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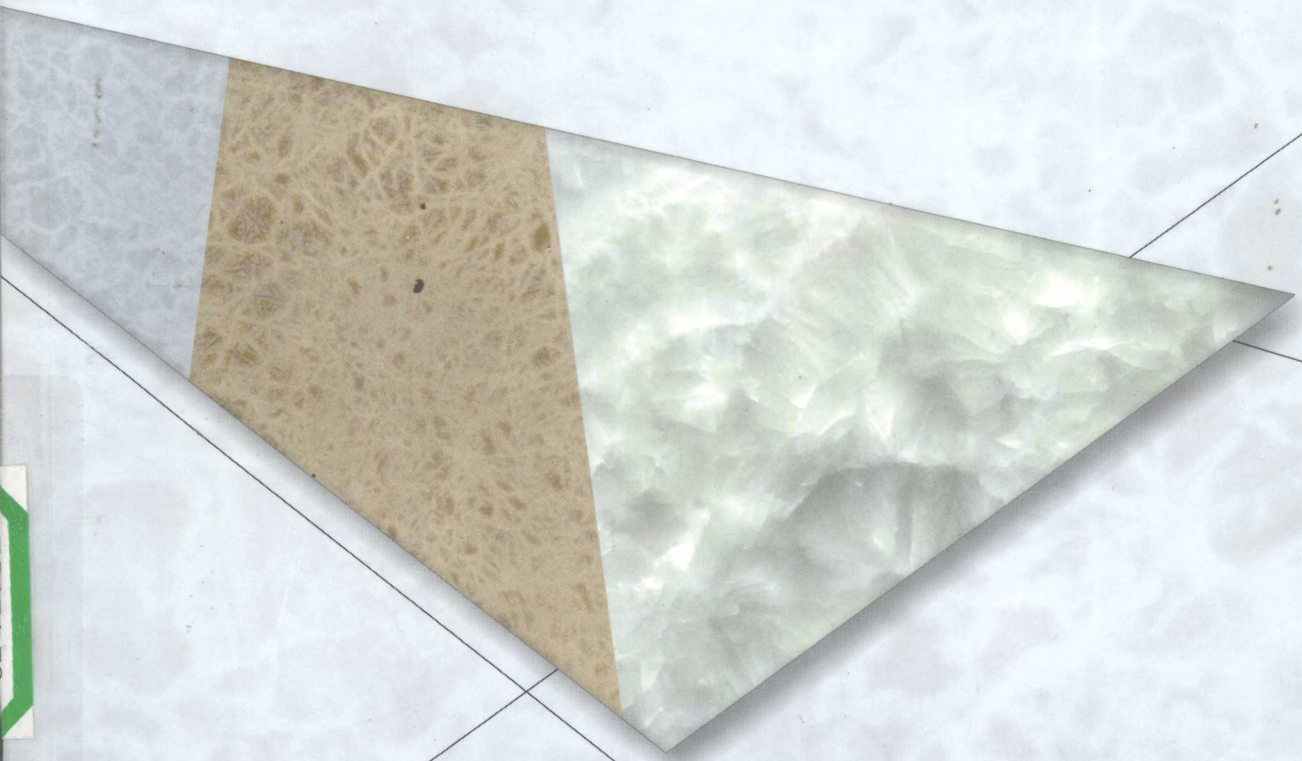
Preparation of Decorative Building Glass-ceramics by Cracked-glass Crystallization Process

周俊 王焰新 著



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# 摘 要

建筑装饰用微晶玻璃是由特定组成的母玻璃在可控条件下进行热处理，在玻璃基质上生成一种或多种晶体，使原来单一、均匀的玻璃相变成了有晶体相和玻璃相交织在一起的多相复合材料。

