Original Paper

Drawing of oxynitride glass fibers[1)]

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Glass fibers were drawn from three $MgO-Al_2O_3-Y_2O_3-SiO_2$-based oxynitride glass melts. A single-hole bushing process was used to spin the melts containing nitrogen contents between about 13 and 16 at.%. The drawing process is described in detail, and it is shown that besides melt viscosity the high surface tension of the oxynitride glass melts strongly controls the fiberization. This is analyzed in terms of Reynolds and Weber numbers. Glass fibers up to a length of about 30 cm can be drawn for Reynolds numbers between about 0.01 and 0.2 and Weber numbers between about 2.6 and 3.1, however, even there the fiber diameter oscillates to some extent. For smaller Reynolds and Weber numbers it is impossible to draw fibers at all. In this instability regime only droplets leave the nozzle outlet. The oxynitride fibers obtained have excellent mechanical properties and a high chemical resistance to alkaline attack.

Ziehen von Oxinitrid-Glasfasern

Drei Oxinitridglasschmelzen auf der Basis von $MgO-Al_2O_3-Y_2O_3-SiO_2$ wurden zerfasert. Ein Einzeldüsenziehprozeß wurde verwendet, um die Fasern mit Stickstoffgehalten zwischen 13 und 16 At.% zu spinnen. Der Ziehprozeß wird im Detail beschrieben, und es wird gezeigt, daß neben der Viskosität auch die hohe Oberflächenspannung der Oxinitridglasschmelzen die Zerfaserung stark beeinflußt. Dies wird durch Reynolds- und Weber-Zahlen beschrieben. Glasfasern bis zu einer Länge von etwa 30 cm können bei Reynolds-Zahlen zwischen etwa 0,01 und 0,2 und Weber-Zahlen zwischen etwa 2,6 und 3,1 gezogen werden. Jedoch schwankt der Faserdurchmesser auch dann noch. Bei kleineren Reynolds- und Weber-Zahlen kann man überhaupt keine Fasern ziehen. In diesem Bereich der Instabilität verlassen den Düsenausgang nur Tropfen. Die erhaltenen Oxinitridfasern haben sehr gute mechanische Eigenschaften und eine hohe chemische Beständigkeit gegen alkalischen Angriff.

1. Introduction

Oxide glass fibers are important technical materials. They are used in a variety of forms, e.g. as mats, strands or chops for insulation, or as fiber bundles in composites to strengthen polymers, metals, plaster or cement. Industry offers fibers of different compositions, however, E-glass fibers are the most commonly used technical fibers [1]. The drawing conditions of continuous oxide glass fibers, both with technical and laboratory compositions, are relatively well established, e.g. [1 to 10]. In contrast, the potential of oxynitride glass fibers is much less proved thus far. It is well-known that the incorporation of nitrogen into silicate glasses may result in strongly improved physical and chemical properties [11 to 14]. Thus, it is to be expected that high-performance fibers might be available, e.g. high-modulus fibers with extremely high chemical resistance, but Messier et al. [15] reported the failure of continuous fiber drawing from the melt with nitrogen contents >3.2 wt%. Oxynitride glass fibers have also been prepared by the ammonolysis of silica gels [16], however, this unconventional method is of special importance still.

It is the aim of this work to elucidate the drawing conditions of oxynitride glass fibers with higher nitrogen contents. A single-hole bushing method is used. Both viscosity and the high surface tension of the melts to be fiberized are important, and it is shown how the drawing conditions of oxynitride glass melts are correlated to the two dimensionless numbers, the Reynolds (*Re*) and the Weber (*We*) numbers.

