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Review
In Situ high-temperature optical microscopy

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High-temperature optical microscopy is an essential *in situ* characterisation and monitoring technique with wide applications in different areas of materials science. The devices used include commercial available instruments, known as heating microscopes, and custom-made devices, usually called "high-temperature processing microscopes" or "thermo-optical instruments". The different areas of applications of high-temperature optical microscopy are discussed on the basis of practical examples drawn from the literature. Besides the classical use of the technique to study the melting and softening behaviour of glass, slags, ashes and other silicate and ceramic materials, this review covers alternative applications, in particular the use of heating microscopes as "optical dilatometers" to investigate the sintering kinetics of powder compacts. In this regard, the advantages of the technique over conventional dilatometry are emphasised. A variety of custom-made devices is described, developed to investigate particular problems, such as delamination and curling of laminate composites during densification, cosintering of multilayer metal-ceramic and ceramic-ceramic systems, and wetting behaviour of liquid phases on rigid substrates. As a particular example of such a custom-made equipment, a novel, multi-purpose high-temperature processing microscope is described, and its application potential, which is well beyond that of commercial devices, is outlined. This instrument is unique in that it combines both vertical and horizontal sample observation capability, as well as the possibility to investigate samples of relatively large sizes (65 mm^3), i.e. about 10 times larger than those suitable for commercial heating microscopes.

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1. Introduction

With the aid of heating devices attached or surrounding the stage of a microscope, physical and chemical phenomena occurring in materials at high temperatures can be observed *in situ*. A hot stage is a compact heating device which provides the necessary temperature and thermal environment while allowing observation of the specimen.

According to Chamot and Mason [1], the first *in situ* microscopy investigation at high temperatures was conducted as early as 1865. A Bunsen burner flame was used to heat the extreme of a copper bar placed in an ordinary microscopy stage and the sample to be observed was held in a bore-hole. The development of electrically heated stages at the beginning of this century brought a significant impulse to high-temperature microscopy: the devices became simpler and compact, allowing the use of objectives of relatively short working distance [1, 2]. Moreover a wide range of temperatures could be obtained and accurately controlled by means of rheostats, thus providing more flexibility to the researchers.

A great variety of types of high-temperature optical microscopes have been designed and used in different areas of materials science since those early times. Classical applications areas have been for example the determination of fusion, subliming, and transition temperatures of different substances, including vulcanisation of rubber, softening of glasses, coagulation of colloids, chemical reactions at elevated temperatures, etc. Another important application area has been high-temperature metallography.

The present review is limited to high-temperature microscopy investigations in which the sample is placed in a compact furnace and observed and measured with an optical instrument. Thus, the process investigated resembles the real situation of firing (sintering) or melting of materials. Moreover, the parameters of interest in these investigations are usually the macroscopic dimensions and shape of the samples, usually in the range of hundreds of microns to millimetres, so that microscopes of relative low magnification are required (of the order of 10X). The term "microscopy" is kept in this review, in accordance with the current literature, although some of the instruments to be described here resemble more a "telescope" in that a sample situated at a relatively long distance from the observing device (i.e. inside a furnace) is viewed, rather than a conventional

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microscope. It must be noted that a great number of instruments which are available for investigating microscopical samples and for high-magnification observation, i.e. to observe changes of microstructure (in the μm-range) at high temperatures, are not covered in the present review. These devices are usually called hot-stage microscopes and find application in high-temperature metallurgy and other thermoanalytical studies [3]. Information on these instruments and their application fields can be found in several articles [4–9]. Some of these instruments allow for simultaneous X-ray diffraction or differential calorimetric analyses to be carried out [3, 10]. Also not covered here are thermal scanning devices developed to conduct remote mapping of surface temperature distributions, which are used in infrared thermographic studies [11], and other forms of analytical microscopy methods developed for micro-thermal analysis [10].

In general, high-temperature optical microscopy is a powerful characterisation technique in broad areas of materials science and engineering, as we intend to demonstrate in this article. It has been literally ignored, however, in conspicuous, comprehensive treatments of materials characterisation techniques and microscopy (see for example Refs. [12–14]).

In the present review two types of devices are considered and discussed separately on the basis of literature available to date: commercial instruments, which are usually known as heating microscopes (in Section 2) and custom-made devices, which are called “high-temperature processing microscopes” or “thermo-optical systems” (in Section 3). In Section 4 a novel custom-made multi-purpose high-temperature processing microscope is described in detail, including examples of its application.

2. The heating microscope

2.1. Description and history of the apparatus

The heating microscope is by far the best-known device in both industry and research for observation of thermal processes. Fig. 1 is a simplified schema showing the components of a heating microscope. The apparatus consists of three principal units mounted on an optical bench approximately 1.50 m long: the light source, the electric furnace (about 200 mm in length and 20 mm in diameter) with specimen carriage and the observation unit with the microscope itself and the recording facility, either a photographic or a video camera. The light source is either a low-voltage filament or a halogen lamp. The specimen to be observed is placed on a small ceramic plate. The microscope projects the image of the specimen situated in the furnace in approximately 5X magnification onto a groundglass screen and onto the recording device. Usually, the furnace is constructed so as to permit the use of any desired gas in order to allow the investigation of oxidation and reduction processes. The temperature is normally controlled with an automatic furnace control unit, incorporating a program for variable heating rates and several dwell times. Current commercial devices offer a working temperature capability of up to 1750 °C and the system is water-cooled. More details about the illuminating, optical and thermal systems can be obtained from manufactures [15, 16].

Heating microscopy has its origin in a series of optical instruments developed to study the melting behaviour of coal ashes early in this century, as reviewed by Radmacher (1949) [17]. In particular, a device constructed in the early twenties, and described by Endell [18], and a similar one, developed by Ebert in 1930 [19], can be considered to be the for-runners of present days heating microscopes. Instruments essentially identical to those commercially available today [15, 16] were used by Radmacher [17], Mann [20], Schor [21], Zwetsch [22] and Metz [23] during the forty and fifty years to study the heating behaviour, softening and melting of glasses, slag, flyash and other silicate systems. The basic features of the heating microscope, as depicted in Fig. 1, have not varied since they were introduced commercially some fifty years ago. However, modern equipments are now available with a number of computer assisted accesories and fully automatic data and image recording systems, in order

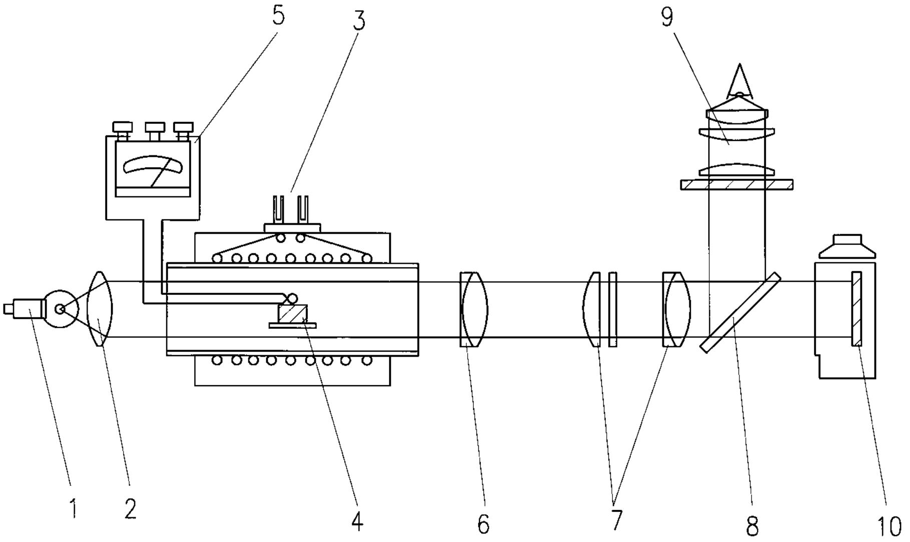


Figure 1 Simplified schema of a heating microscope [20]: (1) light source, (2) condenser lens, (3) electric furnace, (4) sample and thermocouple, (5) temperature controller, (6) objective, (7) ocular, (8) rotating mirror allowing visual observation and image recording (photograph or video recording), (9) optical assembly for visual inspection, (10) image recording system (photo or video camera).

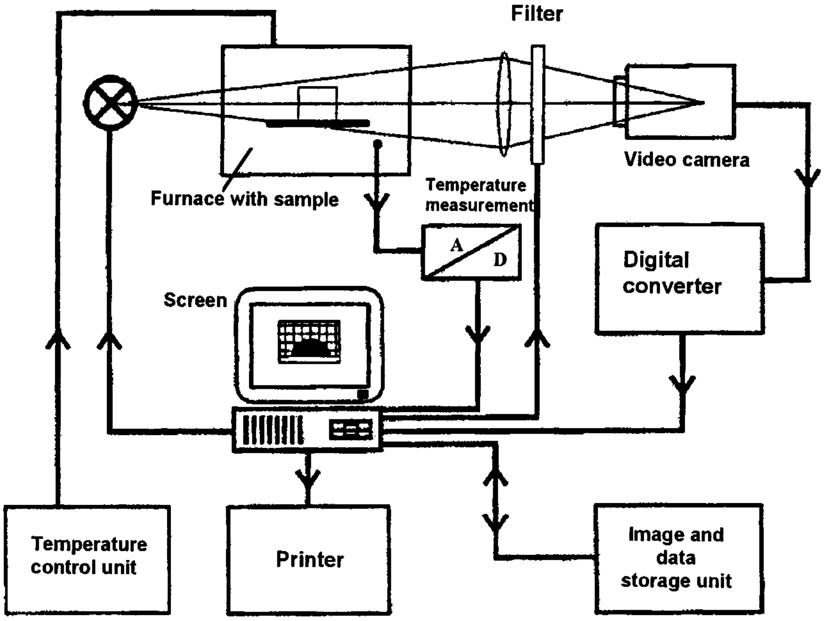


Figure 2 Computer assisted automatic measuring system for the image analysis and data processing in heating microscopy, as developed by Görke and Leers [24].

