

PERITECTIC-LIKE REACTIONS INVOLVING GLASSY PHASE

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Abstract. This paper aims to review our recently obtained data on the reactions which look like peritectic though there is a difference between them and classical peritectic reactions. Such phase transformation involving a glassy/amorphous/supercooled liquid phase was initially observed in the rapidly-solidified $\text{Ge}_{60}\text{Al}_{25}\text{La}_{15}$ alloy in which an amorphous and a crystalline phase produce another crystalline phase. Another rapidly solidified $\text{Zr}_{65}\text{Ni}_{10}\text{Al}_{7.5}\text{Cu}_{7.5}\text{Ti}_5\text{Nb}_5$ alloy has a mixed structure containing glassy and a submicron β -Zr solid solution phase. The glassy+bcc β -Zr solid solution structure transforms to a mixture consisting of residual glassy and icosahedral phases after the completion of the first exothermic reaction, and this reaction is also a single-type reaction. A common feature of these phase transformation is that they are diffusion-controlled. The reactions described above look, in general, similar to the peritectic one though the absence of the diffusion transfer through the product phase, lack of a common interface and absence of inherited structure differentiate such type of reactions from a classical type peritectic reaction. The structure changes observed and the kinetics of these phase transformations are discussed in detail. Compared to the above-mentioned a reaction "glassy+nanoscale I-phase \rightarrow cF96 Hf₂Fe phase" observed in the melt-spun $\text{Ti}_{40}\text{Zr}_{20}\text{Hf}_{20}\text{Fe}_{20}$ alloy is closer to typical peritectic one.

1. INTRODUCTION

Following invention of conventional metallic glasses [1] bulk metallic glassy alloys were obtained by stabilization of the supercooled liquid against crystallization at the relatively low cooling rate of less than 1000 K/s from liquid state [2-4]. As these alloys exhibit high mechanical strength, high hardness, good fracture toughness, good corrosion resistance and so on, the study of their properties and devitrification behavior is essential in view of their practical usage.

Four types of phase transformations were found to occur during devitrification of the glassy alloys [5,6] polymorphous (a product phase has the same composition as the glassy phase), primary (a product phase has a composition different from that of the glassy phase), eutectic devitrification (two or

more phases nucleate and grow conjointly) and spinodal decomposition involving a phase separation of the glassy phase prior to devitrification. The kinetics of the devitrification process of glassy alloys has been analyzed [7,8]. An unusual eutectic-like reaction was observed in several Al-RE-Ni-Co (RE denotes rare-earth element) glassy alloys. Two crystalline phases, which were found to precipitate simultaneously in these glassy alloys, did not have a common interface and had a large size difference [9].

However, some amorphous and glass-forming alloys form glassy-crystal or glassy-quasicrystal composites which in some cases possess better properties than the single-phase alloys [3]. On heating these alloys exhibit different phase transformation behaviour. In binary crystalline alloys peritectic

