Heating Microscopy and its Applications

Chiara Venturelli
Expert System Solutions, Viale Virgilio 58/L, 41123 Modena, Italy
c.venturelli@expertsystemsolutions.it

Introduction

Heating microscopes were commercially introduced 60 years ago, and they immediately gained an important role in material science and engineering thanks to their wide field of application [1]. Nowadays, these instruments are used in both industry and research in many sectors: traditional and advanced ceramic industries, the glass industry, power plants, the metallurgical sector, and, generally, in all fields where the melting behavior of materials has to be determined. Heating microscopy techniques can be successfully applied to the direct characterization of glazes, glasses, frits, ashes, mold powders for continuous casting, coals, slags, etc.—during a heat treatment.

A full understanding of the physical–chemical behaviors of these materials is often out of reach because of their complexity. To cite an example, a ceramic glaze may contain more than 20 chemical elements. This makes it almost impossible to obtain meaningful results *ab initio*, that is, beginning from the fundamental properties of the single components forming the material, especially when new phases develop during the process. Experimental methods prove to be most effective for the study of the behavior of these materials during firing, allowing a good comprehension of behavior in an actual industrial firing cycle, thanks to direct observation of the sample.

When heating microscopes first appeared, manual analysis was extremely laborious and was often limited to recording the "softening temperature," and, in any case, they gave very subjective measurements. Furthermore, with the old manual heating microscopes it was not possible to reach high heating rates. The new generation models are completely automatic and can simulate industrial heat treatments up to 1600°C, with heating rates as high as 80°C/min or even "flash" heating. "Flash" or instantaneous heating means that the kiln is always kept at the desired temperature and, thanks to a motorized slit, in a few seconds the kiln moves over the sample, which is at room temperature.

Methods

The Heating Microscope Misura® HSM produced by Expert System Solutions (see Figure 1a) consists of three principal units mounted on an optical bench: a halogen lamp light source, an electric furnace (100 mm in length and 20 mm in diameter) with sample carriage, and an observation unit with microscope and recording facility. The sample is placed on a small alumina plate at the end of a thermocouple. Figure 1b represents a sample inside the kiln during a test. The microscope projects the image of the sample situated in the furnace at ~5× magnification through a quartz window and onto the recording camera [2]. This instrument is able to acquire images of a specimen subjected to a heating cycle, at predetermined time or temperature intervals, while all the dimensional parameters (height, length, etc.) are measured automatically during the test, in order to identify and measure certain characteristic parameters of the material.

The system software automatically analyzes the sample images acquired during the test. Thanks to calculations using geometric parameters based on the shape of the test piece (height, width, contact angle), it is able to determine the characteristic points of the material. All such data are available in graphic form immediately after the test.

The most important features of this analytical technique are the capacity to follow the behavior of materials at the same temperature gradient, as well as in the industrial kiln, without entering and having to contact the sample. The use of small samples allows very high heating rates and ensures a homogeneous heating of the specimen.

