Microstructure of the Ni–Fe–Cu–P melt-spun ribbons produced from the single-chamber and from the double-chamber crucibles

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ABSTRACT

The aim of the work was to investigate the influence of the processing on the final microstructure and properties of the melt-spun Ni–Fe–Cu–P, Ni–Fe–P and Ni–Cu–P alloys ejected in two ways. In the first case, the alloy was molten in a simple single-chamber crucible, then ejected as uniform liquid. In the second case the double-chamber crucible was used, and the flux composed of the two Ni–Fe–P and Ni–Cu–P liquids was cooled on a copper roller before forming a uniform mixture. The two component melt spinning (TCMS) was performed starting from the Ni50Fe50P20 and Ni50Cu50P20 alloys. Three of the alloys i.e. Ni50Fe20Cu30P20, Ni50Fe30Cu20P20 and Ni50Cu30Fe20P20 were melt-spun from the traditional single-chamber crucible. The methods applied in this study for microstructural investigations include scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Mössbauer spectroscopy. Thermal stability of the melt-spun alloys was tested using differential scanning calorimetry (DSC). The results of the investigations are described and discussed in terms of the unique features of the TCMS amorphous microstructure. It is shown that this complex phase composition of the amorphous alloy favors formation of the ductile fracture and the multiple shear band formation.

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1. Introduction

The potential of the metallic glasses as an engineering material in many applications is still strongly restricted due to such reasons as poor tensile ductility connected with the formation of brittle fracture and difficult production of glassy metallic composites. On the other hand, the manufacture of the alloys containing a ductile crystalline phase encouraging the formation of multiple shear bands can be helpful in improving the ductility [1,2]. The composites can be produced by introduction of the second phase “ex situ” prior to casting [2–6], “in situ” by the partial crystallization of the glassy matrix or by crystallization of precipitates during solidification of castings. Amorphous/crystalline composites can be produced using precursor elements with positive heat of mixing between some of them [7–10]. There are reports on formation of two-phase amorphous composites obtained by liquid phase separation in such systems as La–Zr–Al–Cu–Ni [11], Nd–Zr–Al–Co [12], Ni–Nb–Y [13]. In the latter case, the mechanical behavior of the two-phase metallic glass, consisting of a Y-rich softer matrix and a harder globular Nb-rich phase, has been investigated by nanoindentation. It was found that the propagation of shear bands mainly initiates in the softer matrix during deformation. Consequently, the plasticity and the hardness of the two-phase alloy are enhanced with respect to the single softer amorphous alloy. Unfortunately, in these cases [11–13] the production of the two-phase metallic glasses is restricted to the alloys with a special composition. Besides, the microstructure of these alloys is very heterogeneous with a large scatter of particle size. However, a new variation of the melt spinning with the double-chamber crucible proposed in the present work enables the production of a composite with heterogeneous amorphous structure from the simple Ni–Fe–P and Ni–Cu–P melts of a relatively low glass forming ability in or-

La–Zr–Al–Cu–Ni [11], Nd–Zr–Al–Co [12], Ni–Nb–Y [13]. In the latter case, the mechanical behavior of the two-phase metallic glass, consisting of a Y-rich softer matrix and a harder globular Nb-rich phase, has been investigated by nanoindentation. It was found that the propagation of shear bands mainly initiates in the softer matrix during deformation. Consequently, the plasticity and the hardness of the two-phase alloy are enhanced with respect to the single softer amorphous alloy. Unfortunately, in these cases [11–13] the production of the two-phase metallic glasses is restricted to the alloys with a special composition. Besides, the microstructure of these alloys is very heterogeneous with a large scatter of particle size. However, a new variation of the melt spinning with the double-chamber crucible proposed in the present work enables the production of a composite with heterogeneous amorphous structure from the simple Ni–Fe–P and Ni–Cu–P melts of a relatively low glass forming ability in order to produce a lamellar microstructure. The aim of this work was to investigate the microstructure, thermal stability and the fracture appearance of the ribbon melt-spun from the double-chamber crucible in comparison with the melt-spun ribbons ejected from the single-chamber crucible.
2. Experimental