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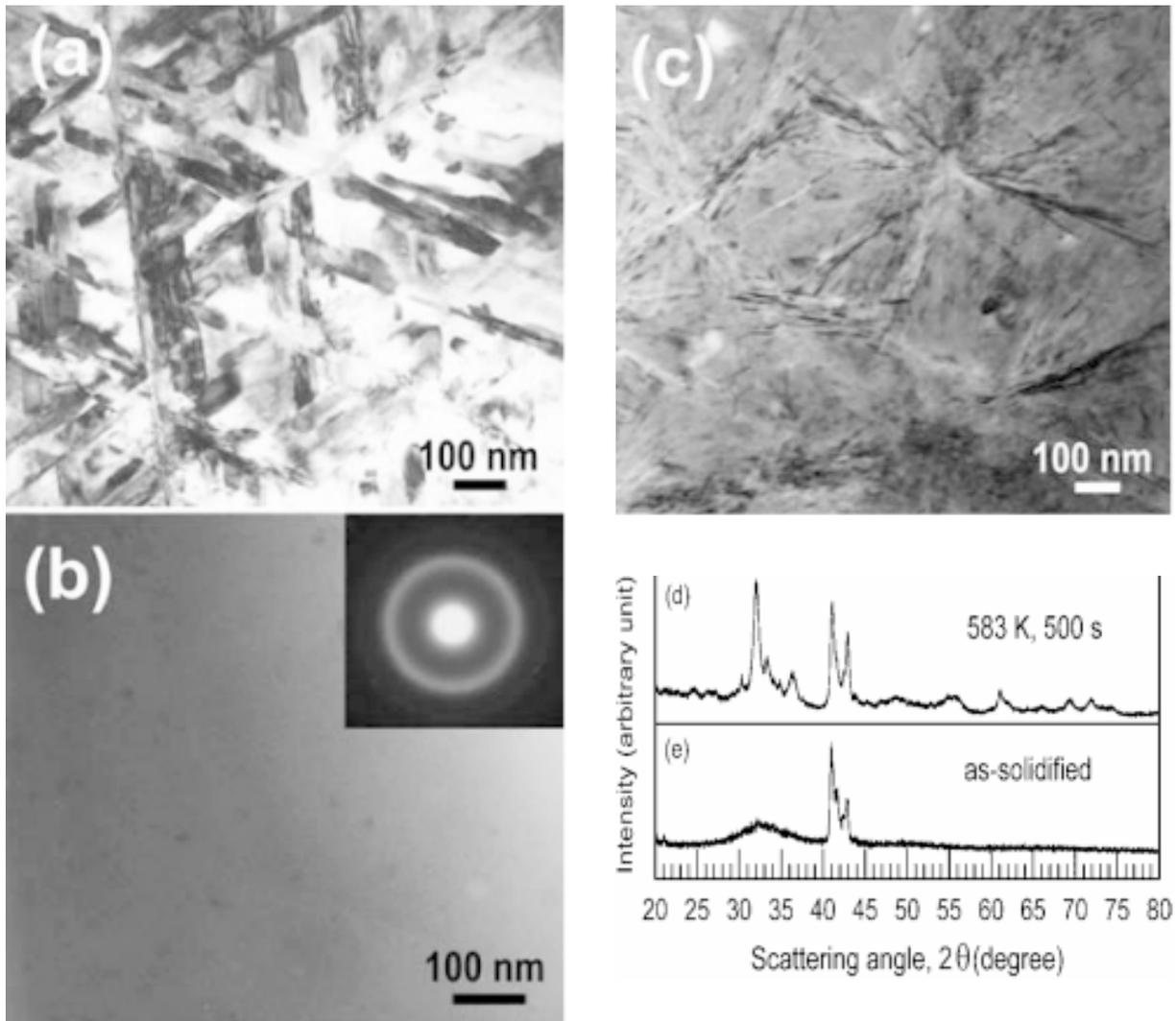


Fig. 1. Bright-field TEM images of the $\text{Ge}_{60}\text{Al}_{25}\text{La}_{15}$ alloy (a,b) in as-solidified and (c) annealed (583K, 1.2 ks) state. The insert – SAED. (d,e) XRD patterns in different states. (d) represents the moment at which three phases coexist according to Fig. 2b when the reaction is not complete.

reactions involving a liquid and a solid phase upon the completion yield a single solid phase. Its analogue peritectoid reaction involves two solid phases producing another solid. The product solid phase forms at the interface between the two reactants which is a diffusion barrier and generally causes such reactions to proceed much more slowly than eutectic or eutectoid transformations. For example, in the iron-carbon system the δ phase combines with the liquid to produce γ austenite. Peritectic reactions in binary systems have been studied extensively [10]. In ternary and multicomponent al-

loys binary peritectic reactions (like binary eutectics) may take place in a temperature interval. Some reactions in ternary alloys in which a liquid and a solid phase react to form two new phases are called quasi-peritectic [11] but in such a case common interface is still observed between parent and product phase.

Recently we observed peritectic-like reactions in three-types of glassy alloys. In the present paper we describe these reactions and point out their difference from the classical peritectic one.

