Fragility Overcome

Using controlled crystallization, a team from the city of São Carlos develops glass-ceramics for telescopes, computers and ear bones

Yuri Vasconcelos

A group of researchers at the Federal University of São Carlos (UFSCar) has been studying and developing new glass materials for 35 years, including glass-ceramics that can be used to manufacture products as diverse as mirrors for gigantic telescopes, substrates for laptop hard drives, artificial bones and teeth, luxury flooring imitating rare stones, transparent pans resistant to thermal shock, and plates for modern electric stoves. The group is led by the materials engineer Edgar Dutra Zanotto, coordinator of the Vitreous Materials Laboratory (LaMaV) in the Materials Engineering Department.

One of the products created by the team, a bio-glass-ceramic for manufacturing small human bones—such as the malleus, the stapes and the incus in the ear—are already being evaluated in clinical tests in humans. This work was carried out together with the University of Florida. In the late 1990s, a patent was licensed to the US company American Biomaterials. "In the patent process, due to our naiveté, we were identified only as the inventors of the product and not the owners—the holders of the rights to the patent," laments Zanotto. "We had a key role in the innovation, but never received a penny in royalties. We learned a valuable lesson, and now we take care to avoid repeating that mistake."

Another biocompatible material created at LaMaV was biosilicate, a bioactive glass-ceramic consisting of silicon,

Thick stained-glass windows in churches show that glass cannot flow at ambient temperature

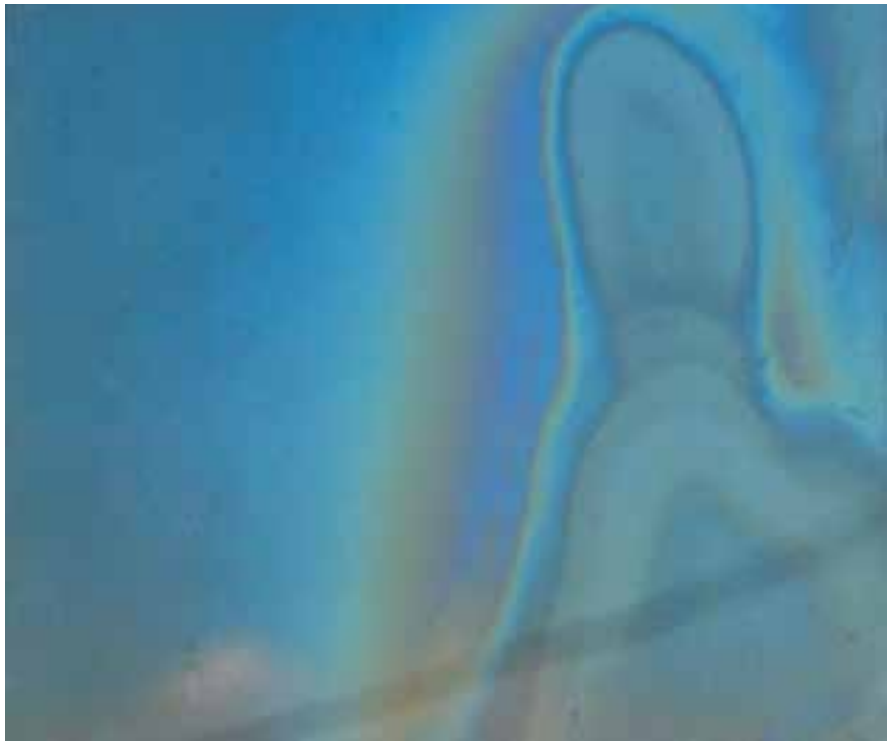
GLOW IMAGES

sodium, potassium, calcium and phosphorus. Produced in powder form, it is used in dental treatment. When bound to dental enamel, it cures dentin hypersensitivity. The product is already sold in small quantities for experimental tests by research groups and is awaiting a green light from the National Health Monitoring Agency (Anvisa) for large-scale marketing. A patent filed in 2003 was recently approved by the Brazilian Industrial Property Institute (INPI). Studies for the development of biosilicate received funding from the FAPESP Innovative Research in Small Businesses (Pipe) and Intellectual Property Support programs.

The UFSCar researchers have also made scaffold glass-ceramics—a sponge-like, bioactive material, which can be used as a base for the growth of bone cells—and a new material for producing plates for electric stoves to replace traditional gas burners. UFSCar filed two patents related to these developments in 2010 and 2011, respectively. According to Zanotto, two companies have already shown an interest in manufacturing the stove plates.

