

# Process of Amorphization Induced by Mechanical Alloying of Iron with Tungsten and Niobium

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Mechanical alloying method was used to synthesise powders of iron with tungsten and niobium. Mössbauer spectroscopy and X-ray diffraction have been applied to monitor the progress in solid-state reactions. In the case of Fe–W system, exhibiting a positive heat of mixing, no trace of amorphization was observed for 20 and 33 at.% of W, as the calculations of phase diagram (CALPHAD) method suggest. During the mechanical alloying process, two solid solutions Fe(W) and W(Fe) were obtained. Mössbauer measurements allowed to recognise the Fe(W) solid solution as a ferromagnetic phase, while the W(Fe) solid solution as a paramagnetic one. In the case of Fe–Nb system, exhibiting a negative heat of mixing, single phase amorphous alloys were synthesised during mechanical alloying of iron with 48 and 64 at.% of Nb. For both investigated compositions, the final products of mechanical alloying processes were amorphous paramagnetic alloys.

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## 1. Introduction

Solid-state amorphization reactions include besides other irradiation, hydrogen-assisted amorphization, pressure-induced vitrification, and mechanical deformation. These methods allow us to obtain amorphous state of solids without passing through the liquid state. Recently, it has been shown that mechanical alloying (MA), through ball milling of initially elemental blended powder mixtures, can provide amorphous materials. A process of amorphization induced by MA is commonly achieved in systems exhibiting a negative heat of mixing [1]. However,

theoretical calculations, confirmed by some experiments, predict an amorphization process in binary systems, which are characterised by a positive heat of mixing [2, 3]. In order to find possible applications, amorphous materials fabricated by the MA process are consolidated to obtain bulk body maintaining the original state, e.g. without recrystallization or decomposition, using for example shock compression [4] or the plasma activated sintering method [5].

In this study, Fe–W and Fe–Nb systems were chosen as representative systems exhibiting a positive and a negative heat of mixing, respectively. Mössbauer spectroscopy and X-ray diffraction have been used to observe the formation of an amorphous phase. Structure and some magnetic properties of the final products of milling of iron with tungsten and niobium are discussed in this paper.

## 2. Experimental details

The following mechanical alloying processes were performed: Fe<sub>80</sub>W<sub>20</sub> in the high-energy ball mill Spex 8000 D, Fe<sub>67</sub>W<sub>33</sub>, Fe<sub>52</sub>Nb<sub>48</sub>, and Fe<sub>36</sub>Nb<sub>64</sub> in the high-energy planetary ball mill Fritsch Pulverisette P5. In all cases stainless-steel balls and containers were used. Solid-state reactions of iron with tungsten and niobium were carried out under argon atmosphere in a glove box. More experimental details are described elsewhere in [6, 7].

X-ray diffraction (XRD) measurements were performed on a Philips PW 1830 diffractometer using Cu  $K_\alpha$  or Co  $K_\alpha$  radiation. Mössbauer spectroscopy (MS) studies were carried out in the transmission geometry at room temperature using the source of <sup>57</sup>Co in the Rh matrix.

## 3. Results and discussion

### 3.1. Structure

For selected times the mechanical alloying process was interrupted and a small quantity of the milled powders was taken out and examined by XRD. The obtained XRD patterns allowed monitoring the progress in solid-state reaction of iron with tungsten and niobium. Figure 1 presents the XRD patterns registered for the final products of milling. As the XRD analysis proved, during the mechanical alloying process of iron and tungsten, two solid solutions of W in Fe lattice Fe(W) and of Fe in W lattice W(Fe) were formed (Figs. 1a and b). In the case of Fe–Nb system, a single homogeneous amorphous phase was obtained after 70 h of milling (Figs. 1c and d).

XRD measurements allowed us to calculate the lattice parameters of Fe(W) and W(Fe) solid solutions versus milling time for Fe<sub>80</sub>W<sub>20</sub> and Fe<sub>67</sub>W<sub>33</sub>. In both cases the lattice parameter of Fe(W) solid solution increases with milling time, while the lattice parameter of W(Fe) solid solution decreases with milling time [6]. It may be assumed that the Vegard law is realised in the Fe-rich and W-rich

