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Effect of deferrization on continuous basalt fiber properties

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Deferrized glass was produced by the reduction smelting of basalt batch in a graphite crucible at a high temperature. The deferrized continuous fiber has higher glass transition and drawing temperatures, lower crystallization ability and enhanced thermal stability in comparison with those of the original basalt fiber.

The use of basalt fiber as a thermal insulation material requires its high-temperature stability. Crystallization of fiber at temperatures above the glass transition leads to its significant embrittlement. Therefore, the development of methods for the inhibition of fiber crystallization during heat treatment is of practical importance.

One of the main distinctions of basalt fiber from synthetic glass fiber is a high iron content (8–16 wt% Fe_2O_n). The iron content and Fe^{3+}/Fe^{2+} ratio influence the viscosity, density, mechanical and crystallization properties *etc.*[1,2] It is believed that iron cations play a key role in crystallization processes in basalt fiber since an iron-containing spinel phase has lower activation energy of crystallization in comparison with chain and tectosilicates.[3–5] High iron percentage may even cause spontaneous crystallization in a glass melt during fiber formation.

As we reported earlier,[1] the properties of a melt, which determine the fiber fabrication conditions, are better at low Fe content. The presence of Fe ions ($\geqslant$ 2.5 wt%) in glass markedly raises the service temperature of iron rich glass fibers under weak loads and vibrations.

Here, we propose a method of producing fiber with lowered crystallization ability and enhanced thermal stability based on the deferrization of basalt glass (BG).

The original BG was obtained by smelting a basalt[†] batch in a platinum crucible in a high temperature furnace under the following thermal conditions: (1) heating to 1473 K at a rate of 300 K h^{-1}; (2) heating in a temperature range of 1473–1873 K at 50 K h^{-1}; (3) homogenization at 1873 K for 20 h; and (4) rapid quenching of melted glass in water.[3] The glass with lowered iron content (deferrized basalt glass, DBG) was prepared in three steps. First, the basalt batch was smelted in a graphite crucible at 1773 K for 24 h. The graphite crucible was put into an alundum one to prevent its combustion in air. During the reducing treatment, iron oxides in melted basalt reacted with graphite to form metallic iron:

$$Fe_2O_n + nC \rightarrow 2Fe\downarrow + nCO\uparrow.$$

Moreover, silicon carbide formation at the given temperature is also possible:

$$SiO_2 + 3C \rightarrow SiC + 2CO\uparrow.$$

After the reduction smelting, deferrized glass was poured out. Iron balls formed during the smelting settled at the graphite crucible bottom [Figure 1(*b*)]. At the second step, the deferrized basalt glass [Figure 1(*c*)] was heat treated in air at 1473 K for 24 h to remove an excess of graphite and fine iron particles. After all the annealed deferrized glass was heated in a Pt/Rh crucible at 1873 K for 24 h to fuse phases crystallized on the previous step and release gas inclusions formed by the thermal decomposition of silicon carbide. The homogenized melt was quenched in water. The chemical composition and density[‡] of BG [Figure 1(*a*)] and DBG [Figure 1(*d*)] glasses are given in Table 1.

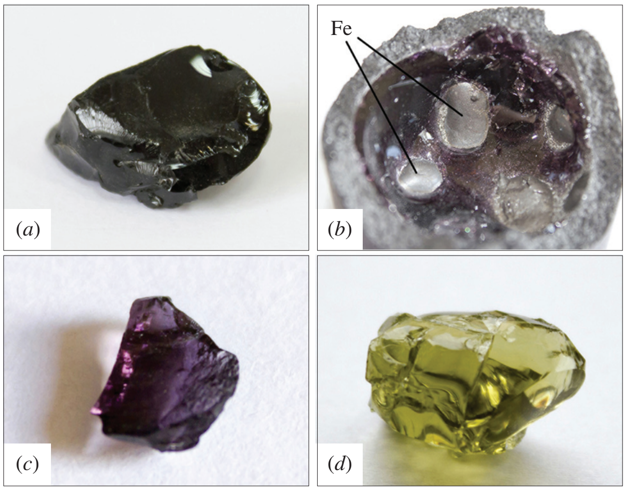

Figure 1 (*a*) Original basalt glass; (*b*) iron sediment on the graphite crucible bottom; (*c*) reduced glass; (*d*) deferrized glass after remelting.

Original and deferrized continuous fibers (BCFs and DBCFs, respectively) were produced by pulling from BG and DBG melts using a laboratory scale system.[6] We used fibers 10–11 μm in diameter.

