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Sintering of waste of superalloy casting investment shells as a fine aggregate for refractory tiles

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Abstract

Powders obtained by milling ceramics shells, already used as investment material in casting processes, were sintered to investigate their possible re-use in the production of ceramic refractories. The sintering behaviour of these powders, consisting essentially of silica and mullite, were analysed both in a heating run by conventional contact dilatometry and in an isothermal process via optical dilatometry. The mechanical properties of sintered composites formed with a matrix of fine powders and an inert coarse phase of the same material are evaluated and discussed in view of possible use in the production of refractory tiles.

Keywords: A. Sintering; C. Mechanical properties; D. Mullite; E. Refractories

1. Introduction

In many industrial casting processes ceramic shells are used as investment materials. After use, a large amount of ceramic wastes are produced which in turn affects the overall production costs. The re-use of these materials in the form of powders to be used in new sintering processes could be recommendable in spite of additional milling costs.

The refractory lining in the combustion chamber of gas turbine plants is normally made of sintered tiles of traditional mullite/alumina refractory. The microstructure of such a refractory is rather heterogenous, including coarse mullite [1] and alumina grains (over 1 mm in size) with large macropores, bounded by a fine microporous alumina matrix. Microcracks of a size comparable with that of the coarser grains are present to some extent throughout the matrix, sometimes crossing the mullite grains. The large amount of open porosity (beyond 18%) allows to keep low both the thermal conductivity and the weight of the tiles. As a consequence, however, the mechanical strength is very low (flexural strength around 13 MPa and fracture toughness $K_{Ic} = 0.7$ MPa $m^{1/2}$). During their service (typically 20,000 h between two consecutive maintenance stops) the tiles, which are normally grafted to the steel hull, undergo both thermal cycling and mechanical vibrations. On inspections during the maintenance stops, it is not infrequent to find the more exposed tiles damaged and these have to be replaced on site with difficult and expensive interventions. Typical damages are: surface degradation caused by exposure to the hot combustion gas and formation of through thickness cracks of considerable lengths which, however, are kept under control by an effect of grain bridging opposing crack propagation.

The use of powders of waste shells containing a vitreous phase could be beneficial under two aspects. On one hand, vitrification at the hot side of the tiles may protect the surface from erosive actions, while viscous flow in the refractory matrix may improve its resistance to crack propagation [2].

The main problem in this application of the shell waste is, however, the sinterability of the powders when used as the fine matrix of refractory composites. The large grains behave as an inert reinforcement in all cases, so that any low-cost material could be considered for this purpose, including coarser powders of the same waste.

In the present work sintering experiments in both traditional and optical dilatometry have been carried out on powders

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obtained from milling of waste materials. The sinterability of such powders at 1400 °C appears to be comparable to that of alumina powders of similar size and the small scale mechanical properties are compatible with those of a common refractory. An attempt also was made to obtain a refractory composite by mixing fine powders with coarse grains of the same material and sintering at 1400 °C. This composite was also tested in bending and the results are compared to the behaviour of a traditional refractory.

2. Materials and methods

All samples in the present work were prepared starting from a waste ceramic material based on molochite whose phase composition derived from EDS and XRD spectra is: 53 wt.% vitreous SiO_2, 45 wt.% mullite, 0.7 wt.% Fe_2O_3 and 1.3 wt.% K_2O.

Fine powders (1–10 μm), obtained from this ceramic material by planetary milling, have been used to create samples for sintering tests; a slurry, obtained by addition of Polyvinylpyrrolidone acting as a lubricant, has been uniaxially pressed (60 MPa) to get cylindrical samples with 5 and 13 mm diameter. Before the experimental tests, samples were pre-heated at 450 °C for 2 h in order to remove any organic compounds; a slow heating/cooling rate (3 °C/min) was used to avoid thermal stress or forced gas release. Their green relative density, measured by the Archimede's technique, is 0.69.