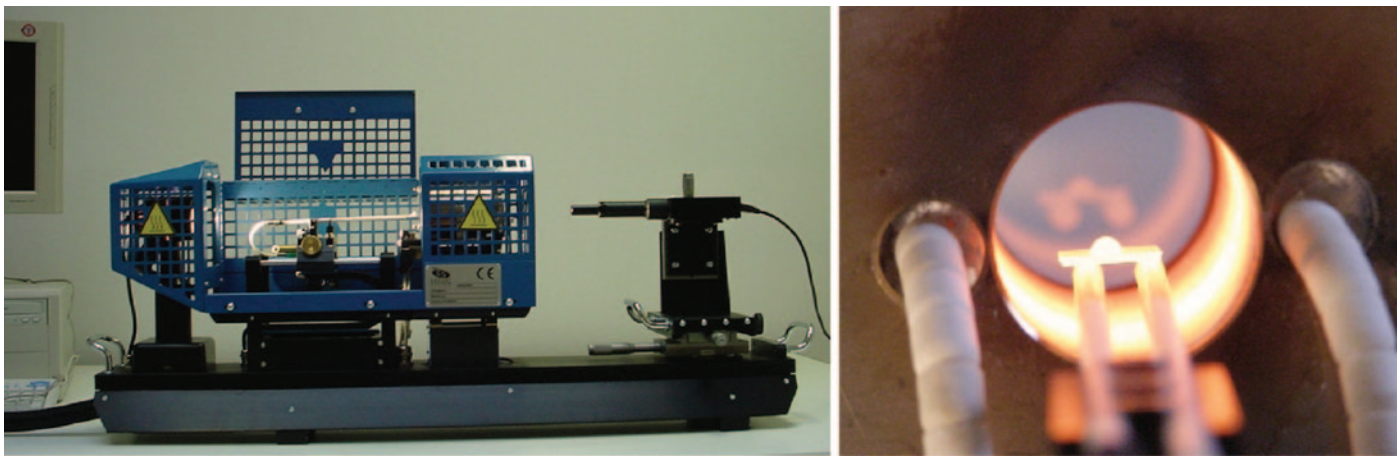
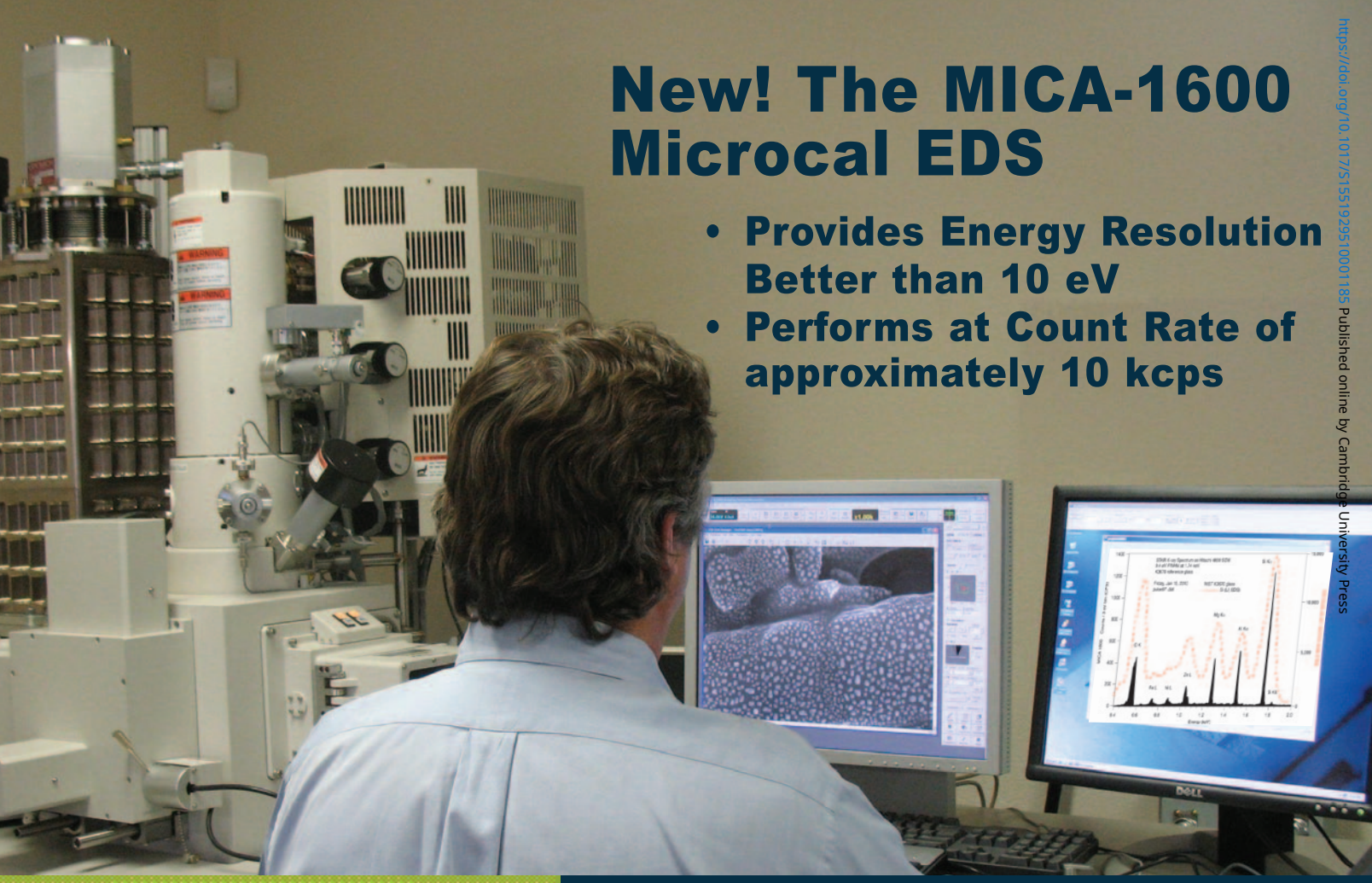