本书首先对建筑装饰用微晶玻璃的发展、特性、现役制备工艺、以及利用污泥和其它固体废弃物制备建筑装饰用微晶玻璃等方面作了较系统的介绍；再针对现役制备工艺的不足，特别是烧结法容易出现气孔缺陷，压延法产品又没有明显纹理的不足，提出利用裂纹玻璃作为微晶玻璃前躯体，基于 $CaO-Al_2O_3-SiO_2$ 系统母玻璃易表面析晶、裂纹玻璃易从裂纹处优先析晶原理，经烧结、晶化而制备成微晶玻璃产品，并将该工艺命名为“裂纹玻璃晶化法”。该工艺制得的微晶玻璃产品具有与现役烧结法完全不同的类似古生物残骸的不规则树枝状、颗粒状、丝缕状、星状、扇贝状纹理，故将产品命名为“仿生物碎屑微晶玻璃”。

裂纹玻璃晶化法的工艺路线是：配料→混合→玻璃熔制→浇注或压延成型→水淬惊裂→裂纹玻璃板→烧结→晶化→磨抛→仿生物碎屑微晶玻璃成品。其中，最关键的工艺步骤是裂纹玻璃的烧结和晶化。为此，本书设计出两个系列的实验，即烧结实验和晶化实验，同时进行了样品的性能参数测试。主要表征项目包括：DTA 测试各配方母玻璃的析晶趋势；计算机扫描仪记录样品的表观形貌；阿基米德法（悬浮法）和比重瓶法联测样品的密度和气孔率；XRD、SEM 测定样品的晶化度、晶体种类及显微结构；万能材料试验机测定晶化样品的抗折强度；热膨胀仪测定母玻璃和微晶玻璃的热膨胀系数；母玻璃和微晶玻璃的耐化学腐蚀性对比测试。

利用石英砂、长石、石灰石及其它辅助原料，通过配料、熔融后制成裂纹玻璃和玻璃颗粒，再对裂纹玻璃进行系统的烧结实验和晶化实验，目的在于探索裂纹玻璃晶化法的关键工艺参数。同时，将玻璃颗粒与裂纹玻璃进行烧结对比试验，以作为分析和评估裂纹玻璃烧结性的参照对象。

## 一、烧结实验研究

烧结性不同的配方的裂纹玻璃均能实现很好的烧结，尤其是难烧结配方也能烧成表面平整光滑的烧结体，且烧结下限温度低；裂纹玻璃的烧结受初始析晶的影响小，烧结上限温度可以很高，因此，裂纹玻璃的烧结温度范围很宽。在较佳烧结温度区间烧成的裂纹玻璃烧结体的致密度很高，闭口气孔率小于 0.5%；相反，玻璃颗粒的烧结效果受母玻璃料的烧结难易程度和初始析晶的影响很大，烧结温度范围窄，致密度低，最佳烧结温度下的烧结体的闭口气孔率也在 1.0%以上。裂纹玻璃和玻璃颗粒烧结体的闭口气孔率均随烧成温度的升高而增大，但前者的增幅很小，基本稳定在 0.5%附近；而后者的增幅很大，可升至 2.0%以上。裂纹玻璃烧结体的闭口气孔率比玻璃颗粒烧结体低的主要原因在于：①前者的孔隙度远小于后者；②前者的裂纹间隙呈楔形，而后者的颗粒空隙呈堆积型。

此为试读，需要完整PDF请访问：www.ertongbook.com

裂纹玻璃的烧结速度快，烧结性不同的配方均能在较短的时间内实现烧结；在相同的合理烧结温度下，裂纹玻璃的烧结速度比玻璃颗粒快 10～30min，且烧结体致密度更高。裂纹玻璃在烧结温度下转化为牛顿型流体，通过粘滞流动机理实现烧结，用 Frenkel 烧结公式可以解释裂纹玻璃比玻璃颗粒更易烧结的原因，即前者的烧结对象玻璃碎屑的半径可被看作无穷大，远大于玻璃颗粒的半径。

