Chapter 6

FORMATION OF QUASICRYSTALS IN BULK METALLIC GLASSES AND THEIR EFFECT ON MECHANICAL BEHAVIOR

Jenő Gubicza and János Lendvai
Department of Materials Physics, Eötvös Lorand University
H-1117, Pázmány Péter sétány 1/A, Budapest, Hungary

ABSTRACT

The annealing of bulk metallic glasses (BMGs) at elevated temperatures usually leads to partial or full crystallization. The crystallization in several systems starts with the formation of metastable quasicrystalline (QC) particles and then the material can be regarded as a composite of QC and amorphous phases. The appearance of QC particles significantly affects the mechanical properties of BMGs. In this chapter, the morphology, structure and chemical composition of QC particles formed during heat-treatment of BMGs are reviewed according to the relevant literature. Special attention is paid to the influence of the formation of QC particles on the mechanical behavior at room and high temperatures. It was found that during heat-treatment of a commercial ZrTiCuNiBe BMG above the glass transition temperature nanosized spherical QC particles containing smaller grains were formed. Depending on the annealing temperature the volume fraction of the QC phase varied between 25 and 37%. The QC particles contain Ti, Zr and Ni in high concentration, while the amorphous matrix is enriched in Be. The high temperature viscosity increases mainly due to the hard QC particles but
there is also a slight contribution from the compositional changes of the supercooled liquid matrix. The bending strength measured at room temperature decreases in consequence of QC formation, most probably mainly due to the loss of free volume in the amorphous matrix.

1. INTRODUCTION

Due to their unique mechanical properties the deformation behavior of bulk metallic glasses (BMGs) has been intensively studied in recent years [Waniuk, 1998; Inoue, 2001; Wei, 2004; Schuh, 2007]. BMGs usually have lower elastic modulus, higher strength, and reduced plasticity compared to their crystalline counterparts of the same chemical composition [Schuh, 2007]. The application of BMGs at high temperatures often leads to partial or full crystallization. It was suggested [Frank, 1952; Kelton, 2006] that the ability of metals to form amorphous structure by fast cooling is enhanced by the dominance of icosahedral short-range order (ISRO) in melts that is incompatible with translational periodicity of crystallographic structures. An icosahedral packing of twenty slightly distorted tetrahedra is more dense than fcc or hcp packings, therefore although it is incompatible with translational periodicity it might be a natural choice for liquid and amorphous structures [Kelton, 2004; Kelton, 2006b]. The existence of ISRO in the supercooled liquid state brings about an extremely small interfacial free energy between an icosahedral quasicrystalline phase (i-phase) and a metallic glass of the same composition [Holzer, 1991]. Consequently, the nucleation of the i-phase during annealing of BMGs is easier than the formation of the more stable crystalline phases. In support of this, the i-phase is frequently reported as the primary devitrification phase, particularly for the Zr- and Hf-based bulk metallic glasses [Xing, 2000; Saida, 2001, Chang, 2006].

