

# METASTABLE PHASES AND NANOSTRUCTURING OF Fe-Nb-Si-B BASE RAPIDLY QUENCHED ALLOYS

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**Abstract.** Primary precipitation phases in amorphous Fe-Si-B-Nb alloys with compositions around FINEMET and bulk amorphous alloys have been investigated. On the base of new and previous TEM and XRD results concentration areas and condition for formation of the metastable phases have been determined. Role of the primary metastable phases with compositions close to the mean composition of the alloys in the processes of nanostructuring is discussed, in particular the role of hexagonal phase with the distorted  $\alpha$ -Mn type structure is emphasized.

## 1. INTRODUCTION

Recent progress in investigation of amorphous metal alloys is connected to the problems of specific structure and properties of alloys with high glass forming ability (GFA) and nanocrystallization (NC). These problems are related to each other [1,2]. Formation of nanostructures occurs either at the optimal compositions for bulk metallic glasses (BMG) or at slightly changed compositions (with increased concentration of the main component or with small additions of some elements, e.g. Pd, Pt, Ag in ZrNiAlCu alloys [1]).

Fe-Si-B-Nb system is an example of Fe base alloys with similar relationships. The system is the base for extensively investigated FINEMET alloys (with addition of 1 at.% Cu) and for metallic glasses  $Fe_{75}Si_{10}B_{15}$  with 2 - 4% Nb [3]. The same holds for other iron base metallic glasses: Fe-Zr(Nb)-B, Fe-Al(Ga)- metalloids (in the latter case addition of 1% Cu promotes formation of a nanocomposite [4]).

Information on metastable phases formed during the primary precipitation process is essential for understanding physical nature of BMG, NC and

relations between them. The following facts are emphasized in [1]. There are only a few (three) kinds of metastable phases formed as primary crystallization phases in multicomponent metallic glasses, i.e. I-phase in Zr(Ti, Hf) based alloys and two different big cubic phases in Zr and in Fe based alloys. Formation of specific phases and their fast nucleation is associated with similarity between local structures of the metastable and amorphous phases. On the other hand there are high activation barriers for long range rearrangement necessary for formation of primary phases in stable supercooled liquid. Surface energy also plays an important role in the processes of nanostructuring.

For Fe-Si-B-Nb alloys with compositions close to FINEMET alloys we have observed a number of phases which form during primary precipitation process either by rapid quenching or by annealing of amorphous precursor. Structures of these phases are related to  $\alpha$ -Mn structure type, among them are aperiodic phase with cubic symmetry on the base of  $\alpha$ -Mn structure – cubic quasicrystal (CQ phase) and hexagonal H-phase which can be represented as distorted  $\alpha$ -Mn structure [5].

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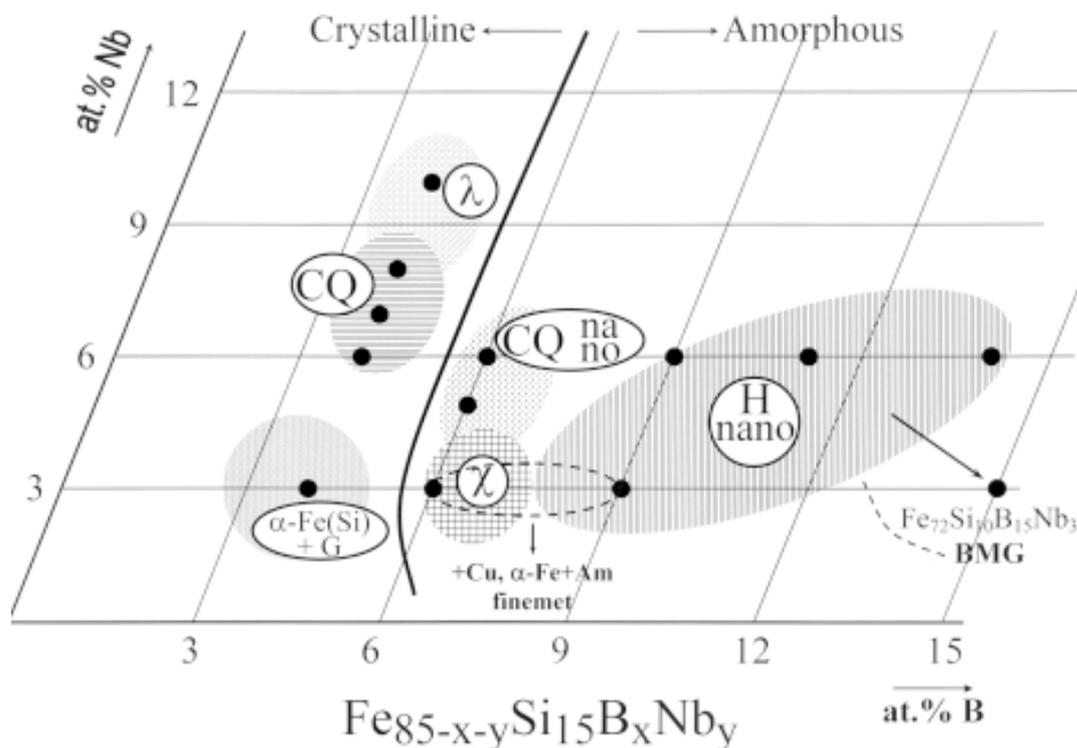


Fig. 1. Formation of metastable phases in the primary crystallization processes.