裂纹玻璃烧结的实质是裂纹在表面张力作用下愈合。本书将裂纹分为 3 类：无间隙裂纹、中下层间隙裂纹、表层间隙裂纹。3 类裂纹的烧结均是在表面张力的作用下实现的，但具体作用形式不同，同时也受到了其它辅助作用力：无间隙裂纹是在玻璃受热膨胀和表面张力作用下实现烧结；中下层间隙裂纹主要受玻璃的膨胀软化作用、上层玻璃的软化挤压作用及表面张力而烧结；表层间隙裂纹则借助间隙中的细小玻璃碎屑的桥接作用、先期裂纹愈合面的扩展来实现烧结。不同裂纹形态对闭口气孔的形成贡献不同，无间隙裂纹和表层间隙裂纹均不会生成气孔，而中下层间隙裂纹是裂纹玻璃烧结体中闭口气孔生成的根源，但表层间隙裂纹先行愈合而将中下层气体通道堵塞则是闭口气孔生成的前提。裂纹玻璃烧结体的气孔生成受到烧结时板材上下层温差和落入表层间隙裂纹中的细小玻璃碎屑的桥接作用的严重影响，因为这二者是导致表层间隙裂纹先行愈合的环境条件。

## 二、晶化实验研究

裂纹玻璃的原始裂纹处易于优先非均匀成核，其原因在于：在裂纹玻璃生成过程中，水-热玻璃相互作用有利于在裂纹面（玻璃碎屑表面）生成活性基团和异相物质；同时，裂纹面也会富集和吸附冷淬水和空气中的矿物质及杂质，致使裂纹处具有丰富的成核位和成核能量优势；此外，属于 $CaO-Al_2O_3-SiO_2$ 系的玻璃碎屑本身也具有表面成核趋势。

在晶化热处理时，优先非均成核的玻璃碎屑表面有利于晶体的析出，但由于析晶释放出的凝固潜热、CaO 的消耗、CaO 含量本身低于母玻璃全部晶化所需的化学计量等因素的影响，致使先期析出的晶体向玻璃碎屑内部生长时将遵从枝晶生长机理。

裂纹玻璃晶化法微晶玻璃磨抛光后呈仿生物碎屑纹理，纹理形成的机理在于裂纹玻璃的非均匀成核和析晶。①裂纹玻璃中的玻璃碎屑表面易于核化，先期析晶；而玻璃碎屑内部不能自行成核、析晶，仅能借助表面晶体向其内部的生长而逐渐晶化。该晶化过程因受到晶化时间、凝固潜热和 CaO 消耗的影响，越靠近玻璃碎屑表面，三者的影响越小，晶化度越高；反之，越靠近玻璃碎屑中心，晶化度越低。②玻璃碎屑表面先期析出的晶体沿径向朝玻璃碎屑内部析出主干枝晶时，受到的凝固潜热的影响小，CaO 供应充沛，生长快，析晶量大；而沿周向析出二次及多次枝晶生长将受到主干枝晶释放的凝固潜热和 CaO 消耗的影响，生长较慢，析晶量少。正是由于裂纹玻璃的原始裂纹与玻璃碎屑、玻璃碎屑表层与中部、玻璃碎屑径向和周向等部位的晶化度差异，构成了宏观仿生物碎屑纹理的基础。影响仿生物碎屑纹理的外部因素主要有水淬温度和化学成分，前者影响着裂纹玻璃的原始裂纹量和玻璃碎屑的形态及大小，后者通过影响母玻璃的析晶能力而影响纹理风格。

母玻璃中的 CaO 含量对裂纹玻璃晶化法微晶玻璃的宏观形貌、总析晶量及显微结构影响很大。当 CaO 含量高时，主干、二次及多次枝晶析出趋势均较大，裂纹玻璃可在较短的时间内晶化透，且总析晶量高，微观晶粒密集；当 CaO 含量低时，主干、尤其是二次及多次枝晶难析出，裂纹玻璃难以晶化透，且总析晶量偏低，微观晶粒稀疏。

晶化温度是影响裂纹玻璃晶化状态的主要因素。在由低至高的晶化温度下，裂纹玻璃将依次生成不同组织结构的微晶玻璃，即晶化不透的微晶玻璃，完全晶化的微晶玻璃，过烧的微晶玻璃，其中完全晶化的微晶玻璃是裂纹玻璃晶化法所探求的最佳工艺条件下的产品形态。各类微晶玻璃的生成机理、机械强度及其变化规律如下：