The sintering behaviour was analysed both during heating with a linear temperature ramp via conventional dilatometry and in an isothermal process via optical dilatometry. The latter technique allows not only to use larger samples but also to avoid any compression of the sample by the dilatometer rod [3]. These tests have been performed in a tubular furnace, designed and built for wettability and surface tension studies (sessile drop method), which allows to introduce the sample in a very short time, typically 30 s, when all process parameters are stable; in this way we can simulate a quasi-isothermal heating process. During the tests, the sample profile could be monitored continuously by means of a CCD Camera in order to acquire images and subsequently measure any change in diameter. The diameters are calculated by means of the software Astra-VIEW2.0, originally developed by CNR-IENI staff [4,5] for surface tension and contact angle measurements. Calculations are made by comparison with a reference material, a disk of sapphire, previously measured by means of a micrometric system with the precision of 1 μm; the thermal expansion coefficient of the reference disk is taken into account. Special attention has been paid in order to get good quality images with high contrast, high resolution and absence of any reflections by means of filtering, focusing and backlighting; in particular, backlighting allows acquiring the shadow of the sample avoiding dimensional uncertainties due to the effect of sample radiance.

In each picture the diameter has been evaluated as the mean value of 14 measurements at different heights of the sample by the computer program and dimensions have been checked after each experiment using a micrometric system.

Moreover, a set of cylindrical samples have been sintered in a muffle furnace at 1350 °C reaching a final relative density of 0.77; these specimens were mechanically tested in radial compression (Brazilian test) to determine the tensile strength.

Finally, in order to evaluate the feasibility to produce a refractory with improved characteristics from this molochite based waste material, a composite was made by slip casting mixing together 20% of fine powder (1–10 μm), 70% of coarse grains (0.5–1.5 mm) and 10% of pure alumina (1–10 μm). After sintering in muffle at 1350 °C the material reached a final apparent density of 1.6 g/cm^3 (without pressing). From this composite, three specimens with dimensions 10 mm × 23 mm × 105 mm were cut for mechanical testing.

3. Results

3.1. Sintering

Samples with a diameter of 5 mm were sintered in a dilatometer up to 1460 °C with a linear temperature ramp of 10 °C/min in order to define the optimal temperature for the further isothermal sintering tests. The dilatometer curve shows the start of sintering at 1100 °C, a quite steady state rate in the range 1200–1400 °C, while from 1400 °C the process has a sharp acceleration (see Fig. 1).

Then, for isothermal sintering, two temperatures have been chosen: 1300 °C and 1400 °C; samples were kept at constant temperature for 2 h and then cooled. In Fig. 2 the plot of shrinkage against time is presented, the first point (the big black circle) represents the initial diameter as measured before the experiment; the lag between this point and the first measured point is due to the procedure required for the image optimization (focusing, filtering, etc.). The final microstructures of samples sintered at the two temperatures are shown in the SEM micrographs of Fig. 3.

3.2. Mechanical tests

Ten cylindrical samples sintered in a muffle furnace at 1350 °C were mechanically tested in diametral compression (Brazilian test). A mean tensile strength of 20 MPa was obtained,

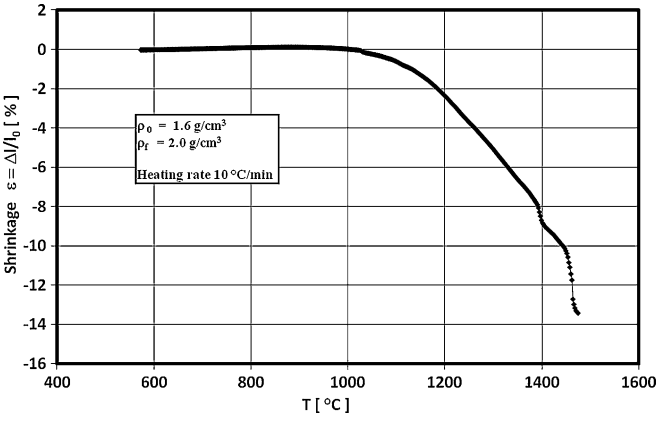

Fig. 1. Dilatometer curve for sintering up to 1460 °C.