The goal of this work was to obtain data on structural transformations with formation of  $\alpha$ -Fe, CQ and H phases as primary precipitation phases in alloys with compositions adjacent to FINEMET alloys in order to shed light upon the processes of nanostructuring and also to compare them with the results for bulk metallic glass  $\text{Fe}_{72}\text{Si}_{10}\text{B}_{15}\text{Nb}_3$ .

## 2. EXPERIMENT

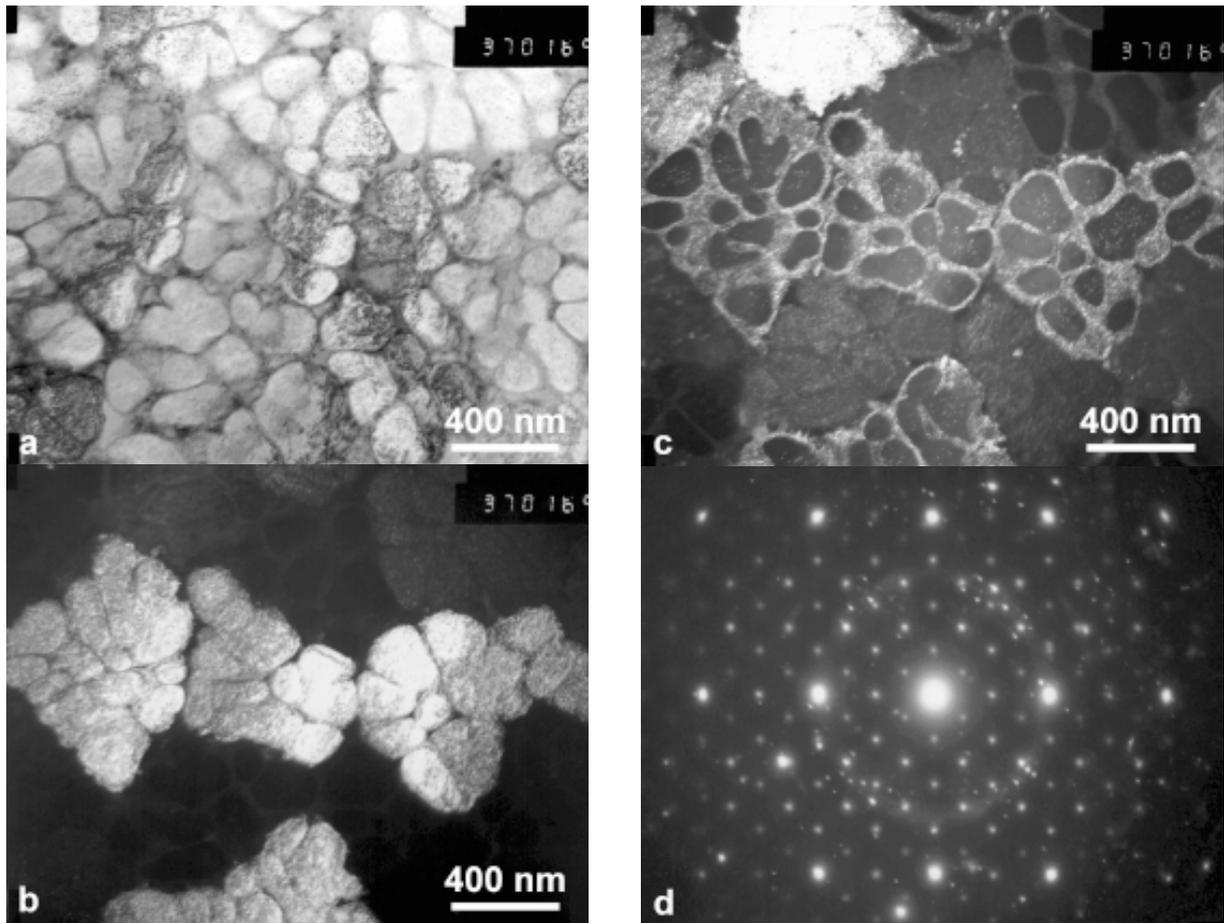
Rapidly quenched alloys were prepared by melt spinning. Temperatures of phase transformations were estimated by differential thermal analysis (DTA). Structure was investigated by transmission electron microscopy (TEM), X-ray diffraction (XRD).