The precipitation of an icosahedral quasicrystalline phase upon devitrification of Zr-based BMGs has been reported for ZrCuAl [Fan, 2006], ZrCuNiAl [Köster, 1996], ZrCuAlNiTi [Xing, 1998] and ZrTiCuNiBe alloys [Wanderka, 2000; Mechler, 2004]. It was found that the chemical composition of BMGs has a deterministic influence on the local atomic order in the glassy state and therefore on the crystallization sequence during annealing [Saida, 2007]. Comparing Zr_{70}Ni_{30} and Zr_{70}Cu_{30} metallic glasses, the former shows a tetragonal atomic order while the latter exhibits an icosahedral local atomic configuration. As a consequence, in Zr_{70}Cu_{30} the supercooled liquid state has a higher stability (larger temperature difference upon heating between the glass
transition and the primary crystallization) and as a first step quasicrystalline i-
phase forms while Zr$_{70}$Ni$_{30}$ crystallizes into tetragonal Zr$_2$Ni phase during
heat-treatment. It is suggested that structural differences in the glassy phase
is caused by a strong chemical affinity of a Zr–Ni pair compared with that of a
Zr–Cu pair. The sensitivity of local atomic order to the chemical composition
was demonstrated by adding 1 at.% Pd into a Zr$_{70}$Al$_{10}$Ni$_{20}$ metallic glass
[Saida, 2007]. Without the Pd addition, tetragonal Zr$_2$Ni was observed in the
initial stage of transformation, however, the primary crystallization process
changes markedly into single i-phase formation by the addition of 1 at.% Pd.
Addition elements, such as Ag, Pd, Au or Pt, to ZrAlNiCu glasses are believed
to generate inhomogeneous atomic configuration regions including ISRO
configurations in the supercooled liquid [Inoue, 1999; Chen, 1999; Murty,
2000; Saida, 2000; Saida, 2003b], which then promote the precipitation of an
icosahedral phase. It was also found that the addition of Ti to bulk amorphous
Zr$_{62-x}$Ti$_x$Cu$_{20}$Ni$_{8}$Al$_{10}$ alloys resulted in the formation of a metastable
quasicrystalline phase in the first transformation step but only in the
composition range of 2 ≤ x ≤ 4 [Kühn, 2006]. Additions of oxygen or
palladium to Zr-based bulk amorphous alloys may also induce quasicrystallization [Köster, 1996; Eckert, 1998; Murty, 2000b]. When oxygen
is added to metallic glasses with high glass forming ability, it increases the
stability of the icosahedral phase during crystallization. On the other hand, Pd
stabilizes the amorphous phase in Zr-based metallic glasses in which
icosahedral clusters are presumed to be stable [Murty, 2001]. Thus,
nanoquasicrystallization occurs even from binary Zr–Pd binary metallic glass
[Murty, 2001]. The size of the QC domains usually falls in the nanometer
range, however formation of micrometer-sized icosahedral quasicrystalline
particles has also been reported for Zr–Ti–Nb–Cu–Ni–Al alloys [Kühn, 2000;
Kühn, 2005].

The local atomic structure in metallic glasses can be changed by
mechanical disordering (MD). It was demonstrated that ball milling a
Zr$_{65}$Al$_{7.5}$Ni$_{10}$Cu$_{12.5}$Pd$_5$ glassy alloy resulted in the formation of the fcc Zr$_2$Ni
instead of the icosahedral QC phase in the primary crystallization step, due to
the MD-induced distortion of the local structure [Saida, 2003]. On the other
hand, the appearance of QC particles in the amorphous matrix results in
significant changes in the mechanical properties which depend strongly on the
chemical composition of BMGs as well as on the temperature of annealing
[Xing, 2001]. In this chapter, the effect of QC phase formation in a
commercial ZrTiCuNiBe metallic glass on the deformation behavior at room
and elevated temperatures is summarized. First the evolution of the
microstructure during annealing is characterized in detail. Then the viscosity as a function of QC phase content is investigated by indentation creep testing in the supercooled liquid region (the temperature range between the glass transition temperature and the onset temperature of crystallization). The deformation behavior at room temperature is studied by three-point bending tests.

