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The Effect of Combined Compressive and Torsional Strain on the Crystallization of Hbani Glass

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Abstract

The crystallization process of fluoride glass HBANI after combined deformation (compressive and torsional strain) of ε = 4 and annealing to crystallization temperatures was studied by differential scanning calorimetry and X-ray diffraction. The glass transition temperature and the crystallization temperature, the sequence of the crystalline phases emerging was determined. It is shown that the crystallization rate of fluoride glass decreases after combined deformation.

Keywords: combined deformation, fluoride glass, crystallization

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1. Introduction

Severe plastic deformation changes the characteristics of phase transitions in metallic glasses. This was shown by the example of the crystallization of metallic glasses $CoFe_{3.2}Si_{2.5}Mn_{3.1}B_{15.7}$ after ion irradiation [1] and $CoFe_{4.9}Si_{14.9}B_{10}$ after barocryodeformation [2].

Irradiation by 30 keV Ar^+ ions with a current density of 50 μA/cm^2 to irradiation dose of $1.5 \cdot 10^{18}$ ion/cm^2 at a temperature of 200°C leads to nanostructuring of the metallic glass. The radiation-induced nanostructure is a structure of severe plastic deformation [3]. The crystallization heat of irradiated glass is increased by 30% compared with the crystallization heat of initial unirradiated glass.

On the contrary the crystallization heat of metallic glass after barocryodeformation (all-round compression of 2.5 GPa at a temperature 77K) is decreased by 35% compared with the crystallization heat of initial glass. This is due to the fact that crystallization kinetics of amorphous alloy is affected by internal strain. Severe all-round compression induces positive residual internal strain and ion irradiation (stretching deformation) induces negative residual internal strain.

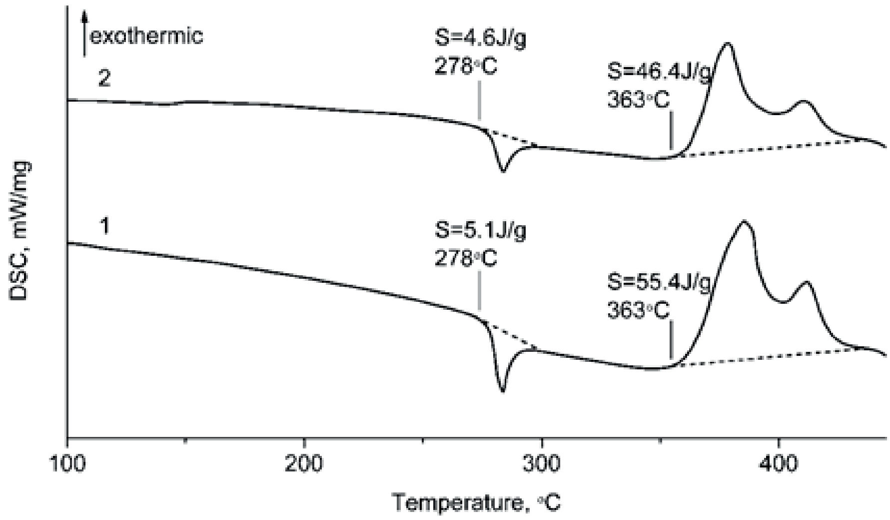

Figure 1: DSC of the HBANI glass samples №1, in initial state (1), after combined deformation (2). S – peak area.

In this paper the crystallization process of dielectric fluoride glass HBANI after combined deformation (compressive and torsional strain) was studied.

2. Materials and Methods

HBANI glasses were obtained from glasses with low crystallization temperatures by the technique of forced low-temperature materials forming carried out at high pressures [4]. Glasses had the form of cylinders with a diameter of 3 mm. Glass composition was as follows: HfF_4 - 53.8%, NdF_3 - 1.5%, InF_3 - 1.2%, AlF_3 - 4.0%, BaF_2 - 22.0%, NaF - 10%.