## 3. RESULTS

Fig. 1 shows schematically concentration areas corresponding to formation of different phases in the primary crystallization process for Fe-Si-B-Nb alloys with fixed Si content of 15 at.%. It is based on the results obtained previously and described in more detail in [5] for the following compositions:  $\text{Fe}_{85-x-y}\text{Si}_{15}\text{B}_x\text{Nb}_y$  with  $x=4, y=6, 7, 8, 10$ ;  $x=6, y=3,$

$5, 6$ ;  $x=4, 6, 9, 11, 14, y=6$ . Results for some new compositions ( $\text{Fe}_{79}\text{Si}_{15}\text{B}_3\text{Nb}_3$  and  $\text{Fe}_{72}\text{Si}_{10}\text{B}_{15}\text{Nb}_3$ ) and more detailed data for initial stages of devitrification of  $\text{Fe}_{73}\text{Si}_{15}\text{B}_6\text{Nb}_6$  alloy are added. Besides, alloys with partial substitution of Fe for Mn ( $\text{Fe}_{63}\text{Mn}_{15}\text{Si}_{15}\text{B}_4\text{Nb}_3$  and  $\text{Fe}_{61}\text{Mn}_{15}\text{Si}_{15}\text{B}_2\text{Nb}_7$ ) have also been investigated.

To the left from the solid nearly vertical line in Fig. 1 there are alloys which crystallize during melt quenching, to the right are alloys with higher boron content which are amorphous in the quenched state and crystallize during annealing. The following phases have been observed:  $\chi$ -phase – BCC  $\alpha$ -Mn structure type with  $a = 0.882$  nm; CQ-phase – cubic quasiperiodic phase on the base of  $\alpha$ -Mn structure; H-phase – hexagonal phase (rhombohedral distortion of  $\alpha$ -Mn structure,  $a \sim 1.23$  nm,  $c \sim 0.77$  nm); CQ nano and H nano – nanocrystalline structures; G-phase - FCC structure (space group Fm3m,  $a = 1.122$  nm,  $\text{Co}_{16}\text{Nb}_6\text{Si}_7$  structure type) and  $\lambda$ -phase – Laves phase (hexagonal,  $\text{Fe}_2\text{Nb}$  structure type,  $a=0.477$  nm,  $c=0.772$  nm). Areas of compositions close to FINEMET alloys and to bulk metallic glasses (BMG) are also shown (Fig. 1).

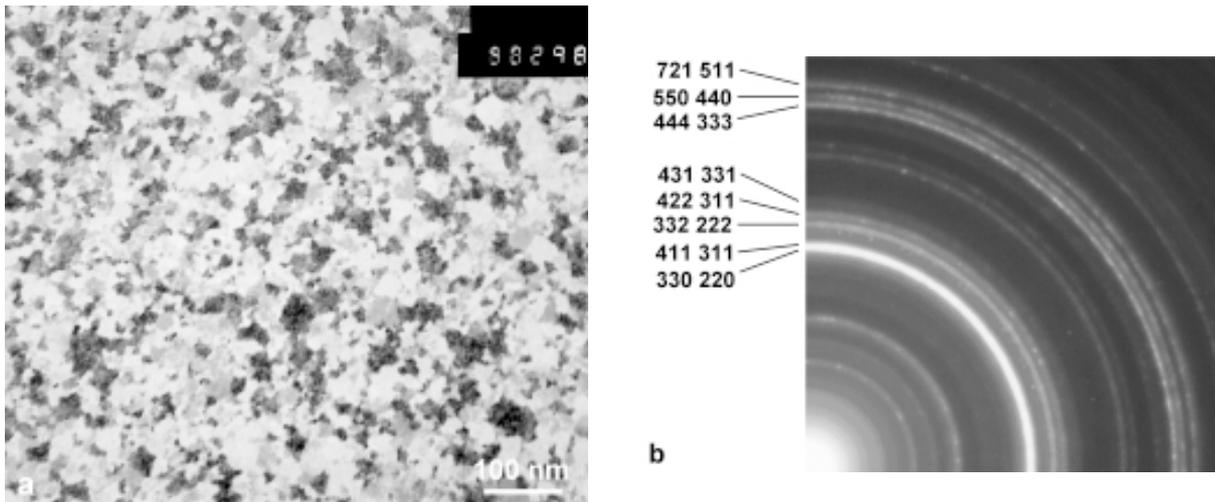


**Fig. 2.** TEM images for the as-quenched  $\text{Fe}_{78}\text{Si}_{15}\text{Nb}_3\text{B}_4$  alloy: bright-field image (a); dark field image taken with a BCC  $\alpha\text{-Fe(Si)}$  phase reflection (b); dark field image taken with a G-phase reflection that does not coincide with the fundamental and superlattice reflections of the  $\alpha\text{-Fe(Si)}$  phase (c). Selected area diffraction (SAD) associated with the area shown in Fig. 2b, (110) planes of the reciprocal lattices of G and  $\alpha\text{-Fe(Si)}$  phases (d).