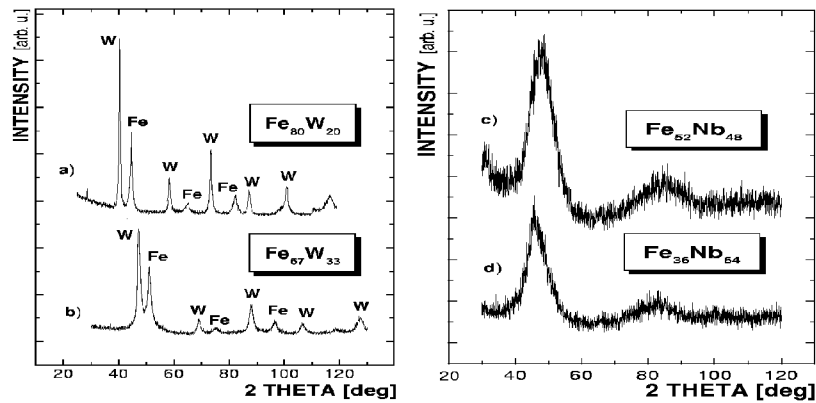


Fig. 1. XRD patterns of the final product of the mechanical alloying processes: a)  $\text{Fe}_{80}\text{W}_{20}$  milled for 10 h in Spex mill,  $\text{Cu } K_{\alpha}$  radiation; b)  $\text{Fe}_{67}\text{W}_{33}$  milled for 115 h in Fritsch mill,  $\text{Co } K_{\alpha}$  radiation; c)  $\text{Fe}_{52}\text{Nb}_{48}$  milled for 70 h in Fritsch mill,  $\text{Co } K_{\alpha}$  radiation; and d)  $\text{Fe}_{36}\text{Nb}_{64}$  milled for 70 h in Fritsch mill,  $\text{Co } K_{\alpha}$  radiation.

regions of the Fe–W system [8, 9]. On the basis of this assumption, it was possible to estimate the final concentrations of iron and tungsten in the obtained solid solutions. In the process of mechanical alloying  $\text{Fe}_{80}\text{W}_{20}$  in Spex mill the final compositions of solid solutions were  $\text{Fe}_{97}\text{W}_3$  and  $\text{W}_{95}\text{Fe}_5$ , while in the case of  $\text{Fe}_{67}\text{W}_{33}$  synthesised in Fritsch mill, the  $\text{Fe}_{80}\text{W}_{20}$  and  $\text{W}_{97}\text{Fe}_3$  solid solutions were finally formed. This estimation allowed us to state that the mechanical alloying process extends the solid solubility limit of tungsten in Fe lattice up to 20 at.% (in equilibrium conditions W practically does not dissolve in Fe lattice), while the solid solubility limit of iron in W lattice was extended up to 5 at.% (in equilibrium 2.6 at.%).

During milling, the sizes of the powder particles diminish which was reflected by the broadening of the diffraction lines. The average grain sizes were roughly estimated using Scherrer's formula. In the case of  $\text{Fe}_{80}\text{W}_{20}$  the average grain sizes of the final product of milling were about 20 nm, while in the case of  $\text{Fe}_{67}\text{W}_{33}$  they were about 10 nm. The decrease in the grain size to the level of tens nanometers was accompanied by the increase in the lattice strains [6]. For Fe–Nb system the average grain sizes were calculated for the samples just before the amorphization process. In the case of  $\text{Fe}_{52}\text{Nb}_{48}$  the average sizes of grains were about 10 nm for Fe and Nb, while for  $\text{Fe}_{36}\text{Nb}_{64}$  they were about 25 nm and 10 nm for Fe and Nb, respectively.

Concluding, XRD measurements proved that in the mechanical alloying process of  $\text{Fe}_{80}\text{W}_{20}$  and  $\text{Fe}_{67}\text{W}_{33}$  performed under above-mentioned conditions two solid solutions Fe(W) and W(Fe) were formed instead of an amorphous phase. This result is inconsistent with that obtained by the calculation of phase diagram

(CALPHAD) method, which predicts in Fe–W system an amorphous phase formation for tungsten concentration from 18 to 43 at.% [2]. In the case of  $\text{Fe}_{52}\text{Nb}_{48}$  and  $\text{Fe}_{36}\text{Nb}_{64}$  single phase amorphous alloys have been synthesised during MA processes. Results are consistent with the thermodynamic data, which predict the amorphization process in binary alloy systems exhibiting a large negative heat of mixing [10].

### 3.2. Magnetic properties

Mössbauer measurements allowed us not only to monitor the progress in solid-state reactions of iron with tungsten and niobium but also to determine the magnetic properties of the phases formed during milling and their relative abundance. In general, the Mössbauer spectra for shortly milled samples are similar to that for  $\alpha$ -iron. Further milling leads to the gradual formation of different magnetic phases. Figure 2 presents the Mössbauer spectra of the final products of milling of  $\text{Fe}_{80}\text{W}_{20}$  (Fig. 2a),  $\text{Fe}_{67}\text{W}_{33}$  (Fig. 2b),  $\text{Fe}_{52}\text{Nb}_{48}$  (Fig. 2c), and  $\text{Fe}_{36}\text{Nb}_{64}$  (Fig. 2d).