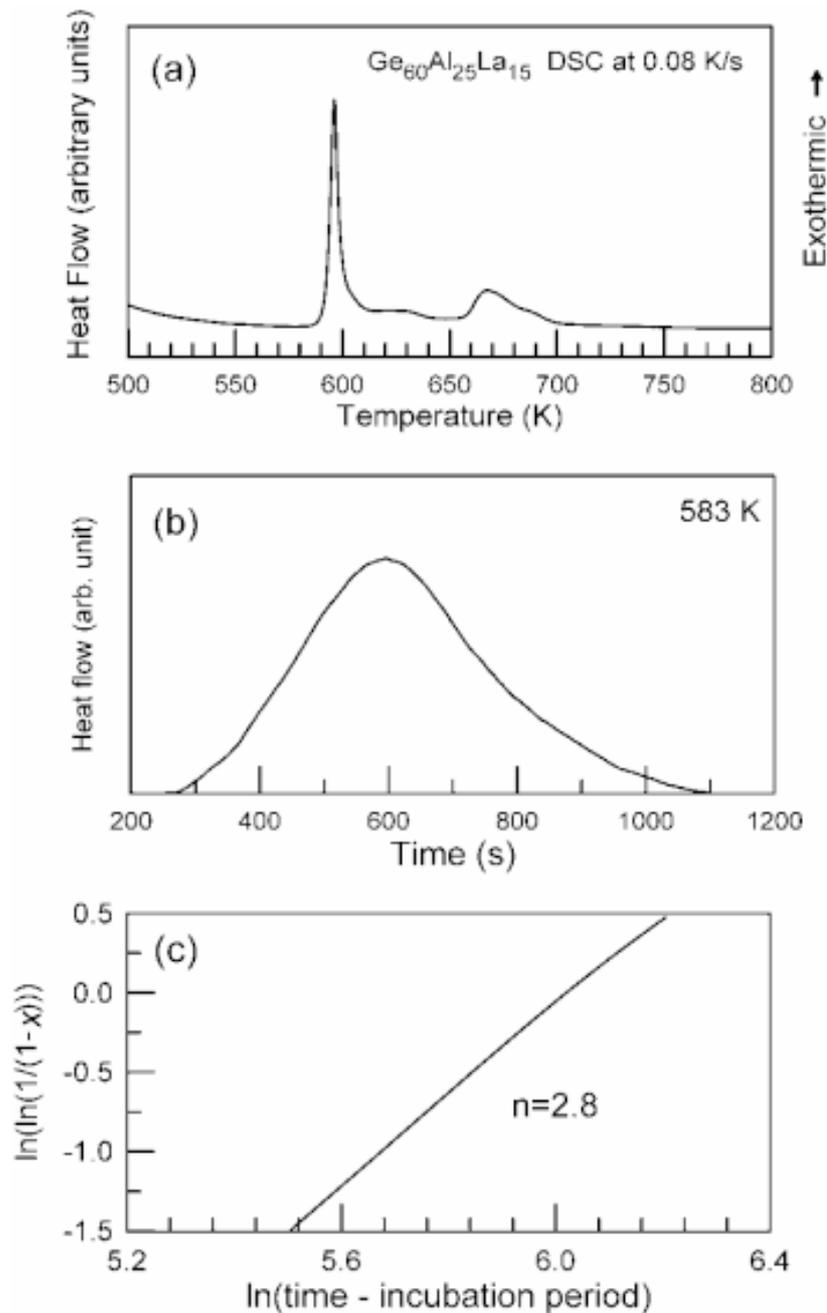


Fig. 2. (a) DSC trace, (b) isothermal differential calorimetry trace and (c) the corresponding Avrami plot for the $\text{Ge}_{60}\text{Al}_{25}\text{La}_{15}$ alloy.

2. EXPERIMENTAL PROCEDURE

The studied alloys have been produced in the form of melt-spun ribbons by so-called melt-spinning technique and studied by X-ray diffractometry, transmission electron microscopy and differential calorimetry. The details can be found in the papers cited below.

3.1. Ge-Al-La alloy

The structure of the $\text{Ge}_{60}\text{Al}_{25}\text{La}_{15}$ alloy [12] in the as-solidified state consists of the colonies of a crystalline phase (Fig. 1a) crystallized separately from the amorphous matrix (Fig. 1b). Some nanosize crystalline particles are also present in the amorphous matrix, but their volume fraction is low. The

