JOURNAL OF MATERIALS SCIENCE **34** (1999) 3991 – 3996

Mechanical behavior of metaphosphate glasses used as coating on metals in relation to their structure and preparation method

A. IOST*, R. BIGOT
Laboratoire de Métallurgie Physique et Génie des Matériaux, CNRS UMR 8517 and Ecole Nationale Supérieure d'Arts et Métiers, 8 boulevard Louis XIV, 59046 Lille cedex, France

F. BARBIEUX, P. VAST
Laboratoire de Chimie appliquée, Bât. C4, Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq, France
E-mail: iost@lille.ensam.fr

The purpose of the present work was to investigate the mechanical behavior of metaphosphate glass coatings of the Na_2O-CaO-P_2O_5 system on steel substrates. These coatings may be used as thermal barriers or to give anti-corrosion protection. Coacervates of glasses under consideration were obtained by a coacervation process, from Graham's salt and deposited on aluminized steel substrate. Chemical composition of coacervate phases was improved by the choice of cations and addition of a filler to reduce the residual stresses in glass metal joints due to the thermal expansion coefficient mismatch. The chemical and mechanical properties of both the coating and the interface were studied by energy dispersive spectrometry (EDS) and hardness measurements. It was shown that an alumina layer is formed by the reaction between the phosphates compounds during curing. This layer acts as a barrier for the iron diffusion. The fracture toughness of the glass coating was investigated by Vickers indentations. Inasmuch the cracks are of the Palmqvist form, the Evans and Charles formula holds for calculating K_{IC}. A value near 0.85 MPa $m^{1/2}$ was found for all the glasses investigated. Residual stress distribution was calculated. The glass coating was in compression and residual stresses were reduced by the interlayer formation. A good adhesion was found since cracks produced by indentation near the glass steel interface propagated in the coating rather than along the interface.

---

1. Introduction

Certain interest exists concerning industrial applications of metaphosphate glasses and ceramics [1–3]. Although their chemical durabilities are generally less than that of silicate glasses in the presence of water, their low melting point and glass transition temperature [2] offer a possibility of using them as sealing agents or coatings on metals or ceramics substrates. Their reactivity in the liquid state with metal oxides is being currently used to generate coatings or sealing with many oxidized metals or ceramics [4]. One major potential use of metaphosphate glasses involves the enamelling of ceramics and metals. For this purpose we have developed a coating for steel surfaces, with a 500 to 1000 μm thickness, for use as a thermal barrier in the range of 700 to 1000 °C. In this case, metaphosphate glasses are used at the same time as a sealing agent for ceramic particles, which generate a thick coating by the formation of a glass ceramic composite, and for the adhesive bond of this composite to the metal substrate.

Among the different criteria for the adhesive bond, mechanical behavior is the principal and essential consideration. As a consequence, the metaphosphate glasses and the glass metal interface were studied by indentation measurements to determine the fracture toughness of glasses and to measure the adhesion. These measurements were performed on glass without ceramic fillers.

2. Experimental

2.1. Sample preparation

The coating of steel substrates was obtained by using a soft chemistry route viz the coacervation of polyphosphates [3–5]. In this method the starting compound is Graham's salt from which, with the addition of different kinds of cations, a colloidal phase is formed by polymeric long chains of polyphosphates, called coacervate [5]. These coacervates may be formulated by the addition of several cations at the same time [6]. Therefore,

---

* Author to whom all correspondence should be addressed.

it is possible to obtain different precursor formulation of various glass compositions with addition of metal oxide during the formation of coacervates [4].

Polyphosphate coacervates are liquids with viscosities from 10 to 10,000 cP depending on the water content and the kind of cation [2, 6]. The first step of preparation consists of a partial hydrolysis of the long metaphosphate chains by heating, and then the glass is generated by melting the mixture. In order to coat the metal substrate by the metaphosphate glass, the coacervate is deposited on the substrate by brushing, dipping or spraying. By heating, the coacervate generates a cement-like material (around 150–300 °C) which sticks to the substrate before forming a glass coating at the higher temperature.

Different conditions must be considered in order to obtain a good coating. Firstly we have to match the coefficient of thermal expansion of glass to the coated metal. This is accomplished both by the choice of cations that cause the coacervation phenomenon, and by the addition of a filler. Secondly, the glass substrate interface must be controlled.

For metaphosphate glass coatings, one should not start directly from a steel substrate, because the interaction between coacervates and metal leads to the formation of ferric oxides and poor adherence. As we have shown in earlier studies (for example, about coating on titanium by metaphosphate glasses), the presence of phosphide (or oxiphosphide) at the interface increases the mechanical strength of the interface [3]. The reason for our choice of using aluminized steel for this kind of coating is the important reducing capability of Al. We have also used the same method with another reducing agent like titanium in order to obtain coating for hip prosthesis [7].