Nickel–iron–phosphorus Ni₄₀Fe₄₀P₂₀, nickel–copper–phosphorus Ni₇₀Cu₁₀P₂₀ and nickel–iron–copper–phosphorus Ni₅₅Fe₂₀Cu₄P₂₀ alloys were prepared starting from 99.95 wt% Ni, 99.95 wt% Fe, 99.95 wt% Cu, Ni–P, Fe–P and Cu–P master alloys. The precursors were melted in the arc furnace under argon gettered protective atmosphere. Then the alloys were melt-spun in helium atmosphere with the linear velocity of 40 m/s, ejection pressure 150 kPa, and crucible hole diameter 1.2 mm. The four ribbons were produced. The first one was obtained by the two component melt spinning (TCMS), i.e. the ejection of alloys was preceded by heating and melting the Ni₄₀Fe₄₀P₂₀ and Ni₇₀Cu₁₀P₂₀ alloys separately in the double-chamber crucible with a partition barrier between the two melts (Fig. 1). However, the three remaining alloys i.e. Ni₄₀Fe₄₀P₂₀, Ni₇₀Cu₁₀P₂₀ and Ni₅₅Fe₂₀Cu₄P₂₀ were ejected after re-melting in a simple single-chamber crucible and then ejected into the copper roller.

The tensile tests were performed. Tensile specimens with a gauge length of 40 mm, a width of 1.6 mm, and a thickness of 15 ± 3 μm were prepared, and were tested at room temperature at a crosshead speed of 1 mm/min. Following tensile tests, the fracture surfaces of tested specimens were characterized by SEM with EDS.

The free surface of the two component melt-spinning (TCMS) alloy as well as the fractures of the TCMS, Ni₄₀Fe₄₀P₂₀, Ni₇₀Cu₁₀P₂₀ and Ni₅₅Fe₂₀Cu₄P₂₀ ribbons after tensile breaking were observed by means of scanning electron microscope with EDS (JOEL 6610. Then the ribbons were investigated by means of the JEOL 300 kV transmission electron microscope (TEM). X-ray diffraction was performed on Rigaku Miniflex-2 diffractometer using Cu Kα radiation filtered by the LiF bent single crystal on the detector side. The scattering angle 2θ varied between 30° and 60°. Scans were performed in the θ–2θ mode. Differential scanning calorimetry (Perkin Elmer DSC7) in argon atmosphere was used for characterizing the crystallization behavior of amorphous ribbons with the heating rate of 40 K/min. For the alloys containing iron Mössbauer spectra were collected at room temperature in transmission mode using 14.41-keV line of ⁵⁷Fe. The MsAa-3 spectrometer was used with the Kr-filled proportional counter and commercial ⁵⁷Co(Rh) source. Velocity scale was calibrated by the Michelson–Morley interferometers equipped with the He–Ne laser. Spectra were calibrated and processed by means of the Mosgraf-2009 suite proper applications [14]. All spectral shifts are reported versus room temperature α-Fe.

3. Results and discussion

The scanning electron microscope image and EDS analysis done at the free surface (Fig. 2a) and at the cross-section (Fig. 2b) of the melt-spun ribbon obtained by the two component melt spinning (TCMS) reveal the presence of bands with differentiated chemical composition. Lighter and darker bands are arranged along the longitudinal direction of the ribbon. The EDS mapping indicates that the brighter bands are enriched in Ni and Cu, however the darker bands are enriched in Fe. On the other hand, the mapping of P presents uniform distribution of this element. Therefore, in spite of the fact that P has a different affinity to each of the metallic elements (the enthalpies of mixing, see Table 1, ΔH⁰_{(Cu–P)} = −17.5 (kJ/
The essential alloy reveals two different nearest neighbor environments and Ni–Fe–Cu–P ribbons ejected from the crucible shows the brighter areas marked “A” and the darker areas marked “B” is smooth as shown by the solid black and white arrows. It is worth to note that the transition between the areas correspond to the range of the d values between 1.9 Å and 2.3 Å. It is worth to note that the transition between the areas “A” and “B” is smooth as show the solid black and white arrows on Fig. 3b. Due to the content of the species with the different atomic number, one can expect, that the “A” areas contain more Fe (Z = 26) and “B” areas are enriched in Ni (Z = 28) and Cu (Z = 29). Smooth transitions from one area to another without any traces of crystals between may be due to the fact that the intermediate compositions between “A” and “B” are also amorphous.