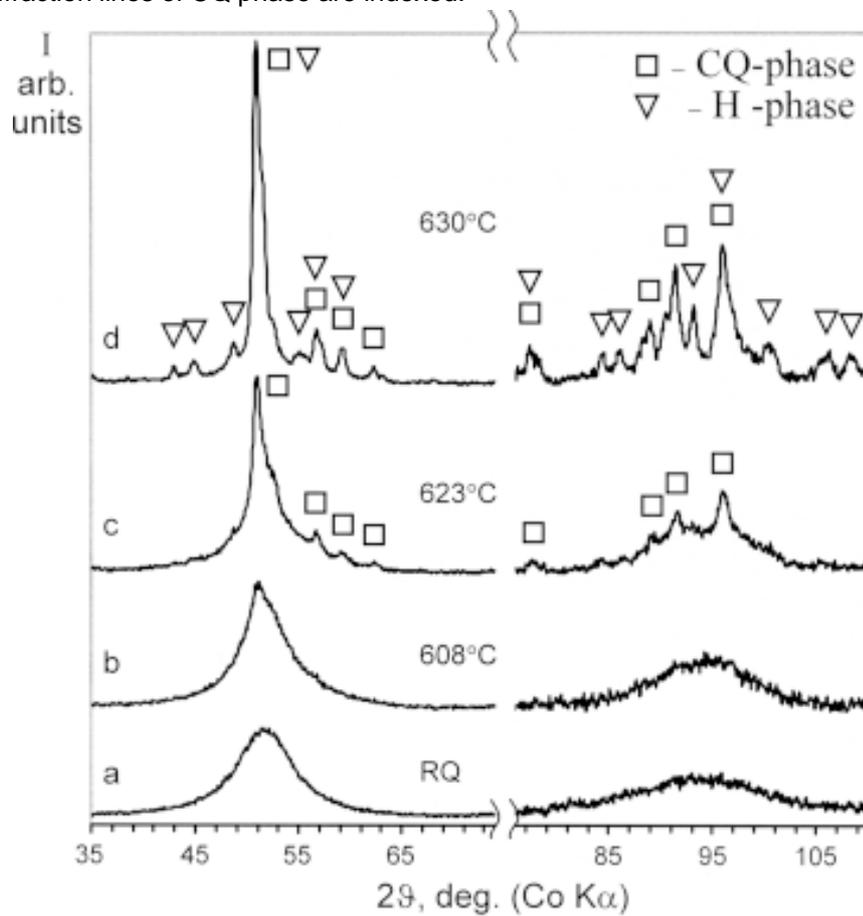
CQ phase is formed by polymorphous crystallization during rapid quenching, G phase is formed by eutectic crystallization in a mixture with  $\alpha\text{-Fe}$ ,  $\chi$ -phase ( $\alpha\text{-Mn}$  type) and H-phase are formed by annealing of amorphous precursors. Areas CQ and CQ nano in Fig. 1 correspond to one and the same phase but with different morphology.

Most of the investigated alloys belong to one of the two groups: alloys with low boron content and relatively high niobium content where formation of CQ phase is observed and alloys with enhanced boron content where H phase is formed. In alloys with reduced concentrations of both B and Nb eutectic mixture of  $\alpha\text{-Fe}$  and G phases is formed. For example, in quenched  $\text{Fe}_{78}\text{Si}_{15}\text{Nb}_3\text{B}_4$  alloy  $\alpha\text{-Fe}$  precipitates in the form of dendrites surrounded by

FCC phase with lattice parameter  $a=1.12$  nm. Between the two cubic lattices – BCC  $\alpha\text{-Fe}$  and FCC – certain orientation relations are observed: 4-fold symmetry axes of both lattices are parallel (Fig. 2). Besides lattice parameter of the FCC phase is  $a_{\text{FCC}} \approx 4a_{\text{BCC}}$ . Lattice parameter of the FCC phase for  $\text{Fe}_{78}\text{Si}_{15}\text{Nb}_3\text{B}_4$  alloy varies from 1.1232 to 1.1250 nm, the smaller value corresponding to the contact surface of the ribbon, the larger – to its free surface. The value of lattice parameter and relative intensities of XRD reflections suggest that structural analog of the phase is silicide  $\text{Co}_{16}\text{Nb}_6\text{Si}_7$  with the space group Fm3m and lattice parameter 1.122 nm. There is a phase of the same structure type in Fe-Nb-B system (lattice parameter for com-