2. Formation of Quasicrystalline Phase in the BMGs During Heat-Treatments

The formation of QC phase during annealing was studied in a commercial Zr-based bulk metallic glass with the composition of Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25} (LM-1B, manufacturer: Liquidmetal Technologies, Inc). The diameter and the length of the cylindrical specimens were 9 and 85 mm, respectively. Heat effects were detected by differential scanning calorimetry (DSC) during isothermal heat-treatments at 677, 682 and 687 K which are slightly above the middle temperature of the supercooled liquid regime, \((T_g + T_{xo})/2\), where \(T_g = 625\) K is the glass transition temperature and \(T_{xo} = 725\) K is the onset temperature of crystallization. The heat flow versus time curves, recorded during isothermal annealings at 677, 682 and 687 K are shown in Figure 1. The curves display two exothermic peaks. The phase composition was determined by X-ray diffraction on samples cooled rapidly to room temperature after different annealing times. Figure 2 shows the X-ray diffractograms corresponding to the as-received state as well as to four annealing times at 682 K, marked by dots on the DSC thermogram in Figure 1. In the as-received state only a halo was observed indicating that the initial sample is fully amorphous. The X-ray diffraction pattern obtained after annealing for 1300 s contains an amorphous halo and the peaks of a QC phase [Gubicza, 2008]. The diffractograms corresponding to shorter annealing times (not shown here) have the same characteristics with weaker reflections of the QC phase. Consequently, the first exothermic peaks on the thermograms of Figure 1 are related to the formation of a QC phase. The X-ray diffractograms in Figure 2 shows that the second exothermic peak on the DSC thermogram corresponds to the crystallization of stable phases, namely \(\text{Be}_2\text{Zr}, \text{Zr}_2\text{Ni}, \text{Zr}_2\text{Cu}\) and \(\text{NiTi}\). At the end of the second crystallization peak (the annealing time is 4900 s at 682 K) a significant amount of QC phase remained in the microstructure which disappeared completely only after prolonged (55000 s)
heat-treatment while the fractions of Zr$_2$Cu and Be$_2$Zr increased. This transformation of the remaining QC phase is so slow and the released heat so small, that it could not been detected in the DSC measurements. It is noted that similar two-step devitrification sequence was detected for other alloys, such as Zr$_{65}$Ni$_{10}$Cu$_{10}$Al$_{15}$Ag$_{10}$ where the first reaction corresponds to the formation of a QC phase from the amorphous matrix, while the second one results from the formation of a non-stoichiometric Zr$_2$Cu-like phase from the previously formed quasicrystals [Liu, 2004; Liu, 2004b]. It was also observed that the DSC peak related to the formation of QC phase was shifted to a lower temperature if the Zr$_{44}$Ti$_{11}$Cu$_{10}$Ni$_{10}$Be$_{25}$ amorphous alloy had been deformed before heat-treatment [Révész, 2010]

The heat released in the first exothermic peak during isothermal annealing was used to estimate the relative fraction of the QC phase. Integrating the heat flow versus time function, the heat released during crystallization ($H$) can be calculated at any time of annealing. It is found that the total heat released during crystallization, i.e. the area under the two DSC peaks is the same within the experimental error for all the three temperatures, $H_{\text{total}} = 60\pm1$ J/g. The total heat was distributed between the two peaks by separating them at the time value where the heat flow is minimal after the first peak (see Figure 1). The heat fractions related to the two peaks are different for the three temperatures as it is shown in Figure 3.

![Figure 1. The heat flow as a function of time during isothermal annealing at 677, 682 and 687 K. The dots on the curve for 682 K mark the states where the crystalline phase composition following rapid cooling to room temperature was investigated by X-ray diffraction (see Figure 2).](image-url)
During the first peak corresponding to the formation of QC phase, 37, 30 and 25% of the total heat are released at 677, 682 and 687 K, respectively. Complementary TEM investigations have shown that the ratio of the heat released in the first exothermic peak to the total heat is very close to the volume fraction of QC phase formed up to the end of the first DSC peak. The higher the temperature of annealing, the shorter the incubation time before the formation of stable crystalline phases, therefore the maximum volume fraction of QC phase is smaller and correspondingly the fraction of the first peak in the total heat is also lower.
3. MORPHOLOGY, STRUCTURE AND CHEMICAL COMPOSITION OF QUASICRYSTALS FORMED DURING ANNEALING BMGS