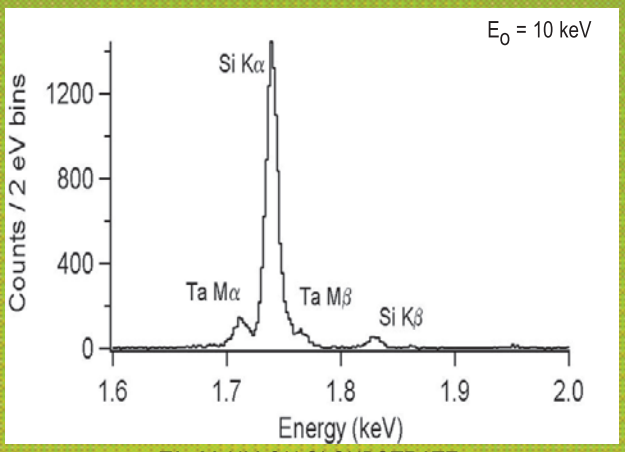
Figure 1: (a) The heating microscope Misura® HSM, and (b) the sample inside the furnace.

New! The MICA-1600 Microcal EDS

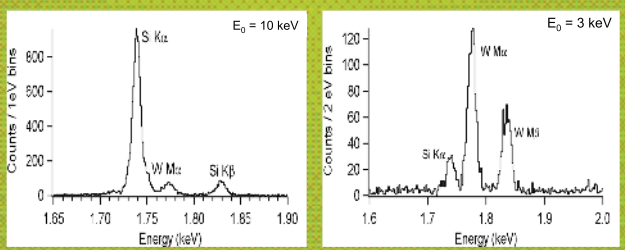
- **Provides Energy Resolution Better than 10 eV**
- **Performs at Count Rate of approximately 10 kcps**



NANOSCALE MATERIAL ANALYSIS SERIES



TA, 20 NM ON SI SUBSTRATE



W, 20 NM ON SI SUBSTRATE

SEND US YOUR SAMPLES.
TRY OUR NEW **MICA-1600** DATA SERVICE WHERE WE TAKE YOUR SAMPLES, PROCESS IT AND GET YOU THE DATA YOU NEED...**FAST!**
CALL **408-722-8478** FOR DETAILS.

Next Generation EDS Combines Conventional EDS with WDS Resolution

The new MICA-1600 X-Ray Spectrometer from STAR Cryoelectronics is a next-generation EDS that combines conventional EDS with WDS resolution into a single instrument to provide the high resolution, throughput, uptime and ease-of-use required for materials characterization and analysis. Its unique microcalorimeter easily resolves line overlaps, detects light elements and characterizes the thinnest, smallest features at very low beam voltages.

•ENERGY RESOLUTION BETTER THAN 10 EV FWHM AT 1.7 KEV

•COUNT RATE OF APPROXIMATELY 10 KCPS

•A large sensing area of up to **4mm^2**

•Works to within approximately **45 mm** of the sample

•Operates with a 0.1 K refrigerator that only consumes clean electricity

•Absolutely no liquid cryogens are used

For more information, contact Hideo Naito, Marketing Director, STAR Cryoelectronics today at 408-722-8478 or microcal@starcryo.com

25-A Bisbee Court, Santa Fe, NM 87508 Tel 505.424.6454 Fax 505.424.8225 info@starcryo.com www.starcryo.com

STAR Cryoelectronics

Results

Analysis of fuel ash samples according to DIN 51730. The definition of characteristic parameters identifiable with the heating microscope is contained in the German rule DIN 51730, referring to a specific ash fusibility test of fuel. This test is important in power plants because the maximum temperature of the combustion chamber must be regulated to be always lower than the softening temperature of ash. If the temperature is too high, ash will start to melt and stick on the walls of the chamber, damaging the burner. This rule was published for the first time in 1954, and it is widely used [1]. The specified specimen shapes are: cylinder 3 mm high and 3 mm in diameter; cube with an edge length of 3 mm, or truncated cone. Equivalent American rules ASTM D 1857 and the International Standard ISO 540 are additional common norms for ash and use test pieces with sharp edges to facilitate the typical shapes observed (generally pyramidal shapes with height up to 19 mm or cubic samples up to 7 mm on a side). The heating microscope Misura® HSM is designed to respect all these international standard test methods for the determination of ash melting behavior.

