Quasiperiodic and Frank-Kasper phases formation during primary crystallization of Fe-base amorphous alloys

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Abstract. Initial stages of devitrification were investigated for iron based amorphous alloys: Fe-P-C-(Cr, Mn, Mo); Fe-B-Si-Nb with 67 – 80 at.% of Fe and 15-25 at.% of P+B+Si+C. Primary precipitated phases of α-Mn or related tetrahedrally close packed structure types, in particular aperiodic structures, were observed. They are characterized by fast nucleation and formation of nanostructures. In some cases specific precrystallization state is formed for which diffraction patterns are consistent with the existence of nano-clusters with local TCP structure. Structure of the liquid or amorphous state can be presented as composition of the same clusters but with the different, noncrystallographic long range order.

1. Introduction

Most of iron based practically important alloys are multicomponent. Among them are alloys on the base of Fe-Si-B and Fe-P-C systems with additions of transition metals and Fe-B-Cr, V, Nb alloys. For Fe-based bulk metallic glasses and numerous nanocomposites (which are also multicomponent, as a rule) the importance of investigation of primary precipitating phases for understanding the origin of high stability of supercooled liquid and nanostructuring processes has been emphasized [1]. Useful information concerning local atomic configurations in amorphous alloys can be obtained via investigation of structure of the metastable phases forming in the primary precipitation process, and this is the main aim of our work.

2. Experiment.

Amorphous alloys obtained by melt spinning (ribbons 20-30 μ thick) were heat treated either by constant rate heating to the temperature of beginning of the exothermic reaction followed by immediate cooling in air or flash annealing, i.e. dipping into salt bath at 20 - 50ºC above the main crystallization peak for 1 - 2 s or local impulse laser annealing [2]. Structure was investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD).

3. Results.

Phases forming in the primary precipitation (PP) process for the investigated alloys together with some previous results are listed in the table 1. For the first group of alloys (with phosphorus as the main
alloying element) \( \chi \)-phase with \( \alpha \)-Mn type structure is observed at the first stage of crystallization [3]. An example is given in figure 1 (Fe\(_{77.5}\)Mn\(_{2.5}\)P\(_{14}\)Si\(_{4}\)C\(_{2}\), BCC, \( a=0.8765 \text{ nm} \)). Volume fraction of the phase exceeds 50% and the particle size is \( \sim 20 \text{ nm} \). Particle size in the range 10-50 nm depends on composition and heat treatment. Smaller particles are observed in multicomponent alloys and at higher heating rates. The same \( \chi \)-phase precipitates together with dendrite like \( \alpha \)-Fe in the Fe\(_{74}\)Mn\(_{5}\)B\(_{8}\)Si\(_{7}\)P\(_{4}\)C\(_{2}\) alloy (No 2, table 1), see figure 1. On the other hand, for the alloy No 3 (with Al and Ga additions) which can be classified as bulk metallic glass (BMG) [4], no TCP phases are observed.

| No | Alloy | PP phases                           |
|----|-------|-------------------------------------|
| 1  | Fe-P-Si-C-Me, 70-80 at.% Fe, P+Si+C 18-25 at.%, P – 13-18 at.% C, 0-3% Si, 2-10% Cr, Mn | \( \chi \) (nano) |
| 2  | Fe\(_{75}\)Mn\(_{5}\)B\(_{8}\)Si\(_{7}\)P\(_{3.5}\)C\(_{1.5}\) | \( \chi + \alpha \)-Fe |
| 3  | Fe\(_{72}\)Al\(_{5}\)Ga\(_{3}\)P\(_{11}\)C\(_{5}\)B\(_{4}\)Si\(_{1}\) | Fe\(_{(P,B)}\)+ FCC Fe\(_{3}\)AlC |
| 4  | Fe\(_{80}\)P\(_{15}\)C\(_{7}\)(Cr,Mn,Mo), \( x = 5-10 \) | Am', \( \chi \) (nano), CQ* |
| 5  | Fe\(_{80}\)P\(_{15}\)C\(_{7}\)Si\(_{1}\) | Am', CQ* |
| 6  | Fe\(_{72}\)Si\(_{10}\)B\(_{15}\)Nb\(_{3}\) | H (nano) |
| 7  | FeSi\(_{15}\)B\(_{2}\)Nb\(_{3}\), \( x = 6 - 11, y = 3 – 6 \) | \( \chi, \ H, \ CQ \) (nano) |

* - phases forming by flash annealing only

Table 1. Primary precipitating phases formed during devitrification of amorphous alloys.

For phosphorus bearing alloys with enhanced C content (No 4, table 1) specific transient structural state (Am') is formed at the initial stages of transformation of amorphous phase. Formation of this state is characterized by separate exothermic peak on DTA curves, as well as narrowing and/or asymmetry of diffraction halo and enhanced contrast of dark field TEM images [2]. Both effects enhance gradually with increasing temperature or holding time below the peak of the main exothermic reaction, and then are followed by heterogeneous nucleation of \( \chi \)-phase nanoparticles and formation of stable phases.

Decrease of width of amorphous halo becomes more evident if flash annealing is used. Figure 2 shows XRD patterns near the first and the second amorphous halos for Fe\(_{79}\)P\(_{13}\)C\(_{7}\)Si\(_{1}\). These changes of the halo can be compared to XRD pattern for rapidly quenched Fe\(_{75}\)Si\(_{15}\)B\(_{4}\)Nb\(_{6}\) alloy in which a specific aperiodic structure (CQ-phase) is formed [5]. The structure of the phase can be represented as constructed from the domains of \( \alpha \)-Mn structure with quasiperiodically arranged defects and possesses cubic symmetry. Indexes of the main reflections from CQ-phase are shown in figure 2. Characteristic feature of XRD pattern is splitting of the most strong reflection (411) + (330) of \( \alpha \)-Mn structure and shifting of (444), (550), (721) reflections from their positions in case of \( \alpha \)-Mn structure. These features can also be noticed in XRD patterns of flash annealed Fe\(_{79}\)P\(_{13}\)C\(_{7}\)Si\(_{1}\) samples, their structure can be represented as the same CQ-phase but with particle size \( \sim 5 \text{ nm} \). Thus formation of CQ-phase by flash annealing can be observed in iron base alloys with metalloids only.