The samples were industrial low carbon steel ($C < 0.03$ wt %) with an aluminum-silicon alloy coating having an average thickness of about 22 μm that was obtained by hot dipping followed by a skin pass. Two kinds of glasses were used for the coating (Table I). The first was obtained from a coacervate without filler and the second one with Fe_3O_4 as the filler. The coating curing temperature range was 800–900 °C.

2.2. Hardness and fracture toughness experimental

Indentation measurements were carried out with a standard Vickers diamond indenter using loads, P, from 0.05 to 20 N. All loads were applied in 30 s with a 15 s holding time. Before indentation, the specimens were polished by mechanical grinding to remove any compressive stresses in the surface which reduced the crack length. The crack length and indentation print, d, were measured by optical or confocal microscopy immediately after the removal of the load. Approximately ten measurements were made at every indentation load.

3. Results

3.1. Observation of the glass coating and of the interface

If we start from coacervate without filler, good wettability of the glass on the substrate is obtained. Nevertheless, many bubbles appear in the glass arising from the reaction between aluminum and phosphate in the presence of water, and forming as phosphine. Because of the glass viscosity, bubbles tend to remain near the interface and may decrease its mechanical properties. So it was considered necessary to stay at the curing temperature for an extra hour to eliminate the bubbles. The Fe_3O_4 filler reacts with glass at its melting point, decreases the bubble formation, and consequently enables one to obtain a glass coating without bubbles in within twenty minutes [3]. Fig. 1 shows a scanning electron micrograph of a sample cured at 900 °C without Fe_3O_4. The EDS analysis along the line AB (Fig. 2) gives the following results:

(i) The diffusion of iron, aluminum, and silicon is weak and has the same value along the glass layer.

(ii) At the interface, an aluminum-iron layer exists, but alumina presence has been found by scanning electron spectroscopy (SEM) or EDS.

In each case, even with filler added, an alumina layer is formed by the reaction between the system coacervate and glass during curing, which constitutes a barrier for the iron diffusion.

3.2. Hardness and fracture toughness

The Vickers hardness is first studied as a function of the applied load. The plot of hardness versus the reciprocal length of the indentation print is linear and corresponds to the Fröhlich *et al.* [8] relation. As reported previously [9], an indentation size effect appears in both glasses, where the hardness decreases with increasing the applied load.

It therefore becomes interesting to identify the different types of cracks in the vicinity of the indent. The profiles were determined by serial polishing with diamond grit and observing the crack patterns. Fig. 3 shows typical profiles resulting from indentation with loads of 0.5 to 2 N. The geometry obtained resembles more to the so-called Palmqvist type [10] than to the half-penny one. It can be seen that the Palmqvist-like cracks do not penetrate deeper than the indent itself as

TABLE I Glass composition and physical properties of the materials investigated

Glass composition	T_g (±10 °C)	T_s (±10 °C)	T_c (±5 °C)	T_f (±5 °C)	α ($\pm 0.2 \times 10^{-6}$ °C^{-1})
$70P_2O_5$-$20CaO$-$5MgO$-$5Na_2O$	420	470	580	830	12.6
$64P_2O_5$-$19CaO$-$4MgO$-$3Na_2O$ $10Fe_3O_4$	450	510	600	810	11.5

T_g: glass transition temperature, T_s: softening temperature, T_c: devitrification temperature, T_f: melting temperature, α: coefficient of thermal expansion.

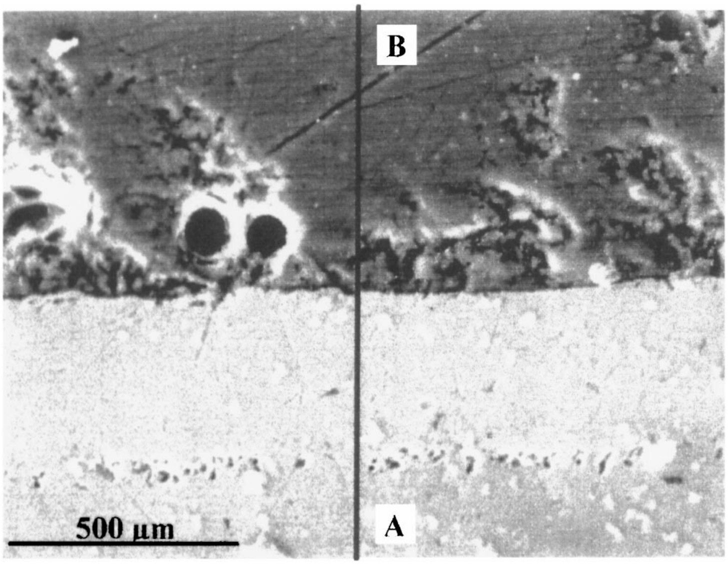


Figure 1 Scanning electron micrograph of the cross section interface between glass and steel.