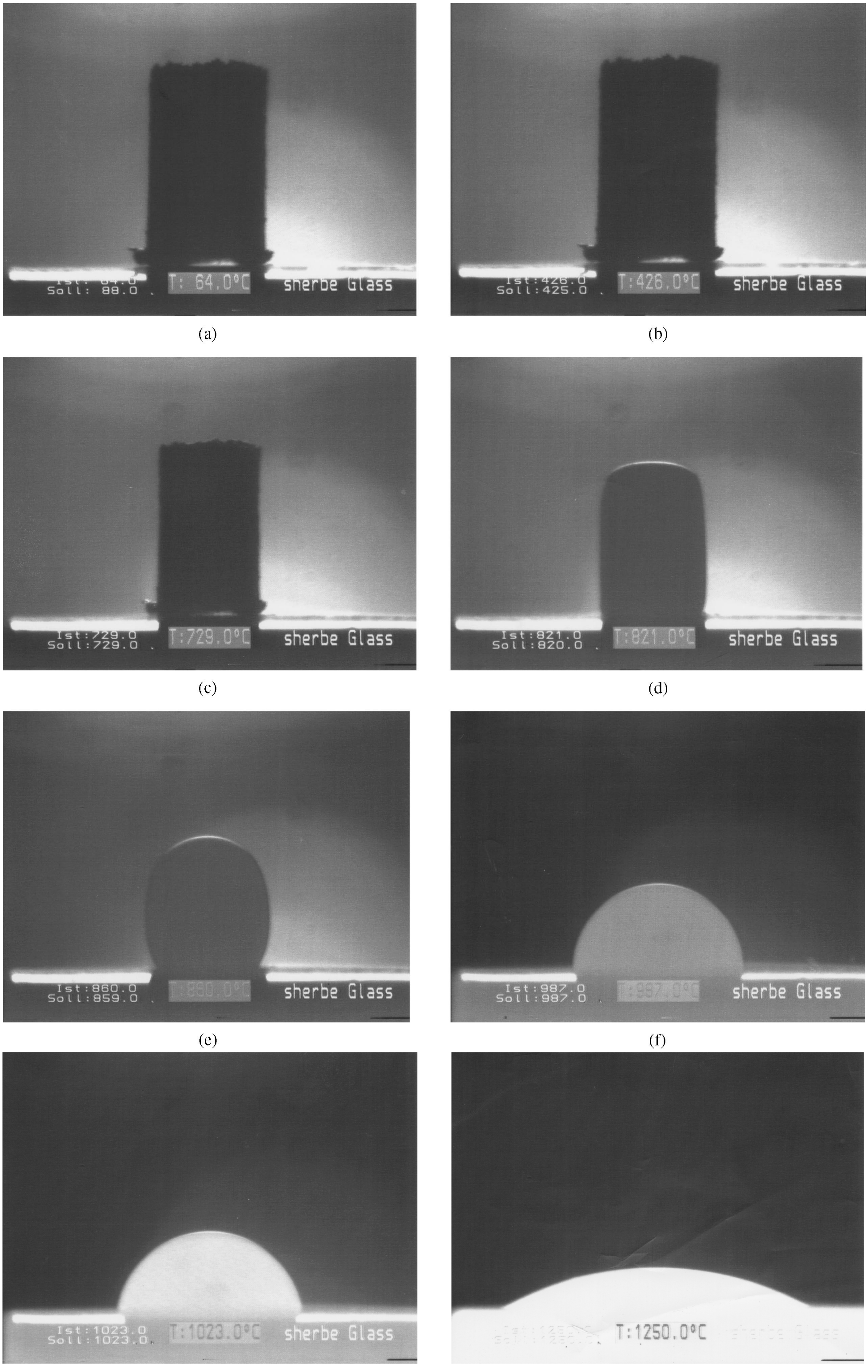
to make the measurement and analysis easier for the operator [15, 16]. Such a computer assisted automatic measuring system is shown schematically in Fig. 2, as developed by Görke and Leers [24]. It incorporates an extensive software package which supports sample image analysis and tracing protocol and evaluation of the temperature dependent sample shape change. An interesting modification of the basic design of the commercially available heating microscope was described by Metz in 1962 [25]. In this configuration, the furnace was constructed to allow the exertion of controlled uniaxial loads (of up to 1 kg) on the sample by means of changeable weights during the high-temperature experiment. Surprisingly, this heating microscope, which would have been very useful for measuring thermal processes under mechanical pressure, for example the sintering kinetics of powder compacts under controlled loads, did not enjoy commercial success [26].

2.2. Classical applications

Heating microscopes are standard, well-know devices in ceramic and glass laboratories in both research institutions and industry, including ceramic and glass manufacturing plants, coal power stations, colleries, gas works, minerals research establishments, etc. Traditionally, the instrument has found application mainly to assess the thermal behaviour, particularly softening and melting, of glasses, slags, flyash, carbons, ceramic frits, glazes, clays, feldspars, vitrified bonded ceramics, refractory phases and other silicate materials. [17, 20, 21, 23, 25–43]. The extension of those traditional applications of heating microscopy to study the melting kinetics of raw material batches for glass melting has been demonstrated recently [35]. In this application, the heating microscope allows for direct *in situ* observation of silicate grain-to-grain reactions during melting and provides a complementary measurement tool to other quantitative thermochemical techniques.

In general, silicate materials are commonly of complex composition, and they do not show a fixed melting point but fuse and soften as they are heated, melting over a relatively wide range of temperatures until reaching the liquid state. These processes can be monitored by heating microscopy, as they progress with changes of the shape of the sample. The melting and softening behaviour of other materials, including metals, plastics, salts, etc., has been much less investigated by heating microscopy, probably due to the need of non-oxidising atmospheres [36], or simply because the instrument is little known beyond the area of glass and ceramics.

For the kind of investigations referred above, samples in powdered form are normally used to hand-press small cylindrical (about 3 mm diameter × 3 mm height) or cubic (27 mm^3) specimens, which are then observed during heating. The different stages of the process are recorded photographically or by means of a video camera. A typical series of photographs showing the evolution of a borosilicate glass compact during heating is shown in Fig. 3. In these investigations, the shape change of the silhouette of the sample is the indicator used for assessing the physical changes occurring in the material (softening, melting). The apparatus allows also for conducting standardised tests: for example, for fuel ashes, the temperature at which the sample shows the hemispherical point (see Fig. 2f) is considered to be the melting point of the material (German norm DIN 51730). One of the main advantages of the heating microscope is that the specimen is at no time in contact with an external measuring element (e.g. a contact rod such as in dilatometers). Thus, no external load is applied which could alter the softening process. This point is particularly important when considering investigations of sintering kinetics, as discussed further below.



(a) (b)

(c) (d)

(e) (f)

(g) (h)

Figure 3 A typical series of video images showing the evolution of a borosilicate glass sample with increasing temperature in a heating microscope. The shape change of the silhouette of the sample is the indicator used for assessing the physical changes occurring in the material (e.g. sintering, softening, melting). $T = 64\,^{\circ}\mathrm{C}$ (a), 426 °C (b), 729 °C (c), 821 °C (d), 880 °C (e), 987 °C (f) 1023 °C (g) and 1250 °C (h).

2.3. Investigation of sintering and related processes in powder compacts

2.3.1. Potential of the technique for sintering studies

Powder processing is the technology of choice to obtain not only traditional ceramic products, but also a variety of novel materials including glass, ceramic and metal matrix composites and functionally gradient materials. Thus, studies of the sintering behaviour of powder compacts have, besides the long-standing academic interest, increasing practical and economical justification [44]. The process of sintering represents for many products the most critical fabrication step in the general aim of obtaining fully controlled microstructures, and thus the required material's properties, in addition to the desired shape and dimensional tolerances. Shrinkage during sintering is related to the rate of energy gain due to the reduction of surface area, at a microscopic scale, of the porous, densifying body. Thus, an accurate *in situ* measurement of the macroscopic shrinkage of the sintering bodies and the appropriate evaluation of the acquired data provide valuable information to understand the kinetics of the sintering mechanisms [45]. Certainly the idea of observing a sample and documenting the change of its dimensions and shape during sintering densification is not new. For example, a number of investigations have been conducted in the area of traditional ceramic firing, i.e. in tile production plants, in particular with the aim of assessing the change of the shape of the products as they densify [46]. *In situ* investigations of sintering conducted using optical instruments other than heating microscopes are reviewed below in Section 3.