(1)晶化不透的微晶玻璃。当晶化温度偏低时，玻璃粘度高，主干枝晶的生长速率缓慢，难以生长至大玻璃碎屑中央部位，裂纹玻璃整体晶化不透，残留着宏观透明玻璃颗粒。通过热膨胀系数测试显示，宏观透明玻璃区的热膨胀系数大于宏观晶相区，在前者易形成张应力，产生裂纹；分层抗折强度测试结果也证实，宏观透明玻璃颗粒直接导致了微晶玻璃整体抗折强度的偏低。

(2)完全晶化的微晶玻璃。当晶化温度合理时，主干枝晶生长速度快，能使裂纹玻璃在较短的时间内晶化透，而二次及多次枝晶析出也较快，使裂纹玻璃的总析晶量达到适宜水平。完全晶化的微晶玻璃不存在宏观透明玻璃颗粒，而由宏观晶相区和宏观浮浊玻璃区构成，仍为组织结构不均匀体，决定着其抗折强度不会非常高，但测试值仍大于 35MPa，能满足建筑装饰材料的强度要求。

完全晶化的微晶玻璃在不同方向上存在着晶化度差异。垂直方向上，表层晶化度高于中部；水平方向上，宏观晶相区的晶化度高，而宏观乳浊玻璃区的晶化度低，前者对后者呈包围态势，且前者的含量比率高于后者。热膨胀系数证实，晶化度越高，热膨胀系数越低。对完全晶化的微晶玻璃的分层抗折强度测试也显示，切削厚度达 2mm 及以上时，将导致抗折强度的急剧下降。这些结果表明，晶化度高的表层和宏观晶相区受到压应力，为微晶玻璃整体的机械强度的主要贡献者，有利于确保抗折强度达到较高值，最佳工艺条件下稳定在 40MPa 以上。

完全晶化的微晶玻璃的闭口气孔率小于 1%，切削抛光板表面仅显示出微小针孔，未见 1mm 以上大气孔，表明裂纹玻璃晶化法产品的气孔缺陷低，符合建筑装饰用微晶玻璃优等品的气孔缺陷要求。

完全晶化的微晶玻璃的耐水性和耐碱性均很好，且耐碱性略优于相应的母玻璃；但耐酸性较差，较佳工艺条件下的耐酸性仅能低至 0.2%，其主要原因在于：①硅灰石晶体本身的耐酸性不强；②样品的组织结构为不均匀体，宏观晶相区过度集中、晶体密集、残余玻璃相少，受耐酸性好的残余玻璃相的掩护作用小，在酸侵蚀下易整体脱落。

(3)过烧的微晶玻璃。当晶化温度偏高时，玻璃粘度很低，主干枝晶的生长速率快，能使裂纹玻璃晶化透；但二次及多次枝晶受凝固潜热影响大，析出速率和析晶量远低于主干枝晶，加之晶体的二次熔解趋势增大，致使裂纹玻璃的整体析晶量不足，残余玻璃相过高，发生过烧现象。残余玻璃相中微裂纹的扩展及脆性断裂将占主导地位，因此降低了微晶玻璃的整体抗折强度。

在完成裂纹玻璃晶化法系统研究基础上，改用污泥作为主要原料，经重新调整配方后，进行了污泥微晶玻璃的制备和性能表征实验，尤其增加了毒性特征浸出实验(TCLP)，以评估微晶玻璃对污泥重金属的固化效果。

以污泥作为主要原料制备的裂纹玻璃的烧结性优于相应的玻璃颗粒，烧结温度更低，在 800℃就能实现烧结；致密度更高，较佳条件下的闭口气孔率小于 0.3%，表明以裂纹玻璃作为微晶玻璃的前躯体进行热处理，可以克服污泥杂质对烧结性的影响。