The X-ray diffraction results are shown in Fig. 4. Generally, all of the studied ribbons show the presence of the broad diffraction maxima located between 40° and 50° without any trace of the sharp peaks. Such patterns can be associated with the amorphous structure in these alloys. The Ni–Fe–Cu–P ribbons reported in this study, i.e. the Ni₄₀Fe₄₀Cu₂₀P₂₀ melt-spun ribbon ejected from the single-chamber crucible and the one obtained by the two component melt spinning (TCMS) have the diffusive diffraction maximum at 44.8° (2.021 Å). These values are close to the diffraction maximum obtained for amorphous Ni–P [16] close to d = 2.02 Å and amorphous Fe–P [17] close to d = 1.97 Å. The amorphous Ni₄₀Fe₄₀P₂₀ alloy has the peak at 44.4° (2.039 Å) and the Ni₇₀Cu₁₀P₂₀ alloy at 45.1° (2.008 Å). Therefore, the diffraction maxima obtained for the quaternary Ni–Fe–Cu–P amorphous alloys cannot be distinguished on the basis of the X-ray diffraction. In spite of the fact that the TCMS amorphous ribbon was formed from the melts with strongly differentiated chemical compositions i.e. Ni–Fe–P and Ni–Cu–P (see Fig. 2), they have separated diffusive peaks neither on electron diffraction patterns nor X-ray diffraction patterns, as it was reported for the two-phase amorphous liquid immiscible alloys [5,11]. This can be due to two possible reasons. The first one is because the two amorphous alloys (i.e. Ni₄₀Fe₄₀P₂₀ and Ni₇₀Cu₁₀P₂₀) have quite similar densities and give broad diffusive peaks for very close diffraction angles, i.e. 44.4° and 45.1°, respectively. The second reason is that there is no distinct interfacial boundary between the regions of the two different chemical compositions. Consequently, intermediate amorphous regions have the diffraction diffuse rings also for intermediate diffraction angles between 44.4° and 45.1°. On the other hand, the observation confirms that the microstructure of the partially mixed regions is also amorphous.

The measured and fitted Mössbauer spectra for the three of the amorphous alloys containing iron i.e.: TCMS Ni–Fe–Cu–P, Ni₅₃Fe₂₀Cu₄P₁₀ and Ni₄₀Fe₄₀P₂₀ are shown in Fig. 5. The essential Mössbauer parameters of the spectra are given in Table 2. The Ni₇₀Cu₁₀P₂₀ alloy was not investigated by Mössbauer spectroscopy, because there was no iron in the sample. The spectrum for Ni₅₃Fe₂₀Cu₄P₁₀ alloy reveals two different nearest neighbor environments.

Table 1
Calculated enthalpies of mixing ∆Hmix for equiatomic liquids containing Fe, Cu, Ni and P in binary systems, kJ/mole [15,16].

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cu</th>
<th>Ni</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>–</td>
<td>+13.0</td>
<td>–</td>
<td>–31.0</td>
</tr>
<tr>
<td>Cu</td>
<td>–</td>
<td>+4.0</td>
<td>–</td>
<td>–17.5</td>
</tr>
<tr>
<td>Ni</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–26.0</td>
</tr>
</tbody>
</table>

Fig. 3. TEM micrographs for the TCMS ribbons formed by ejection of the separately molten Ni₄₀Fe₄₀P₂₀ and Ni₇₀Cu₁₀P₂₀ alloys; (a) TEM image with the brighter areas marked as “A” and the darker areas marked as “B”; arrows with the dashed lines link the electron diffraction patterns with the broad diffusive rings and the “A” and “B” areas; (b) higher magnification of the area visible on (a) with the smooth transition between “A” and “B” marked by arrows with the solid lines.

