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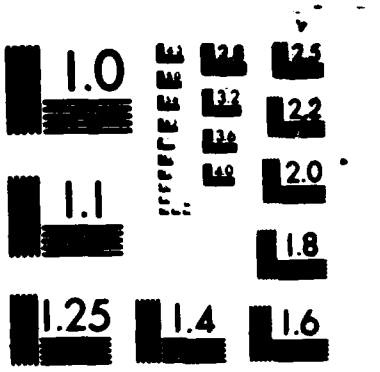

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Ceramic-Ceramic Composites Meeting in Belgium

Dr. Louis Cartz

4 August 1987

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The problems of obtaining homogeneous dispersions of multicomponent systems were frequently discussed at this conference. The use of acoustic emission was shown to be a useful NDT analytical tool to detect the presence of microcracks in different places. The composite systems considered at the meeting included: zirconia-toughened aluminum (ZTA), SiC fiber-reinforced pyrex, SiC fiber-reinforced silicon (SiO_2) glass matrix, mullite-zirconia-Al_2O_3-SiC, C-fiber-reinforced reaction-bonded SiC, ionic conducting NASICON-glass insulator composites, and γ-AlON-Al_2O_3 composites. The zirconium oxycarbide system, ZrO_2-ZrC_xO_y and ZrC-ZrC_xO_y composites are interesting, novel systems.

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CERAMIC-CERAMIC COMPOSITES MEETING IN BELGIUM

A conference on Ceramic-Ceramic Composites was held at the Université de l'Etat in Mons, Belgium, from 13 through 15 April 1987. It was organized by Le Centre de Recherche de l'Industrie Belge de la Céramique (CRIBC) and the Association Belge pour Favoriser l'Etude des Verres et des Matériaux Céramique (ABVC). Participants and speakers came from most of the Western European countries, in particular, Belgium, France, Germany, and the UK. Papers were presented on the following topics:

- Homogeneous dispersions of multicomponent systems
- SiC-fiber-reinforced composites
- Composites containing an ionic conducting component
- Zr-C-O system
- The use of acoustic emission testing.

Homogeneous Dispersions

An important part of the meeting was concerned with the homogeneity of ceramics of complex compositions which might contain several phases or be reinforced by a dispersion of fibers, whiskers, or other shaped particles. Several speakers discussed the problem of obtaining such homogeneous dispersions, particularly where extensive grinding might damage the fibers or whiskers.

R.J. Brooks (University of Leeds, UK) reviewed the different types of inhomogeneities, which may arise from grain-size differences, density differences, or different chemical compositions. Even where the inhomogeneities are due simply to local density differences in the green body, different rates of sintering, can be caused because the rate of density increase is greatest for low-density bodies. Different sintering rates due to density differences in the green body can lead to local stresses building up in the sintered material. To avoid this, the initial density differences in the green body, should be kept small, initial density should be as high as possible, and low-density inclusion--and, in particular, nonsintering inclusions--should be avoided. Brooks compared the sintering of composites with the sintering rate of the green body with and without nonsintering inclusions. As little as 20 percent of inclusions in the green body can reduce the matrix sintering rate to zero. This happens when the back-stress due to the presence of nonsintering inclusions equals the sintering stress; it arises from the fact that the nonsintering component does not change dimension, while the sintering component shrinks.

Brooks set out to estimate the back-stress due to the inclusions. To do this, he assumed a viscous system where the densification rate is proportional to $\sigma(E)/\eta$ or $[\Sigma-\sigma(B)]$, where $\sigma(E)$ is the effective driving stress and equal to $\Sigma-\sigma(B)$, Σ is the sintering stress and $\sigma(B)$ the back-stress due to the inclusion, η the viscosity, and ρ the density. Using a Maxwell model for a viscoelastic solid, the change in the stress $\dot{\sigma}$ can be related to the difference between the stress developed less the stress released. That is:

$$\dot{\sigma} = G\dot{\Delta\rho} - G\sigma/\eta$$

where G is the shear modulus, $\Delta\rho$ the strain rate due to different densification rates due to different densities, and $G\sigma/\eta$ is the stress release due to vision flow. The stress release $\dot{\sigma}$ is dependent on G/η, and this is used as a figure of merit for sintering behavior (see Hsueh et al., 1986, for a further discussion of back-stresses due to nonsintering inclusions). Brooks pointed out that ZrO_2 and Al_2O_3 have low figures of merit and so have poor sintering characteristics, while glass with a high figure of merit has good sintering behavior.

