

Technology Brief

DENSIFICATION, CRYSTALLIZATION, AND STICKING BEHAVIOR OF CRUSHED WASTE GLASS SINTERED IN REFRACTORY MOLDS WITH RELEASE AGENTS

Ceramic products, such as tile, are currently processed from recycled waste glass by sintering crushed glass in refractory molds. This processing method uses the unique low temperature viscous phase sintering characteristic of glass particles. The development of this method has been limited by processing problems of crystallization of the glass and sticking of the glass to molds. Release agents have been used, but sticking problems still occur.

This report documents research performed to provide an understanding of the crystallization and sticking problems that occur when sintering recycled glass in refractory molds coated with release agents.

Fusing

Fusing glass particles into a dense product occurs by viscous phase sintering at temperatures much lower than the melting temperatures of crystalline materials of the same composition. This sintering mechanism is controlled by glass composition, impurities, surface area, packing efficiency, and crystallization behavior. Some glass compositions densify easily by viscous phase sintering, while other compositions do not densify well. The viscosity has to decrease sufficiently for glass flow to occur, but not too rapidly to cause crystallization. If crystallization occurs, the viscosity will increase and further densification will be inhibited. Impurities or additions of crystalline materials to the glass particles will also adversely affect the sintering behavior.

Key Words	
Materials:	Crushed soda-lime glass.
Technologies:	Glass fusing.
Applications:	The manufacture of glass tile and other kiln-fired fused glass products.
Market Goals:	To increase the quality and economic competitiveness of fused glass products.
Abstract:	To provide an understanding of the crystallization and sticking problems that occur when sintering recycled glass in refractory molds coated with release agents.

The purpose of this experimental work was to develop an understanding of the current practice of sintering crushed glass in refractory molds with release agents, and to determine if a processing window exists where a satisfactory product can be produced. The results are specific to the particular glass studied, but some general conclusions can be made.

Sticking Behavior of Glass at High Temperatures

Glass softening and flow is required for glass particles to sinter into a dense product, and to produce a smooth surface. However, this also causes the glass to tend to stick to materials that come in contact with the glass, such as refractory mold or even a release agent. For sticking to occur, the glass has to wet the surface of the material it is in contact with. This is similar to a liquid wetting a solid, which is



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controlled by the differences in surface tensions (or surface energies) between the materials.

The release should be bonded well to the refractory mold to keep the release from separating when some sticking occurs. How well the release particles are bonded together is also an important factor in the performance of the release. If no sticking occurs, then ideally the release particles should be strongly bonded together. However, if sticking occurs, then weakly bonded release particles will limit the amount of release that sticks, and extend the number of repeat firings possible. The strength of the refractory mold may also be important. Ideally the weakest link should be as close as possible to the glass-release interface. A final factor that may be important is the stability of the release on repeat firings. Reactions and phase changes in the constituents of the release can occur during repeat firings. The release should be designed to limit adverse changes that would degrade the release performance.

For this project alumina hydrate, silica, and kaolin were chosen for investigation as release agent constituents for use with soda lime glass. The data developed in this study show that for all ratios of the three test releases, a composition consisting of 60% alumina hydrate and 40% kaolin gave the best results, but eventually degraded after repeated firings.

Crystallization of Glass

Glass is metastable and will transform to the stable crystalline state if enough thermal energy is available. This transformation is called devitrification or crystallization, and occurs by a two-step nucleation and crystal growth process. As glass is heated the viscosity decreases, which increases the tendency for structural rearrangement and crystallization. When the temperature is increased high enough (usually just above the softening point), crystal nuclei begin to form. The nuclei are simply tiny regions in the glass structure where the crystalline structure has formed. As the temperature is further increased, the rate of nuclei formation, or nucleation, increases to a maximum at some temperature, depending

on the composition. At higher temperatures additional thermal energy causes the nuclei to grow by crystal

growth mechanisms. The rate of crystal growth increases with increasing temperature to a maximum at some temperature, and then the rate decreases to zero at the liquidous temperature.

The initial temperature of crystal growth for a soda lime glass was found to occur at about 1380F (750C), with the maximum rate of crystal growth at about 1780F (970C). The crystallization occurred on the surface. These results show that soda-lime glass will crystallize at relatively low temperatures, which may be difficult to avoid at the temperatures required to sinter crushed glass in a loosely filled mold.

The objectives of this work were to determine if the test could be fired to produce a smooth surface without a hazy appearance, and to further understand the crystallization behavior of soda-lime glass. Reducing the hold time decreased the crystallization, but in all cases where a smooth surface was produced crystallization and a surface haze also occurred. These indicate that for the particular glass and processing conditions used, some degree of crystallization will occur when the glass flow is enough to produce a smooth surface.

Conclusions

Sintering of crushed soda-lime glass without sticking and crystallization problems is technically very challenging, because of the conflicting effects of a reduction in glass viscosity. Glass flow is required to fuse and sinter the particles together. The amount of viscosity reduction and flow that is needed increases with greater particle size and less efficient particle packing. Glass flow also has the negative effects of promoting sticking and crystallization. So the processing challenge involves producing enough glass flow to sinter the particles, but not enough to cause sticking and crystallization problems. With the particular glass and release agents used in this project, it does not appear possible to completely separate the densification process from the sticking and crystallization problems. A balance is required between the required degree of densification and the amount of sticking and crystallization that can be tolerated.

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For More Information

For a copy of the report, *Densification, Crystallization, and Sticking Behavior of Crushed Waste Glass Sintered in Refractory Molds With Release Agents*, or for more information, call the CWC at (206) 443-7746 or visit the or visit the CWC Internet Website at www.cwc.org.

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