Samples were subjected to combined deformation via tensile-testing machine ИР 5047-50. Compressive strain with pressure 650 MPa was 25%. Shear deformation $\varepsilon = 4$ according to computational procedure [5]. The structure and composition of the initial and subjected to combined deformation samples was studied using a differential scanning calorimeter Q20 and X-ray diffractometer DRON-8.

3. Results

Fig. 1, 2, 3 show results of differential scanning calorimetry (DSC) with heating rate of 10°C/min in the temperature range from 100 to 450°C.

The glass transition can be observed on the DSC curves of the samples at temperature of 278°C. The exothermic peaks at temperatures of 385°C and 410°C correspond to two-stage crystallization process of fluoride glass.

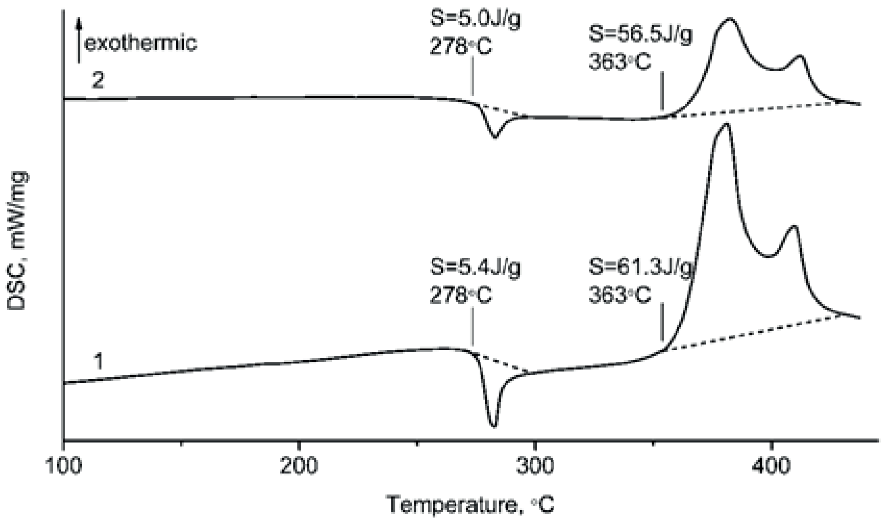

Figure 2: DSC of the HBANI glass samples №2, in initial state (1), after combined deformation (2). S – peak area.

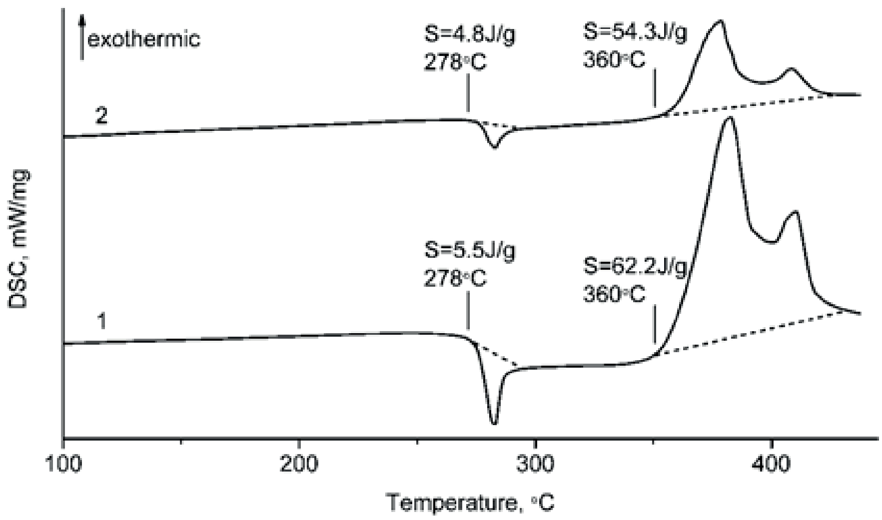

Figure 3: DSC of the HBANI glass samples №3, in initial state (1), after combined deformation (2). S – peak area.