Brooks discussed the following ways to improve sintering:

1. Reduce $\dot{\Delta\rho}$; that is, the change of density differences with time. One method of doing this is to coat fibers with, for example, an organic coating which will be driven off at high temperatures, so that the fiber can be considered to be shrinking in size comparable to the sintering shrinkages.

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2. Use reaction sintering--for example, $Si+N_2$ to produce Si_3N_4.

3. Reduce the viscosity of the system. This requires smaller grain sizes, higher temperatures, or the use of liquid phase sintering.

4. Increase the sintering stresses by applying high pressure, as in hot isostatic pressing (HIP).

The analysis that Brooks presented showed that there are ways of sintering other than resorting to HIP. Replying to questions, Brooks pointed out that fibers in composites should be under compression, not under tension.

Zirconia Ceramics

A review of the mechanical behavior of composites reinforced by particles was presented by G. Fantozzi (Institut National des Sciences Appliquées [INSA], Villeurbanne, France). He discussed the toughening of composites using the tetragonal (T) to monoclinic (M) transformation of ZrO_2. Zirconica is cubic above 2350°C, tetragonal down to 1170°C, and monoclinic at lower temperatures. There is a 3-percent decrease in volume on increase of temperature through the M→T transformation, though the metastable tetragonal form can exist at lower temperatures. A reinforcement of the toughness of the ceramic can result, depending on the amount of metastable tetragonal form present. The transformation T→M depends on several factors--in particular, the difference of surface energies of the M and T forms--and there is a critical particle size below which the transformation does not occur. Fantozzi pointed out that the toughness of the composite depends on the particle size of ZrO_2 used, and he described the effects of very small particle-size ZrO_2 on the composite. He reviewed the properties of the composite zirconia-toughened-alumina with addition of Y_2O_3 (ZTA or Y-ZTA).

P. Mathieu (Céramiques Techniques, Desmarquest, France) described work on SiC-whisker-reinforced zirconia-toughened alumina (ZTA). He discussed the difficulties of obtaining good dispersions where there is the possibility of damage to the SiC whiskers during extensive grinding. The effect of the aspect ratio and how specimens may be densified by HIP were also discussed. ZTA ceramic composites were also discussed by G. Orange (INSA, Villeurbanne) and by L. Mazerolles (Centre d'Etudes de Chimie Métallurgique [CECM], Vitry-sur-Seine, France).

Zeta-Potentials

The importance of matching zeta potentials to obtain good dispersions was discussed by G. Moortgat (CRIBC); where the two powders have the same ζ-potential, a homogeneous dispersion of the two powders becomes possible. The change of ζ-potential with pH and the case of $ZrO_2+Al_2O_3$ where both have the same ζ-potential at very low pH were discussed. Moortgat described an electrolytic method where good dispersions of homogeneous powders are obtained; some questioners commented that other investigators have found this method to be unsatisfactory.

SiC-Based Composites

D.M. Dawson et al. (Harwell Laboratory, Didcot, UK) described the "Fabrication and Evaluation of Nicalon SiC fiber-reinforced Glass" (Dawson et al.; 1986). The matrix is of pyrex glass and the fibers are aligned, continuous SiC (Nicalon) tows. The method of preparation permits the formation of a dense composite with minimum porosity, using the flow properties of the glass under hot pressing. The stages in the preparation are as follows:

1. An organic protective coating on the SiC fibers is removed by heating.

2. The SiC fibers are passed through a suspension of glassy particles in H_2O, so that the fibers become impregnated with glassy particles.

3. The filaments are wound around a flat wheel and dry out to form flat ribbons up to 6" wide.

4. The ribbons are cut, giving sheets of material called "pre-preg."

5. The sheets of pre-preg are stacked as required and hot pressed up to 1600°C.

6. The finished composite now consists of layers, each with aligned SiC fiber; different orientations can be chosen for the sequence of stacked layers.

The mechanical properties of this composite depend on the following fabrication parameters: conditions of burn-off of the organic coating of the fiber, slurry composition, fiber tension and winding conditions, hot pressing temperature, time, and pressure. Following a systematic analysis of these factors, composites have been prepared of fiber volume fraction 0.5 having flexural strength of 1.25 GPa, Weiball modulus 30, elastic modulus 120 GPa, and fracture energy above 50 kJm^{-2}. Fatigue testing has shown the material to undergo no degradation of properties after 1000 hours at stress levels of 1 GPa. Pyrex softens above approximately 500°C when deformation of the composite occurs. However, specimens held at 500°C for 1000 hours in air under a load of 0.5 GPa, showed no subsequent significant degradation at room temperature.