The first work reporting on the systematic application of heating microscopy on sintering studies was published by Harkort and Paetsch in 1960 [47]. They studied the change of the height of powder compacts made of feldspar during sintering. Later Buist conducted similar investigations on several ceramic powder compacts [34]. However, that earlier research was limited to measuring the compact volume or height contraction with sintering time and no further parameters of the sintering kinetics were determined. In fact, the vast majority of studies on sintering kinetics are carried out using standard dilatometry [44, 48–51]. It was only in the early nineties that the heating microscopy technique started to be applied intensively to study sintering phenomena in a variety of material systems [52]. In most investigations, however, only *qualitative* observations were conducted, for example related to shape distortion or bloating effects in ceramic and glass powder compacts and films during sintering [53–55], or simple measurements of shrinkage curves [30, 56–59] were carried out. Although more complex thermo-optical devices for studying the sintering kinetics of powder compacts have been constructed and utilised, as described further below, the standard heating microscope, most probably available in every materials science laboratory, represents a very useful apparatus for sintering investigations. In recent works, for example, heating microscopy was shown to be an excellent alternative experimental technique to carry out detailed *quantitative* studies of sintering kinetics [52, 60–65]. For these studies, the possibility of *in situ* monitoring the shrinkage process without the exertion of external loads, thus minimising friction with constraints and other external influences is paramount, and this can be achieved using heating microscopy. Moreover, using heating microscopy, only one sample for each sintering run is necessary since the entire sintering process can be observed and recorded. A further advantage, if the samples have cylindrical geometry, a common practice in sintering studies, is that both axial and radial shrinkage can be recorded simultaneously, and anisotropy effects during sintering can be accurately assessed. The phenomenon of sintering anisotropy is relevant, for example, when studying the sintering kinetics of metal [66] and glass powder compacts [62–64, 67], glass-ceramics [61, 65] and ceramic matrix composites [68, 69], where accurate experimental data are necessary to validate theoretical models. Fig. 4 shows, as an example, the evolution of the sintering axial and radial shrinkage in borosilicate glass powder cylindrical compacts that had been pressed uniaxially, as measured in an earlier heating microscopy investigation [64]. It is seen that the sample shrinks anisotropically during sintering, with a more pronounced shrinkage in the axial than in the radial direction. The occurrence of shape distortion during sintering, as a consequence of shrinkage anisotropy, has a very important practical significance both in traditional firing of ceramics (e.g. tiles) [46] and in modern powder technology [66, 70–72]. In particular the control of dimensional accuracy of expensive sintered parts is necessary to avoid or minimise post-sintering machining and specimen rejections [73, 74]. In this regard, heating microscopy provides a very convenient tool for the *in situ* monitoring of dimensional changes

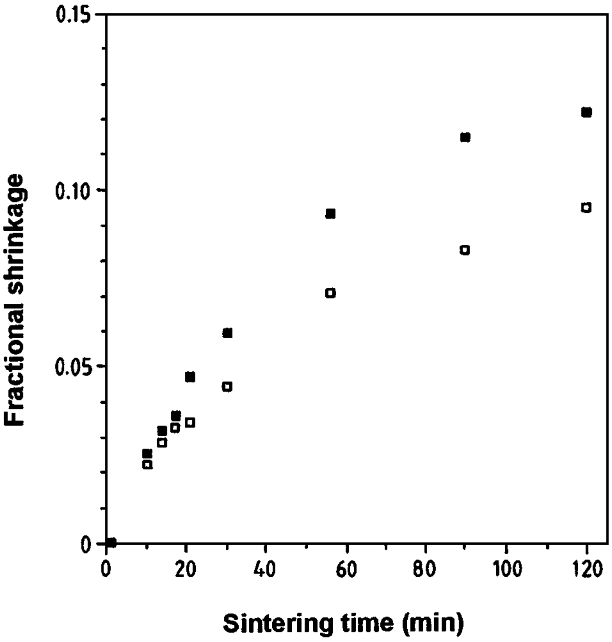


Figure 4 Evolution of the axial and radial shrinkage of borosilicate glass powder cylindrical compacts during sintering, as measured in a heating microscopy investigation [64]. The instrument allows the detection of shrinkage anisotropy, i.e. the sample exhibited more pronounced shrinkage in the axial (■) than in the radial (□) direction.

during sintering, as demonstrated in a recent investigation on particle reinforced glass-ceramic products [69]. A further problem that can be investigated by heating microscopy is the interaction between densification and crystallisation when sintering glass-ceramic materials. Here, knowledge of the influence of heating rates on the onset of crystallisation is necessary in order to design the optimal heating schedule for achieving full densification of the material [65]. Other group of sintering phenomena which can be assessed by heating microscopy is related to the effect of inhomogeneities or rigid inclusions on the densification kinetics of powder compacts [51, 60]. The use of heating microscopy for investigating this particular problem is briefly described below, using a glass matrix composite system as an example, in order to clarify the application of the instrument and the required data analysis.

2.3.2. *Case study: Influence of hard inclusions on the sintering of glass matrix composites*

Cylindrical compacts of the powders to be examined (5 mm in diameter by 5 mm) are obtained by pressing in a die at room temperature, usually without the addition of any binder. For isothermal experiments the furnace of the heating microscope is first heated to the sintering temperature and subsequently the compacts are inserted quickly, in order to provide isothermal conditions for the whole stage of sintering. The samples are placed on a small ceramic plate with the longitudinal axis coinciding with the vertical direction. Usually two specimens are used for each run and the results are averaged. Sintering time, temperature and atmosphere depend in general on the material and kind of investigation to be conducted. By measuring the changes of length and diameter of the samples during the sintering process, either by taking photographs of the sample at pre-chosen time intervals during the sintering process, or by video recording the whole experiment, it is possible to obtain the axial and radial shrinkage and, thus, the density of the sample with enough precision at any time. The height and diameter of the photographed or video-recorded sample images can be measured with a relative error $<1\%$ on suitable enlargement.

The instantaneous density of the composites during the sintering process can be obtained by means of the following relation:

$$\rho_c = \frac{\rho_{c0}}{\left(1-\dfrac{\Delta D}{D_0}\right)^2\left(1-\dfrac{\Delta L}{L_0}\right)} \qquad (1)$$

where ρ_{c0} represents the initial (green) density of the composite, $\Delta D = D_0 - D$ and $\Delta L = L_0 - L$. D_0, L_0 are the initial sample diameter and length, and D, L are the instantaneous diameter and length, respectively. The instantaneous absolute density of the matrix ρ_m may be obtained by [75]:

$$\rho_m = \frac{(\rho_{c0} - \rho_i c_D)\rho_c}{(\rho_{c0} - c_D\rho_c)} \qquad (2)$$

where ρ_i is the density of the inclusion phase and c_D is the volume fraction of the dispersed phase in the initial compact, thus including the porosity. The volumetric fraction of inclusions which corresponds to the fully dense composite, F, and c_D are related by the following relationship:

$$c_D = \frac{(\rho_{c0} - F_{\rho_i})F}{(\rho_{c0} - F_{\rho_i})F + (1-F)^2\rho_M} \qquad (3)$$

where ρ_M is the theoretical density of the matrix. From Equation 2 and its time derivative follows the volumetric strain rate of the glass matrix as

$$\frac{\dot{\rho}_m}{\rho_m} = \frac{\left(\dfrac{\dot{\rho}_c}{\rho_c}\right)\rho_{c0}}{(\rho_{c0} - c_D\rho_c)} \qquad (4)$$

Using heating microscopy and this data reduction method, the sintering of barium magnesium aluminosilicate glass-ceramic matrix composite containing alumina platelet inclusions has been studied recently [69]. Fig. 5 shows the density of the composites, normalized to the theoretical density given by the rule of mixtures ($\rho_M = 2.74$ g/cm^3, $\rho_i = 3.99$ g/cm^3), as function of sintering time for different volume fractions of platelets F. Sintering was conducted at 950 °C. The values were calculated using Equation 1, the data for radial and axial shrinkage from heating microscopy measurements, and the green density of the samples. The data shown are an average of two runs under the same conditions and have a maximum relative error of 4%. As Fig. 5 shows, the presence of the rigid inclusions has a significant detrimental effect on the densification kinetics of the composite and on the final composite density. For an inclusion volume fraction as low as 10 vol%,

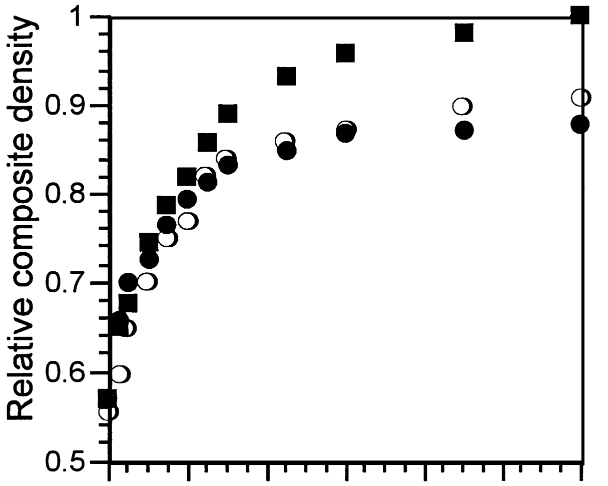


Figure 5 Relative density of BMAS glass matrix composites containing alumina platelet inclusions versus sintering time for different volume fraction of inclusions (F), as determined from heating microscopy measurements: (■) $F = 0$, (○) $F = 0.10$, (●) $F = 0.30$.

only a relative density of 90% of the theoretical can be achieved.

