Interplanar spacings of complex Fe-Ni phases in rapidly quenched Fe-Ni-Nb-B systems

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Abstract. Formation of phases in the course of crystallization from amorphous state in rapidly quenched Fe-Ni-Nb-B was investigated with respect to the ratio of Fe/Ni and content of B in a wide compositional interval. A transition from nanocrystalline bcc-Fe formed during first crystallization stage into fcc-FeNi and Fe₂₃B₆ fcc-type structure with large unit cell accompanied by a distinct change in the transformation kinetics was observed with increasing Ni content. The emergence of these phases during (nano)crystallization is investigated with respect to the changes of local order induced by large variations of Fe/Ni and to the presence of large atoms of Nb. Diverse methods of high-resolution structure characterisation are used to identify and quantify phases with similar interplanar spacing. A deviation from a typical two-stage pattern leading to a rapid single-stage crystallization with direct formation of stable phases, incidentally present also in the structure of the precursor master alloys, is interpreted within the framework of a model of cluster structure of amorphous state. Links between the expected local ordering in amorphous state and the structure of crystallizing phases are followed and compared with similar phenomena observed in Nb-containing Co-rich Fe-Co-Nb-B system.

1. Introduction
Alloys rich in Fe in combination with another ferromagnetic element such as Co, Cr or Ni represent attractive systems both for basic investigation as well as for potential magnetic applications. Substitution of Fe by Ni in rapidly quenched Hitperm-type Fe-Ni-Zr-B systems is known [1] to lead to a change of structure of nanograins from bcc to fcc and to formation of fcc-type (Fe-Ni)₂₃B₆ lattice with large unit cell.

Our aim is to follow the evolution of phases during crystallization of amorphous Fe-Ni-Nb-B system over a broad range of Ni/Fe ratio and for varying content of B in order to obtain information about the relationship between transformation mechanisms and possible structural units active in the observed changes of the structure of the forming phases.

2. Experimental
Master alloys of (FeₙNiₓ)₆₁Nb₇B₁₂ system for y/x = 0/1, 1/6, 1/3, 1/2, 1/1, 2/1 a 3/1, (Fe₉Ni₁₂)₉₃⁻ₓNbₓBₓ and (Fe₉Ni₁₃)₉₃⁻ₓNbₓBₓ for z = 12, 15, 17 and 20 were prepared from elements with purity better than
99.9%. Amorphous ribbons 6 mm wide and approximately 20-25 microns thick were prepared by planar flow casting. Chemical composition of the ribbons was assessed by inductively coupled plasma spectroscopy, while their amorphous state after casting was verified by X-ray and electron diffraction.

Transformation from amorphous state was monitored by four-probe electrical resistivity measurement (accuracy better than 0.01%) with spring-loaded needle contacts in vacuum using linear (10K/min) heating and isothermal annealing (long-term stability ±0.1K). Consistency of transformation data from electrical resistivity measurements was verified and complemented by differential scanning calorimetry (DSC) using Mettler 822°.

Samples for X-ray diffraction measurements and high-resolution electron microscopy (HREM) analysis were annealed isothermally at selected temperatures (stability ±0.1K over annealing periods of 1000min) and re-annealed at 623K in vacuum furnace at pressures better than 10⁻³ Pa for 30min to relieve eventual internal stresses induced by heat treatment. Standard 3mm discs for HREM cut from amorphous ribbons were thinned after heat treatment by ion beam milling using the GATAN PIPS. HREM analysis was performed using JEOL 2010 electron microscope.

X-ray diffraction measurements were performed in Bragg-Brentano geometry using CuKα radiation with a graphite monochromator in the diffracted beam. The lattice parameters were calculated from the angular positions of all available X-ray diffraction peaks by linear extrapolation, using least squares fitting [2] as well as by total pattern analysis (Rietveld refinement) using Bruker TOPAS software with the accuracy better than ± 0.0003 nm.

3. Results and discussion

Transformations for system with z=12 at% B are shown in figure 1. Alloys with ratio Ni/Fe < 1 exhibit a typical decrease of resistivity upon nanocrystallization followed by a second stage at temperatures close to 900 K. Increasing Ni-content leads to decrease of the onset of nanocrystallization and to narrowing of the interval between the first and the second stage of crystallization, which is accompanied by rather sharp increase of resistivity. This effect becomes even more pronounced with increasing B-content (figure 2), where for z>15 only a fast single-step transformation is observed, taking place over very narrow temperature range regardless of the heating rate.