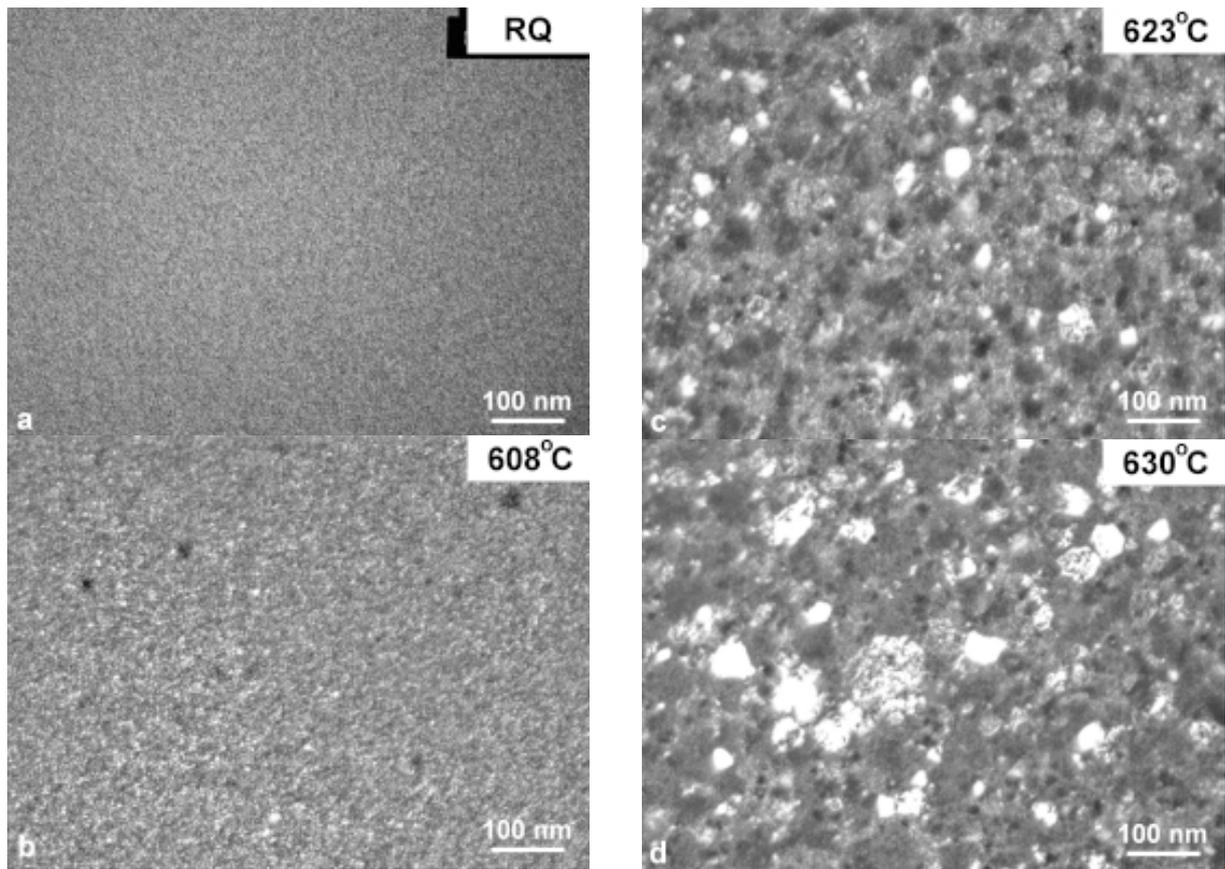
**Fig. 3.** TEM results for rapidly quenched  $\text{Fe}_{63}\text{Mn}_{15}\text{Si}_{15}\text{B}_4\text{Nb}_3$  alloy. Bright field image (a) and SAD pattern (b), circular diffraction lines of CQ phase are indexed.



**Fig. 4.** XRD patterns for  $\text{Fe}_{63}\text{Si}_{15}\text{B}_6\text{Nb}_6$  alloy: a – rapidly quenched; b, c, d – heated to the indicated temperatures at a rate  $10^\circ/\text{min}$ . Intensity in the high angle part of the patterns is multiplied by 3.

position  $\text{Fe}_{76}\text{Nb}_6\text{B}_{18}$  is 1.081 nm). This phase is usually designated as G-phase.