From the experimental data and using Equation 4 it is also possible to determine the hydrostatic component of the stress in the matrix caused by the inclusions, σ, normalised to the sintering pressure, Σ, according to the following expression [75]:

$$\frac{\sigma}{\Sigma} = 1 - \frac{\dot{\rho}_{\mathrm{m}}/\rho_{\mathrm{m}}}{\dot{\rho}_{\mathrm{fm}}/\rho_{\mathrm{fm}}} \tag{5}$$

where the subindex *fm* corresponds to the data of the unreinforced matrix ($F = 0$). The determination of the hydrostatic stresses developed during sintering with rigid inclusions is relevant for the fabrication of this kind of composites because they may lead to high shear stresses at the particulate-matrix interface, which could in turn cause the formation of cracks, and hence lower the mechanical strength of the sintered bodies. Finally it should be mentioned, that the experimental data obtained by heating microscopy may be conveniently used to validate theoretical predictions of models developed to predict the sintering kinetics of composites containing rigid inclusions [76, 77]. In summary, this case study demonstrates that heating microscopy is a powerful, yet simple, technique for investigations of the sintering behaviour of powder compacts.

2.3.3. Advantages over conventional dilatometry

In comparison with standard dilatometry, which is by far the most applied experimental technique to investigate sintering phenomena [48–51, 78], heating microscopy offers important advantages. Firstly, some difficulties may appear when studying the sintering behaviour using dilatometers due to the presence of an extra external stress on the sample, caused by the dilatometer push rod. This external load may have a non-negligible effect on the sintering kinetics, especially if the matrix densifies by a viscous flow mechanism, as in glasses [79–82], or for compacts made of salt powders, such as sodium fluoride [45]. A fictitious shrinkage anisotropy may be measured in these cases. The effect of external compressive stresses, even as low as those caused by the load of dilatometer push-rods (∼5 kPa), has been shown to lead to a pronounced anisotropy effect in sintering glass powder compacts [81], thus confirming the advantage of heating microscopy. In addition, these external loads, always present in dilatometry, can result in the destruction of weak powder compacts or ceramic gels [83], making dilatometry measurements unsuitable. Moreover, standard dilatometers allow for recording the sintering shrinkage in one dimension only, not being possible to monitor *in situ* the transverse shrinkage, and thus, to detect true anisotropy effects. This results in a further disadvantage of standard dilatometry since a large number of samples are required, if the instantaneous values of the shrinkage in direction normal to the dilatometer push-rod are to be determined [45, 84]. In order to determine the instantaneous radial shrinkage, and thus to study shrinkage anisotropy, separate set of experiments must be conducted, known as interrupted sintering experiments. In these experiments, the sintering is interrupted at several times (or temperatures) before completion, and the radius of the sample is measured with a micrometer [45, 84, 85]. However, this practice is usually not followed (it is certainly time and sample consuming) and isotropic shrinkage behavior is assumed. Otherwise, especial and complex devices allowing the detection of length changes in different directions have to be used, including 3-dimensional dilatometers [86] and laser scanning micrometers [87]. Another point that may lead to accuracy problems in dilatometric measurements is the fact that some friction always exists at the contact areas between the sintering compacts and the dilatometer push rods. This may cause, for example, "barreling" of the samples, as reported in the literature [84].

2.4. Other applications of heating microscopy

There is a variety of further *in situ* high-temperature optical investigations which can be conducted by means of the heating microscope. Some interesting investigations were reported by Raask and co-workers in the sixty years [88, 89]. They studied for example the development of a miscibility gap in certain silicate systems at temperatures of ∼1300 °C [89], and the rate of evaporation of molten salts at temperatures of up to 1500 °C [88] using heating microscopy. In these applications, droplets of molten glass and molten salt, respectively, are introduced into the furnace hanging from the sample carrier. The miscibility gap in silicate melts can be qualitative assessed by *in situ* observation of the phase separation in the drops [89], while the volume change of the drops as a function of time was used to obtain evaporation rates in molten salts [88]. The authors are not aware of more recent work in the literature dealing with the observation of these phenomena in heating microscopes.

Other important application area of the heating microscopy technique is in studies of wettability between solid and liquid phases. This is of particular importance in the development of coating technologies, including plastic or resin coatings and paints [90] and in the development of glass/metal seals and glazes [34]. The wettability of intermetallic substrates by liquid alloys has been investigated using heating microscopy recently [91]. Moreover, interfacial phenomena related to the adhesion between a solid and a liquid phase can be investigated with the heating microscope, as showed for example in a recent study on glass/polymer systems [92]. The heating microscope has also been used to study the wetting/non-wetting transition temperature of feldspar melts on silica sands [31]. Also the interaction between clinker and refractory lining bricks can be investigated with this instrument by observing the wetting behaviour of the low-melting constituents of Portland cement clinker and the principal components of refractory bricks (e.g. magnesia) [34].

3. Custom-made high-temperature optical devices

Materials scientists have constructed during the last 40 years numerous devices for *in situ* high-temperature optical microscopy. The main reasons behind the design and construction of such especial instruments have been on the one hand the particular need of the specific investigation conducted, frequently impossible to be carried out using a commercial apparatus, e.g. a heating microscope, or, on the other hand, the need to investigate large samples, frequently much bigger than those that are suitable for commercial heating microscopes. Many of the devices built were just a combination of an open furnace and an optical and image recording system, other devices have been more complex, incorporating, for example, an image analysis capability. A brief review of these instruments will be given in this section, focusing on those devices designed for investigations of firing and sintering of ceramic, metals and composites; and on liquid phase-solid phase wetting studies. In the next section a modern apparatus constructed recently [93], known as high-temperature processing microscope, will be described in detail and some typical examples of the novel use of the instrument in materials science will be presented.

3.1. Studies of melting, sintering, densification and dimensional change at high-temperatures

The observation of the shape change of relatively large samples (10–20 mm height) at temperature has been used traditionally to assess the fusion and melting behaviour of ash and slag. According to a British Standard (BS 1016–PT 113), for example, ash samples in the form of cones or pyramids are placed in a tube furnace and observed through a telescope at one minute intervals while the furnace is heated up at a rate of 5 or 8 °C/min. The standards require that the temperature of initial rounding of the cone tip is recorded, as well as the softening temperature (when the cone has softened to 2/3 its original height) and the temperature when the cone has melted into a hemisphere. Novel commercial instruments are nowadays available for this kind of tests, which, having a larger furnace diameter, accept a larger number of samples at one time, facilitating the test [94].

Probably the first reports on the use of "optical dilatometry" to assess *in situ* the sintering behaviour of powder compacts were those originated in Finland, authored by Mäkipirtti [95] and Tikkanen [96]. The measuring equipment consisted of a sintering furnace with its power supply and temperature control device, a protective gas purifier, a temperature measuring instrument, and a photographic apparatus. The specimen was photographed at certain intervals during sintering. The objective used was such that the image on the film was equal in size to the test specimen. The measurements were conducted on W-Ni-Cu and Ni powder compacts of about 18.5 mm diameter and 10 mm length at temperatures of up to 1450 °C [95, 96]. Although the system offered capability to investigate anisotropy effects, shrinkage in only one dimension (diametral) was measured.

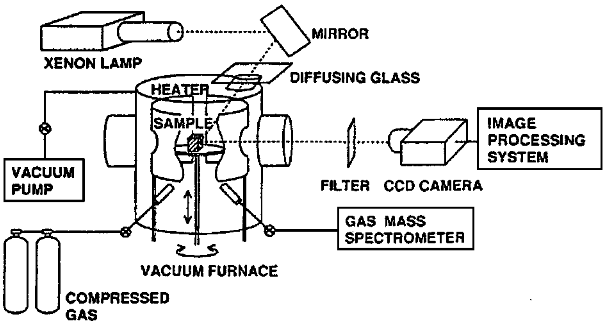


Figure 6 Schema of an *in situ* monitoring system of sintering shrinkage of powder compacts after Mizuno *et al.* [98]. (Published with permission of The Minerals, Metals and Materials Society).

With the increasing requirements for dimensional accuracy control and minimisation of shape distortion in expensive sintered parts [71, 72, 74, 97, 98], a variety of optical and digital image processing systems have been developed for the reliable accurate *in situ* monitoring of the sintering process. Mizuno *et al.* [73, 98] have developed a non-contact measuring system, which includes a digital image analysis facility. The apparatus is shown schematically in Fig. 6. It consists of an atmosphere-controllable furnace, a light source to illuminate the specimen located in the heating zone, a camera to monitor the image of the specimen and an optical mirror, all of which are placed in on a vibration isolated desk. In this monitoring system, the reflected image of the specimen illuminated from outside the furnace is received. A photographic camera is connected to the image processing system for *in situ* recording and analysis of the experiment. The image of the specimen mapped on the film or photographic paper is then input to the image system via a charge coupled device (CCD) camera. Die-pressed cylindrical powder samples (14 mm diameter) made of a stainless steel/zirconia functionally gradient material were investigated [98]. In a further investigation, both cylindrical (10 mm in diameter and 12 mm in height) and cuboid (30 × 10.5 × 5 mm) specimens made of carbonyl Ni powder were considered [73]. The innovative aspect of the device is indeed the digitalisation facility allowing for a highly accurate measurement of the silhouette (outline) of the samples. Thus, the occurrence of non-uniform shrinkage during sintering can be assessed with high precision.

