Dependence of Hardness of Silicate Glasses on Composition and Thermal History
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Introduction

From an industrial point of view, it is desirable if the hardness of a glass can be predicted from its composition and manufacturing conditions.

Hardness of crystals may be calculated using a semi-empirical approach. So far, this is not possible for glasses. The aim of this study is to discuss the factors that should be taken into account in the calculation of hardness of glass.

Effect of thermal history: E-glass (aluminoborosilicate) is annealed at $\theta_g$ for different durations $t_a$ and Vickers hardness ($H_v$) measured

Effect of chemical composition

Polymerisation effect: SiO$_2$-Al$_2$O$_3$-Na$_2$O of different Na$_2$O-content $\rightarrow H_v$ measured

Modifying ion effect: 68SiO$_2$-1Fe$_2$O$_3$-8A$_2$O-23RO (A = alkali, R = alkaline earth) $\rightarrow H_v$ measured

Thermal History

To study the annealing effect of the E-glass on the fictive temperature $\theta_f$, the heat capacity ($C_p$) –temperature curves are measured on the glasses annealed for various durations ($t_a$) at $\theta_g$. $\theta_f$ is determined by Moynihan’s enthalpy-matching approach.

$H_v$ increases with duration of annealing, whereas it decreases with increasing $\theta_f$. Trend is confirmed by nanoindentation on E-glass fibres ($\theta_f = 1166$ K) [Lonnroth et al., JNCS 354, 3887 (2009)]

Chemical Composition

The four SiO$_2$–Al$_2$O$_3$–Na$_2$O glasses contain different amounts of Na$_2$O. The Na$_2$O excess is calculated as the amount of Na$_2$O that does not participate in AlO$_4$–charge balancing. $H_v$ decreases with the excess amount of Na$_2$O, i.e., the network depolymerization degree.

The effect of the type of network-modifying cation on hardness for 68SiO$_2$–8Na$_2$O–1Fe$_2$O$_3$–23RO glass series (R = Mg, Ca, Sr, and Ba) and 68SiO$_2$–23CaO–1Fe$_2$O$_3$–8MZO series (M = Na, K, Rb, and Cs). The opposite trends for the two series are observed.

Conclusions

1) Annealing lowers $\theta_f$ and thereby increases the structural density of glasses. This leads to an increase of hardness.
2) For alkali ions, hardness increases with increasing ionic radius, whereas the opposite trend is observed for alkaline earth ions.
3) The structural changes of the network occurring at the atomic scale must be taken into consideration when predicting the effect of chemical composition on hardness.

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