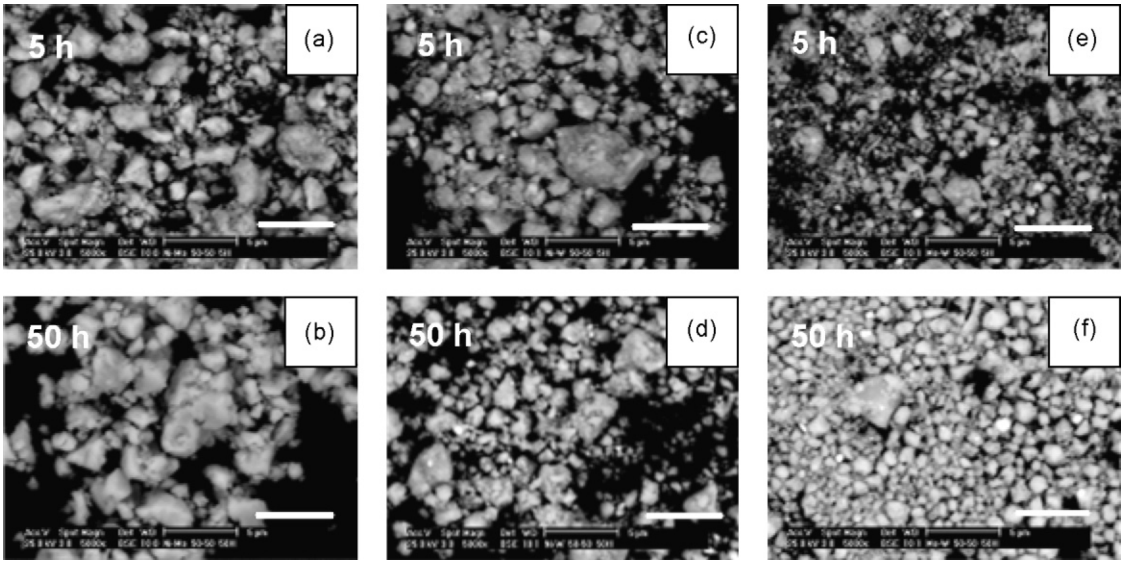

Fig. 1. SEM electron backscattered images of: (a and b) NiMo, (c and d) NiW, and (e and f) MoW milled for 5 and 50 h.

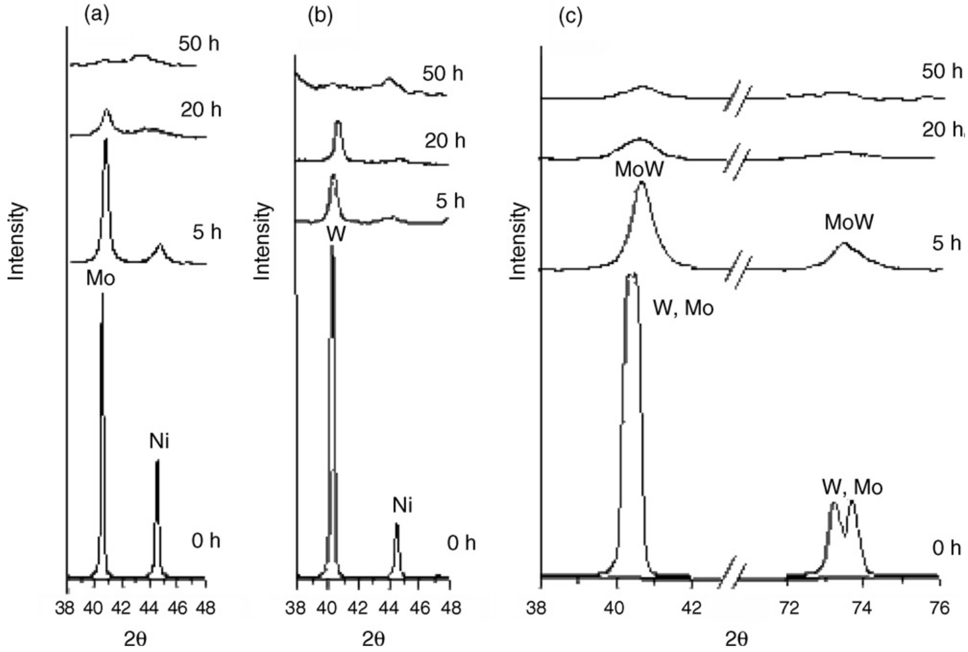

Fig. 2. X-ray patterns for different periods of milling: (a) NiMo, (b) NiW, and (c) MoW.

is obtained. Fig. 4 is a TEM analysis showing the evolution of the microstructures with milling time. After 50 h the materials are completely amorphous.