Another group of studies concerned the investigation of the sintering behaviour of polymers using high-temperature optical microscopy [99, 100]. In these investigations, the coalescence of polymer particles, placed on transparent substrates, was observed by means of an optical microscope and recorded photographically. Also the shrinkage of polymer fibres during thermal treatment has been investigated using an optical instrument [101].

The sintering of fiber reinforced ceramic composites, ceramic laminates, films and coatings has been observed *in situ* using custom-made visual inspection instruments. Ostertag [102, 103], for example, assessed

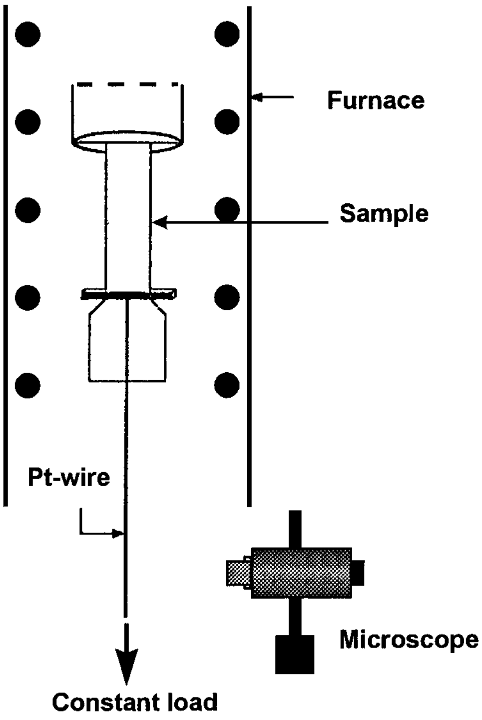


Figure 7 Experimental set up for high-temperature visual inspection, developed by Cheng and Raj [105], to measure the sintering pressure in ceramic films.

the development of stresses due to differential densification of the constituents in a model composite sandwich compact by optical inspection of the bending of the specimen during sintering. The device consisted simply of a video-camera mounted in front of an open tube furnace where the sample was placed. A similar simple device consisting of a tube furnace and a photographic camera was used by Cai *et al.* [104] to study constrained densification of alumina/zirconia hybrid laminates. In their studies, the development of sintering mismatch stresses was determined from the curling of asymmetric laminates, which were observed *in situ* during sintering. Another experimental set up for high-temperature visual inspection, shown in Fig. 7, was developed by Cheng and Raj [105] to measure the sintering pressure in ceramic films. In these investigations the change in length of the specimen as a function of sintering time was measured by observing the position of the tip of a platinum wire attached to the bottom of the specimen with a travelling microscope, i.e. the specimen was not observed directly. The same authors used another custom-made optical set up [106] to study the generation of flaws during constrained sintering of metal-ceramic and metal-glass multilayer films. This instrument is shown in Fig. 8. Small penny-shaped samples, 1 mm in diameter were observed during sintering by means of an optical microscope of long working distance lens. The image of the specimen was recorded continuously through a video camera. The magnitude of interest was the change of the specimen diameter with sintering time, which was possible to be determined with high accuracy by measuring the instantaneous diameter of the recorded image of the sample by means of an image analyser.

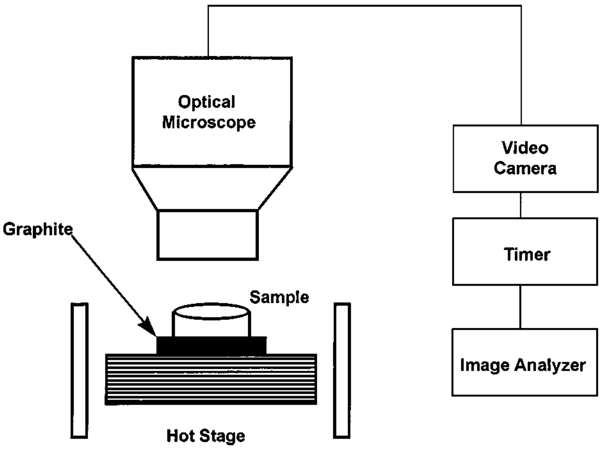


Figure 8 Schema of an optical set up developed by Cheg and Raj [106] to study the generation of flaws during constrained sintering of metal-ceramic and metal-glass multilayer films. Small penny-shaped samples, 1 mm in diameter, are tested.

In situ noncontact optical setups have also proven to be powerful instruments to study the effect of densification mismatch during co-firing of multilayer ceramic/ceramic and ceramic/metal systems, e.g. ceramic capacitors or electronic packages [107–110]. In this instruments, the sample is not directly observed, but the change of its shape and dimensions is detected optically using a laser beam. For example, Jean and coworkers have used a laser optical set-up to determine *in situ* the linear shrinkage and camber development of $Ni/BaTiO_3$ laminates of 100 μm in thickness during sintering [109]. The technique provided useful information to verify their model, in which camber development was explained on the basis of the densification-rate mismatch between the laminate components. The same laser optical set up was used in another work by the same authors [110] to study the cofiring kinetics and mechanisms of Ag/ceramic filled glass electronic packaging systems. The device was used to determine "*in situ*" the linear shrinkage of the laminates and Ag films. Unfortunately, the detailed description of the instrument used in these investigations was not provided by the authors [110]. Another laser optical instrument was described by Lu and co-workers [107, 108]. The instrument is shown in Fig. 9, and it is similar in principle to another apparatus used previously by Garino and Bowen [111] in sintering studies. The instrument was used to measure the thickness shrinkage profiles of constrained films in the system borosilicate + silica during sintering [108]. The thickness of the films investigated was between 0.2 and 0.6 mm. The aim of the study was to gain an understanding of the kinetics of constrained sintering in these films, which find applications in microelectronic packaging. Referring to the schema of Fig. 9, it is seen that a miniature assembly consisting of a small rectangular piece of polished silicon and two alumina spacers was mounted over the sample. A thinner alumina spacer is placed directly on top of the constrained film and a thicker spacer on the exposed substrate. The polished silicon piece is carefully bridged across the two alumina spacers. The tilt angle of the polished silicon changes as the constrained

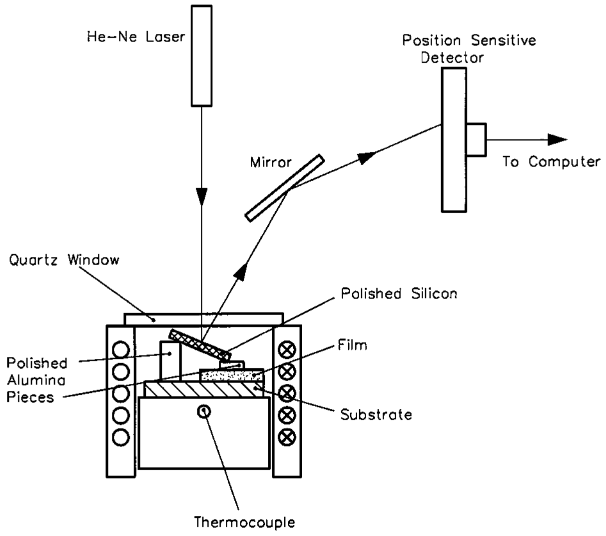


Figure 9 Schematic drawing of the optical-scanning instrument for *in situ* measurements of linear shrinkage profiles in ceramic and metal films and tapes, after Bang and Lu [108].

film thickness decreases upon densification. This angle variation is determined by reflecting a He-Ne laser beam off the silicon surface into a position sensitive detector. The detected signal is thus directly proportional to the shrinkage in the film thickness. The technique allows for the determination of sintering shrinkage of thin films with a very high precision. The same instrument was used to measured unconstrained shrinkage profiles of metal films and ceramic tapes [107]. In this configuration, the contrast between the reflective surface of the polished alumina setters and the rough surface of the sample was exploited to measure the dimensional changes of the sample that occur during sintering. More recently, the instrument was employed to investigate the sintering of cordierite glass-ceamic films (150–200 μm thickness) on silicon substrates [112]. Another thermo-optical measuring system was developed by Raether and Müller [113] with the aim of optimising sintering processes. The device can be used not only to measure the change of dimensions of the sample during sintering, but also other properties, for example the thermal conductivity, can be measured *in situ* as sintering proceeds. It can be used at temperature of up to 1700 °C in reducing atmospheres and 2200 °C in inert atmospheres and vacuum. Certainly the most interesting characteristic of this instrument is the possibility of simultaneous measurement of shrinkage and thermal properties during sintering. The description of the apparatus as well as examples of its use in sintering studies of different ceramics (e.g. alumina) can be found in the original work of Raether and Müller [113].

3.2. Studies of wetting and bonding in liquid-solid systems

A number of studies have been presented in the literature regarding the direct measurement of the wetting angle at liquid-solid interfaces at high temperatures. Examples are the cases where the angle is determined goniometrically from observations of the solid-liquid meniscus system, either *in situ* or from photomicrographs or recorded images [113, 114]. The studies published include for example measurements of the contact angle of liquid glasses or metals on ceramic and metal substrates by the so-called sessile drop method [115–122], or the measurement of the liquid meniscus of a fluid polymer contacting a vertical flat metallic plate [114]. The wetting of fibres by different fluids has also been studied by direct measurement of the contact angles on fibres embedded in the fluid of interest [123]. Also the surface tension of different substances, including liquid oxides [124], metals [125] and polymers [115, 126] can be obtained by the direct measurement of the shape of a drop attached to a substrate either in a sessile drop or a pendant drop configuration. In the simplest set-up for these measurements, the samples, situated in a furnace at the desired temperature, are viewed through fused silica windows. The solid-liquid contact angles and the shape parameters of the drops are measured using telegoniometers [116] or from photomicrographs or recorded images. For the most common sessile drop method, the parameters of interest are indicated in Fig. 10 [92].