X-ray diffractometry (XRD) spectra of HBANI glass in initial state and after annealing at 400°C and 435°C are shown on fig. 4, 5, 6.

All initial samples were in an X-ray amorphous state (fig. 4). Peaks on XRD spectrum after annealing at 400°C (fig. 5) correspond to crystalline phases of HfF_4, $Na_7Hf_6F_{31}$ и $BaHfF_6$. The XRD spectrum of HBANI glass after annealing at 435°C (fig. 6) contain crystalline phase peaks of HfF_4, $Na_7Hf_6F_{31}$ и $BaHfF_6$ with more intensity and new peaks corresponding to crystalline phase Na_3HfF_7. These crystalline phase peaks appear against the background of an amorphous halo which indicates partial crystallization of the samples.

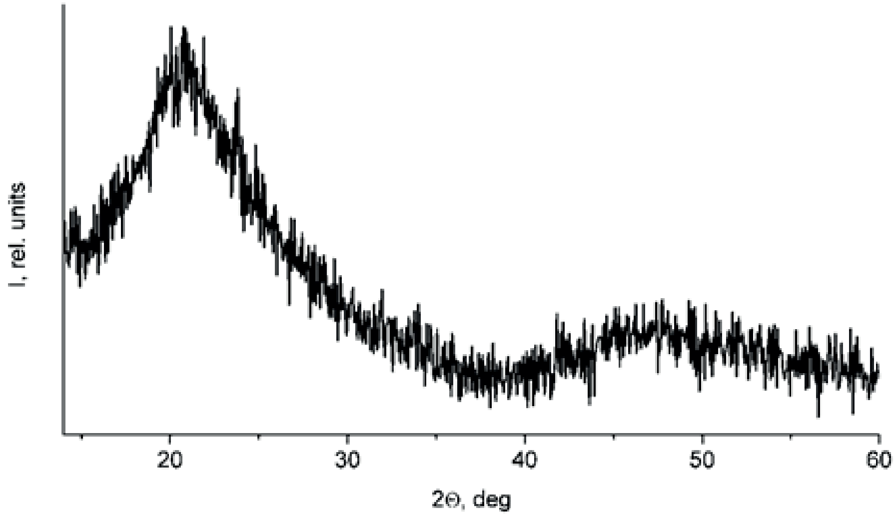

Figure 4: XRD spectrum of HBANI glass in initial state (CuK_α).

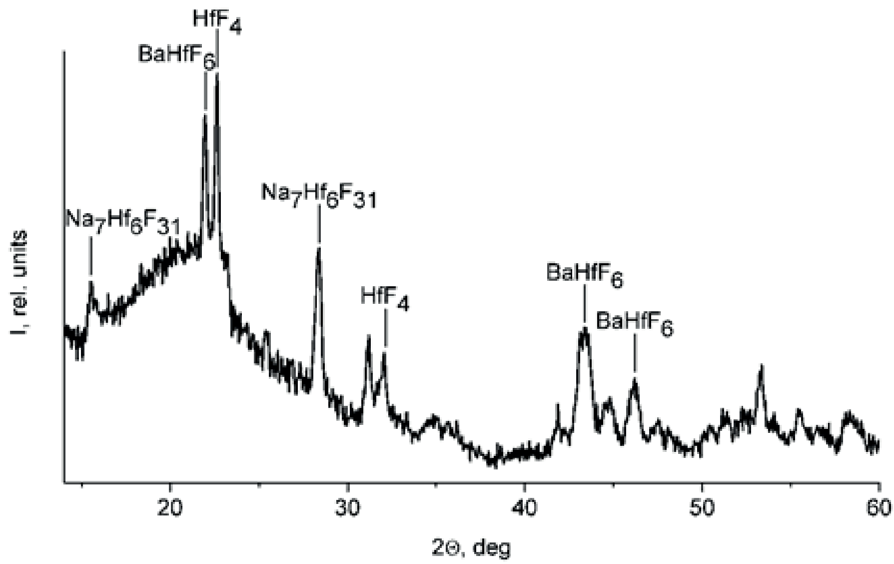

Figure 5: XRD spectrum of HBANI glass after annealing at 400°C (CuK_α).