在较佳晶化温度下制备的污泥微晶玻璃的致密度高，闭口气孔率稳定在 0.35%附近，磨

抛样品表面也未见大于 1mm 的气孔，产品表观质量好；抗折强度大于 35MPa，符合建筑板材的要求；污泥微晶玻璃的耐水性和耐碱性好，但耐酸性很差。耐酸性差的原因并不在于晶相，而在于残余玻璃相的耐酸性很差，这可能是由于母玻璃中的碱金属离子($Na^+$)和网络中间体($Al_2O_3$、$B_2O_3$)含量过高所致；毒性特征浸出实验(TCLP)测试结果显示，污泥微晶玻璃的重金属浸出量极低，表明污泥经微晶玻璃方式而被资源化利用后可有效固化重金属离子，消除其对环境的二次污染。

纵观本书有关裂纹玻璃晶化法的烧结和晶化系统试验研究及样品性能测试结果分析，可以认为，裂纹玻璃晶化法能够制备出具有仿生物碎屑纹理、闭口气孔率低、表观气孔缺陷少、各项性能指标能满足建材质量要求的建筑装饰用微晶玻璃；该工艺还能适应成分多变且含有杂质的固体废物特性特征，利用该工艺可将污泥等固体废物制备成微晶玻璃产品而得到资源化利用。

**关键词**：裂纹玻璃晶化法；裂纹玻璃；微晶玻璃；烧结；晶化；建筑装饰材料

# ABSTRACT

Glass-ceramics used as decorative building materials are prepared by heat-treating parent glass with specific composition to deposit crystals under controlled conditions, which are jointly composed of single or multiple crystals and residual glass so as to be referred to as composite materials.

In this book, the development, characteristics and fabrication technology of decorative glass-ceramics are systematically reviewed; subsequently, the use of sewage sludge and other solid wastes for production of glass-ceramics is also overviewed. Finding out the shortage of conventional technologies preparing glass-ceramics, especially gas pore defects of glass grain sintering technology and non-textures for the products of rolling technology, the authors proposed a new process, in which cracked glass is used as a precursor and sintered and crystallized for glass-ceramics; accordingly, the process is named for short as QICGC process, i. e. a process of preparing glass-ceramics by crystallization of the glass with cracks induced by water-quenching (abbr. cracked glass). The glass-ceramics prepared by the QICGC process show specific appearance with dendritic, granular, silk-like, stellate and shell-like textures so as to be called as pseudo-bioclastic glass-ceramics.

QICGC process flowchart is as follows: mix-design and weighing → blending → melting parent glass→ forming by cast or rolling → water quenching → cracked glass → sintering → crystallizing → polishing → pseudo-bioclastic glass-ceramics. The key procedures of QICGC process are sintering and crystallizing of cracked glass. Therefore, two series of experiments, i. e. sintering experiments and crystallizing experiments, were designed and carried out, and, at the same time, the properties of corresponding samples were tested or characterized, using differential thermal analyzer for probing crystallization tendency of the parent glass of all batches, computer scanner for recording the appearances of the samples, Archimedes method (suspension method) and pycnometer method jointly for measuring densities and porosities, X-ray diffractometer and scanning electron microscope for determining crystal composition, type and micro-structure of crystallized samples, universal testing machine for measuring three-point bending strength, thermo-mechanical analyzer for testing coefficient of thermal expansion, and chemical resistance tests of parent glass and glass-ceramics.

After the cracked glass is prepared using quartz, feldspar, limestone and other additives by mix-designing, blending, melting and water-quenching, systematic sintering experiments and crystallizing experiments were carried out respectively, in order to determine the key parameters of QICGC process. At the same time, glass grains, prepared by the same method of

cracked glass, were sintered as a parallel and contrast experiment of cracked glass sintering. Results of sintering and crystallization of cracked glass of two series of experiments are as follows.