Fig. 4. The XRD of the of the TCMS and single-chamber crucible melt-spun Ni₄₀Fe₄₀P₂₀, Ni₇₀Cu₁₀P₂₀ and Ni₅₃Fe₂₀Cu₄P₁₀ ribbons; the positions of the diffusive maxima and d values were indicated by arrows.
Fig. 5. The Mössbauer transmission spectra for the TCMS Ni–Fe–Cu–P, Ni$_{40}$Fe$_{20}$Cu$_{5}$P$_{20}$ and Ni$_{40}$Fe$_{20}$P$_{20}$ amorphous alloys.

Table 2
The essential Mössbauer parameters for the three of the amorphous alloys containing iron i.e. the TCMS Ni–Fe–Cu–P, Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$ and the Ni$_{40}$Fe$_{20}$P$_{20}$. The symbol $A$ denotes relative contribution of the given iron site to the whole spectrum, $IS$ stands for the isomer shift of the particular sub-spectrum, $QS$ denotes the absolute value of the quadrupole splitting. The symbol $B$ stands for the value of the hyperfine field in the ferromagnetic phase.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A$ (%)</th>
<th>$IS$ (mm/s)</th>
<th>$QS$ (mm/s)</th>
<th>$B$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCMS Ni–Fe–Cu–P</td>
<td>53</td>
<td>0.27</td>
<td>0.39</td>
<td>–</td>
</tr>
<tr>
<td>Ni$<em>{55}$Fe$</em>{20}$Cu$<em>{5}$P$</em>{20}$</td>
<td>47</td>
<td>0.28</td>
<td>–</td>
<td>12.7</td>
</tr>
<tr>
<td>Ni$<em>{40}$Fe$</em>{20}$Cu$<em>{5}$P$</em>{20}$</td>
<td>42</td>
<td>0.37</td>
<td>0.58</td>
<td>–</td>
</tr>
<tr>
<td>Ni$<em>{40}$Fe$</em>{20}$P$_{20}$</td>
<td>58</td>
<td>0.17</td>
<td>0.56</td>
<td>–</td>
</tr>
<tr>
<td>Ni$<em>{40}$Fe$</em>{40}$P$_{20}$</td>
<td>100</td>
<td>0.27</td>
<td>–</td>
<td>16.6</td>
</tr>
</tbody>
</table>