The Mo–W system forms a complete solid solution according to the phase diagram; both elements have very similar atomic radii and a bcc crystal structure with a very similar crystal parameter. After 5 h of milling a nanocrystalline solid solution is formed. This is observed by XRD and electron diffraction analysis. In the first stage of milling two separate peaks of Mo and W are observed which after 5 h of milling develop into only one peak, indicating the formation of a solid solution. The bright field image shows nanocrystals with an average size of 20 nm forming agglomerates (Fig. 5a). As milling proceeds up to 50 h, peaks decrease in intensity and broaden, reaching an amorphous state coexisting with some nanocrystaline particles, as can be observed in the electron diffraction pattern. Peak shifting towards higher angles is observed with milling, suggesting the type I mechanism according to Weeber and Bakker [4].

Different authors have proposed various conditions for amorphisation. Koch [5] establishes that one element should be a fast diffuser; the system should have a large negative heat of mixing and large difference in atomic radius. On the other hand, Weeber and Bakker [4] considered the system as an asymmetric diffusion couple (the smaller atom in the diffusion couple is the moving species) and also a large negative heat of mixing. Liu et al. [14] presents the formation of amorphisation in binary metal systems by reaction of metallic multilayers with special

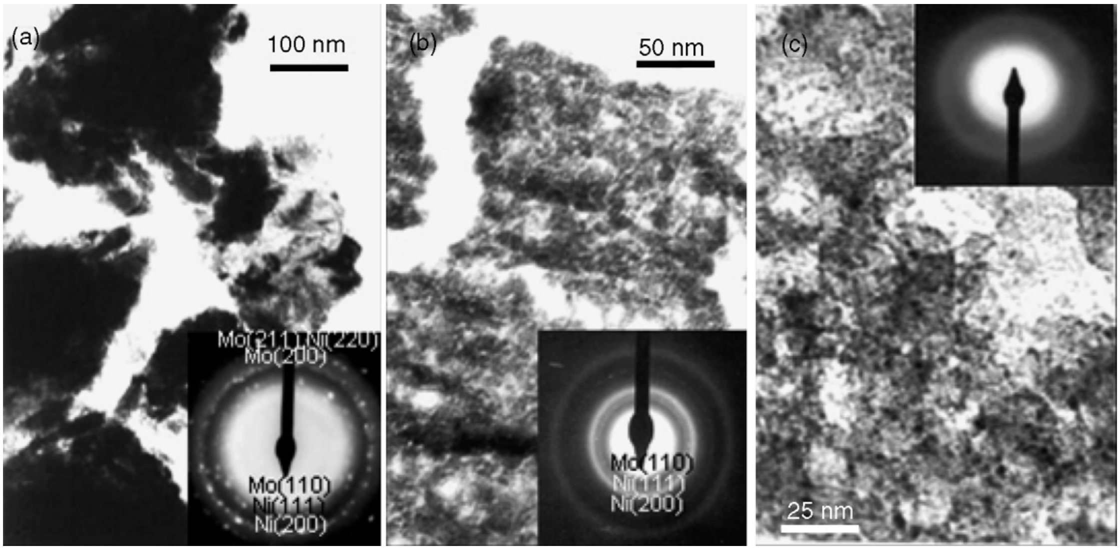

Fig. 3. TEM bright field images for different periods of milling for NiMo: (a) 5 h, (b) 20 h, and (c) 50 h.

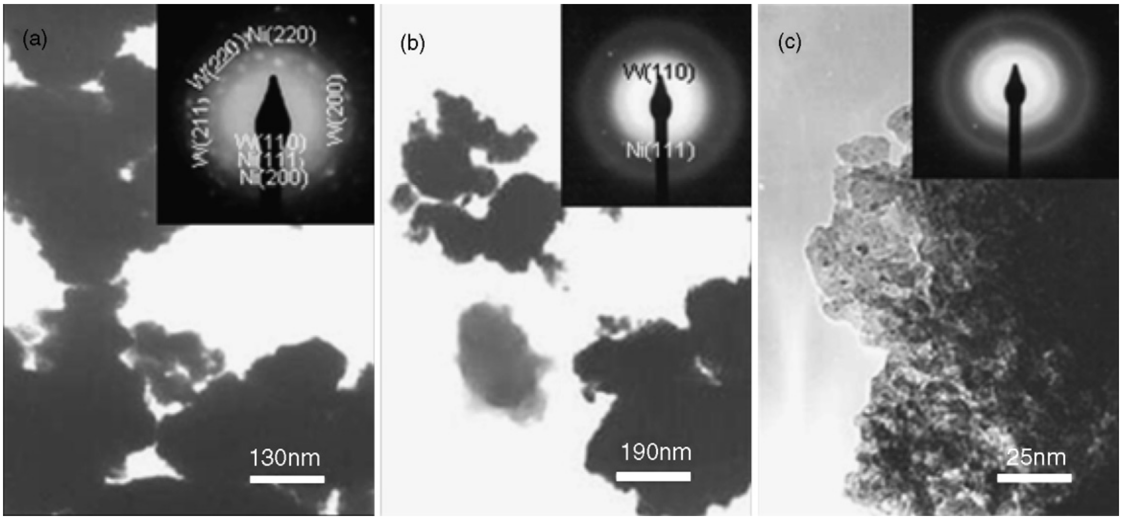

Fig. 4. TEM bright field images for different periods of milling for NiW: (a) 5 h, (b) 20 h, and (c) 50 h.

consideration to excess interfacial free energy and the presence of growth barriers resulting from the interfacial texture.