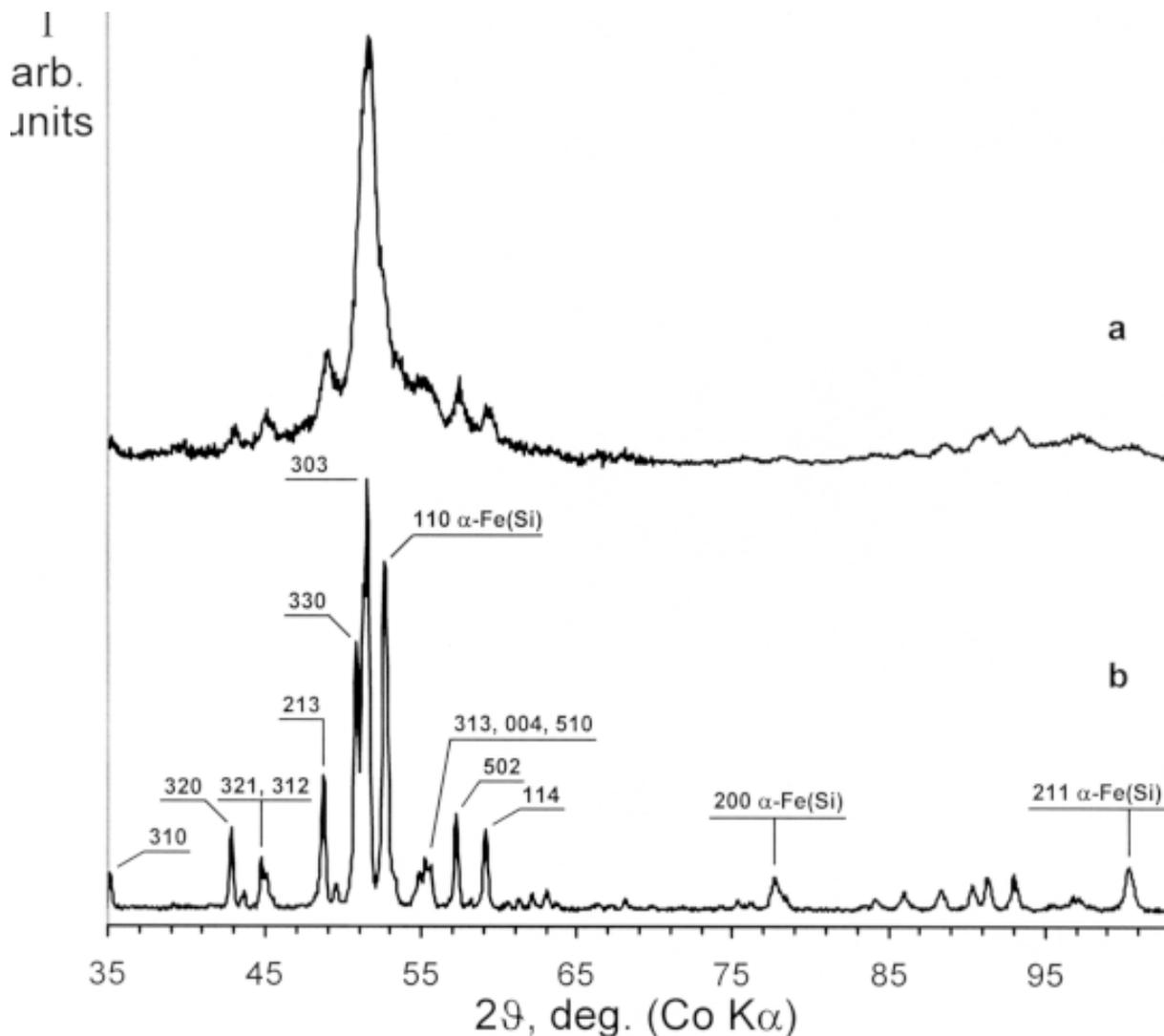
Partial substitution of Fe by Mn in alloys with low content of boron and niobium leads to essen-



**Fig. 5.** Dark field image for  $\text{Fe}_{63}\text{Si}_{15}\text{B}_6\text{Nb}_6$  alloy heated to the indicated temperatures (corresponding to Fig. 4).

tial changes of crystallization processes during melt quenching. For  $\text{Fe}_{63}\text{Mn}_{15}\text{Si}_{15}\text{Nb}_3\text{B}_4$  alloy single-phase fields of nano-sized ( $\sim 50\text{-}70\text{ nm}$ ) grains of CQ-phase formed by polymorphous crystallization (Fig. 3) is observed for relatively high cooling rates. All the circular diffraction lines in SAD (Fig. 3) belong to the CQ phase, they are indexed as in [5]. For lower cooling rates two-phase structure consisting of dendrite like particles of CQ phase and H-phase can be obtained. In alloys with Mn additions CQ phase can form also at boron content less than 4 at.%. Particles of CQ-phase formed by polymorphous crystallization were observed for rapidly quenched  $\text{Fe}_{61}\text{Mn}_{15}\text{Si}_{15}\text{Nb}_7\text{B}_2$  alloy. Positions of reflections which depend on Nb concentration (according to [5] shift of the main reflections from  $\alpha\text{-Mn}$  positions is roughly proportional to Nb content) corresponds to the mean Nb content in the alloy. Structures of alloys with Mn additions are described in more detail in [6].