PARTNERSHIPS WITH INDUSTRY

The laboratory works closely with a network of collaborators abroad and with the private sector, carrying out basic and applied research and creating new glass materials. In the last three and a half decades, a few dozen projects have been undertaken in conjunction with more than 40 companies, among them Italian tire manufacturer Pirelli, American aluminum multinational Alcoa, Brazilian glass manufacturer Nadir Figueiredo, French multinational Saint-Gobain, also in the



The mystery of the saint, now resolved: human form in a window in the city of Ferraz de Vasconcelos, São Paulo

A new material, biosilicate, is already being produced in small quantities for tests

glass industry, Companhia Baiana de Pesquisas Minerais (CBPM), American company OptiGrate, in the photonics sector, and Brazilian steelmaker Usiminas. With the latter, the team developed a glass-ceramic to be used as flooring, wall covering or in interior design. It is produced from steel slag, a byproduct of the metallurgical industry with a high silica and metal oxide content.

The work, which began around the year 2000, was carried out in partnership with the Usiminas Research and Development Center, located in Ipatinga, Minas Gerais. At that time, the company generated about 125,000 metric tons of blast furnace and mill slag per month, a waste of serious environmental concern. "The production of steel slag glass-ceramics could potentially rid the environment of these byproducts, and at the same time replace natural rocks and other raw materials," says Zanotto. Thanks to the INPI's recent granting of the patent and good results, Usiminas plans to build a pilot plant to manufacture glass-ceramics. Technical and economic feasibility studies are being performed to this end.

AN ACCIDENTAL DISCOVERY

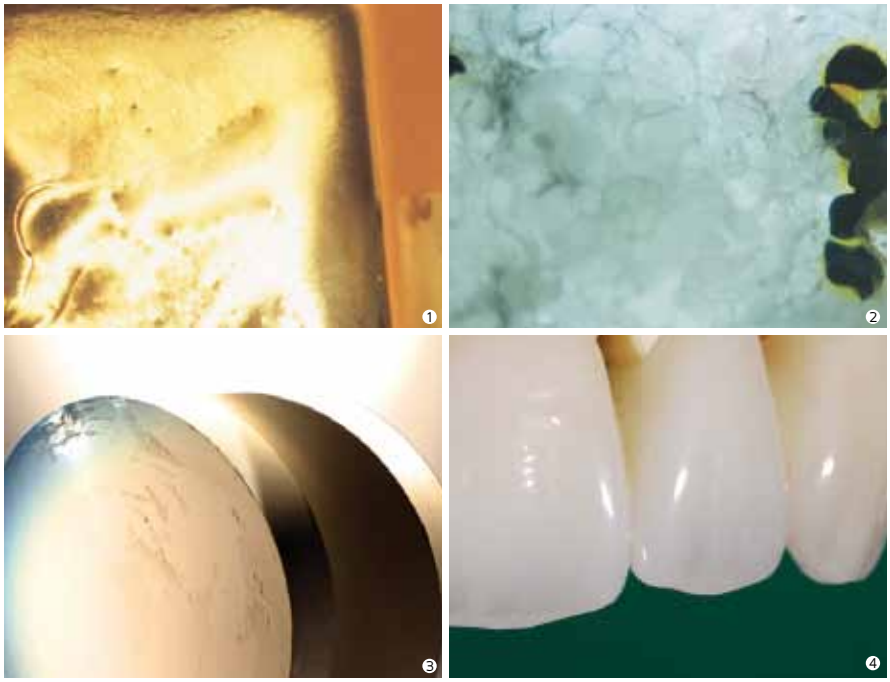
Glass-ceramics are sophisticated polycrystalline materials that originate from glass and always contain a vitreous phase, with content varying from 1% to 99%. Discovered accidentally at the American company Corning Glass and first synthesized in 1953, glass-ceramic materials are produced from the controlled crystallization of vitreous materials, a phenomenon which occurs when glass containing a dissolved nucleating agent, such as titanium oxide, zirconium oxide, phosphorus oxide or silver is subjected to high temperatures, between 500 and 1000 degrees Celsius. As a result of this process, the glass partially crystallizes and becomes a new material, with different characteristics.

"Glass-ceramics are smooth and much more resistant than glass. Furthermore, they can be produced with low or high electrical conductivity, a thermal expansion coefficient close to zero—equal to that of metal—high chemical durability and zero porosity," explains Zanotto**.** According to the researcher, due to these properties, glass ceramics can be used, for example, as electrical insulators, a characteristic needed for substrates of computer hard drives, and may be used in situations where expansion of the material is undesirable because it would cause damage to the equipment, as in telescopes or stove plates. The first scientific paper on glass-ceramics was published in 1957. To date, the Scopus database contains records for about 10,900 scientific and technological articles in the area and Free Patents Online lists more than 5000 related patents.