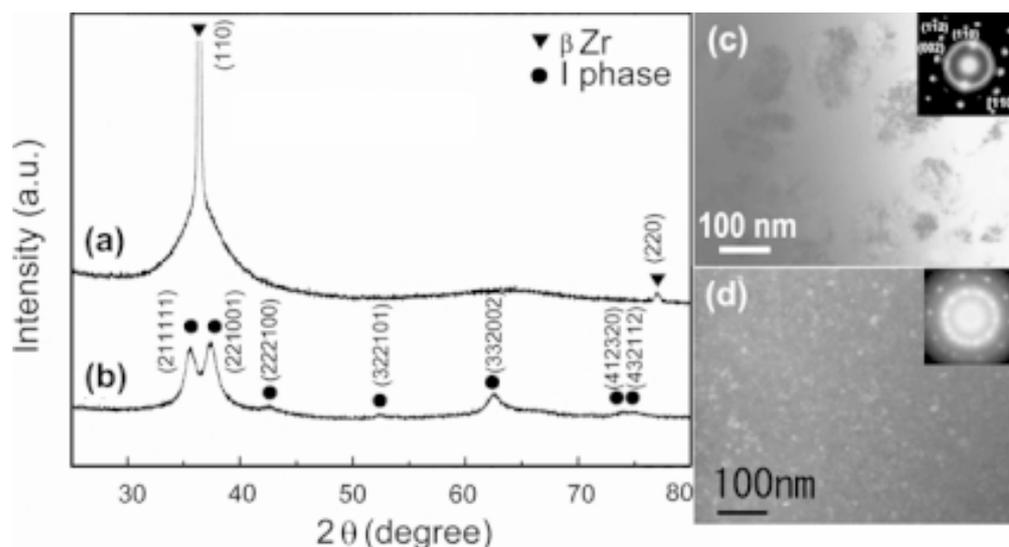


Fig. 3. X-ray diffraction patterns of the $Zr_{65}Ni_{10}Al_{7.5}Cu_{7.5}Ti_5Nb_5$ amorphous alloy: (a) in as solidified state and (b) annealed for 300 s at 723K. (c,d) bright-field TEM images: (c) in the as solidified state (the insert: SAED pattern), (d) annealed for 300 s at 723K (the insert: NBD pattern).

selected-area electron diffraction pattern (SAED) in Fig. 1b illustrates the existence of the amorphous phase.

The as-solidified crystalline phase (phase 1) has an unknown structure and transforms on heating. The DSC curve taken at a sufficiently low heating rate is displayed in Fig. 2a. The reaction related to the first exothermic heat effect at 590K was found to be: Amorphous phase + crystalline phase 1 \rightarrow crystalline phase 2 and residual amorphous phase. This reaction is similar to a peritectic reaction in binary systems with the amorphous phase instead of the liquid one. It can also be called a peritectoid-like one as the amorphous phase is solid, though disordered. An isothermal differential calorimetry curve taken at 583K is shown in Fig. 2b. Fig. 1d illustrates the time period at which the crystalline phases 1 and 2 coexist.

The structure of the $Ge_{60}Al_{25}La_{15}$ alloy after the first phase transformation changes greatly. The inhomogeneous as-solidified structure consisting of the separate amorphous (Fig. 1b) and colonies of crystalline (Fig. 1a) phases transforms to a relatively uniform one (Fig. 1c) in which the plate-shaped particles of the $GeAlLa$ phase 2 (crystalline phase 2) of about 10 nm in thickness are homogeneously distributed in the residual amorphous matrix. Such a structural change takes place in a relatively short period of time of 800 s at 583K.

The metastable crystalline phase 2 was found to have a tetragonal lattice with lattice parameters of $a=0.559$ nm and $c=0.528$ nm. According to EDX analysis the composition of three different crystals of crystalline phase 2 was found to be $Ge_{52}Al_{31}La_{17}$, $Ge_{64}Al_{20}La_{16}$ and $Ge_{59}Al_{25}La_{16}$. An average composition ($Ge_{58}Al_{26}La_{16}$) is very close to alloy's composition and can be written as $Ge_{12}Al_5La_3$. During the subsequent two reactions pure cF8 Ge precipitates from the amorphous matrix and crystalline phase 2 ($Ge_{12}Al_5La_3$) being metastable transforms into a crystalline phase 3.

3.2. Transformation from glassy + β -Zr to glassy + icosahedral structure in Zr-based alloy

The X-ray diffraction (XRD) pattern of the melt-spun $Zr_{65}Ni_{10}Al_{7.5}Cu_{7.5}Ti_5Nb_5$ [13] ribbons is shown in Fig. 3a. The diffraction pattern consists of broad diffraction peaks produced by the glassy phase (it exhibits T_g upon heating) and the sharp diffraction peaks identified as (110) and (220) of a bcc β -Zr solid solution. The particles have submicron size (Fig. 3c). The distribution of the diffracted intensities of β -Zr particles indicates that they have a strong orientation relationship with the ribbon surface (Figs. 3a and 3c).