## 1. Sintering experiments

Cracked glass of the batches with different sintering abilities, especially of difficult sintering batches, can be well sintered at the relatively low temperature. On the other hand, when sintering temperatures are high, the sintering quality of cracked glass is only slightly influenced by the initial crystallization, and phenomena of sintering quality worsening don't occur. Accordingly, it is obvious that the QICGC process enjoys a wide range of sintering temperature. Compactness of sintered bodies of cracked glass fired in the optimal sintering temperature interval is high, and their closed porosities are smaller than 0.5%. On the contrary, the sintering state of glass grains is severely influenced by sintering ability of batches and initial crystallization, so that sintering temperature range becomes narrow and the compactness of the sintered bodies is low. As a result, the closed porosities of sintered bodies at the optimal temperature are over 1.0%. The closed porosities of sintered bodies of cracked glass and glass grains increase with heat-treatment temperature, however, the increase extent of the former is low, holding at about 0.5%, while that of the latter is very high, up to 2.0%. The reasons of the compactness of sintered bodies of cracked glass being greater than that of glass grains ones can be attributed to: ①The original porosity of the cracked glass is far less than the glass grain before sintering; ② The shape of the crack gap in cracked glass is wedge-like, and that of glass grains is inter-particle porous.

Sintering of cracked glass is quick so that the sintering procedure of the cracked glass of different batches can finish in a short time. The sintering rate of cracked glass is 10～30min quicker than that of glass grains at the same proper temperatures, and the compactness of the former is higher than that of the latter. In the sintering temperature interval, cracked glass transforms into Newton fluid and accomplishes sintering. According to Frenkel formula, the fact of cracked glass sintered more easily than glass grains can be attributed to the difference of the radius of the objects heat-treated, i. e. the radius of the former infinitely bigger than that of the latter.

The sintering of cracked glass is essentially accomplished in the action of surface tension. In this book, cracks in the cracked glass are divided into three kinds: non-gap cracks, gap cracks in middle-layer and bottom-layer, and gap cracks in surface layer. Three kinds of cracks are all sintered as a result of different model of surface tension and other associated actions: non-gap cracks are healed under glass thermo-expansion and surface tension; gap cracks in middle-layer and bottom-layer are sintered under the synergetic effect of glass thermo-expansion, compressive effect loaded by surface layer glass and surface tension; gap cracks in surface-layer are sintered under bridging act of small glass debris and extension of front edges of cracks healed previously. Three kinds of cracks have different contribution to

the formation of closed gas pores: no gas pores will be formed in non-gap cracks and gap cracks in surface layer; gap cracks in middle-layer and bottom-layer are the origin of closed gas pores; it is the premise of forming closed gas pores that gap cracks in surface-layer before hand healed before the gap cracks in middle-layer and bottom-layer being fully healed. The formation of closed gas pores is severely influenced by the temperature difference and the bridging act of the small glass debris fell into surface gap crack, both being environment conditions for gap cracks in surface-layer before hand healed.

## 2. Crystallizing experiments

The cracks of cracked glass are favorable for heterogeneous nucleation. The reason is that, during the fabrication of cracked glass using water quenching, water-glass thermal interaction is to produce active radicals and hetero-matters at the surface of the glass debris constituting cracked glass, and mineral impurities of water and dusts of air could also be absorbed at the surface of the glass debris. The active radicals, hetero-matters, mineral impurities and dusts can act as the nucleating positions of cracked glass and lower the nucleation energy; in addition, glass debris pertaining to parent glass of $CaO-Al_2O_3-SiO_2$ family has a tendency of surface nucleation by itself.

During crystallizing, the crystal will in advance deposit at the surface of the glass debris of cracked glass owing to the surface preferentially nucleating; but under the synergestic effects of the latent heat released by crystallization, expense of CaO, and CaO content lower than the stoichiometric amount needed for complete crystallization of parent glass, the mechanism of dendritic crystal growth works when the crystals preferentially deposited grow continually to the interior of the glass debris.