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2. Experimental

2.1 Glasses

Table 1 displays the compositions of the glasses used to draw fibers. They were developed from the composition of glass N 21, which was found already to have an excellent chemical resistance to alkaline attack [17]. The raw materials MgO (reagent grade) and Al_2O_3 (water-free) were from Merck, Darmstadt (Germany), AlN (powder, 99%) and Si_3N_4 (powder, Si 58%) were from Ventron, Karlsruhe (Germany), and Y_2O_3 (0.8 to 3.0 µm) and SiO_2 (ground quartz crystal <100 µm) were from Starck, Goslar (Germany) and Heraeus, Hanau (Germany), respectively. The raw materials were mixed in acetone according to their compositions, and – after drying – they were pressed into cylinders of 25 mm diameter with a pressure of 325 MPa. They were then placed into the graphite crucible of the fiber drawing set-up (see section 2.2) and heated inductively at 40 K min^{-1} to 1600 °C. The melts were held there for 15 min to reach a sufficient

Table 1. Composition of the batch for oxynitride glass melts used for fiber drawing (in mol %), analyzed nitrogen content (in wt%) in the glass. The table also contains some property data.

glass	composition of batch						analyzed nitrogen content	ϱ in g cm^{-3}	T_g in °C	E in GPa
	MgO	Al_2O_3	Al_2N_2	Y_2O_3	SiO_2	$SiN_{4/3}$				
N 21	40	10.0	5.0	–	41.25	3.75	3.69	2.882	820	116
NY 27	40	–	7.5	41.25	41.25	3.75	4.27	3.311	826	189
NY160	–	7.6	17.0	25.1	50.3	–	4.37	3.941	940	136

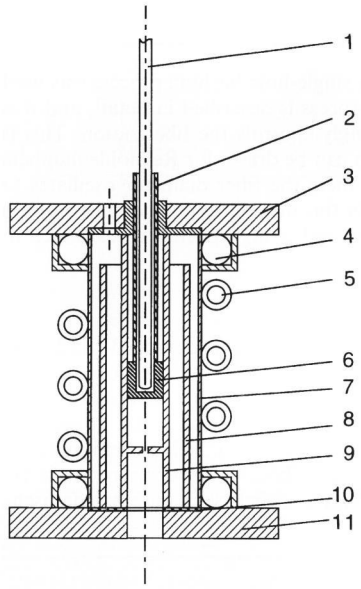


Figure 1. Schematic of drawing furnace. 1: thermocouple, 2: Al_2O_3 tube, 3: upper part of furnace with nitrogen inlet, 4: seal, 5: induction coil, 6: graphite plug, 7: silica glass tube, 8: Al_2O_3 tube for heat insulation, 9: graphite crucible with orifice, 10: graphite seal, 11: lower part of furnace.

homogeneity for fiber drawing. Then the melts were cooled to the fiberization temperatures in a range of melt viscosities between $10^{2.2}$ and 10^3 dPa s.

The glasses and glass melts were investigated independently for several properties. Among others these were the densities, ϱ, the Young's moduli, E, and the glass transition temperatures, T_g [18] (table 1). Furthermore, the melt viscosities, η, were determined between T_g and 1600 °C and the surface tensions, σ, could be estimated by two independent methods, the drop weight and the drop geometry methods, respectively [19]. σ values of about 500 to 600 N mm^{-1} were obtained, which are nearly twice as high as those known for most oxide glass melts.

2.2 Drawing process

A single-hole bushing process was used to draw the oxynitride glass fibers (figure 1). Although the apparatus looks similar to set-ups used to draw oxide glass fibers, e.g. [1], it does have some important differences. Thus, an N_2 atmosphere is used as a protective gas in the furnace chamber during the fiberization to prevent oxidation and bubble formation [20] at the surface of the oxynitride glass melts. In a first attempt it was tried to draw the fibers without the graphite plug (see position 6 in figure 1) by simply increasing the N_2 pressure above the melt up to 300 hPa. Although this is a hydrostatic pressure used commonly in spinning set-ups [7], this method was not very successful to prepare oxynitride fibers. Instead, the melt jet formed spherical droplets only after leaving the crucible orifice. A comprehensive investigation [21] showed that not only the pressure but also the other common spinning parameters, e.g. the orifice diameter and the flow rate [7 and 8], as well as also the regime of Reynolds numbers [6], valid for oxide glass melt fiberization, are no appropriate parameters for oxynitride melt fiberization.