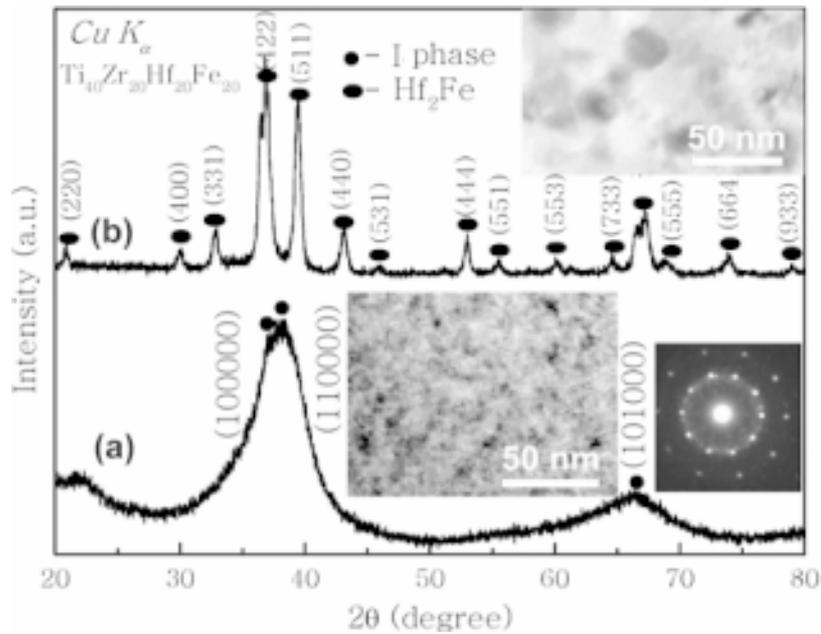


Fig. 4. XRD patterns of the $\text{Ti}_{40}\text{Zr}_{20}\text{Hf}_{20}\text{Fe}_{20}$ alloy (a) in as-solidified and (b) annealed for 1.8 ks at 841K state. The inserts in (a) and (b) are the corresponding TEM images and SAED.

As shown in Fig. 3b, the X-ray diffraction pattern of the sample annealed for 300 s at 723K consists of broad peaks caused by the glassy phase and sharper peaks with higher intensities produced by the precipitated nanoscale quasicrystalline particles. Indexing of this icosahedral phase in Fig. 3b has been done according to Ref. 14. A typical nanobeam electron diffraction (NBD) pattern shown in the insert of Fig. 3d is taken from an icosahedral particle. The icosahedral phase is common in such alloys [15]. The Avrami plots obtained from the isothermal differential calorimetry curves corresponding to the initial exothermic reaction taken at different temperatures were reasonably linear and gave the Avrami exponent values ranged from 2.5 to 2.9 [13].

Glassy+bcc β -Zr solid solution \rightarrow icosahedral phase + residual glassy transformation takes place on heating from the supercooled liquid region while in $\text{Ge}_{60}\text{Al}_{25}\text{La}_{15}$ alloy it took place from the amorphous state. As in $\text{Ge}_{60}\text{Al}_{25}\text{La}_{15}$ alloy this initial transformation in $\text{Zr}_{65}\text{Ni}_{10}\text{Al}_{7.5}\text{Cu}_{7.5}\text{Ti}_5\text{Nb}_5$ alloy was found to obey the following kinetic law [16] for the volume fraction (x) transformed as a function of time (t):

$$x(t) = 1 - \exp[-Kt^n]. \quad (1)$$

The existence of the residual glassy phase and the average Avrami exponent value of 2.7 indicate that the transformation “glassy+bcc β -Zr solid solution \rightarrow icosahedral phase” is diffusion-controlled and takes place at nearly constant nucleation rate.

The above-described transformation seems to be in general close to that of a peritectic one. However, one can see a large size difference of the precipitates in the annealed (see Fig. 3d) and the as-solidified sample (Fig. 3c). The relatively large grains of β -Zr solid solution of 100-150 nm in size dissolve in the supercooled liquid during the phase transformation accompanied by the formation of fine 3-15 nm precipitates of the icosahedral phase. No inherited structure is observed in Fig. 3 as it should be in the case of classical peritectic reaction. Thus, β -Zr solid solution is a less stable phase than the icosahedral phase in the $\text{Zr}_{65}\text{Ni}_{10}\text{Al}_{7.5}\text{Cu}_{7.5}\text{Ti}_5\text{Nb}_5$ alloy below about 650K. At room temperature diffusion is very slow and β -Zr solid solution particles remain in the structure. On heating of the as-solidified sample above T_g the diffusion rate increases, the β -Zr solid solution particles dissolve in the supercooled liquid and the icosahedral phase starts to precipitate. However, in the present case such a transformation takes place like a solitary reaction.