Fig. 6 presents the DSC traces performed for the TCMS Ni–Fe–Cu–P and single-chamber crucible melt-spin Ni$_{40}$Fe$_{40}$P$_{20}$, Ni$_{70}$Cu$_{10}$P$_{20}$ and Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$ ribbons at a heating rate of 40 K/min. All of the DSC heating traces show a substantial exothermic crystallization effects (Table 3). For the amorphous Ni$_{40}$Fe$_{40}$P$_{20}$ alloy single stage crystallization is observed. In this case, a crystallization onset is at $T_p = 678$ K which is followed by the peak value associated with the maximum speed of the crystallization at $T_p = 681$ K and enthalpy of $H = –83.66$ J/g. However the amorphous Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$ alloy has a three-stage crystallization with the onset of the first stage at $T_{x1} = 600$ K and its peak value at $T_{p1} = 615$ K with exothermic effect of $H_1 = –7.08$ J/g. For this alloy the largest crystallization enthalpy $H_2 = –46.50$ J/g is associated with the second stage which starts at $T_{x2} = 664$ K and has a peak located at $T_{p2} = 668$ K. The third stage begins at $T_{x3} = 738$ K with the peak at $T_{p3} = 756$ K and the value of exothermic effect $H_3 = –3.73$ J/g. The amorphous Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$ alloy crystallizes in one stage with the onset at $T_x = 667$ K, the peak at $T_p = 670$ K and with exothermic effect $H = –62.71$ J/g. Similarly the TCMS Ni–Fe–Cu–P amorphous ribbon has one stage crystallization with the onset at $T_x = 671$ K and the peak at $T_p = 674$ K. The exothermic crystallization effect is $H = –63.34$ J/g. Comparison of the onset and the peak value of the largest crystallization exothermic effect indicates that the Ni$_{40}$Fe$_{40}$P$_{20}$ amorphous alloy has the highest thermal stability, i.e. the highest crystallization temperature range. The main crystallization exothermic effect has also the highest value of the enthalpy. On the other hand, the main...
crystallization effect for the Ni$_{70}$Cu$_{10}$P$_{20}$ amorphous alloy occurs at the lowest range in terms of crystallization onset and the peak temperature. Also, the exothermic effect for the alloy is the lowest. This observation correlates well with the values of mixing enthalpies $H_{\text{mix}}$ for the equiatomic liquids [15,16]. It is worth noting that for the Ni-Fe-Cu-P system, the largest negative values of $H_{\text{mix}}$ correspond to Fe–P $H_{\text{mix}} = -31 \text{ kJ/mol}$ and Ni–P $H_{\text{mix}} = -26 \text{ kJ/mol}$, whereas the value of mixing enthalpy for Cu–P is $H_{\text{mix}} = -17.5$. This can be associated with the lower affinity of Cu to P than Fe and Ni to P and to lower enthalpy of the main crystallization effect. The value of the crystallization enthalpy for the largest crystallization peak in the Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$ alloy is $H_{\text{e}} = -83.66 \text{ J/g}$ and in the TCMS Ni–Fe–Cu–P alloy is $H_{\text{e}} = -83.34 \text{ J/g}$. Therefore, the values are basically at the same level. This may be expected due to the similar average chemical composition. However, the temperatures $T_x = 671 \text{ K}$ and $T_p = 674 \text{ K}$ of the main crystallization peak for the TCMS Ni–Fe–Cu–P alloy have distinctly higher values than the corresponding values for the Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$ alloy ($T_x = 667 \text{ K}$ and $T_p = 670 \text{ K}$). Taking into account that the former alloy in its amorphous state consists of the Ni–Fe–P rich and Ni–Cu–P rich compositions, it is quite obvious that the Ni–Fe–P rich part of the alloy crystallizes at the temperature range closer to the one for Ni$_{40}$Fe$_{40}$P$_{20}$ alloy whereas the Ni–Cu–P rich composition crystallizes at lower temperatures. The shifting of the crystallization peak of the TCMS Ni–Fe–Cu–P alloy to the higher temperatures than the peak position of the Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$ alloy is in accordance with this interpretation.

Fig. 7(a–c) show the fractures of the ribbons melt-spun after ejection from the single-chamber crucible. All of the fractures presented for the Ni$_{40}$Fe$_{40}$P$_{20}$, Ni$_{70}$Cu$_{10}$P$_{20}$ and Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$ alloys have the smooth brittle glassy appearances typical for the brittle glassy alloys. There are also a few deformation markings (Fig. 7a–c shown by white arrows) observed on the free surfaces of the samples near the fractures. The observation is consistent with the findings of Spaepen [20] that the deformation behavior of glassy materials at low temperatures and high stresses is extremely inhomogeneous and plastic flow is highly localized in thin shear bands.

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_x$ (K)</th>
<th>$T_p$ (K)</th>
<th>$\Delta H$ (J/g)</th>
<th>$T_x$ (K)</th>
<th>$T_p$ (K)</th>
<th>$\Delta H$ (J/g)</th>
<th>$T_x$ (K)</th>
<th>$T_p$ (K)</th>
<th>$\Delta H$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{40}$Fe$</em>{40}$P$_{20}$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>678</td>
<td>681</td>
<td>-83.66</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ni$<em>{70}$Cu$</em>{10}$P$_{20}$</td>
<td>600</td>
<td>615</td>
<td>-7.08</td>
<td>664</td>
<td>668</td>
<td>-46.50</td>
<td>738</td>
<td>756</td>
<td>-3.73</td>
</tr>
<tr>
<td>Ni$<em>{55}$Fe$</em>{20}$Cu$<em>{5}$P$</em>{20}$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>671</td>
<td>674</td>
<td>-63.34</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>TCMS Ni–Fe–Cu–P</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</table>