![Figure 1](image1.png)  
**Figure 1.** Temperature dependence of electrical resistivity in (FeNi)₃₁Nb₇B₁₂ system where Fe/Ni content is y/x=0/1, 1/6, 1/3, 1/2, 1/1, 2/1 and 3/1. Arrow demonstrates the shift of the first crystallization to lower temperatures.

![Figure 2](image2.png)  
**Figure 2.** Temperature dependence of electrical resistivity in (Fe-Ni)₉₃₋𝑧Nb₇B₇ systems for z=12, 15, 17 and 20 at.% and Ni/Fe = 2 and 3. Transformation shift to lower temperatures and its sharpening leading to a single step transformation is visible with increasing B and Ni content.
The transition from the two-stage crystallization into a single-stage reaction is shown for Ni-rich alloys with varying B-content also by DSC (figure 3). A marked difference in the heat flow between alloys with \( z=12 \) and 15 and alloys with \( z>15 \) is observed although the total heat evolved is not significantly different (inset in figure 3).

The evolution of crystalline phases at the end of the first crystallization stage for different Ni/Fe for \( z=12 \) is shown in figure 4. While for Ni/Fe<1 clearly a bcc structure with grains below 10 nm is formed, higher Ni-content leads to formation of (Fe-Ni)\(_{23}\)B\(_6\) phase; the signature of fcc-FeNi is very unclear and present only in the intermediate compositions (Ni/Fe=1, 2) and the grains as observed by HREM are very small. Higher content of fcc-FeNi is seen clearly only at elevated temperatures. Such single-stage single-phase transformation behaviour is enhanced in alloys with higher B-content; for \( z=20 \) the formation of fcc-FeNi is seen only well above 873K (figure 5). Its content does not exceed significantly 1/3 of the total crystalline volume content while its grain sizes remain low even above 1000 K (figure 6); the major crystalline phase is (Fe-Ni)\(_{23}\)B\(_6\) with grain sizes up to 100 nm.

**Figure 3.** DSC-curves for (FeNi\(_3\))\(_{81}\)Nb\(_7\)B\(_z\) system, \( z=12, 15 \) and 17 at.\%, illustrating overlapping of crystallization peaks and translation in temperature with respect to B content. Inset: concentration dependence of peak positions (\( T_{M_2} \)) for the first and second (I, II) transformation stages and enthalpy evolution \( \Delta H_{cryst.} \). Arrows show transition from double stage to single stage transformation.

**Figure 4.** XRD pattern of (Fe\(_x\)Ni\(_y\))\(_{73}\)Nb\(_7\)B\(_{12}\), \( y/x=0/1, 1/6, 1/3, 1/2, 1/1, 2/1 \) and 3/1, annealed at selected temperatures. De-composition of bcc structure and formation of fcc-FeNi and fcc-(Fe-Ni)\(_{23}\)B\(_6\) is presented.

**Figure 5.** XRD pattern of (FeNi\(_3\))\(_{73}\)Nb\(_7\)B\(_{20}\) annealed at selected temperatures. No further growth of (Fe-Ni)\(_{23}\)B\(_6\) phase is visible after the first crystallization step. Similarity with master alloy is obvious but with respect to fcc \( \gamma \)-FeNi.
The lattice parameter of \((\text{Fe-Ni})_{23}\text{B}_6\) phase exhibits a pronounced dependence on the ratio of Ni/Fe (figure 7), decreasing from the values tabulated for pure Fe\(_{23}\text{B}_6\), down to 1.0584 nm for the highest Ni/Fe. It is interesting to note that the lattice parameter exhibits no evolution with annealing time or temperature and remains constant to within the limits of the accuracy of used methods. The evolution of grain size of the \((\text{Fe-Ni})_{23}\text{B}_6\) phase is shown on figures 8 and 9 from the onset of transformation (~5 nm) up to fully developed grains of several tens of nanometers while the interplanar spacings remain unchanged. Figure 8 shown also the possible presence of small particles with interplanar spacings close to those expected for fcc-FeNi; these particles, however, are quite tiny and indistinct and were not detected at later stages of the transformation. The evolution of the overall microstructure and lattice parameter of the fcc-Fe\(_{23}\text{B}_6\) type phase is similar to that observed in Fe-Co-Nb-B system [3].