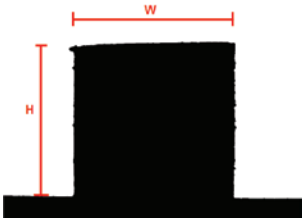


Figure 2: Cylindrical specimen (3 mm high, 3 mm in diameter) used for the determination of ash melting behavior according to the German standard DIN 51730.

Here, the melting behavior of fuel ash is studied with the heating microscope Misura® HSM, using the DIN 51730 standard. Referring to this standard and Figure 2, it is possible to define the following characteristic temperatures:

- Deformation temperature: the first sign of ash deformation (rounding of the edges, start of swelling)
- Sphere temperature: the edges of the sample become completely round, with H=W
- Hemisphere temperature: the sample is approximately hemispherical, with W=2H
- Flow temperature: the sample has spread out such that its height is one-third that of the hemisphere temperature.

With the addition of some water drops for increasing the plasticity, the ground ash was pressed with a manual press to obtain a cylinder 3 mm high and 3 mm in diameter, which is then placed on an alumina plate. Data acquisition intervals are temperature-based, every 5°C. The results are shown in Figure 3, where the dimensional variations of the specimen are expressed as a percentage with respect to its initial size (taken as 100%) and reported as a function of the temperature. The deformation point is identified as the onset of swelling. During the test the ash sample, in fact, develops a non-negligible quantity of gas.

Analysis of glazes, glasses, and frits. In the ceramic sector, heating microscope testing has never been ruled by a specific law, even though since the first years of its introduction on the market, a standard analysis method has been sought [1]. The aim of the study of Paganelli in 1997 [3] was understanding if the common practice of running laboratory tests with 3-mm high, 2-mm diameter samples at 50°C/min can provide valuable information about the behavior of the samples in industrial firing conditions. All tests were performed using the heating microscope MISURA HSM. Paganelli found that the test method is quite reliable because it gives results within a very narrow range, even comparing industrial firing cycles with a typical laboratory cycle at a constant heating rate. The sample size was developed considering the balance between gravitational, viscous, and surface tension forces acting on the glaze during the melting process.

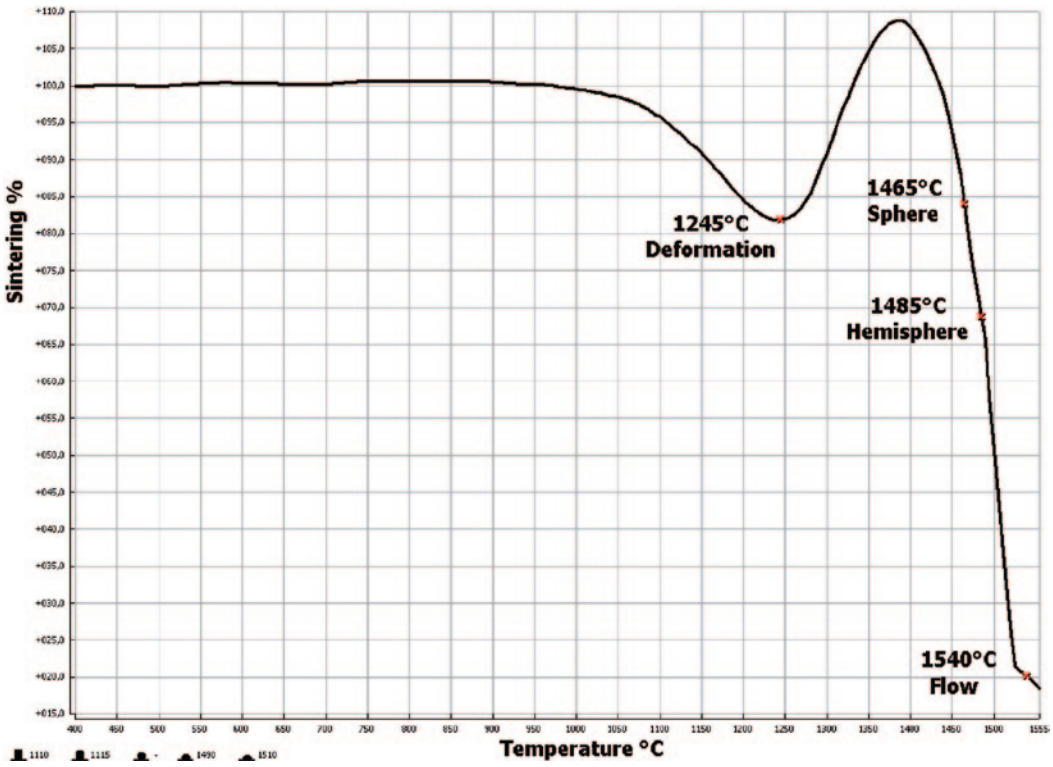
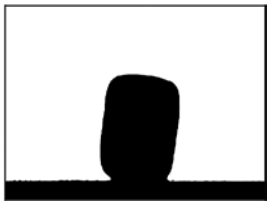
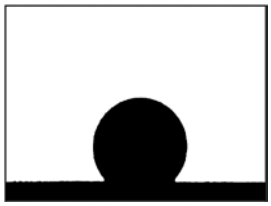
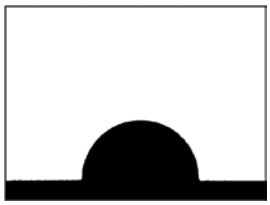
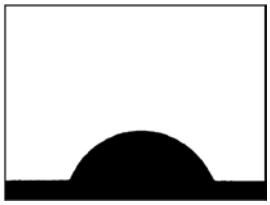