As shown in Table 1, the reduction smelting described in this work makes it possible to obtain clarified mineral glass with significantly lowered iron content and density in laboratory scales. Note that in industry it is more practical to produce deferrized glass by smelting basalt rock with coal in a cupola furnace. The lower drawing temperature limit[§] for DBCFs is higher by 30 K than that for BCFs and equals 1723 K because of an increased viscosity of glass melt after deferrization.

The glass transition and crystallization processes in BCFs and DBCFs were analyzed by differential scanning calorimetry

[†] In this work, we used andesitic basalt from the Sil'tsevskoe deposit (Carpathians, Ukraine).

[‡] Density was measured by hydrostatic weighing on a Sartorius YDK 01 LP balance using distilled water as an immersion liquid.

[§] As the lower fiber drawing temperature limit, we took the temperature at which fibers up to 20 μm in diameter could be drawn for 30 min without breakage.

Table 1 Chemical composition and density of original and deferrized basalt glasses.

Glass sample	Content (wt%)								Density/g cm^{-3}
	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	$\Sigma(Fe_2O_n)$	
BG	56.1±0.6	15.5±0.4	8.7±0.3	4.0±0.1	2.4±0.1	2.3±0.2	1.1±0.1	9.9±0.2	2.70±0.01
DBG	61.7±0.6	17.3±0.4	9.7±0.3	4.5±0.1	2.5±0.1	2.5±0.2	1.2±0.1	0.5±0.2	2.51±0.01

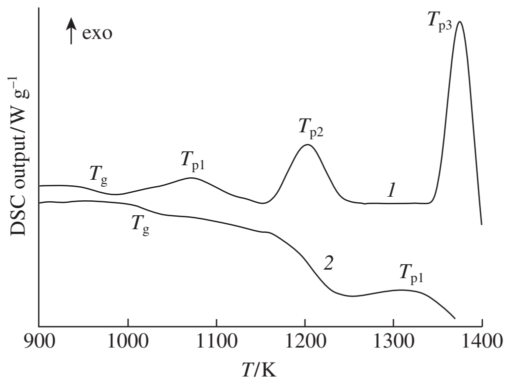

Figure 2 DSC curves of (*1*) BCFs and (*2*) DBCFs in air at a heating rate of 10 K min^{-1}. T_g is the glass transition temperature; T_{p1}, T_{p2} and T_{p3} are the exothermal peak temperatures.

(DSC).¶ Figure 2 shows the DSC output signal as a function of temperature. The DSC curve of BCFs contains the glass transition range with the inflection point (T_g) at 975 K and three exothermal peaks at T_{p1} = 1075 K, T_{p2} = 1198 K and T_{p3} = 1374 K, which correspond to crystallization processes in BCFs. The glass transition temperature on DSC curve of DBCFs is higher by 50 K. The broadened endothermic effect at temperatures above 1100 K is connected with the gradual decrease in the viscosity of the amorphous matrix of DBCFs. In a temperature range of 1240–1360 K, this effect is overlaid by the crystallization exothermal peak (T_{p1} = 1329 K).

The phase transformation sequence in BCFs and DBCFs during heat treatment was investigated by X-ray diffraction (XRD) analysis.†† In accordance with the DSC data, fiber samples were annealed at 973, 1073, 1173 and 1273 K for 24 h; their XRD patterns are presented in Figure 3.

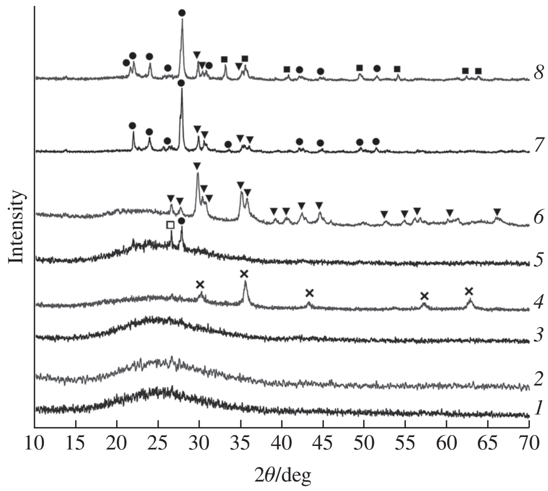

Figure 3 XRD patterns of DBCFs heat-treated at (*1*) 973, (*3*) 1073, (*5*) 1173 and (*7*) 1273 K and BCFs heat-treated at (*2*) 973, (*4*) 1073, (*6*) 1173 and (*8*) 1273 K for 24 h in air. The peaks have been assigned to spinel (×), pyroxene (▼), hematite (■), plagioclase (●) and quartz (□).