More sophisticated devices for *in situ* measurements of wetting and bonding at liquid-solid interfaces at high temperatures have been also constructed. The careful control of the furnace atmosphere is a characteristic feature of all devices designed to conduct wettability studies, as the gas surrounding the droplet and substrate will have a strong influence on the measured liquid-solid contact angle [92]. One of such novel instruments designed to perform wetting studies is shown schematically in Fig. 11 [127]. The device was constructed after an earlier instrument developed in the early sixties [117]. The sample is placed on a special sample holder made of graphite in a high-frequency induction furnace. The device allows for conducting measurements

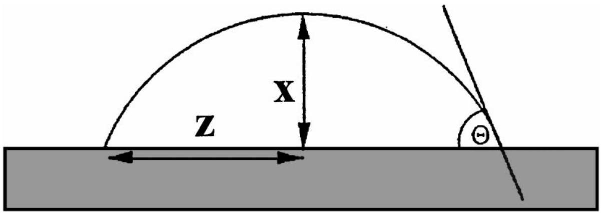


Figure 10 Parameters of interest in the sessile drop method to investigate wetting angle and surface tension of liquids.

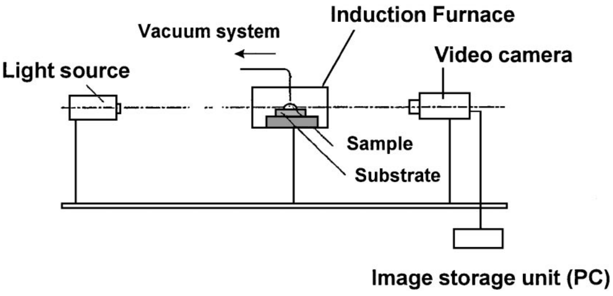


Figure 11 Schema of a novel device for *in situ* measurements of contact angle at liquid-solid interfaces at high temperatures, after Nitsche [127]. The sample is placed on a special sample holder made of graphite in a high-frequency induction furnace. The device allows for conducting measurements in vacuum and in different gas atmospheres.

in vacuum and in different gas atmospheres. The special sample holder, which contains the thermo-element, allows for a precision of ±2 °C in the measurement of the working temperature. The optical system allows for a magnification of 5X and the experiment can be video-recorded. The shape of the drops on the solid substrates can be determined from the recorded images with a precision of 0.01 mm. The instrument was used to determine the contact angle of different metals (e.g. Co, Ni, Cu, Pd and Sn) on ceramic substrates such as titania and mullite [127] and to determine the surface energy of polymers [92]. Similar devices allowing high-temperature measurement of wetting angles with high-precision have been constructed by others and are commercially available, allowing measurements at extremely high temperatures (up to 3000 °C in vacuum or He atmospheres) [128]. High temperature X-ray imaging instruments have also been developed [119]. By using X-rays to image the drops on a solid substrate, most of the image distortion problems associated with light optics can be eliminated.

4. The high-temperature processing microscope

4.1. Description

In this section, a novel instrument is described, which has been specially constructed for the observation of thermal processes in relatively large samples. The device, called High-Temperature Processing Microscope (HTPM), is a multipurpose equipment: it enables to conduct both standardised thermal tests (such as the determination of the melting behaviour of ashes under the German norm DIN 51730) and many other thermal experiments of scientific interest, as described below. This apparatus was designed originally for the investigation and optimisation of melting processes occurring during the recycling of contaminated float glass residues [93, 129]. A schema of the HTPM, including peripheral devices, is shown in Fig. 12. Due to its especial, novel construction, horizontal (such as in commercial heating microscopes) and vertical observation of the sample is possible. Fig. 13 is a detailed schematic drawing of the furnace, in vertical position, showing the illumination and video-recording devices also. The furnace can be rotated up to 90 degrees on an horizontal axis, so that horizontal observations can be done. A more complete description of the apparatus and technical constructive details can be found elsewhere [93, 129]. Working temperatures between room temperature and 1600 °C are possible, and the maximal dimensions of the samples are 40 mm in diameter and 50 mm in height. Due to these relatively large sample dimensions, and the possibility of using reflected and transmitted light, volume effects in transparent samples are visible, e.g. crystallisation of glass. In most cases, the microscope also allows the identification and separation of surface and volume effects. Within a sample, resolutions of the order of 50–100 μm are possible, the exact value depending on the magnification chosen and the achieved contrast. The working atmosphere is air, however it is possible also to carry out experiments in vacuum other in other special gas atmospheres. The process evolution is recorded by means of a CCD camera. This allows for a rapid and reliable documentation of the process, enabling the further data evaluation by a suitable software.

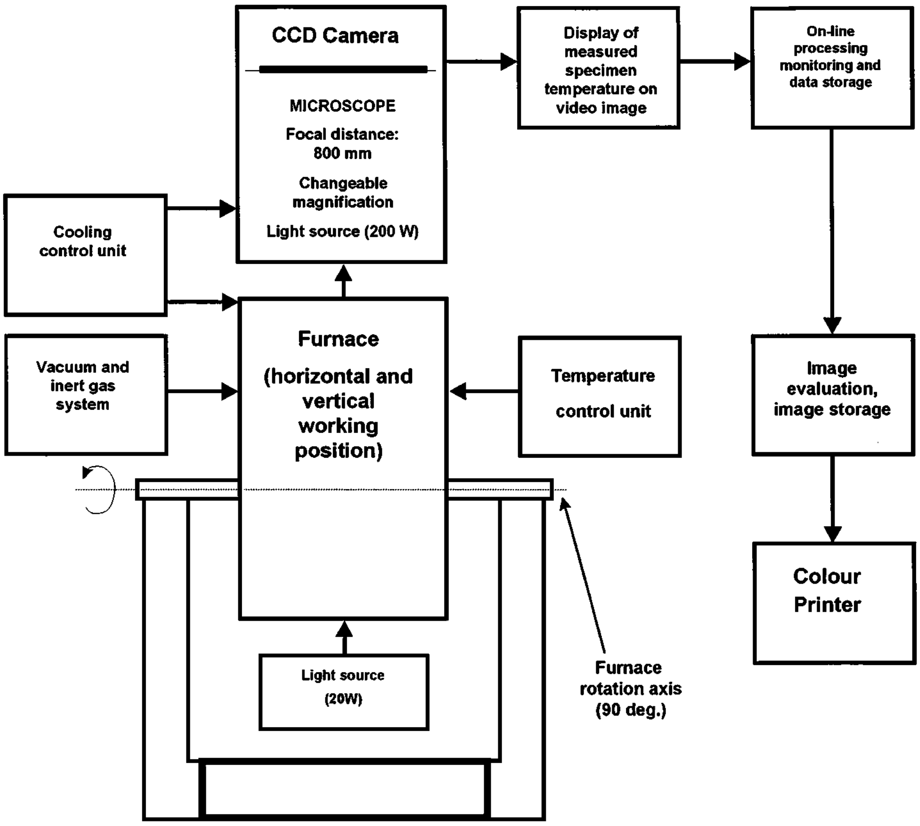


Figure 12 Schema of the High-Temperature Processing Microscope, including peripheral devices [129].

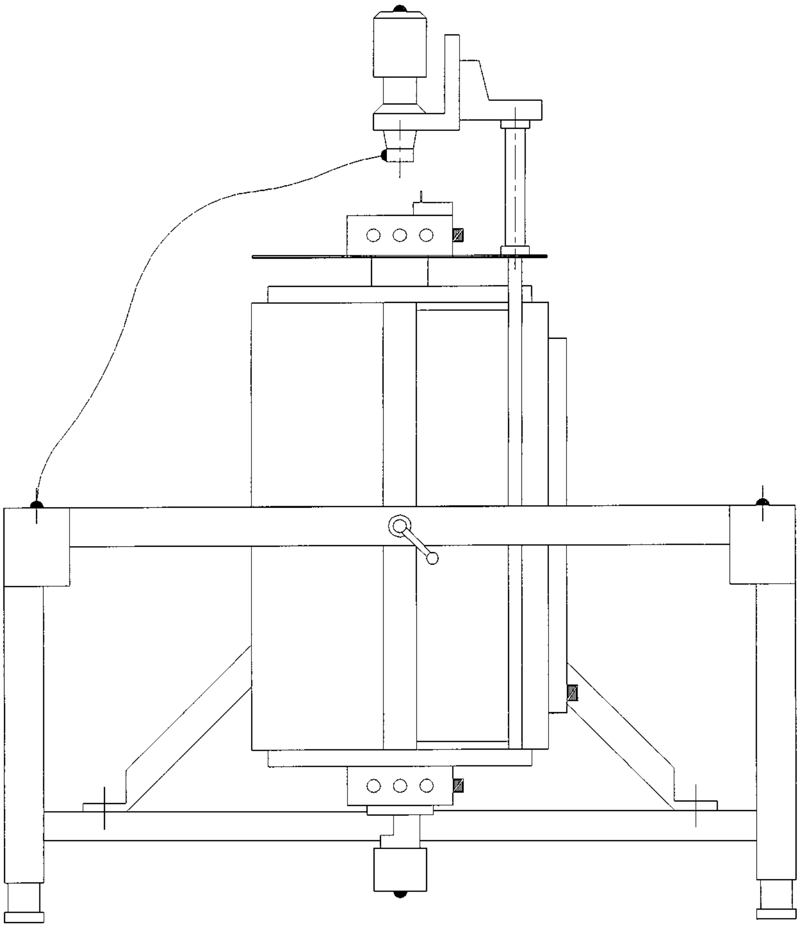


Figure 13 High-Temperature Processing Microscope: detailed schematic drawing of the furnace assembly, in vertical position, showing the illumination, optical and video-recording devices. The furnace can be rotated around an horizontal axis, so that horizontal observation of the sample is possible [129].