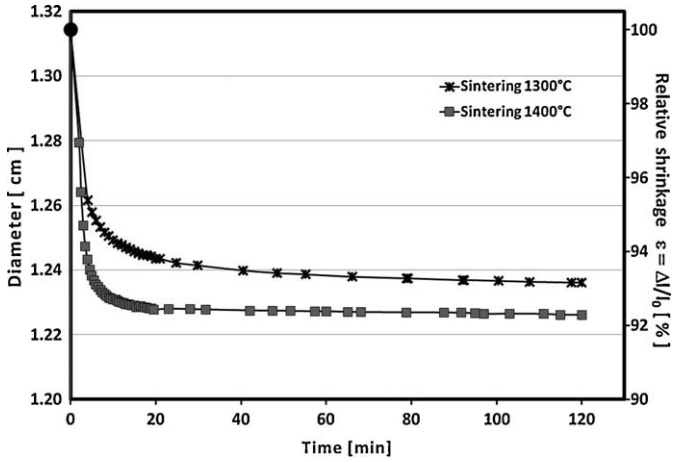

Fig. 2. Diameter vs. time (a) and shrinkage vs. time (b) curves for isothermal sintering.

comparable to that of a standard refractory. The Weibull curve shows a certain dispersion of data with a low value of the Weibull parameter m (Fig. 4), as expected for this type of testing.

In order to investigate the mechanical properties of the composite material made by fine powders and coarse grains, elastic modulus and flexural strength have been measured on the three specimens described in Section 2. The dynamic elastic modulus was evaluated by means of the resonance method resulting in a mean value of 18 GPa while the flexural strength, evaluated in 4-point bending by a testing machine INSTRON8501 in displacement control (0.1 mm/min), gave a mean value of 9.9 MPa. All samples broke apart instantaneously after reaching the rupture load.

4. Discussion

The dilatometric curves for isothermal sintering described in the previous section can be converted into semi-logarithmic plots of $\ln(\mathrm{d}\rho/\mathrm{d}t)$ vs. ρ, the relative density of the compact. These plots, typically, appear as descending straight lines in the initial/intermediate stage of sintering and bend down in the final stage, when the sintering rate decreases, tending asymptotically to a final density ρ_f. The main features of the plots are therefore ρ_f and the (negative) slope S of the linear part. The higher is S, the faster is the process.

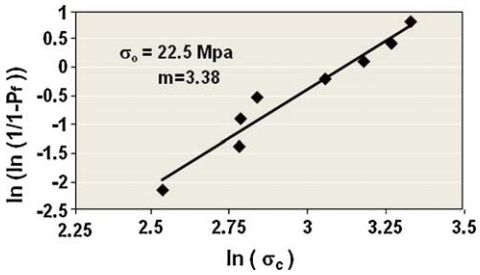

Fig. 4. Weibull curve for Brazilian tests for samples sintered at 1350 °C.

When a unique diffusion mechanism is involved, the isothermal sintering follows a kinetic law relating the densification rate to actual density, according to Eq. (1) [6]:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = k(T)\frac{\Sigma}{r_{\mathrm{m}}^{n}} f(\rho) \tag{1}$$

where

- $k(T) \propto \exp((-Q_i/k_{\mathrm{B}}T))/k_{\mathrm{B}}T$ is a thermodynamic factor, Q_i is the activation enthalpy of the dominating diffusion mechanism and k_{B} is the Boltzmann constant;
- r_{m} is the mean particle radius and the exponent n depends on the diffusion mechanism;
- Σ is the so-called *sintering stress* [7], a thermodynamic parameter which plays the role of driving force of the process, nearly temperature independent and inversely proportional to r_{m};
- $f(\rho)$ is a function describing the kinetics of the process depending on the dominating diffusion mechanism and, implicitly, on the microstructure. At constant microstructure, i.e. in the absence of grain growth or particle rearrangement, this function is independent of both temperature and particle size. It follows that, starting from equal green compacts, the semi-logarithmic plots should have the same shape, being only translated along the vertical axis. In particular the slopes in the stationary part of the kinetics should be equal. The final parts of the curves could be different, however, if grain growth occurs.

In the case of the present experiments the final microstructures of the two compacts show that no grain growth had occurred.