NOTRE-DAME'S STAINED-GLASS WINDOWS

In addition to the development of new glass-ceramics, LaMaV is responsible for important contributions to basic research, particularly in studies related to nucleation and crystal growth in glass and the physical-chemical properties of glass. "Our research made significant contributions to understanding the processes that control nucleation and crystal growth in many different types of glass. In the scientific field, we described kinetic processes and we tested, improved and developed various theoretical models," says Zanotto. Examples of the contributions in this area were two articles published by Zanotto, in 1998 and 1999, in the *American Journal of Physics*, the first one also reported in *Science*, dismantling the myth that medieval churches such as Notre-Dame, in Paris, were proof that glass can flow at room temperature because their stained glass is thicker at the bottom than at the top. The researcher does not dispute that glass is a viscous liquid, but he demonstrated that flow to the extent necessary to achieve the thickness seen in the churches would take millions and millions of years. Based on the analysis of the composition of 350 medieval stained-glass windows, he concluded that the observed differences in thickness were actually due to glass manufacturing defects.

MIGUEL BOYAYAN



The four faces of new materials: 1. glass-ceramic made from steel slag turns waste into luxury material 2. imitation marble material creates luxury floors and wall coverings 3. bioactive ceramic revolutionizes surgical implant systems 4. artificial teeth boost oral aesthetics

An innovation that is beginning to take shape: glass-ceramics made of steel slag

The work done by Zanotto and his group—which also includes professors Ana Cândida Rodrigues and Oscar Peitl—began in 1977 with the researcher's master's thesis at the São Carlos Institute of Physics (IFSC-USP), and continued with his doctoral studies, conducted at the University of Sheffield, in the UK. Thirty-five years later, the laboratory, with an area of 800 square meters and outfitted with modern equipment, has been the source of 200 scientific papers published in journals, 12 patents filed and 60 masters and PhD student theses—another 15 are in process. Over the years, the laboratory's research has been supported by various funding agencies, such as FAPESP, the National Council on Scientific and Technological Development (CNPq) and the Coordinating Agency for the Improvement of Higher Education Personnel (Capes). Zanotto coordinated two thematic projects, *Current problems in glass crystallization*, now finished, and *Kinetic processes in glass and glass-ceramics*, which is ongoing.

GLASS CRYSTALS

The LaMaV operates in a network of 30 institutions, including 20 overseas, and is at the same level as laboratories at the universities of Nagaoka, Japan, Missouri, USA, Jena, Germany, and private research institutes at Nippon Electric Glass, also in Japan, Corning Glass, in the United States, and Schott Glass, in Germany. The network of international collaborators brings together scientists from France, Spain, Portugal, Germany, Bulgaria, the Czech Republic, the United Kingdom, the United States, Russia, Colombia and Argentina, among others. At the start of this year, to commemorate the laboratory's 35 years of activity, Zanotto published the book *Cristais em vidro – Ciência e arte* [Glass Crystals - Science and Art], which features a collection of scientific and artistic photomicrographs of glassy materials generated during this period—in total, the collection has more than 40,000 images.■

PHOTOS 1, 2 AND 3. VLAD FOKIN/LAMAV/UFSCAR. PHOTO 4 ® THAYER DENTAL LABORATORY, INC

PROJECTS

1. *Current problems in crystallization of glass* – No. 1999/00871-2 (1999-2004)
2. *Kinetic processes in glass and glass-ceramics* – No. 2007/08179-9 (2008-2012)

GRANT MECHANISM
1. and 2. Thematic project

COORDINATOR
1. and 2. Edgar Dutra Zanotto (UFSCar)

INVESTMENT
1. R$935,421.42
2. R$1,772,804.02

SCIENTIFIC ARTICLES

1. PEITL, O. *et al.* Compositional and microstructural design of highly bioactive P2O5-Na2O-CaO-SiO2 glass-ceramics. **Acta Biomaterialia**. v. 8, n. 1, p. 321-32, 2012.
2. Nascimento, M. L. F. *et al.* Dynamic processes in a silicate liquid from above melting to below the glass transition. **Journal of Chemical Physics**. v. 135, p. 1-18, 2011.
3. Zanotto, E. D. A bright future for glass-ceramics. **American Ceramic Society Bulletin**. v. 89, n. 8, p. 19-27, 2010.

FROM OUR ARCHIVES

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Issue No. 191 – January 2012

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Issue No. 178 – December 2010

Mystery Revealed
Issue No. 79 – September 2002

The saint in the window – Yet another myth of glass
Issue No. 79 – September 2002

Much More Than Simple Glass
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