Numerous applications of the HTPM in several areas of materials science and engineering are possible, as described below.

4.2. Applications

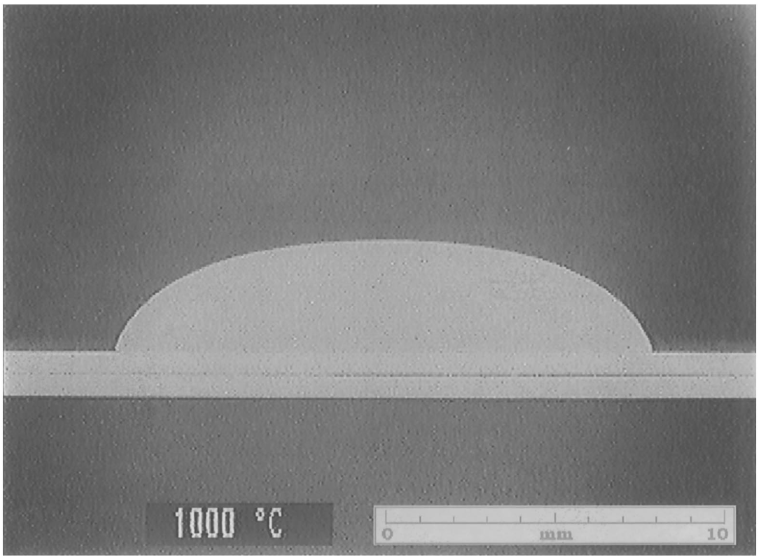
4.2.1. Horizontal working position

In the horizontal working position, the HTPM allows to investigate sintering, softening and melting processes in powder samples and solid compacts which are 10 times larger than those commonly suitable for heating microscopes (see Section 2.1). Of particular interest is the observation of the flow and melting behaviour of glass samples at different temperatures in order to obtain viscosity (η) values. This method was introduced by Reich and Panda [39, 40] and extensively used by Scholze [28]. Although the standard heating microscope can be used also for these measurements, as shown in the literature [32], the larger samples suitable for the HTPM permit the attainment of higher accuracy. In particular, the hemispherical point (fluxing point) can be determined with very high reliability using the present apparatus, so that the temperature at which the viscosity reaches a fixed value ($\log \eta = 4.2$, with η in dPa) can be assessed accurately. The influence of external conditions including sample preparation, heating rate, furnace atmosphere and substrate material on the temperature for hemispherical condition can be investigated also. In addition, the melting behaviour of a glass on different substrates, which depends on the surface energies of the solid and liquid phases, can be also investigated. Fig. 14 shows, for example, the different flow behaviour of a standard NBS glass on different substrates (alumina and platinum) at 1000 °C. Similarly, the determination of contact (wetting) angles between a solid and a liquid phase by the sessile drop method is possible, as well as the study of the flow behaviour of glazes on ceramic substrates (e.g. procelain).

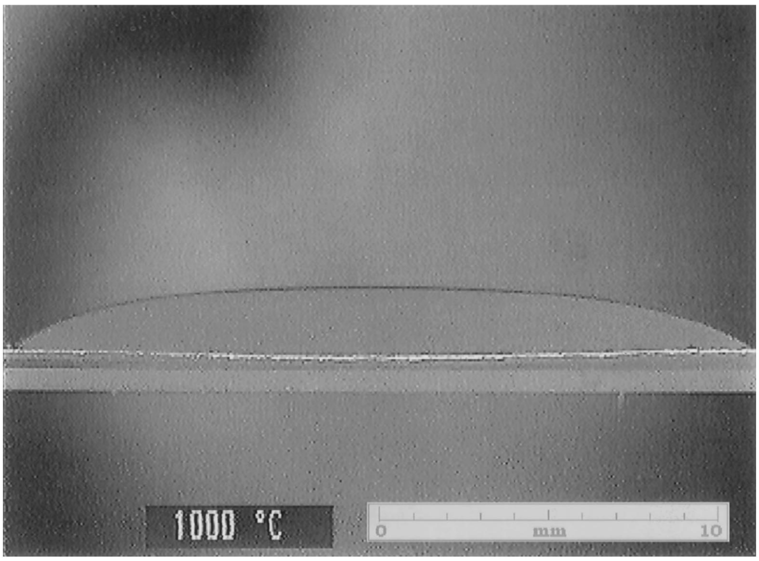
Phase transformations, in particular crystallisation, of glass samples can also be investigated using the HTPM. While thermoanalytical (DTA) measurements provide the temperature of the onset of a crystallisation reaction, observation of a sample at temperature supplies information on the progress of crystallisation and on its effect on the sample dimensions and shape. Other uses of the HTPM include the determination of the thermal expansion of dense samples and the assessment of oxidation processes at different temperatures.

4.2.2. Vertical working position

In the vertical working position the HTPM offers the possibility of direct observation of the melting process of raw materials, powders and glass cullet, including the investigation of bubble formation, and the measurement of bubble size and distribution during melting.



(a)



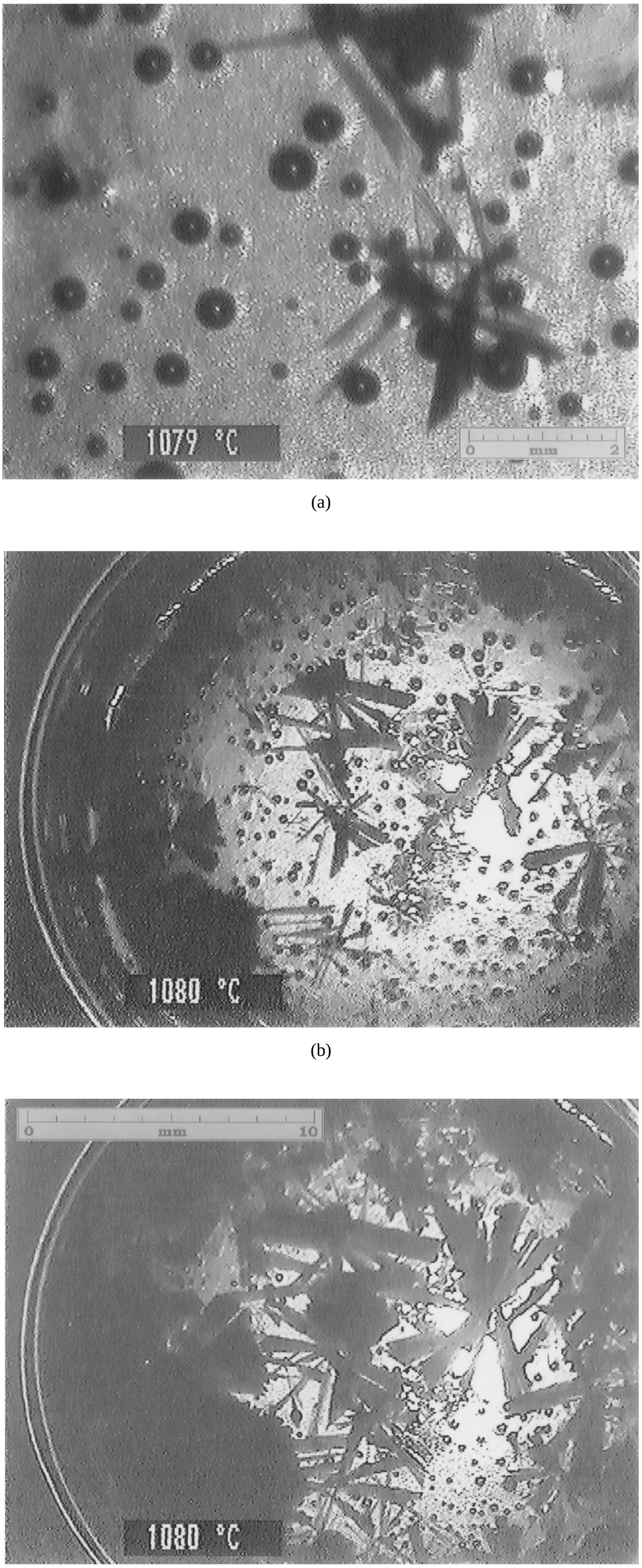
(b)

Figure 14 Video images obtained in the HTPM, showing the different flow behaviour of a standard NBS glass on (a) alumina and (b) platinum substrates at 1000 °C.