Figure 3: Heating microscope data curve obtained for a fuel ash sample. Characteristic points are identified according to DIN 51730.

The cylindrical sample was chosen because this is the only shape that enables the microscope to focus on a plane that does not change during the shape transformations induced by heating. The use of prismatic samples should be avoided because they require continuous changes of the focus.

The characteristic points typical of glasses, glazes, and frits identifiable with the heating microscope are defined in Table 1. Figure 4 shows the comparison between the curves obtained for two different ceramic frits subjected to a heating rate of

Table 1: Definition of characteristic points for glasses, glazes, and frits identifiable with the heating microscope Misura® HSM.

	**Onset of data acquisition:** The image analyzer automatically takes as 100% the height of the sample, measured considering the sample holder (alumina support) as a base reference.
	**Sintering:** As the temperature increases, the viscous flow activation threshold is overcome and the material undergoes the sintering phase: the sample decreases in size, but its shape does not substantially change. In the case of glasses, glazes, and frits, the driving force of the sintering process is the surface tension of the vitreous phases. The sintering phase ends when the sample reaches its maximum density. The sintering temperature identified by the instrument is the temperature at which the sample has reached a dimensional variation corresponding to the 5% with respect to the first image acquired, which is taken to be 100%.
	**Softening:** The softening point is reached when liquid phases appear on the surface of the sample. From this point on, the shape of the sample undergoes substantial changes caused by the surface tension of the liquid phases. To find this point, the rounding of the corners of the sample and the smoothing of the upper part of the walls of the sample are taken into consideration.
	**Sphere:** At the sphere temperature the sample is formed almost entirely of liquid phases, and the shape of the sample is controlled by the surface tension. While the surface tension tends to reduce the surface to a minimum forming a sphere, the hydrostatic pressure related to the density of the liquid phase tends to flatten the shape. Some glasses do not reach the sphere point: for example, glasses with a high density and a low surface tension (lead silicates). In detecting the sphere temperature, every image analyzed is compared with a theoretical sphere.
	**Half Sphere:** The half sphere temperature is reached when the height of the sample is half the width of the base. If the glass behaves normally, at the half sphere temperature the contact angle is approximately 90°. However, at this temperature the contact angle is often much higher, and in some cases the shape of the sample can resemble a bell. These anomalies can be attributed to the formation of non-homogenous phases inside the sample, such as crystallization or glass-glass separations.
	**Melting:** When the height of the sample shrinks to under a third of the base, it is assumed that the sample has completely liquified and has reached the melting point.

50°C/min. The cylindrical samples (3 mm high and 2 mm in diameter) were obtained pressing the powders with a manual press into a cavity of suitable dimensions with some water.