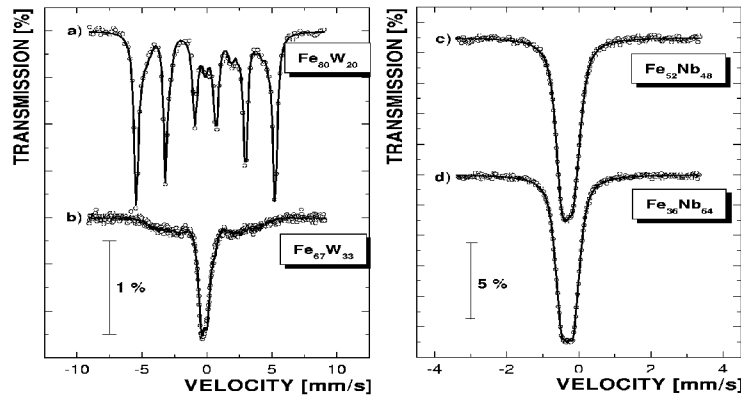


Fig. 2. Room-temperature Mössbauer spectra of the final product of the mechanical alloying processes: a)  $\text{Fe}_{80}\text{W}_{20}$  milled for 10 h in Spex mill, b)  $\text{Fe}_{67}\text{W}_{33}$  milled for 115 h in Fritsch mill, c)  $\text{Fe}_{52}\text{Nb}_{48}$  milled for 70 h in Fritsch mill and d)  $\text{Fe}_{36}\text{Nb}_{64}$  milled for 70 h in Fritsch mill.

In the case of  $\text{Fe}_{80}\text{W}_{20}$  Mössbauer measurements revealed that not the whole amount of iron dissolves in tungsten lattice.  $\alpha$ -iron component had a significant contribution (67%) in the spectra of the sample milled for 10 h (see Fig. 2a). Besides  $\alpha$ -iron component, three sextets and two doublets were fitted to the spectrum. The total abundance of these three sextets was estimated as 17%. On the basis of the simple dilution model and the literature data [11] it was proved that three sextets represent  $\text{Fe}_{97}\text{W}_3$  solid solution in which three different configurations of iron and tungsten atoms in the nearest neighbourhood of  $^{57}\text{Fe}$  are possible.

The first doublet was recognised as the contribution caused by Fe atoms located at the substitutional sites in the lattice of  $W_{95}Fe_5$  solid solution and its relative abundance was estimated as 10%. The second doublet (contribution of 6%) with the quadrupole splitting  $\Delta > 1.2$  mm/s and a large value of isomer shift (of about 0.57 mm/s) was attributed to  $Fe^{2+}$  in an iron–tungsten oxide formed during milling.

In the case of  $Fe_{67}W_{33}$  Mössbauer spectrum of the final product of milling is the superposition of two doublets (total abundance 75%) and the broad hyperfine magnetic field (HMF) distribution. It was proved that the broad HMF distribution is caused by the ferromagnetic Fe(W) solid solution (e.g.  $Fe_{80}W_{20}$ ), while doublets represent the paramagnetic W(Fe) solid solution (e.g.  $W_{97}Fe_3$ ) in which iron atoms were located both at grain boundaries and substitutional sites of W lattice [6].

As XRD analysis proved, a single homogeneous amorphous phase was obtained after 50 h of milling in the case of  $Fe_{52}Nb_{48}$ , while  $Fe_{36}Nb_{64}$  is amorphous after 35 h of milling. Mössbauer spectra of  $Fe_{52}Nb_{48}$  samples milled longer than 50 h and of  $Fe_{36}Nb_{64}$  samples milled longer than 35 h revealed paramagnetic doublet (Figs. 2c and d). The fitting of the spectra by the doublet distribution allowed calculating the average quadrupole splittings. They are as follows:  $\Delta = 0.19(1)$  mm/s for  $Fe_{52}Nb_{48}$  and  $\Delta = 0.18(1)$  mm/s for  $Fe_{36}Nb_{64}$ . It may be stated that magnetic properties of the final product of milling of  $Fe_{52}Nb_{48}$  and  $Fe_{36}Nb_{64}$  are similar.

#### 4. Conclusions

It was shown that the mechanical alloying process is an effective method of production of amorphous materials, especially in systems exhibiting a negative heat of mixing (e.g. Fe–Nb). The amorphization process was not observed in Fe–W system as the theoretical calculations suggest. The milling conditions may have a significant influence on the formation of an amorphous phase in the case of systems exhibiting a positive heat of mixing.

It is worth emphasising that Mössbauer spectroscopy is a powerful method used in the investigations of materials produced by the mechanical alloying. It allows one to determine the relative abundance of the phases formed during milling and to recognise their magnetic properties.

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