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Tailoring glass surfaces via internal cationic diffusion

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In this paper, we report a new way to create functional surfaces on the transition metal containing oxide glasses. In terms of chemistry and structure, the created surfaces are classified into two groups. One group is the nano-crystalline surface layer enriched in earth alkaline oxides, and the other is the nano-amorphous surface layer enriched in silica. The nano-crystalline surface is generated by subjecting the glass to an oxidation process in atmospheric air at the glass transition temperature for a certain duration. During this process, a fraction of the transition metal ions will be transformed from low to high valence state, and this causes electron holes to migrate from the glass surface towards the glass interior. To maintain the charge neutrality, the network modifying ions must diffuse from the interior towards the surface, i.e., the so-called outward diffusion occurs. At the surface, the modifying cations react with oxygen ions to form the corresponding oxides, the formation of which is driven by the negative Gibbs free energy of the reaction. It is found that the magnesium ions are the most mobile, and hence, the formed periclase (MgO) is the predominant nano-crystalline phase in the surface layer. The origin of this phenomenon is discussed in the present work. As a mirror effect, the nano-amorphous surface layer enriched in silica is generated by subjecting the glass to a reduction process. The direction of the cationic diffusion during reduction is just the opposite of that of the outward diffusion, i.e., the so-called inward diffusion occurs. However, whether the inward diffusion happens strongly depends on the partial pressure of the reducing gas (e.g. hydrogen). The fascinating part of the new approach is that both the direction and the extent of the diffusion are controllable, and hence, the thickness of both types of layers can be tailored. The formation of the nano-layers can considerably contribute to improving physical and chemical functions of glassy materials. We clarify the kinetic and thermodynamic mechanisms of both outward and inward diffusion. We also describe the perspectives of our new approach, in particular, with respect to the potential applications of the approach in creating functional surfaces on non-oxide glasses, and even on crystalline materials.

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