Glassy frit (Figure 4, black curve): Between 650 and 750°C, the first shrinkage in the sample occurs. This is the sintering phase, during which the sample dimensions decrease, but the specimen shape remains unchanged. As the maximum density is achieved, the sintering process cannot proceed anymore and this causes a "sintering plateau" on the curve. The sample dimensions remain constant for a certain temperature interval (770–840°C) even if the sample continues to be heated. As the temperature increases further, the surface tension does not vary much, but the viscosity of the glassy phase decreases exponentially. When the viscosity reaches a sufficiently low value to allow the glassy phases to wet the external surface of the specimen, the material is at the softening point (840°C). Beyond this point the glass begins to behave as a liquid, and the surface tension decreases the

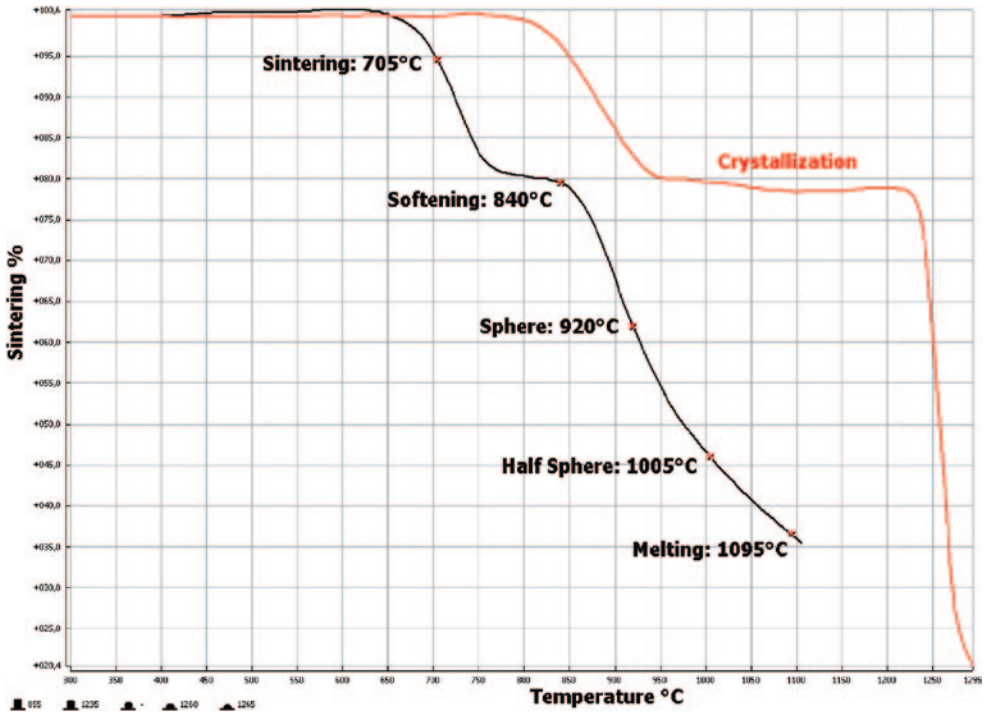


Figure 4: Comparison of data curves for two different ceramic frits: glassy frit (black curve) and crystallizing frit (red curve).