Fig. 7. The SEM images of tensile fractures for amorphous alloys: (a) Ni$_{40}$Fe$_{40}$P$_{20}$; (b) Ni$_{70}$Cu$_{10}$P$_{20}$; (c) Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$; (d and e) TCMS Ni–Fe–Cu–P; (f) EDS maps showing the distribution of Ni, Fe, Cu and P for the SEM image from (e); white arrows show deformation markings on (a–e); black dashed arrows and black dashed lines indicate the coincidence between vein-like pattern (e) and the boundaries of the Ni–Fe–P and Ni–Cu–P areas (f).
However, the fracture surface in the TCMS Ni–Fe–Cu–P amorphous alloy (Fig. 7d and e) is more developed than in the case of the Ni$_{40}$Fe$_{40}$P$_{20}$, Ni$_{70}$Cu$_{10}$P$_{20}$ and Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$ amorphous alloys obtained by ejection from the single-chamber crucible and the free surface near the fracture has the multiple deformation markings (Fig. 7d and e). The appearance of the fracture surface is ductile with the presence of vein-like pattern. The SEM microphotographs and EDS maps show that there are strip-like regions on the fracture parallel to its edge that have the differentiated chemical composition (Fig. 7f). It is worth noting that the course of some segments of this vein-like pattern of the fracture is co-incident with the boundaries of the Ni–Fe–P and Ni–Cu–P areas. These segments and the corresponding boundary regions are indicated by black dotted lines and black dashed arrows on Fig. 7e and f on the Fe map. This suggests that this differentiation of the chemical composition influenced the fracture formation in the TCMS Ni–Fe–Cu–P amorphous alloy. These observations are consistent with the findings of Concustell et al. [13] where the formation of the Ni–Nb–Y amorphous/amorphous double phase composite led to formation of multiple shear bands. The improvement of ductility is attributed to the fact that the precipitation of a second phase in the amorphous matrix may disrupt shear-band propagation and hence improve the ductility of the amorphous material [1,13]. It is possible that in case of the ribbon produced from the double-chamber crucible, the ductile fracture and the multiple shear bands are due to the disruption of the shears bands. The TCMS Ni–Fe–Cu–P amorphous alloy is more ductile than the two amorphous phases of the different chemical composition. Therefore, the possible explanation for the ductile fracture and the multiple shear bands is that this complex phase composition favors formation of the ductile fracture and the multiple shear band formation.

4. Conclusions

1. The microstructure of the TCMS Ni–Fe–Cu–P alloy is amorphous and its unique lamellar band-like morphology is formed during the melt spinning from the partially mixed streams of the glass forming Ni$_{40}$Fe$_{40}$P$_{20}$, Ni$_{70}$Cu$_{10}$P$_{20}$ alloys ejected from the double-chamber crucible. The starting compositions of the alloys were suitable for amorphisation even in case of formation of the intermediate compositions at the regions where the partial mixing occurred.

2. In the case of the TCMS Ni–Fe–Cu–P amorphous alloy, the Mössbauer spectroscopy allowed the identification of the unmixed or poorly mixed Ni–Fe–P regions with the isomer shift $\delta = 0.28$ mm/s and hyperfine field ($B$) = 12.7 T with the contribution of 47%. The other part of this amorphous alloy which is a product of a partial mixing between the Ni–Fe–P melt and the Ni–Cu–P melt has $\delta = 0.27$ mm/s, and gives a contribution of 53% to the whole spectrum. For the latter region, the iron sites have the similar properties as in the Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$ amorphous alloy.

3. The temperatures ($T_h = 671$ K and $T_s = 674$ K) of the main crystallization peak for the TCMS Ni–Fe–Cu–P alloy are distinctly higher than the corresponding values for the Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$ alloy ($T_h = 667$ K and $T_s = 670$ K). It is due to the fact that the Ni–Fe–P rich part of the alloy crystallizes at the temperature range closer to the crystallization of the Ni$_{40}$Fe$_{40}$P$_{20}$ alloy.

4. The tensile fractures of the Ni$_{40}$Fe$_{40}$P$_{20}$, Ni$_{70}$Cu$_{10}$P$_{20}$ and Ni$_{55}$Fe$_{20}$Cu$_{5}$P$_{20}$ amorphous alloys have the smooth brittle glassy appearances typical for the brittle glassy alloys. On the other hand, the TCMS Ni–Fe–Cu–P amorphous alloy presented more developed fractures with the vein-like patterns which can be associated with the boundaries of the Ni–Fe–P and Ni–Cu–P areas resulting from the special method of formation of the amorphous alloy.

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