Manfre' [4 and 5] observed three different stages when the liquid glass leaves a capillary nozzle. The first one is an unstable stage with the formation of drops of liquid glass. The second stage describes the continuous spinning of fibers according to the Hagen-Poisseuille equation. The third stage combines the spinning of fibers with an oscillation of the liquid glass jet. This oscillation is interpreted as a "hindered dropping process". Stehle and Brückner [9] and Brückner et al. [10] described the decrease in diameter and the formation of spheres in the liquid glass melt filaments as a distorted equilibrium between viscosity and surface tension forces. Possibilities to overcome the strongly increased action of the surface tension force in the case of oxynitride melts are either to increase the hydrostatic pressure or to increase the velocity of the liquid glass jet at the nozzle outlet. This latter method was used by a controlled movement of the plug with velocities between 0.2 and 5.8 mm s^{-1}, enabling a range of increased but constant jet velocities. The pressure at the nozzle outlet could be made as high as 3 MPa. After fiberization the filaments were quenched in an atmosphere of sublimating liquid nitrogen below the induction furnace.

The high surface tension force of the oxynitride glass melts may cause both instability and oscillation of the liquid glass jet. Oscillation and instability are dissimilar processes. Oscillation implies a change in the jet shape with time without distorting the continuous formation process of a fiber, whereas an instability leads to a disintegration of the jet and an interruption of the fiber spinning process.

Burgman [6] already analyzed the fiber drawing process in terms of the dimensionless *Re* number. Different

shapes of the liquid glass jet at the nozzle were attributed to different regimes of *Re*. However, Burgman also mentioned explicitly that his analysis in terms of the *Re* numbers is appropriate only for glass melts with the usual surface tensions of 300 to 330 N mm^{-1}. He further mentioned that for the case of strongly dissimilar values of surface tensions both the *Re* and the *We* numbers might give a more appropriate description of the drawing process. However, no further attempts were made.

Since the data are available for the present experiments, such an attempt will be made in the following. The geometry parameters used are diameter, d, and length, L, of the nozzle, which varied around 1.5 and 3.0 mm, respectively. The materials data, i.e. viscosity, η (between $10^{2.2}$ and 10^3 dPa s), density, ϱ, and surface tension, σ, were given in section 2.1 already. The kinematic parameters are the mass flow rate, dm/dt, and the velocity of the glass jet at the nozzle outlet, v_d. The mass flow rate can be calculated using the continuity equation

$$\frac{dm}{dt} = \varrho \cdot D^2 \cdot \frac{\pi}{4} \cdot v_p \qquad (1)$$

where m = mass, t = time, ϱ = density, D = crucible diameter, and v_p = velocity of the plug. The velocity at the nozzle outlet, v_d, is obtained by

$$v_d = \frac{dm/dt}{\varrho \cdot d^2 \cdot \pi/4} . \qquad (2)$$

Re and *We* numbers, which have the physical meaning of the ratios of inertial force to rheological force and inertial force to surface tension force, respectively, can be defined as [22]

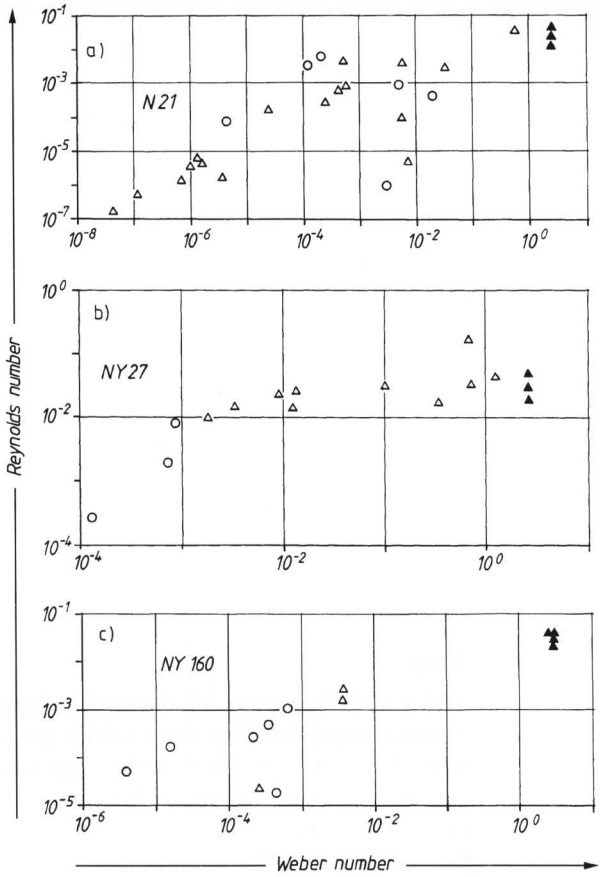
$$Re \equiv (dm/dt)/(\eta \cdot d) = \frac{\varrho \cdot d \cdot v_d \cdot \pi/4}{\eta} \qquad (3)$$