Formation of nanoscale structures by annealing the as quenched amorphous precursors is observed in alloys with 6 at.% Nb and 5-6 at.% B (the field designated as CQ nano in Fig. 1). Figs. 4 and 5 show XRD patterns and dark field TEM images for  $\text{Fe}_{73}\text{Si}_{15}\text{B}_6\text{Nb}_6$  alloy heated to temperatures in the vicinity of the first crystallization DTA peak. Heating to  $608\text{ }^\circ\text{C}$  (onset of crystallization) results in formation of a transient state characterized by smaller width of amorphous halo compared to the initial state alongside with enhancement of contrast in dark field TEM images (Figs. 4b and 5b). Nanoscale structure on the base of CQ phase can be obtained by heating to the peak temperature  $T_{\text{px}} = 623\text{ }^\circ\text{C}$  (Figs. 4c and 5c). From the lattice spacings one can conclude that the precipitated CQ-phase contains less Nb compared to the mean composition of the alloy. As a result of the nanoscale decomposition with precipitation of CQ particles, amorphous phase is also enriched with



**Fig. 6.** XRD for  $\text{Fe}_{72}\text{Si}_{10}\text{B}_{10}\text{Nb}_3$  alloy rapidly quenched and heated to 612 °C at a rate 10<sup>9</sup>/min. (a); XRD for  $\text{Fe}_{72.3}\text{Si}_{13.5}\text{B}_9\text{Nb}_{4.2}\text{Cu}_1$  alloy rapidly quenched and heated to 740 °C (b), indexes of H-phase are indicated to compare with “a”.

boron and during subsequent heating to 630 °C it transforms into H-phase which also forms a nanoscale structure (Figs. 4d and 5d).

TEM dark field images resembling those shown in Fig. 5b have been obtained for FINEMET ( $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ ) alloy by dipping in salt bath (for 1 – 2 sec.). Flash annealing by laser (heating above ~ 700 °C) results in formation of  $\chi$ -phase by heating to lower temperatures and  $\alpha$ -Fe + H-phase by heating to higher temperatures.

According to [5] H-phase which is formed in FINEMET alloys by transformation of nanocrystalline structure contains ~ 13 – 15 at.%

B. It was confirmed by results obtained for  $\text{Fe}_{72}\text{Si}_{10}\text{B}_{15}\text{Nb}_3$  alloy which can be classified as metallic glass iron base alloy [3]. Fig. 6a shows XRD pattern for the sample heated to 612 °C (~ 5° below the crystallization peak). Phase composition is H-phase and some amount of the residual amorphous phase. Positions of the reflections correspond to lattice parameters of the hexagonal phase  $a=1.22$  and  $c=0.76$  nm ( $c/a=0.630$ ). Apparent activation energy (estimated using Kissinger method) of H-phase formation for this alloy is 700 kJ/mol.

XRD pattern for  $\text{Fe}_{73.5}\text{Si}_{13.5}\text{Nb}_{4.2}\text{B}_9\text{Cu}_1$  alloy heated above the second crystallization peak is also

shown (Fig. 6b) for comparison. Phase composition in this case is H-phase and  $\alpha$ -Fe. H-phase reflections are indexed, their positions agree well with the positions calculated for hexagonal phase with  $a=1.23$   $c=0.77$  nm. XRD patterns for the two alloys look similar but for a little smaller lattice parameters and larger width of reflections for  $\text{Fe}_{72}\text{Si}_{10}\text{B}_{15}\text{Nb}_3$  alloy which is in accordance with nanocrystalline structure ( $\sim 20$  nm) of the alloy (Fig. 6a). Thus the two samples contain one and the same hexagonal H-phase.

Nanocrystalline structure consisting of H-phase and residual amorphous phase in  $\text{Fe}_{72}\text{Si}_{10}\text{B}_{15}\text{Nb}_3$  alloy practically does not change after heating to 700 °C. Such thermal stability distinguishes it from nanocrystalline structures in alloys corresponding to H-nano area in Fig. 1. In the latter case roughening of the structure and precipitation of  $\alpha$ -Fe(Si) occurs when the alloys are heated 10 to 50 °C degrees above the temperature of the first crystallization peak (the higher temperature corresponds to higher boron content).

On the base of these and previously obtained results it can be concluded that H-phase has a variable composition and its lattice parameters increase with Nb content at the late stages of transformations. H-phase forming in FINEMET alloys heated to temperatures near the second crystallization peak grows in nanocrystalline structure consuming both  $\alpha$ -Fe and the residual amorphous phase [5]. If the annealing temperature is lower ( $\sim 580 - 600$  °C for 1 – 2 hours) formation of  $\text{Fe}_2\text{B}$  phase is observed. Particles of this phase precipitate in residual amorphous phase surrounding  $\alpha$ -Fe particles.

#### 4. DISCUSSION

On the base of results presented the following mechanism of nanostructuring in FINEMET alloys is proposed. At the initial stages of devitrification amorphous phase decomposes into nanosized clusters enriched and depleted of boron. Local arrangement in B-rich clusters is similar to that in H-phase, in B-poor clusters – to CQ phase (both phases have much in common: their structures are both built on the base of  $\alpha$ -Mn structure from similar atomic configurations but with different arrangement of them). The phases have definite relations between their lattice parameters which enables their coherent precipitation with low interphase surface energy. It is worth mentioning that decomposition into two amorphous phases has been also

shown to govern the process of nano crystallization in Ti base BMG alloy [2].