The icosahedral phase is also metastable and transforms to Zr_2Ni (t12), Zr_2Cu (t16) and other equilibrium phases at high temperature. One can suppose that the β -Zr phase is formed on solidification at the higher temperature than the annealing temperature of 723K, and at this temperature the icosahedral short range order is not well developed yet as it was found to intensify on cooling [17], especially under supercooling.

3.3. Transformation in Ti-based alloy

The phase composition and structure of the $Ti_{40}Zr_{20}Hf_{20}Fe_{20}$ alloy in the as-solidified state and annealed for 1.8 ks at 841K are shown in Figs. 4a and Fig. 4b, respectively [18]. The average size of the quasicrystalline particles dispersed in the amorphous (this alloy does not exhibit T_g on heating) matrix in the as-melt-spun $Ti_{40}Zr_{20}Hf_{20}Fe_{20}$ alloy is 5 nm while the average size of the cF96 Hf_2Fe phase precipitated by the first exothermic peak is 20 nm.

The transformation between the icosahedral phase and $(Zr,Hf,Ti)_2Fe$ phase is as follows: Amorphous + nanoscale icosahedral phase \rightarrow cF96 Hf_2Fe phase. Residual amorphous phase also remains after the transformation. This transformation also shows an incubation period and obeys the kinetic law (Eq. (1)). From the Avrami exponent value $n=2.3$ obtained from the least squares fitting of the Avrami plot [18], one can say that this transformation is suggested to be diffusion-controlled at nearly constant nucleation rate.

4. COMMON DISCUSSION AND CONCLUSION.

The transformations observed in the studied Ge-, Zr- and Ti-based composite alloys start after an incubation period and indicate a diffusive-type nucleation and growth reaction [19-21].

The single-type phase transformation: amorphous/glassy/supercooled liquid phase + crystalline phase \rightarrow crystalline/quasicrystalline phase observed in the studied alloys formally look similar to the peritectic reaction in binary systems. The reactions observed involve metastable crystalline/quasicrystalline phases including the glassy/amorphous one.

However, the reactions in the Ge-Al-La and Zr-Ni-Al-Cu-Ti-Nb alloys are only formally similar to peritectic reaction though the real mechanism is somewhat different from the classical one. A large parent phase in Ge- and Zr-based alloys dissolves during the precipitation of the product phase and

no rim of the product phase is formed around the parent one. These two phases do not have a common interface and the product phase nucleates in the glassy/amorphous one separately from another crystalline one. The absence of the inherited structure, common interface and large difference in the morphology of the precipitated phases differentiates them from a typical peritectic reaction. Here one should mention that some similar peritectic-like reactions without common interface have been observed in oxide materials [22].

Compared to quasi-peritectic reactions the product phase of such reactions is rather single phase. The residual amorphous phase rather indicates that the reaction has not been completed as the composition may be somewhat different from the exact peritectic one.

The phase transition observed in $Ti_{40}Zr_{20}Hf_{20}Fe_{20}$ alloy is closer to classical peritectic reaction as the crystalline phase nucleates close to the quasicrystalline one.

Such transformation behavior in the Zr and Ti alloys may be connected with three reasons: (1) a non-equilibrium state of the amorphous phase/supercooled liquid phase as a result of rapid solidification at a cooling rate of 10^5 - 10^6 K/s, (2) metastable phases involved in the reactions (both parent and product) which presumably have close free energy values, and (3) similar chemical composition of the studied phases enhancing a high reaction rate. These features enhance such types of the reactions while in some other composite alloys the crystalline/quasicrystalline phase embedded in the glassy phase either directly transforms to another phase or glassy phase crystallizes primarily on heating while the coexisting crystalline phase remains untransformed as has been observed in the Zr-Nb-Cu-Ni-Al bulk metallic glassy matrix composite [23]. These two processes may also take place independently in some alloys.

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