and

$$We \equiv \frac{\varrho \cdot v_d^2 \cdot d}{\sigma} . \qquad (4)$$

3. Results and discussion

Re and *We* numbers were calculated according to equations (3 and 4) for each drawing experiment by using the different quantities mentioned earlier. Figures 2a to c show plots of *Re* as a function of *We* for the three different glass melts investigated. Different regimes are clearly to be seen, to some extent similar to the three stages of fiberization reported by Manfre' [4 and 5]. The first is the unstable stage with the formation of spherical drops. This instability regime is documented here mostly by low *Re* and *We* numbers. The second stage, the regime where Manfre' found a stable fiberization process for oxide melts, obviously does not exist at all for these oxynitride



Figures 2a to c. Relation between Reynolds and Weber numbers for the fiber drawing process; a) glass melt N 21, b) glass melt NY 27, c) glass melt NY 160. ○: formation of drops, △: formation of drops with sporadic oscillation, ▲: oscillation regime.

melts. Only sporadically glass jets occurred with a small outcome of fibers. This stage of sporadic oscillation was obtained when the hydrostatic gas pressure method was used. It obviously belongs to Manfre's third stage of oscillation. This third stage, which resulted here in continuous fibers of varying diameters and a somewhat oscillating liquid glass jet, is equivalent to Manfre's third stage of oscillation in the case of oxide glass melts. In this stage glass fibers of 15 to 30 cm length and most probable diameters between 40 and 70 µm could be produced which could be used then for further property measurements [18]. This regime is obtained with the set-up which uses the mechanical plug that enables to reach both extremely high pressure and mass flow rates at the nozzle outlet. The mass flow rates were 2.9 (glass N 21), 3.3 to 3.8 (glass NY 27), and ≈ 3.9 g s^{-1} (glass NY 160), and the velocity of the liquid glass jet at the nozzle outlet amounted to 0.56 m s^{-1} for all compositions. Figure 3 displays this regime of fiber production with *Re* numbers between about 0.01 and 0.2 and *We* numbers between about 2.6 and 3.1. A comparison with the *Re* numbers of 10^{-6} to 10^{-3} Burgman [6] calculated for oxide glass melt spinning reveals that the *Re* numbers for oxynitride melt spinning are much higher. Shkol'nikov's [3] *Re* numbers for the production of oxide staple fibers are

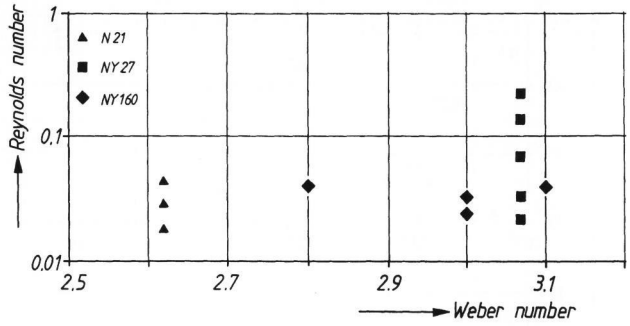


Figure 3. Reynolds and Weber numbers for the oscillation regime, where fiber drawing is possible to some extent for all glass melts.

similar to the *Re* numbers obtained in this work. Because of a lack of data a comparison with the *We* numbers calculated here is not possible thus far.

4. Conclusions

It was shown that the fiberization of oxynitride glass melts is much more complicated than that of oxide glass melts. The reason for that is the high surface tension force of the oxynitride melts. Using a hole-bushing process fibers of up to 30 cm length with most probable diameters between 40 and 70 µm could be drawn. Property measurements on these fibers showed that they have an excellent performance, e.g. Young's moduli, *E*, up to about 200 GPa and a very high stability against alkaline attack [18]. The *E* moduli exceed those of any other existing glass fibers [23].

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