Clusters depleted of boron in accordance with the mean composition of the alloy have less Nb ( $\sim 3$  at.%) than thermally stable CQ phases in alloys with higher Nb content or Mn additions. These particles can further transform into  $\alpha$ -Fe particles, possibly via the stage of formation of CQ phase particles which can be too unstable to be observed in experiment. Possibility of Nb solution in  $\alpha$ -Fe(Si) phase at the first stages of nanostructuring in FINEMET alloys was confirmed in a number of works, e.g. [7].

The suggested model for structure transformations can be illustrated by experimental results for  $\text{Fe}_{73}\text{Si}_{15}\text{B}_6\text{Nb}_6$  alloy with relatively high Nb content. The following sequence of transformations is observed in this alloy: pre-crystallization state – nanoprecipitates of CQ-phase in amorphous matrix – mixture of nanoparticles of CQ and H-phases. Similar pre-crystallization state we have observed for  $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$  alloy after flash annealing.

Further progress is associated with diffusion of Nb increasing its concentration at the periphery of  $\alpha$ -Fe(Si) particles which is in accordance with the previous results [8]. In these layers with high Nb concentration big cubic G-phase is formed which is coherent with the BCC lattice of  $\alpha$ -Fe(Si). Particle growth is retarded not only due to low diffusion rate of Nb but also due to stabilization of structure of these peripheral layers. Due to the high Nb content at the periphery of nano-particles the residual amorphous phase contains less Nb than at the final stage. At the final stage of nanostructuring further diffusion of Nb and B into amorphous phase proceeds, its composition approaching  $\text{Fe}_{60}\text{Nb}_{10}\text{B}_{30}$ . This composition corresponds to bulk metallic glasses [1].

The reported results can be useful for general approach to the problems of GMA and NC which should take into account multicomponent interactions realized in formation of a number of metastable primary precipitation phases, in particular quasicrystalline and aperiodic phases. For Fe-Si-B-Nb system all the primary phases ( $\chi$ , CQ, H, (G)) have a relation to  $\alpha$ -Mn structure type. For Fe based BMG with high boron content, hexagonal H-phase plays the most important role. H-phase is the primary precipitation phase for  $\text{Fe}_{72}\text{Si}_{10}\text{B}_{15}\text{Nb}_3$  alloy for which large ( $\sim 50$  °C) supercooled liquid region has been observed [3]. Formation of nanoscale H-phase in this alloy and high activation energy of this process are connected to similarity of local

atomic configurations in supercooled liquid and H-phase (with tetrahedrally close packed structure) and the difficulty of formation of long range order in arrangement of these configurations.

According to the results discussed above formation of copper nanoclusters is a consequence but not the origin of rapid nucleation of  $\alpha$ -Fe nanoparticles. These clusters can form at the periphery of  $\alpha$ -Fe particles due to positive enthalpy of mixing for copper with Fe and Nb. A number of results for various Fe-based nanocomposites do not contradict these conclusions. For NANOPERM alloys with Zr (enthalpy of mixing for Cu and Zr is essentially negative) no Cu clusters have been observed [9]. For NANOPERM alloys with both Zr and Nb as well as for Co-doped FINEMET and HITPERM (with high Co content) alloys addition of Cu is not a necessary condition for formation of nanocomposite.

At the same time a remarkable property of Cu addition is an essential lowering of crystallization temperature both for alloys where the additions are not necessary for nanocrystallization and for alloys where they cause the transition from one-stage to two-stage crystallization with formation of nanocomposites. It looks probable that copper additions cause transformation of amorphous phase at lower temperatures not (only) for kinetic reasons but due to lowering of enthalpy of amorphous phase. Two competing processes go on simultaneously: decomposition with redistribution of boron and precipitation of  $\alpha$ -Fe and formation of  $\alpha$ -Mn related phases characterized by high activation energy. The former process develops in FINEMET alloys (with Cu) at relatively low temperatures ( $\sim 550$  °C) and low heating rates. Formation of  $\alpha$ -Mn related phases occurs at high heating rates to higher temperatures, e.g. by flash annealing in alloys with Cu additions [5]. Alternatively the phases can be observed at relatively slow heating rates in alloys without Cu.

We can note also that small additions of Pd to ZrNiCuAl BMG [1] also lead to the change of crystallization mechanism. The influence of small additions such as Cu, Pd, Ag on crystallization be-

havior of amorphous alloys on the base of transition metals needs further investigation.

## 5. CONCLUSION

On the base of the results obtained for Fe-Si-B-Nb alloys regarding formation of  $\alpha$ -Mn type and related phases (H, CQ, G), a model for nanostructuring in FINEMET type alloys is put forward. Initial stages of nanostructuring are supposed to be associated with nanoscale decomposition into clusters with compositions close to that of the metastable phases. H-phase (distorted  $\alpha$ -Mn structure) is a primary precipitation phase in BMG alloy with high thermal stability of supercooled liquid. Proximity of H-phase composition to the mean composition of the alloy (compared to composition of residual amorphous phase of nanocomposite) promotes nanoscale decomposition of amorphous precursor.

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