The morphology of QC phase formed during isothermal annealing of Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25} BMG was studied by transmission electron microscopy (TEM) [Gubicza, 2008]. Figure 4 shows TEM images of the microstructure after annealing at 682 K for 600 and 1800 s which correspond to the beginning and the end of the first exothermic DSC peak, respectively (see Figure 1). The images illustrate that the microstructure can be described as a composite consisting of amorphous matrix and spherical QC nanoparticles which were also identified in electron diffraction pattern by the software ProcessDiffraction [Lábár, 2005]. The distributions of particle diameters for 600 and 1800 s are shown in Figs. 4c and d, respectively. The size distribution of QC particles is relatively broad containing particles of 10 as well as 130 nm size. The average sizes of the QC particles are 40 and 51 nm for 600 and 1800 s, respectively, indicating that the increase of the volume fraction of QC particles can be attributed mainly to the increasing number, and not so much to the growth of particles. The average size of the quasicrystalline diffracting domains at the end of the first exothermic peak is 12 nm as estimated from the breadth of the X-ray peak profiles on the basis of the Scherrer-equation. The difference between the particle size and the diffracting domain size suggests that the particles are built up from smaller quasicrystalline grains or subgrains. This is supported by the TEM images in Figs. 4a and b where the areas having different contrasts inside nano-QC particles correspond to grains of 15-20 nm size. This value is in good agreement with the coherently scattering domain size (12 nm) estimated from the breadth of the X-ray peaks. The average size of the QC particles at the end of the first exothermic peak is found to be between 51 and 58 nm for all the three temperatures, indicating that the difference between the annealing temperatures results only in slight variation in the particle size of the QC phase.

The positions of the diffraction peaks of the QC phase in Figure 2 agree well with those of the icosahedral i-phase having the composition of Ti_{x}Zr_{y}Ni_{z} (x=33-37, y=42-46 and z=21) [Kelton, 2004]. The indices of QC peaks are 100000, 110000 and 101000 in the order of increasing diffraction angle in Figure 2. The stoichiometry of the QC phase suggests that the QC particles are enriched in Ti and Ni and depleted from Be and Cu which was also supported by the analysis of their chemical composition by Electron Energy Loss
Spectroscopy (EELS) studies [Gubicza, 2008]. Similar compositional differences between the amorphous and the QC phases were observed for Zr_{46.8}Ti_{16.2}Cu_{7.5}Ni_{10}Be_{27.5} [Wollgarten, 2004; Van de Moortéle, 2004].

Figure 4. TEM images showing the microstructures consist of QC particles and amorphous matrices obtained after annealing at 682 K for 600 (a) and 1800 s (b). The size distributions of QC particles for 600 (c) and 1800 s (d) are also shown.

The chemical heterogeneities suggest that after the nucleation of QC particles their growth is most probably controlled by atomic diffusion supplying the increase of Ti and Ni concentration in the QC particles. At the same time, Figure 4 shows only a limited growth in the particle size when the duration of annealing is increased by a factor of three from 600 to 1800 s at 682 K. This indicates that as the phase transformation proceeds, the growth of larger QC particles is slowed down. The larger the size of a QC particle, the larger the surrounding depleted zone, and correspondingly the diffusion path of the Ti and Ni atoms necessary for its further growing. Therefore, new nucleation becomes preferred to the growth of preexisting particles which is reflected in the slowing down or stop of QC particle-growth.
4. EFFECT OF FORMATION OF QUASICRYSTALLINE PARTICLES ON THE HIGH-TEMPERATURE CREEP OF METALLIC GLASSES

In recent years the deformation behavior of bulk metallic glasses (BMGs) in the supercooled liquid region has been studied over a wide range of strain rates [Waniuk, 1998; de Hey, 1998; Heilmaier, 2001; Lee, 2003; Heggen, 2004; Bletry, 2004]. High temperature creep behavior is traditionally investigated in tension or compression [Heggen, 2004; Bletry, 2004]. At the same time, indentation testing has been also successfully applied in studying the creep of different crystalline materials and glasses [Yu, 1977; Han, 1990; Prakash, 1996; Cseh, 1997]. The most important advantages of this method are the ease of sample preparation and that a small piece of specimen is enough for the measurement. The latter is particularly important feature in the case of bulk metallic glasses where the dimensions of samples are often limited. Recently, it has been shown that the viscosity and the activation energy of deformation determined by compression and indentation tests are in good agreement [Fátay, 2004].