Merging of the two transformation stages and extreme narrowing of the transformation process to narrow temperature intervals (or to very short time periods on logarithmic scales, which have been observed in isothermal annealings) with increasing Ni/Fe and B-content suggests a special arrangement of the original amorphous phase which readily transforms into crystalline state without substantial rearrangement of constituent atoms over longer distances. Such arrangement, containing locally ordered (yet slightly distorted due to rapid quenching from the melt) units similar to figure 10, has been described in [3]. The feasibility of construction of the entire Fe\(_{23}\text{B}_6\) type unit cell from these units only and its stability has been assessed both experimentally [4] and by molecular dynamics [5] with respect to the maximal possible content of Nb atoms, which should not exceed 7 at.% and which is also the case of our investigated systems. Thus it can easily be envisaged that the transformation in presence of Ni atoms is favoured towards a phase with more complex structure and larger unit cell (with fcc structure) instead of a smooth transition from simpler bcc into a more simple fcc-FeNi; a suggestion of this effect is seen on figure 4, where addition of Ni leads to significant decrease of bcc-nanocrystal grain size rather than to formation of fcc-FeNi. The ease of construction of the \((\text{Fe-Ni})_{23}\text{B}_6\) type unit cell from the clusters shown in figure 10 and their availability due to overall chemical composition provides a possibility of nearly instantaneous crystallization by suitable motion of entire clusters and by minute shifts of their constituent atoms into equilibrium positions. It is also noteworthy that polycrystalline master alloy precursors in the Fe-Ni-Nb-B system, which exhibit this behaviour, contain without exception the \((\text{Fe-Ni})_{23}\text{B}_6\) phase (figure 4) with very low content of additional phases such as fcc-FeNi (or bcc-Fe).

![Figure 6](image1.png)  
**Figure 6.** Quantitative Rietveld refinement of Fe\(_{3}\text{Ni}_{16}\text{Nb}_{12}\text{B}_{15}\) annealed at 1013 K/1h. Grain dimensions are approx. 50-100 nm for fcc-(Fe-Ni)\(_{23}\text{B}_6\) phase and 7-15 nm for fcc-FeNi phase.

![Figure 7](image2.png)  
**Figure 7.** Calculated lattice parameters for fcc-(Fe-Ni)\(_{23}\text{B}_6\) and fcc-(Fe-Co)\(_{23}\text{B}_6\) phase with respect to Fe/Ni ratio; the case of (Fe-Co)\(_{23}\text{B}_6\) in Fe-Co-Nb-Si-B [3] shown for comparison.
Figure 8. HREM of \((\text{FeNi}_3)_8\text{Nb}_7\text{B}_{12}\) annealed at 693 K/1h. Small grains belongs to plane (333 or 511) of fcc-(Fe-Ni)$_{23}$B$_6$ phase or to plane (111) of fcc-FeNi phase with \(d=0.205-0.206\) nm, upper area. Lower area corresponds to plane (4-2-2) with \(d=0.216\) nm of fcc-(Fe-Ni)$_{23}$B$_6$ phase.

Figure 9. HREM of fcc-(Fe-Ni)$_{23}$B$_6$ in \((\text{FeNi}_3)_8\text{Nb}_7\text{B}_{12}\) annealed at 773 K/1h. Marked horizontal area corresponds to plane (111) with interplanar spacing \(d=0.607\) nm, perpendicular area corresponds to plane (4-2-2) with interplanar spacing \(d=0.216\) nm.

Figure 10. Possible interstructural arrangement of (Fe-Ni)$_{23}$B$_6$ phase: (a) archimedean antiprism from Fe and/or Ni atoms surrounding B atom, (b) closed archimedean antiprism with possible capping Nb atom, (c) cuboctahedron surrounding Nb atom.

4. Conclusions
The effects of substitution of Fe by Ni in a broad range of Ni/Fe ratios and the effect of boron content on the transformation behaviour in amorphous rapidly quenched (Fe-Ni)-Nb-B system was analysed. A transition from two-stage to a sharp and narrow single-stage transformation was observed with increasing Ni/Fe ratio and increasing boron content. The formation of bcc-FeNi nanograins was observed for alloys with lower Ni-content in the first crystallization stage while the second stage was characterized primarily by formation of (Fe-Ni)$_{23}$B$_6$ phase; the same phase was formed in the single-stage crystallization in alloys with higher Ni/Fe simultaneously with smaller amounts of fcc-FeNi phase.

The readiness to crystallization during which major part of the sample volume crystallizes into (Fe-Ni)$_{23}$B$_6$ phase has been discussed in terms of the existence of possible polyatomic structural units which facilitate the formation of large unit cell phases. The evolution of lattice parameter of the (Fe-Ni)$_{23}$B$_6$ phase with increasing ratio of Ni/Fe was determined by X-ray analysis; no dependence of the lattice parameter on transformation temperature or time has been observed.

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