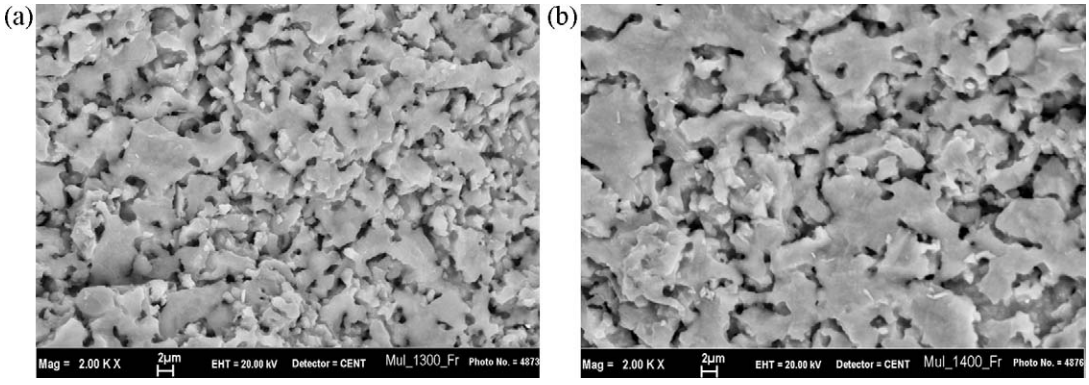

Fig. 3. Microstructure of a fracture surface of a sample sintered at 1300 °C (a) or at 1400 °C (b).

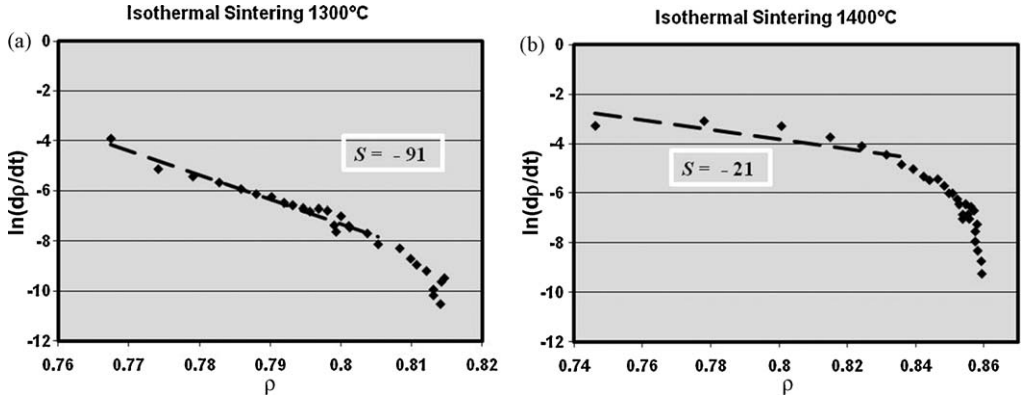

Fig. 5. ln(dρ/dt) vs. ρ curves for isothermal sintering at 1300 °C (a) and 1400 °C (b).

Yet, the two plots are very different in shape: the slopes in the linear parts (evaluated as a linear regression of the points before the bending down) are $S = -91$ for sintering at 1300 °C and $S = -21$ for sintering at 1400 °C, and the final densities are respectively 0.815 and 0.865. An explanation could be a change in the diffusion mechanism. The influence of the diffusion mechanism can be followed in a local sintering law (i.e. the law describing the centre-to-centre approach ε_d of two particles connected by a neck), which can be written, in analogy to Eq. (1), as