Although, the influence of crystallization on the deformation behavior at high temperature has been investigated previously [Galano, 2003; Galano, 2003], the detailed study of the effect of QC phase on creep process was only recently performed [Gubicza, 2008; Lendvai, 2008; Lendvai, 2009]. The effect of the formation of QC phase on the high-temperature creep behavior of Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25} BMG was studied by indentation at 677, 682 and 687 K [Lendvai, 2008]. The experimental setup of the indentation test is shown schematically in Figure 5. Isothermal indentation tests were carried out in a Setaram TMA-92 thermomechanical analyzer. The indentation measurements were carried out on specimens of 3 mm height by using a flat end cylindrical punch of 1.2 mm diameter under constant load of 50 g which corresponds to 0.4 MPa pressure. It has been convincingly confirmed by experimental and theoretical investigations for different metals, alloys and ionic crystals that the equivalent stress ($\sigma$) and strain rate ($d\varepsilon/dt$) in indentation creep tests can be expressed by the applied pressure ($p$) and the indentation rate ($dh/dt$), respectively, as [Yu, 1977; Cseh, 1997]:

$$\sigma = \frac{p}{3}$$  \hspace{1cm} (1)

and
where \( d \) is the diameter of the cylindrical indenter. The viscosity (\( \eta \)) can be determined at any time during the isothermal annealing by the following equation:

\[
\eta = \frac{\sigma}{3} \left( \frac{d e}{d t} \right)^{-1} = \frac{p d}{9} \left( \frac{dh}{dt} \right)^{-1}.
\] (3)
time at 682 K in Figure 7. Complementary TEM and X-ray diffraction experiments have shown that the relative released heat obtained in the first DSC peak was close to the QC fraction as discussed in section 2. As a consequence, the values of \( H_{\text{rel}} \) can be regarded as a measure of the QC fraction. The effect of QC particles on the viscosity was studied at 677, 682 and 687 K up to \( H_{\text{rel}} = 0.2 \), as till this value other crystalline phases did not form according to X-ray diffraction experiments. The dot in the heat flow curve in Figure 7 represents the state corresponding to \( H_{\text{rel}} = 0.2 \) at 682 K.

![Figure 6](image1.png)

**Figure 6.** The heat flow and the indentation rate \((dh/dt)\) as a function of time during isothermal annealing at 682 K.

![Figure 7](image2.png)

**Figure 7.** The heat flow and the corresponding relative released heat, \( H_{\text{rel}} \) as a function of time during isothermal annealing at 682 K. The dot in the heat flow curve represents the state related to \( H_{\text{rel}} = 0.2 \).
In Figure 8 the viscosity as a function of the relative released heat is plotted up to the value of $H_{rel} = 0.2$. As the volume fraction of the QC phase increases, the viscosity of the amorphous–nano-QC composite increases. It is noted that Yan and coworkers [Yan, 2004] have also found that nano-scale crystalline precipitates increase the viscosity of Zr$_{41.25}$Ti$_{13.75}$Ni$_{10}$Cu$_{12.5}$Be$_{22.5}$ bulk metallic glass.

![Figure 8. The viscosity as a function of the relative released heat during formation of the QC phase at 677, 682 and 687 K.](image)

The annealed samples can be considered as a dilute suspension of undeformable spherical QC particles in a viscous liquid phase. A general relationship between the viscosity and the volume fraction of the undeformable spherical particles ($V$) in dilute suspensions was derived theoretically by other authors [Lundgren, 1972; Bedeaux, 1983; Beenakker, 1984; Hsueh, 2005]:

$$\frac{\eta}{\eta_L} = \frac{1}{1 - 2.5V},$$

(4)

where $\eta_L$ is the viscosity of the liquid phase. In these calculations the suspension is treated as a mixture of two fluids, one fluid having an infinitely large viscosity (hard particles) and the other fluid having viscosity $\eta_L$ (liquid). It has been shown that if all the hydrodynamic interactions between the spheres are taken into account, the ratio of $\eta/\eta_L$ differs from eq.(4) by maximum 6% up to $V=0.2$ [Beenakker, 1984]. In order to study the validity of
this relationship for our QC–supercooled liquid composite, the apparent viscosity was normalized by the viscosity of the liquid phase measured before starting the QC formation ($\eta_{l0}$). In Figure 9 the reciprocal of the normalized viscosity, $\eta_{l0}/\eta$ is plotted as a function of $H_{rel}$ which is taken to be equal with $V$.