Crystallization peak areas of HBANI glass after combined deformation decreased by 17%, 8% and 13% for figures 1, 2 and 3 respectively compared with the peak areas of initial glass.

4. Discussion

Crystallization peak area changing on the DSC curves of amorphous alloy after deformation was explained in [2] by example of metallic glasses $CoFe_{4.9}Si_{14.9}B_{10}$. It was

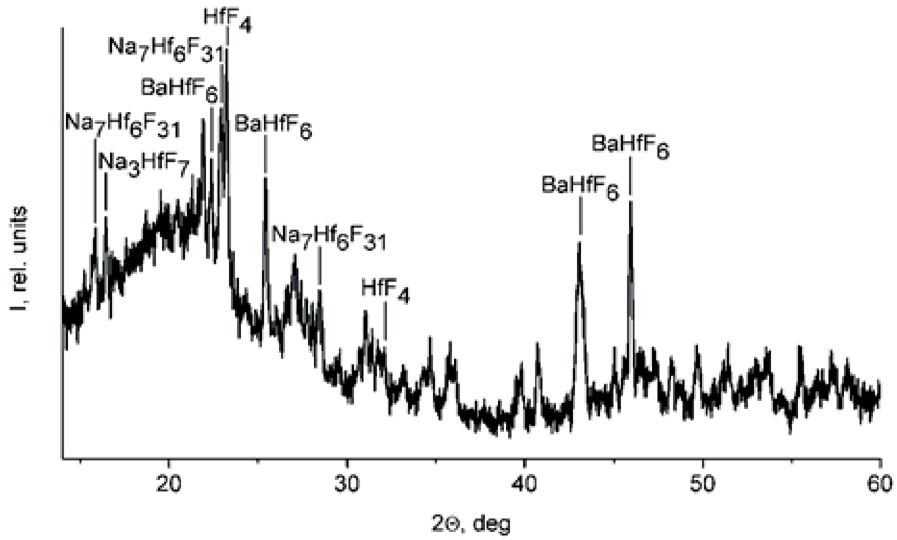

Figure 6: XRD spectrum of HBANI glass after annealing at 435°C (CuK_α).

shown that crystallization peak area (apparent thermal effect) is proportional to crystallization rate. The crystallization rate of metallic glass is defined as the probability of the transition:

$$W \sim \exp\left(-\frac{H}{kT}\right) \tag{1}$$

where H is the transition enthalpy.

$$H = \Delta U + P\Delta V \tag{2}$$

where ΔU is difference of internal energy of the amorphous and crystalline phases. The elastic strain energy is added to (2) in the presence of internal strain P. ΔV is the excess of atom volume in the amorphous phase, which is up to 10% in metal glasses [6]. Thus the kinetics of crystallization of amorphous alloy is affected by internal strain.

Combined deformation induces positive residual internal strain, enthalpy (2) increases, the crystallization rate (1) decreases. Assuming that the crystallization rate ratio of the glass in initial state and after deformation is $W_{in}/W_{def} \sim 1.13$ and using expression (1) gives an estimated value of the residual internal strain in the deformed fluoride glass 200 MPa.

5. Conclusion

It has been shown by differential scanning calorimetry that the glass transition temperature of HBANI glass is T_g = 277°C and and the crystallization temperature is T_{cr} = 365°C.

It has been determined by X-ray diffraction analysis that HfF_4, $Na_7Hf_6F_{31}$ и $BaHfF_6$ phases crystallize in the fluoride glass after annealing to 400°C and Na_3HfF_7 phase crystallizes after annealing to 435°C

Combined deformation ε = 4 of the HBANI glass induces positive residual internal strain. The estimated value of residual strain is 200 MPa. The residual strain decreases the crystallization rate of fluoride glass by 8-17%.

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