Enhancing Shock Resistance and Hardness. C. Baudin (Instituto de Ceramica y Vidrio, Madrid, Spain) described the use of SiC grains as a dispersed phase to enhance the thermal shock resistance and hardness properties of mullite-zirconia-SiC composites. These composites are formed by reaction sintering, heating $ZrSiO_4$ with Al_2O_3 when mullite and ZrO_2 form at 1400°C, as in the following equation:

$$\underset{\text{zircon}}{2ZrSiO_4} + 3Al_2O_3 \xrightarrow{1400°C} \underset{\text{mullite}}{3Al_2O_3 \cdot 2SiO_2} + 2ZrO_2$$

This reaction has been carried out in the presence of excess Al_2O_3 and also MgO and at temperatures ranging from 1450 to 1570°C, forming multicomponent ceramics by a reaction sintering process. The phases present in the composite are $3Al_2O_3 \cdot 2SiO_2$, ZrO_2, Al_2O_3, and SiC.

Baudin discussed the improvement in the thermal shock behavior of zircon-based ceramics by the addition of SiC which has good thermal shock characteristics. Volume changes occur during the reaction, with the final density being lower than that of the starting material. It is necessary to avoid SiC being in contact with ZrO_2 and to enhance the SiC-mullite contacts since this will reduce oxidation effects at high temperature.

Acoustic Emission Testing. The use of acoustic emission to follow the formation of crack surfaces in Al_2O_3-ZrO_2-mullite ceramics was described by L. Delay (Katholieke Universiteit, Leuven, Belgium). The acoustic events have been characterized in terms of their energy. Low-energy acoustic events correspond to cracks in the glass phase, high-energy events correspond to cracks in the alumina phase, and medium-energy events to cracks in the mullite and ZrO_2 crystals. This has been determined by the simultaneous studies of factography and acoustic emission, using a microindentation technique. In the case of the mullite-alumina-zirconia composites--prepared by reaction sintering $ZrSiO_4$-Al_2O_3 containing small amounts of CaO, HgO and TiO_2--a liquid phase enhances the sintering and the reaction rates. By correctly choosing the oxide quantities, the liquid phase should disappear during the heat treatment. The acoustic emission testing is a satisfactory nondestructive testing method for detecting any residual glass phase.

Composites Containing Ionic Conductors

Chorlet (Ecole Nationale de Céramique Industrielle [ENSCI], Limoges, France) presented papers on ionic conductors such as $Na_3Zr_2Si_2PO_{12}$ (NASICON). A sol-gel synthesis of NASICON can be carried out by the polycondensation hydrolysis of alkoxides (Bouquin et al., 1987). The powders obtained remain amorphous up to about 700°C; the crystallization develops between 800 and 1050°C with an increase in Knoop microhardness to a value of about 100 GPa, when the crystallite sizes are typically about 100 nm. Chorlet reported the microstructure and chemical behavior of a composite ceramic containing the conducting phase NASICON and an insulating glass. The structure can be characterized from the electrical

conductivity of the composite. NASICON has an electrical conductivity of approximately $10^{-1}\Omega^{-1}cm^{-1}$ and the glass phase ($Na_2Zr_4Si_{16}P_8O_{61}$) a conductivity less than $10^{-6}\Omega^{-1}cm^{-1}$. The presence of 3 percent of glass reduced the electrical conductivity of the ceramic by a factor 10 and the value approaches that of a glass with approximately 10 percent glass. The electrical properties of the composite are dependent on the sintering temperature. The electrical behavior of the composite can be used as a diffeent way to characterize some features of the microstructure of the composite.

Ceramics of Zr-C-O

F. Thévenot (Ecole Nationale Supérieure des Mines, Saint-Etienne, France) gave an interesting and comprehensive description of ceramics containing the Zr-C-O system (Barnier et al., 1986). They studied, in particular, three materials:

- $ZrC_{0.963}$
- ZrCxOy, a new material
- The composites ZrC_xO_y-ZrO_2 and ZrC_xO_y-ZrC.

Zirconium carbide (ZrC), is fcc of density 6.6 Mg.m-3, m.p. 3420°C. ZrC has a large range of solid solution, is a hard metallic-type material, acid resistant, but it has poor oxidation resistance.

ZrC_xO_y is formed by reacting ZrO_2 with ZrC in vacuum where $ZrO_2 + ZrC \rightarrow ZrC_xO_y + CO$. With an excess ZrO_2, the resulting composite contains a mixture of ZrC_xO_y and ZrO_2 (excess). The reaction starts at 1600°C, and at 2000°C 4 hours are required for the reaction to go to completion. In the Zr-C-O phase diagram, the solid solution phase of ZrC_xO_y has been determined. The cubic lattice parameters of ZrC_xO_y, which has a NaCl-type structure, vary with C and O content and have been determined. The composition of zirconium oxycarbide at the phase boundary with ZrO_2 is $ZrC_{0.64}O_{0.26}$.