Crystallization in BCFs begins with spinel phase formation (magnesioferrite, $MgFe_2O_4$) [ICDD no. 73-2211], which corresponds to the first exothermal effect (T_{p1}) on the DSC curve. Contrastingly, DBCFs remain amorphous at the same temperature.

As stated before,[3] the spinel phase particles in BCFs act as nucleation sites for chain silicate [augite, $Ca(Fe,Mg)Si_2O_6$] [ICDD no. 24-201] crystallization in a range of 1150–1250 K (the second exothermal effect, T_{p2}). In DBCFs small amount of ironless pyroxene [diopside, $CaMg(SiO_3)_2$] [ICDD no. 75-1577] forms only at 1273 K, while the XRD pattern of DBCFs annealed at 1173 K contains only insignificant reflexes of quartz [ICDD no. 78-1252] and plagioclase [albite, $(Na,Ca)Al(Si,Al)_3O_8$] [ICDD no. 41-1480]. At temperatures above 1273 K, plagioclase becomes the dominant crystalline phase both in BCFs (anorthite, $CaAl_2Si_2O_8$) [ICDD no. 2-523] and in DBCFs [albite, $(Na,Ca)Al(Si,Al)_3O_8$] [ICDD no. 41-1480].

Thus, the exclusion of iron cations from basalt melt significantly changes the crystallization process in continuous fibers preventing the formation of the spinel phase and increasing the onset crystallization temperature by ~100 K.

Figure 4 illustrates the results of measurements‡‡ of the tensile strength and elastic modulus of BCFs and DBCFs monofilaments

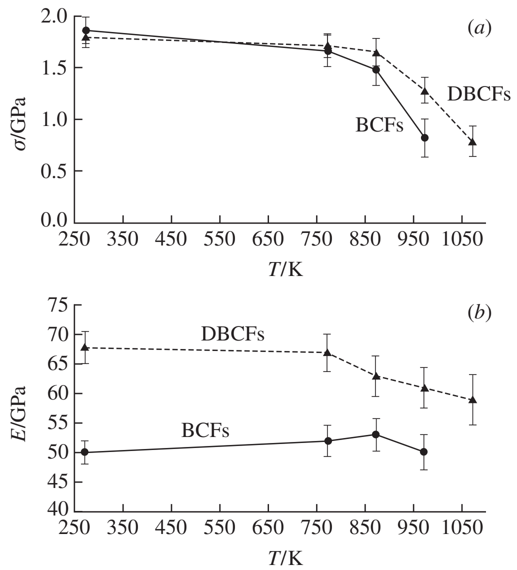

Figure 4 (*a*) Tensile strength, σ, and (*b*) elastic modulus, *E*, of BCFs and DBCFs before and after heat treatment for 1 h in air at different temperatures.

¶ DSC analysis was carried out using a NETZSCH STA 449C Jupiter thermal analyzer. DSC signals were recorded in a temperature range from 298 to 1473 K at a heating rate of 10 K min^{-1} in air. The correction of DSC signals was performed by measuring a baseline with two empty platinum crucibles under the same conditions.

†† X-ray diffraction analysis was performed at room temperature on a Thermo ARL X'TRA powder diffractometer (CuKα1 radiation, λ = 1.54060 Å; CuKα2 radiation, λ = 1.54443 Å; intensity ratio CuKα1/CuKα2 = 0.51) with Peltier-cooled solid-state detector. XRD patterns were collected in the range 2θ = 10–70° with a step 0.02° and a scan rate of 1° min^{-1}. The crystalline phases were identified using the Crystallographica Search-Match software and the International Center for Diffraction Data (ICDD) database.

before and after heat treatment for 1 h in air at 773, 873, 973 and 1073 K. Initial tensile strength values of BCFs and DBCFs are equal and go down after heat treatment at temperatures above 873 K. At 1073 K, the retained strength of DBCFs was ~0.8 GPa, while the mechanical testing of BCFs monofilament annealed under the same conditions is impossible due to its significant embrittlement. The elastic modulus of DBCFs is by ~17 GPa higher than that of BCF; this can be related to increased fiber structure stiffness due to lowered content of network-modifying iron cations and increased percentages of network-forming silicon and aluminum cations.[7] As opposed to the tensile strength, the elastic modulus of both BCFs and DBCFs does not undergo essential changes during the heat treatment.

Therefore, deferrization is proposed as a suitable method for producing glass materials with reduced crystallization ability and enhanced high-temperature stability.

‡‡ The tensile strength and elastic modulus were determined on a Tinius Olsen (Hounsfield) H5KS universal tensile testing machine. Monofilament specimens were fixated on paper support frames using epoxy. The gauge length was 20 mm, and the crosshead speed was 5 mm min^{-1} (ISO 5079).

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