![Figure 9](image)

Figure 9. The reciprocal normalized viscosity in supercooled liquid–QC suspension as a function of the relative released heat at 677, 682 and 687 K.

Figure 9 shows that the $\eta_{l0}/\eta$ versus $H_{rel}$ relationship can be approximated by linear functions with slopes close to -2.5 for all the three temperatures. The slight deviation of the experimental data from the function $1 - 2.5 \times H_{rel}$ (denoted by the dashed line in Figure 9) can be explained by the change of viscosity in the liquid phase i.e. by the deviation of the real values of $\eta_l$ from $\eta_{l0}$ when QC particles are formed. Consequently, these results show that at high temperature the QC–supercooled liquid composite deforms as a dilute suspension and at least up to about 20 % volume fraction of QC, $\eta$ can be given by the following formula [Gubicza, 2008]

$$\eta = \eta_l(H_{rel}) \cdot f(H_{rel}),$$

where $f(H_{rel})$ accounts for the effect of the hard QC particles on the viscosity and it has the following form

$$f(H_{rel}) = \frac{1}{1 - 2.5 H_{rel}}.$$
The viscosity of the liquid phase, \( \eta_L \) was determined as the ratio of the experimentally determined viscosity, \( \eta \), and \( f(H_{rel}) \) given in eq.(6) and plotted as a function of \( H_{rel} \) at 677, 682 and 687 K in Figure 10. It can be seen that \( \eta_L \) increases slightly with increasing the QC fraction.

The temperature dependence of viscosity of the liquid phase was assumed to obey the following relationship:

\[
\eta_L(H_{rel}) = \eta_0(H_{rel}) \exp\left(\frac{Q(H_{rel})}{RT}\right),
\]  

(7)

where \( \eta_0 \) is the pre-exponential factor in viscosity, \( Q \) is the activation energy, \( R \) is the universal gas constant \(( R = 8.31 J \cdot K^{-1} \cdot mole^{-1})\) and \( T \) is the absolute temperature. The values of \( \eta_0 \) and \( Q \) were calculated from the slope of \( \ln \eta_L \) vs. \( 1/T \) plot for different values of \( H_{rel} \) and plotted in Figs. 11a and b, respectively. The pre-exponential factor \( \eta_0 \) increased while the activation energy decreased with increasing fraction of the QC phase. The two effects are largely compensated by each other resulting in only a slight increase of the viscosity of liquid phase with increasing the QC fraction as it was shown in Figure 10. The increase of the pre-exponential factor and the decrease of the activation energy during the formation of the QC phase can be probably attributed to the changes in the chemical composition of the remaining liquid phase. In section 3 we have discussed that the liquid phase was largely depleted in Ti and enriched in Be during the formation of QC particles. It was shown previously that the increase of the fraction of smaller Be atoms in ZrTiCuNiBe bulk metallic glasses usually results in the decrease of the activation energy of diffusion [Macht, 2001]. It was also observed for other compositions that increasing the concentration of smaller atoms among the alloying elements in BMGs leads to smaller values both of the activation energy and the pre-exponential factor, \( D_0 \) of diffusion [Frank, 1994]. The smaller average atomic size in BMGs most probably results in an easier thermal activation of the atomic jump and also reduces the distance of a single jump thereby reducing the activation energy and \( D_0 \), respectively. The pre-exponential factor of the viscosity, \( \eta_0 \) is inversely proportional to \( D_0 \) therefore \( \eta_0 \) increases with increasing the fraction of smaller atoms in the liquid phase due to the formation of QC phase.
Figure 10. The viscosity of the liquid phase in supercooled liquid–QC suspension as a function of the relative released heat at 677, 682 and 687 K.