Glass-ceramics prepared by the QICGC process exhibits an appearance of pseudo-bioclastic texture. The mechanism forming the texture is attributed to heterogeneous nucleation and crystallization. The reasons are as follows: ①The surface of glass debris of cracked glass can easily nucleate and crystallize, but the interior of it can't do so by itself and can only deposit crystals depending on surface crystal developing toward it. The course of the crystal deposition is influenced by the crystallizing time, latent heat and CaO expense. The surface layer of glass debris is crystallized strongly due to the small effects of the three factors, while the center of it weakly due to the great effects. ②When the surface crystals develop primary trunk crystals toward interior of glass debris along the radial orientation of glass debris, the effects of latent heat and CaO expense are so small that primary trunk crystals can develop quickly and the crystallinity is high. On the contrary, when secondary and continually derivative trunk crystals deposit along the circumferential orientation, those effects become so strong that they grow slowly and the crystallinity is low. The differences in the crystallinity between primitive cracks and glass debris, surface and interior of glass debris, radial and circumferential orientation of glass debris, turn into the base of the pseudo-bioclastic texture. External factors influencing the pseudo-bioclastic texture are temperature of water-quenching

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and composition of parent glass, the former determining the crack amount of cracked glass and the morphology and size of glass debris, and the latter affecting the texture fashion by controlling the crystallizability of parent glass.

CaO content of parent glass has large impact on the macro appearance, total crystallinity and micro structure of the glass-ceramics prepared by the QICGC process, because deposition potential of primary, secondary and continually derivative trunk crystals is enhanced with the increase of CaO content. When CaO content is high, cracked glass can be fully crystallized, so that total crystallinity is high and crystal grains are dense; On the contrary, when CaO content is low, primary, especially secondary and continually derivative trunk crystals are difficult to deposit, cracked glass can't be fully crystallized, with low total crystallinity and rare crystal grains.

Crystallization temperature is a main factor influencing crystallizing progress. When crystallization temperature rises from low to high, glass-ceramics with different structures prepared by the QICGC process are generated in succession: partially-crystallized glass-ceramics, fully-crystallized glass-ceramics, and over-fired glass-ceramics. Obviously, preparing fully-crystallized glass-ceramics is the aim of the research on the QICGC process. The formation mechanism, mechanical strength and its change pattern on three sorts of glass-ceramics are as follows.

(1) Partially-crystallized glass-ceramics. While crystallization temperature is on the low side, the viscosity of parent glass is so high that primary trunk crystals are difficult to grow into the center of big glass debris, to result in cracked glass only partially crystallized and macroscopically transparent glass remaining in the glass-ceramics eventually prepared. The result of the test measuring coefficient of thermal expansion shows that coefficient of thermal expansion of macroscopically transparent glass phase is bigger than that of macroscopical crystal phase; accordingly, the tensile stress may form and micro-cracks may generate in the transparent glass phase. And the results of measuring the bending strength of the remainder part of glass-ceramics cut with different thickness indicate also that the transparent glass phase can directly induce the decrease of bending strengths.

(2) Fully-crystallized glass-ceramics. While crystallization temperature is in the proper temperature interval, viscosity of parent glass drops down to medium value, so that primary trunk crystals can easily grow into the center of glass debris, and secondary and continually derivative trunk crystals can also propagate relatively quickly, leading to the total crystallinization of cracked glass to a reasonable degree and final conversion into fully-crystallized glass-ceramics. Though fully-crystallized glass-ceramics don't contain the macroscopically transparent glass phase, they are composed of macroscopic crystal phase and macroscopically opalescent glass phase, and therefore their bending strengths can't reach a very high level. However, more than 35MPa of their bending strength can meet the Chinese standard on the construction and decoration materials.

The crystallinity is different in the different directions of the fully-crystallized glass-ce-

ramic. In the perpendicular direction, the surface crystallinity is greater than that of the interior of the glass-ceramic; in the horizontal direction, the crystallinity of the macroscopic crystal phase is greater than that of macroscopically opalescent glass phase, and the former phase encompasses the latter and the proportion of the former higher than the latter. The result of measuring thermal expansion coefficient shows that the higher crystallinity, the lower coefficient; meanwhile, relationship between bending strength and cut thickness of glass-ceramics reveals that the strength will decrease when the cut thickness exceeds 2mm. Consequently, it is concluded that the surface and macroscopical crystal phase with high crystallinity are compressive stress regions, hereby are the contributors of the mechanical strength to insure the bending strength up to relatively high values. For the samples prepared in the optimal heat-treatment temperature regime, the bending strengths are over 40MPa.