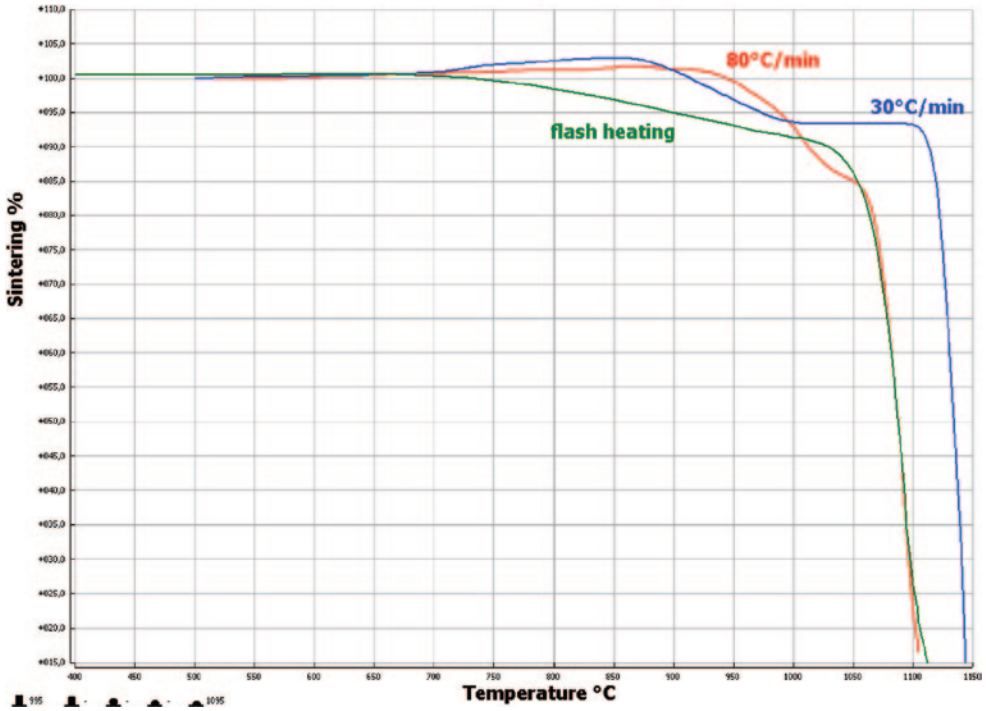


Figure 5: Curves obtained for a sample of mold powders for continuous metal casting applying different heating rates.

surface area to a minimum, causing the formation of a sphere. The specimen shape rapidly becomes spherical (920°C) and then hemispherical (1005°C). Finally, the melting point is reached at 1095°C.

Crystallizing frit (Figure 4, red curve): After the sintering phase, this curve shows a long plateau. (The sample does not change dimension between 950°C and 1250°C). This means that crystallization is taking place inside the material. As the temperature increases (between 1230°C and 1300°C), the material does not behave like a glass (does not exhibit spherical shapes) but melts with the typical behavior of a crystalline material.

Analysis of ceramic mold powders for continuous casting. The application of different heating rates (30°C/min, 80°C/min, "flash" heating) causes different effects on the melting behavior of a material. The example in Figure 5 shows this phenomenon for the case of mold powders for continuous casting. Mold powders, initially fly ash based, were introduced about 40 years ago in the steel continuous casting process. Today synthetic powders consisting of mixtures of various minerals are also used. Considering the chemical composition, the powders are made up of complex mixtures of carbon, some oxides (SiO_2, Al_2O_3, Na_2O, CaO) and other materials. The aims of the powders, when added to the free surface of the liquid steel in the mold, can be summarized as follows: (a) thermal isolation of the steel surface, in order to prevent its solidification; (b) protection of the steel surface from the oxidation; (c) lubrication and heat transfer control between the mold wall and the solid steel shell; and (d) absorption of non-metallic inclusions coming from the steel [4].

When a low heating rate (30°C/min) is applied, a horizontal plateau is observed between 1000 and 1100°C. During this period, specimen dimensions remain constant as the temperature varies. This indicates that a crystallization process is occurring inside the material, which is transforming. The melting temperature of this specimen was identified as 1150°C. The same powder melts at a lower temperature when a higher heating rate is applied. This is because the elements that constitute the material do not have sufficient time to react to compounds with higher melting temperatures. The "flash" or instantaneous heating is the heating rate that best reproduces the thermal stresses that

actually occur in a mold. The melting temperature obtained for a material heated under industrial conditions may be different from the results obtained in a laboratory because the heating rates are likely to be lower in the latter.

Conclusions

Automatic image analysis provided by the heating microscope Misura® HSM allows an accurate measurement of the thermal behavior of ceramics and glasses during heating. This microscope also allows the possibility of applying instantaneous heating to better simulate certain industrial conditions. This new generation of microscopes continues to represent one of the most effective and helpful tools for characterizing thermally induced shape changes.

References

[1] Anonymous, *International Ceramic Journal* 1 (2002) 61–62.

[2] M Paganelli and D Sighinolfi, *Ceramic Forum International (Berichte der Deutschen Keramischen Gesellshaft)* 86 (5) (2009) E18–E21.

[3] M Paganelli, *Industrial Ceramics* 17(2) (1997) 69–73.

[4] KC Mills: "Chapter 8: Mold powders for continuous casting," in *The Making, Shaping and Treating of Steel*, 11th ed., Casting Volume, AISE Steel Foundation, Pittsburgh, 2003.

MT