The sintering of the composite $ZrC_xO_y + ZrO_2$ is carried out under pressure of 40 MPa, in an argon atmosphere. Composites containing up to 17 weight percent ZrO_2 have been prepared. Sintering of the composite is easier when the oxycarbide is richer in oxygen, and when more excess ZrO_2 is present in the composite. Sintering to 99 percent theoretical density has been achieved, and the temperature of sintering decreases from 2100°C to 1765°C as the O/Zr ratio increases up to 0.3.

The mechanical properties of ZrC-ZrC_xO_y and ZrC_xO_y-ZrO_2 composites have been extensively examined and measurements of Young's modulus, toughness, hardness, porosity, and grain sizes reported. As the microhardness increases with composition, the Young's modulus decreases. Fracture characteristics are essentially constant up to 1400°C for ZrC_xO_y-ZrO_2 composite.

Composites formed with an excess of ZrC (that is ZrC_xO_y + ZrC) or an excess of ZrO_2 (that is ZrC_xO_y + ZrO_2) were discussed. The composite with ZrO_2 has a more uniform distribution in ZrO_2 after extensive grinding (up to 16 hours); the ZrO_2 particles develop microcracks. The toughness increases with the grinding time used. Good properties have been obtained for a composite containing 2.4-percent ZrO_2, but this needs to be optimized, and further work is in progress. The very hard ZrC_xO_y is reinforced by ZrO_2. The resulting composite that has high oxygen content is stable to about 1400°C in an oxidizing atmosphere. For composite compositions low in oxygen content, the stability decreased to about 1000°C.

Thévenot discussed other possible systems: TiC_xO_y, HfC_xO_y, TaC_xO_y, and composites such as (Ti, Zr) C_xO_y-ZrO_2.

Thévenot reported during questioning that C appears to stabilize the monoclinic form of ZrO_2.

Other Papers of Interest

R. Gadow (Haldenwanger Technische Keramik, Waldkraiburg, West Germany) gave a brief review of fiber-reinforced, reaction-bonded SiC. Composites have been made from oriented, continuous carbon fibers, coated with SiC by chemical vapour deposition and then infiltrated

with Si liquid. This is followed by carbonization, though Gadow did not describe the procedure, to produce composites that have flexural strengths of 0.7 GPa and fracture toughness 10 MPa$\sqrt{m}$.

A. Hometin (Criceram, Jarrie, France) briefly described the creep behavior of an interesting type of ceramics having superplasticity--a high creep rate with very large strains. This property should permit pressureless sintering as well as high-pressure shaping of the ceramics. The creep behavior of Al_2O_3-ZrO_2-Y_2O_3 was briefly described.

P. Lamidieu (ENSCI, Limoges, France) used elastic wave measurements at high temperatures to determine the variation of Young's modulus with temperature and time. For composites prepared from three-dimensional continuous-fiber SiC in a matrix of SiO_2, he followed the structural and microstructural changes by x-ray diffraction and by electron and optical microscopy.

Goeuriot-Launay (Ecole des Mines, Saint-Etienne, France) described the improvements obtained in the mechanical properties of Al_2O_3 by the presence of a dispersion of γ-AlON. A 10 percent addition of γ-AlON reduced the wear of Al_2O_3 by a factor of 10 in the case of wear due to a metal-ceramic interface under load in H_2O for 2 hours. The γ-AlON tends to block the Al_2O_3 grain movements at high temperature so that the mechanical properties of a composite containing 20 percent γ-AlON are constant to approximately 1400°C, under N_2. The γ-AlON-Al_2O_3 composite is prepared by reaction sintering of α-Al_2O_3 with AlN; the thermal conditions are critical to avoid excessive grain size growth of the α-Al_2O_3 but must be of sufficiently high temperatures to form the γ-AlON.

Summary

The problems of obtaining homogeneous dispersions of multicomponent systems were frequently discussed at this conference. The use of acoustic emission was shown to be a useful NDT analytical tool to detect the presence of microcracks in different places.

The composite systems considered at the meeting included: zirconia-toughened aluminum (ZTA), SiC fiber-reinforced pyrex, SiC fiber-reinforced SiO_2 glass matrix, mullite-zirconia-Al_2O_3-SiC, C-fiber-reinforced reaction-bonded SiC, ionic conducting NASICON-glass insulator composites, and γAlON-Al_2O_3 composites. The zirconium oxycarbide system, ZrO_2-ZrC_xO_y and ZrC-ZrC_xO_y composites are interesting, novel systems.

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