The closed porosity of fully-crystallized glass-ceramics is less than 1%, and the surfaces of the samples cut and polished only display small pinholes and don't show gas pores more than 1mm. It is indicated that the gas pore defect of the glass-ceramics prepared by the QICGC process is low and the product quality can satisfactorily meet the requirements of the relevant Chinese standard.

The water resistance and alkali resistance of fully-crystallized glass-ceramics are excellent, the former being slightly inferior to and the latter slightly superior to that of corresponding parent glass. But acid resistance is poor, and as low as 0.2% of acid resistance can be obtained only under optimal technological condition. The reasons of the poor acid resistance are: ①The main crystal wollastonite in the glass-ceramics is poor to resist acid corrosion; ②The structure of the glass-ceramic is very uneven, because the macroscopical crystal phase aggregates excessively, which leads to dense druses and scarce residual glass phase. When corroded by acid, the crystal aggregations are easy to disintegrate integrally without the protection of residual glass phase.

(3) Over-fired glass-ceramics. While crystallization temperature is high, viscosity of parent glass is so low that primary trunk crystals can grow quickly into the center of glass debris, resulting in complete crystallization of cracked glass. However, affected seriously by the latent heat released in the growth course of primary trunk crystals, the secondary and continually derivative trunk crystals can propagate slowly, and their amount is far less than primary trunk crystals. Moreover, the trend that all crystals are molten again becomes great. The factors mentioned above lead to a deficiency in total crystallinity of glass-ceramics and a very high content of residual glass, so that over-firing phenomenon arises. Owing to the easiness of micro-crack expanding and brittle rupturing in the residual glass phase, bending strength of over-fired glass-ceramics is at a low level.

In this book, on the basis of the systematic research for QICGC process, using sewage sludge as a main material and again adjusting the batches optimized on the base research of QICGC process, the experiments of preparing sewage sludge glass-ceramics and charactering the properties of the samples were subsequently carried out. Toxicity characteristic leaching

procedure (TCLP) experiments were then made to evaluate the effect of solidifying heavy metal ions of the sewage sludge into glass-ceramic products.

Sintering characteristic of cracked glass prepared from sewage sludge as a main material is superior to the corresponding glass grains. For example, effectively sintering temperature of the former is lower than that of the latter, accomplishing the sintering at 800℃, and compactness of the sintered bodies of the former, with less than 0.3% of closed porosity, is lower than that of the latter. Moreover, the results also indicate that the problem of the impact of the impurities from sewage sludge on glass grains sintering, can be solved when using the cracked glass as the precursor of glass-ceramics.

The characteristics of the sewage sludge glass-ceramics prepared at the optimal temperature are as follows: the compactness is high and the closed porosity around 0.35%; surface quality is excellent and no gas pores bigger than 1mm can be observed; bending strength is more than 35MPa to meet the quality requirement of decorative materials; water resistance and alkali resistance are outstanding, but acid resistance is poor which doesn't attribute to the crystal phase but to the residual glass phase that is poor to resist the acid corrosion due to very high contents of alkali metal and net modifying oxides in the residual glass phase; the heavy metals in the sewage sludge glass-ceramics are hardly leached in the TCLP test, which indicates that the heavy metal from the sewage sludge can be solidified so effectively that the secondary environmental pollution of sewage sludge can be avoided when it is fabricated into glass-ceramics.

According to the systematic sintering and crystallizing experiments on the QICGC process as well as the results of characterizing properties of samples, it can be concluded that the glass-ceramics used as decorative building materials with pseudo-bioclastic textures, low closed gas porosities and no gas pore defects can be prepared by QICGC process. This process can also adapt to the composition feature of sewage sludge with a lot of impurities, and sewage sludge can be manufactured into glass-ceramics as a cost-effective way of waste recycling.

**Key Words**: Cracked glass; Glass-ceramic; Sintering; Crystallization; Decorative building materials

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