$$\dot{\varepsilon}_d = A_0 {r_m}^{-(s+1)} {\varepsilon_d}^{-p} \quad (2)$$

where r_m is the arithmetic mean of the two particle radii and A_0 a process constant. This law is perfectly equivalent to that given by Exner and Arzt [8] in integral form. The value of p, involving the term ${\varepsilon_d}^{-p}$, accounts for the diffusion mechanism: the values corresponding to Exner and Arzt's calculations are given in Table 1 for two different shapes of particles. One can see that the lowest values of p correspond to the mechanism of viscous flow. Thus the higher S obtained for samples sintered at 1400 °C can be explained with the activation of viscous flow in the silica phase of the molochite powders. The presence of a slope change at a temperature very close to 1400 °C in the dilatometric curve of Fig. 5 supports such an interpretation. The low value of S for the sample sintered at 1300 °C is due to desintering phenomena [9], namely particle rearrangement followed by ruptures of already formed necks, as suggested also by the aspect of the final microstructure (Fig. 3). Assuming the slope S as an index of the sinterability of a powder compact, it is worthwhile noticing that the sample of molochite powder from re-use of casting shells, when sintered at 1400 °C, has a sinterability quite similar to that of alumina, as demonstrated by the plots of Fig. 6 which were elaborated from the literature data [10,11]. A difference is, however, that the molochite powders seem to have some difficulty to reach a high final density. This point might be not so important in the present case, because the mechanical strength of the sintered powders is at all events sufficient when they are used as a fine aggregate in refractories.

In the mechanical testing of samples obtained by sintering an aggregate of fine powders with coarse grains of the same material, the post-rupture behaviour deserves attention. In fact, this sample breaks apart instantaneously after reaching the rupture load when tested in bending. On the other hand, a sample of standard refractory undergoes progressive fracture with large deflections because of the effect of bridging by the coarse grains [12]. The contribution of crack bridging is totally absent in the new type of refractory. To explain this behaviour, we begin with noticing that sintering between the small particles forming the fine aggregate and the coarse grains is impossible, whichever the materials used, because the sintering stress Σ is too low. Thus the clamping of coarse inclusions in the matrix, which is necessary for bridging fracture surfaces, can occur only by mechanical constraints. One way is to rely on the particle shape: in the present case the particles are normally convex and it would be too expensive to tailor their shapes otherwise. Another way is to take advantage of the thermal mismatch between matrix and inclusions,

Table 1
Values of mechanism parameters p and s.

Diffusion mechanism	Spherical particles		Cubic single crystal particles	
	p	s	p	s
Grain boundary diffusion	2	3	5	3
Volume diffusion	1.5	2	4	2
Viscous flow	0	0	1	0

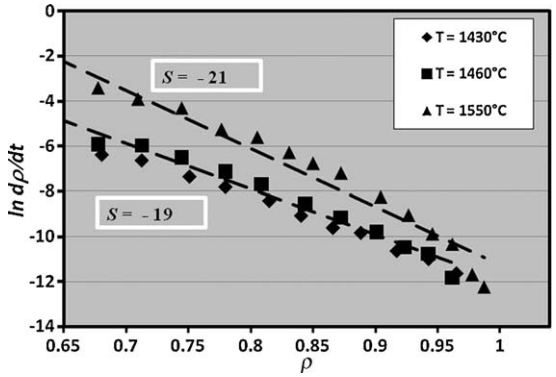

Fig. 6. ln(dρ/dt) vs. ρ curve sintering of alumina powder (redrawn from Refs. [10,11]).

i.e. the difference $\Delta\alpha$ between the coefficients of thermal expansion (CTE) of the two phases. If $\Delta\alpha > 0$, namely the matrix has a CTE higher than the inclusions, on cooling after sintering the inclusions will be under compression. Then friction forces will resist the extraction of inclusions during crack propagation, determining a bridging effect. In the standard refractory the matrix is made of alumina with $\alpha = 8 \times 10^{-6}\ K^{-1}$ and the inclusions are principally mullite with $\alpha = 5\text{–}7 \times 10^{-6}\ K^{-1}$ so that $\Delta\alpha > 0$. In the new refractory, the material of the two phases is the same and there is no effect from thermal mismatch.

5. Conclusions

Powders obtained from waste of ceramic casting investments are essentially molochite with a considerable fraction (53 wt.%) of vitreous silica.

Milled to a size of 1–10 μm such powders have good sinterability at a temperature of at least 1400 °C and can be proposed for use as a fine aggregate in refractory tiles.

The mechanical properties of sintered composites formed with a matrix of fine waste powders and an inert coarse phase of the same material are comparable with those of conventional mullite/alumina refractories.

The choice of the coarse phase, however, is crucial to provide an adequate resistance to crack propagation, which is essential to resist thermal shocks.

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