In our case, we have systems with a very small negative heat of mixing and two of them (NiMo and NiW) form an asymmetric diffusion couple but the moving species is the larger atom, distorting the lattice. The other system (MoW) is a symmetric diffusion couple with very similar electronic characteristics and $\Delta H \cong 0$. However, the three of them amorphize at the same periods of milling with a gradual transition from crystalline to amorphous state, although MoW seems to follow a different amorphisation mechanism. For the NiMo and NiW systems reduction in particle size with milling time and the formation of an amorphous phase at the interface of the crystalline interlayer due to diffusion of an excess concentration of Mo into the Ni lattice causing a large distortion until finally the system amorphizes.

The formation of an amorphous phase in asymmetric diffusion coupled systems is due to the combined effect of two elements: an excess concentration in the solute atoms entering into the structure of one of them and the formation of a critical concentration of defects. Also there is the co-existence of two phases (crystalline-amorphous) in metastable equilibrium and the formation of the amorphous phase nucleating at the interface of the crystalline one and growing by interdiffusion reaction, as has been proposed for thin-film diffusion couples [14,15]. This interfacial region possesses an excess free energy due to the high energy accumulated during ball milling creating a large defect density and accelerating interdiffusion reactions. For Mo–W system the mechanism of amorphisation by MA seems to be due to grain size reduction and defect density until a critical value is reached at which the crystal becomes metastable and transforms to an amorphous phase. Gaffet et al. [16,17] studied the crystal to amorphous phase transition induced by ball milling in Si and Ge powders and attributed this transition to a dynamic equilibrium between the amorphous and the polycrystalline phases. They reported a critical crystal size related

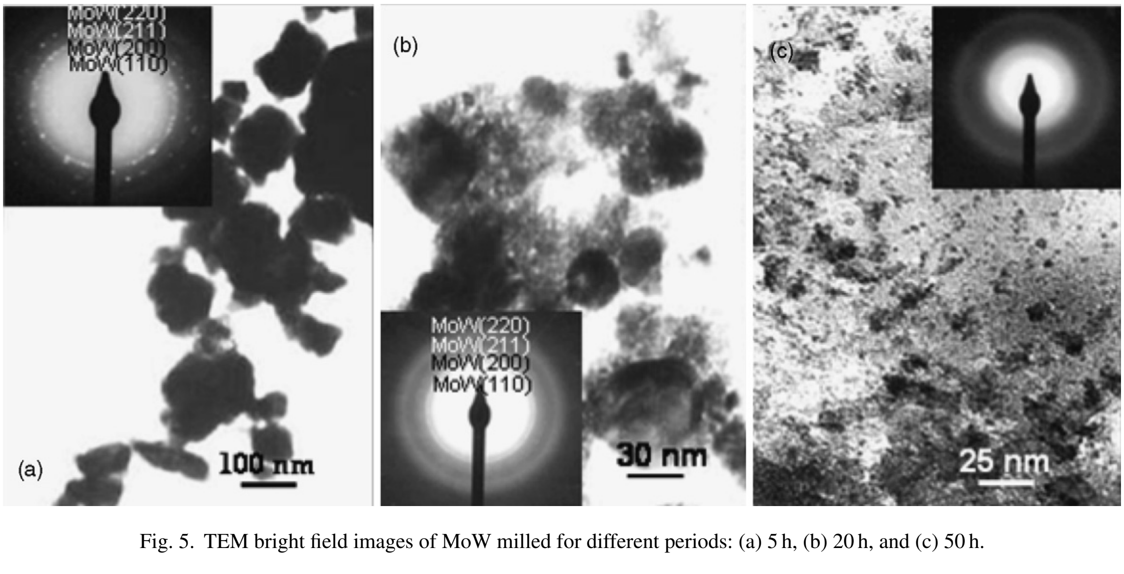

Fig. 5. TEM bright field images of MoW milled for different periods: (a) 5 h, (b) 20 h, and (c) 50 h.

to the lattice parameter change below which the lattice becomes unstable transforming into the amorphous phase. Our results for MoW seem to be in agreement with those presented by these authors.

Therefore, it has been shown that systems with $\Delta H \cong 0$ under intense deformation can become amorphous due to the large density of defects and sharp concentration gradients generated by MA suppressing the driving force for crystallization as has been reported by Desré and Yavari [18].

4. Conclusions

In NiW and NiMo the formation of an amorphous phase at the interface of the crystalline interlayer was observed. MoW showed a continuous reduction of grain size and strain build-up until a critical value was reached and amorphisation proceeded. The three systems amorphized at the same periods of milling with a gradual transition from crystalline to amorphous state.

Systems with $\Delta H \cong 0$ under intense deformation can become amorphous due to the large density of defects and sharp concentration gradients generated by MA inhibiting the driving force for crystallization.

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