Figure 11. The changes of the pre-exponential factor, $\eta_0$ (a) and the activation energy, $Q$ (b) of creep for the liquid phase in supercooled liquid–QC suspension as a function of the relative released heat.
5. Influence of Quasicrystalline Phase Formation on the Room Temperature Mechanical Behavior of BMGs

The effect of formation of QC phase on the deformation behavior of a Zr44Ti11Cu10Ni10Be25 BMG at room temperature was studied by three-point bending tests on 14 mm long samples of 1.6 mm height and 2.3 mm width at a displacement rate of 0.005 mm s\(^{-1}\) [Lendvai, 2008]. Figure 12 shows the results of three-point bending tests carried out at room temperature on samples annealed for different times at 682 K. To permit direct comparison of specimens with slightly different cross-sections, the bending force normalized with the second moment of area (\(F/I\)) is plotted as a function of deflection. It can be seen that while the initial fully amorphous sample shows plasticity, the samples containing different fractions of QC phase failed already in the elastic deformation regime. The large decrease in strength can be explained mainly by a loss of free volume due to structural relaxation in the beginning of annealing [Suh, 2003]. The increase of viscosity in the amorphous phase caused by the changes of chemical composition due to the formation of QC particles may also contribute to the reduction of strength [Schuh, 2007]. The latter effect may make stress relaxation by means of viscoplastic flow more difficult (e.g. in a crack tip region) thereby decreasing the bending strength when QC particles are formed.

It is noted that in the case of a Zr65Al2.5Ni10Cu7.5Pd10 BMG alloy annealed for 60 s at 705K, it was found that the QC phase increased the strength at RT [Inoue, 2001]. The QC phase was identified to have an icosahedral structure with an average particle size of about 30 nm and a high volume fraction of 80–90%. This bulk nanoquasicrystalline alloy shows higher compressive fracture strength (1820 MPa) combined with a significantly improved plastic elongation of 0.5%, as compared with those (1630 MPa and nearly 0%) for the corresponding amorphous single phase alloy with the same alloy composition. Similarly, improved mechanical properties were obtained for bulk Zr56Al3Ni6Cu13Nb10 QC–glass composite processed by conventional copper mould casting [Qiang, 2007], where the QC phase was the majority phase with about 500 nm grain size. The room temperature compression stress–true strain curve exhibits a 2% elastic deformation up to failure, and a maximum fracture stress of 1850 MPa at a quasi-static loading rate of 4.4 x 10\(^{-4}\) s\(^{-1}\). This mechanical behavior is superior to quasicrystal alloys developed earlier, and is
comparable to Zr-based bulk metallic glasses and their nanocomposites which seems to be related to the existence of a glassy phase in between the large-grain QC phases. The synthesis of the in situ QC–glass composite suggests a new approach to develop promising QC materials for engineering applications.

Figure 12. Results of three-point bending tests for samples annealed for different times at 682 K. $F/I$ is the applied force normalized by the second moment of area and $s$ is the deflection. The error bars indicate the uncertainties of maximum values of $F/I$.

6. CONCLUSION

The formation of quasicrystalline phase and its effect on the mechanical behavior was studied in a Zr$_{44}$Ti$_{11}$Cu$_{10}$Ni$_{10}$Be$_{25}$ BMG alloy. During annealing of this alloy, first metastable QC particles and in a second step stable crystalline phases are formed partly from the liquid phase and partly by transformation from the quasicrystals. The nanosized QC particles are spherical and have an internal grain structure. The QC particles formed in ZrTiCuNiBe BMGs during annealing have icosahedral structure and are enriched in Ti and Ni and depleted from Be and Cu.

The formation of the QC phase increases the viscosity of BMGs measured above the glass-transition temperature. The experimental values of viscosity basically follows the theoretical function describing dilute suspensions of hard particles, although the change of chemical composition in the liquid phase also affects the viscosity. As a result of increasing Be/Ti ratio in the liquid phase, the pre-exponential factor and the activation energy of viscosity increased and decreased, respectively, with increasing fraction of the QC phase.
The formation of the QC phase during annealing is accompanied by the decrease of room-temperature bending strength which can be attributed mainly to a loss of free volume and partially to an increase of viscosity in the amorphous phase as a consequence of the change of its chemical composition.

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