Other phenomena which can be observed in situ are the crystallisation of glasses and the melting of crystalline phases in glass melts. Due to the novelty of this kind of observations, examples are presented below.

i) *In situ observation of crystal formation in glass melts*: The *in situ* observation of crystallisation processes in glass melts is of great practical importance. It allows for the determination of relevant crystallisation parameters, such as crystallisation temperature, crystal growth rate, crystal appearance, etc., in a direct simple way. To the authors knowledge, there is very limited work in the literature related to the *in situ* observation of glass crystallisation processes [4]. A typical series of images of a modified float glass melt, as obtained by the HTPM, is presented in Fig. 15. Both crystal formation after 15 min at 1079 °C (Fig. 15a) and crystal growth with increasing time at temperature (Fig. 15b–d) are clearly observed. A series of images such as those of Fig. 15 allows for the determination of several crystallisation parameters, including the volume fraction of a crystalline phase at different processing times, the crystal growth rate, etc.

ii) *In situ observation of melting and dissolution of crystals in glass melts*: The HTPM allows also for a precise determination of the melting temperature of crystalline phases in a glass melt. These measurements are normally conducted by using the standard Differential Thermal Analysis (DTA) technique. However, the identification of the endothermic peaks revealing the melting point of a crystalline phase in a DTA-plot is not always easy, particularly when several crystalline phases are present and the respective peaks can be mounted on each other. *In situ* observation of the process is, then, a useful complementary technique. Fig. 16a–c show, for example, the melting and dissolution of a crystal in a glass melt, as observed by the HTPM. A star-shaped crystal is present in the glass matrix at room

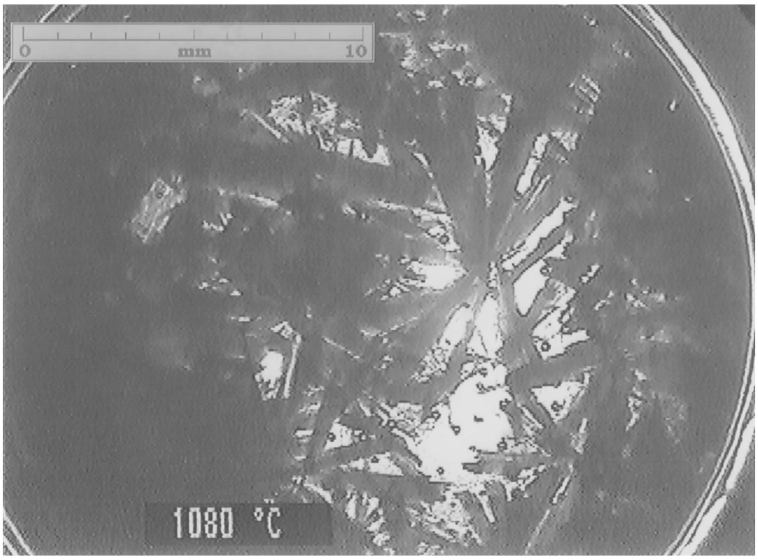


(a)

(b)

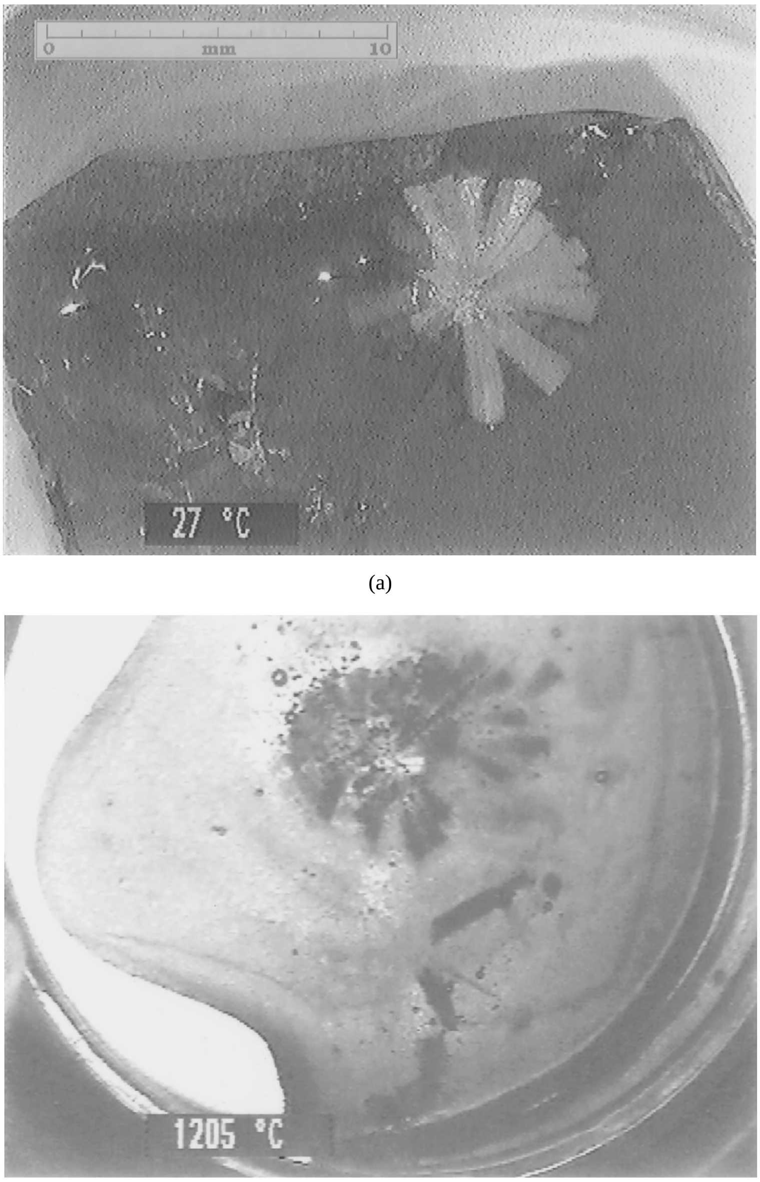
(c)

Figure 15 Series of images of a modified float glass melt, as obtained by the HTPM working in vertical position. The images show: crystal formation after 15 min at 1079 °C (a) and crystal growth with increasing time at temperature (b–d). (*Continued*)



(d)

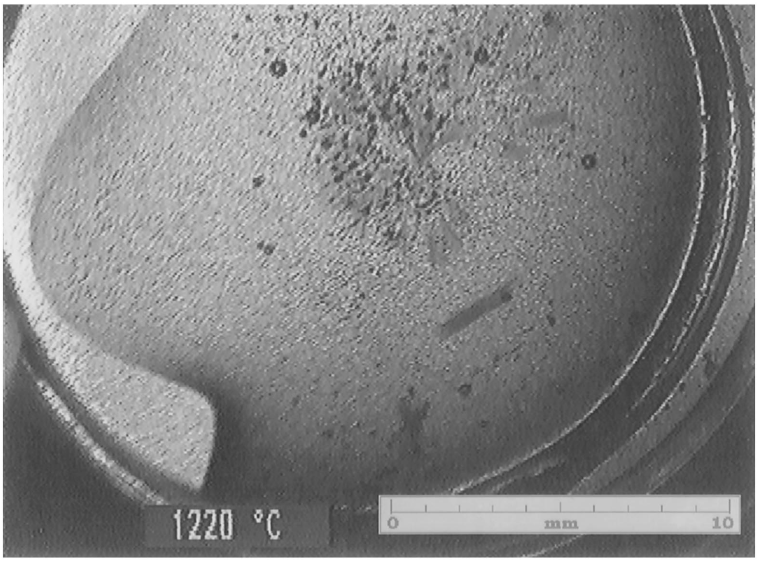
Figure 15 (*Continued.*)



(a)

(b)

Figure 16 Series of images showing the melting and dissolution of a crystal in a glass melt, as observed by the HTPM working in vertical position. A star-shaped crystal is present in the glass matrix at room temperature (a). With increasing temperature, the crystal changes its shape, separates in individual, smaller crystals and dissolves itself in the glass melt (b, c). (*Continued*)



(c)

Figure 16 (*Continued.*)

temperature. It is seen that in a very narrow temperature window (1205–1220 °C), the crystal changes its shape, separates in individual smaller crystals and dissolves itself in the glass melt. Fig. 16b and c show the decrease of the crystal volume with increasing temperature. The microscope allows, thus, for a precise determination of the crystal-free temperature of a glass melt. Similarly, observations of the formation and dissolution of gas bubbles in a glass melt can be conducted using the HTPM. Determination of relaxation processes and of miscibility gaps in glasses may be also possible, as well as the measurement of ion diffusion rates in glass melts.

5. Conclusions

Although often ignored when listing materials characterisation techniques and microscopy methods, *in situ* high temperature optical microscopy is a very important tool in materials science an engineering, as we intended to show in this review. A great number of application examples of high-temperature optical devices was presented, including investigations using very well-known commercial instruments, such as heating microscopes, as well as research conducted using custom-made devices. Certainly, the direct visual observation of a sample while undergoing changes of its external morphology and/or dimensions during a high-temperature process will continue to attract the interest of researchers due to its straightforwardness. The same is true regarding the "*in-situ*" observation of macroscopic modifications in the structure of a sample at high-temperatures, for example the development of large crystals or bubbles in a glass melt. Thus, an increase in the use of high-temperature optical microscopy in diverse areas of materials science and technology can be foreseen. Commercial heating microscopes may be expected to experience modifications in design, with the aim of extending their measurement capabilities, for example by incorporating a high-pressure stage or by including more flexible sample observation systems. Moreover, self-made, high-temperature optical devices or processing microscopes, will most probably continue to be constructed in the future for specialised, mainly scientific, applications.

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