Alloy Fe\(_{72}\)Si\(_{10}\)B\(_{15}\)Nb\(_{3}\) (No 6) can be obtained in BMG form [6]. DTA heating curves show rather large interval of supercooled liquid (\( T_g=585^\circ \text{C}, T_{cryst}=620^\circ \text{C} \) at 50 deg./min.). If the alloy is heated to temperatures between \( T_g \) and 600\(^\circ \text{C} \) no visible change of the first amorphous halo in XRD patterns is observed. Annealing at 600\(^\circ \text{C} \) for 30 sec. results in narrowing and asymmetry of the halo (Am' state). Increasing annealing time at this temperature leads to formation of nanocrystalline structure (figure 3) on the base of H-phase (hexagonal modification of \( \alpha \)-Mn structure [5]).
Structure transformations in FeSi$_{15}$B$_x$Nb$_y$ alloys (No 7, table) are described in more detail elsewhere [5]. For lower boron content CQ phase is formed during rapid quenching (figure 2). For alloys with 6 at.% B heating of the amorphous precursor to 610-630°C gives the following sequence of transformations: Am’ – nano CQ – (χ + H). The first stage of crystallization for alloys with 9-11%B and 6%Nb corresponds to formation of nano- H- phase.

Figure 1. XRD patterns with χ-phase indices for rapidly quenched alloys: Fe$_{77.5}$Mn$_{2.5}$P$_{14}$Si$_4$C$_2$ heated to 450°C (a) and Fe$_{75}$Mn$_5$B$_8$Si$_7$P$_3.5$C$_{1.5}$ heated to 520°C (b), heating rate 20°/min.

Figure 2. XRD patterns for rapidly quenched (a) and flash annealed (in salt bath) at 500°C (b) Fe$_{70}$P$_{15}$C$_{5}$Si$_{1}$ alloy and rapidly quenched Fe$_{72}$Nb$_3$Si$_{10}$B$_{15}$ alloy (c). Indices correspond to quasiperiodic CQ-phase. Right part of the figure shows SAD patterns for the two alloys after laser annealing.

Figure 3. XRD patterns for Fe$_{72}$Nb$_3$Si$_{10}$B$_{15}$ alloy, RQ (a), heated to 600°C and annealed for 0 sec. (b), 30 sec. (c) and 120 sec. (d). Indices of H-phase are indicated.
4. Discussion
The obtained results show that the general tendency for the multicomponent Fe-base alloys is the formation of tetrahedrally close packed (TCP) phases at the first stages of devitrification. The following points are worth to note. If only TCP phase is formed in the PP process then nanocrystallization mode is observed as a rule. Formation of specific Am’ structure by furnace heating correlates with formation of cubic quasiperiodic structure on the base of TCP phase by rapid heat treatments or in the alloys with slightly changed compositions. For BMG alloys nanostructures formed by TCP phases are either observed directly or can be found in the neighbouring compositions. One can suppose that formation of structures at the first stages of devitrification depends on relative stability of TCP phases, quasiperiodic phases and supercooled liquid with short range order characteristic of TCP phases. It seems that the structure of phases forming during PP process shows a large degree of proximity with the structure of liquid and amorphous states.

Structure of condensed phases has received an adequate symmetry description in the framework of the rolling polytope concept [7]. According to this concept, a given type of the structure (crystalline, quasicrystalline, amorphous, liquid, organic liquid crystals) is determined by rolling of the \{3,3,5\} polytope (i.e. 4D-counterpart of an icosahedron) along a set of lines in the 3D Euclidian space. It was shown later that besides ordinary symmetry axes in the symmetry group of the polytope there are non-integer symmetry axes in the symmetry group of the \{3,3,5\} polytope, namely axes \(2\pi/N\) with \(N = 8/3, 10/3, 30/11, 15/4, 15/7, 12/5, 20/7, \) etc. [8, 9]. All non-integer symmetry axes describe non-crystallographic long range order. According to [9], the solidification is the transition from such non-crystallographic order to crystallographic order and the crystal structure of \(\beta\)-Mn is the evidence for this concept since it contains three helical chains of distorted icosahedra. As can be easily shown, this star is the straightened fragment of the \{3,3,5\} polytope, and the \(\alpha\)-Mn structure as a whole can be derived by straightening this polytope along its 15/7 symmetry axis. This is similar to \(\beta\)-Mn structure which can be derived by straightening the \{3,3,5\} polytope along its 15/4 symmetry axis.

5. Summary
Amorphous alloys on the base of Fe-P-C(TM) and Fe-Si-B (TM) systems are liable to devitrification with precipitation of tetrahedrally close packed phases of \(\alpha\)-Mn or related structure types. When such a phase acts as a single primary precipitation phase fast nucleation and formation of nanocrystalline structures is observed. Specific precrystallization state of amorphous phase can be represented as super-nanocrystalline structure formed by cubic quasiperiodic phase. Structures of all the different metastable phases in our report have the same origin: algebraic constructions in higher dimension space. As an example, the \(\alpha\)-Mn structure in our case is not a casual one but is the strict consequence of straightening the \{3,3,5\} polytope structure along the 15/7 symmetry axis.

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