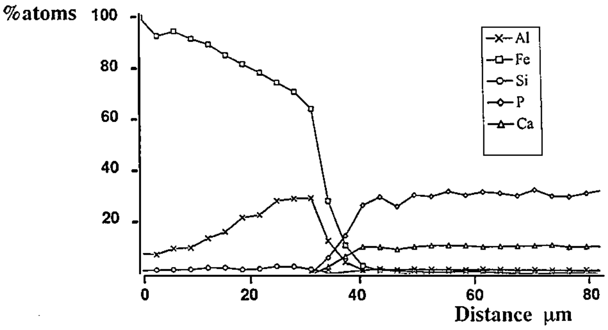


Figure 2 Energy dispersive spectrometry profile analysis along the AB line in Fig. 1. Lines are drawn as guides for the eyes. The interface lies at 35 μm from the left part.

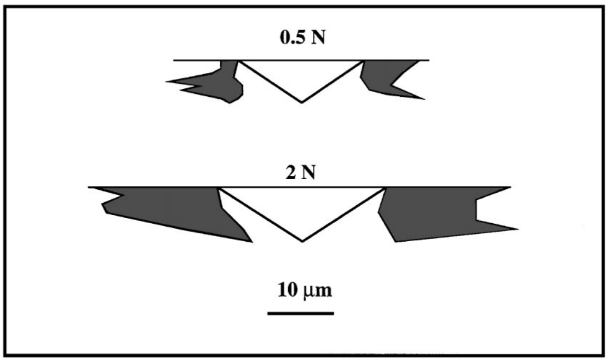


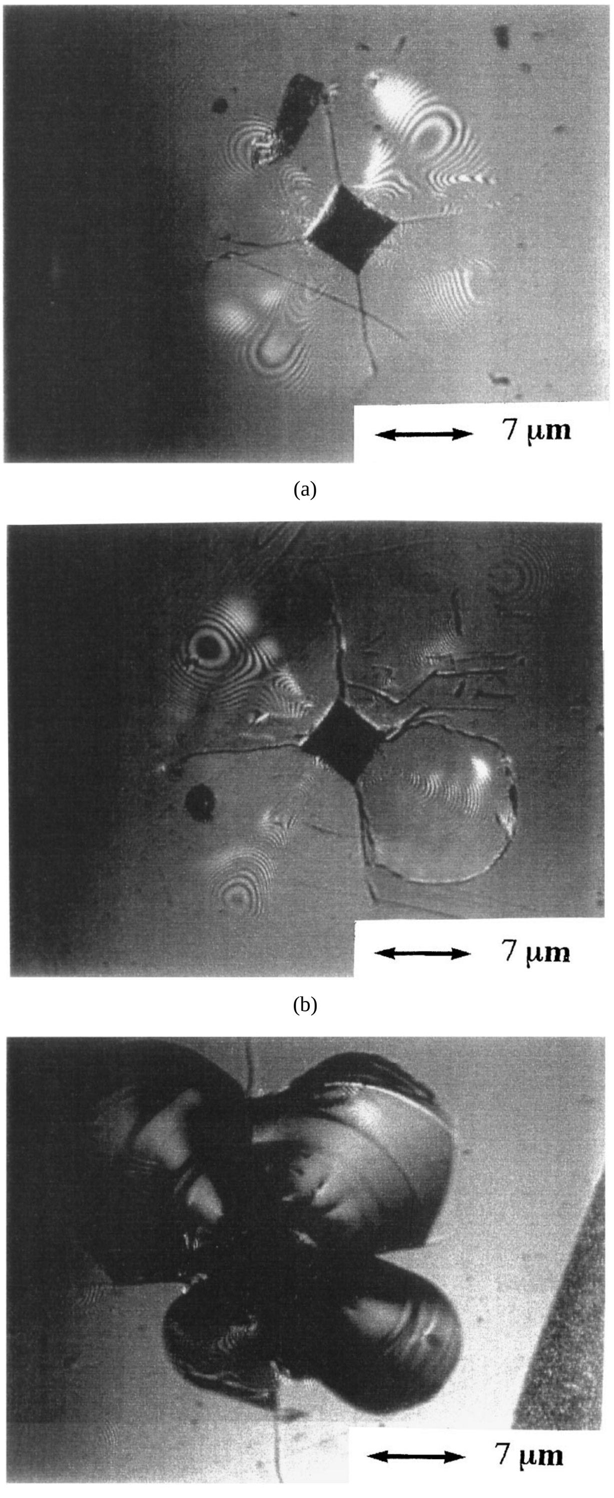
Figure 3 Typical crack profiles as a result of indentation with a Vickers indentation load of 0.5 (top) and 2 (bottom) N. The black area represent the profile crack obtained by serial polishing under the specimen surface.

previously reported for soda lime glass [11] and densified silicate glass [12]. However, it is in contradiction to the results obtained on some ceramic materials where the penetration of the crack is greater than the indentation print [13, 14]. It must also be pointed out that the indentation crack in soda-lime glass was found to be median type [15]. The probability of observing surface cracks emanating from the impression corners depends on the applied load. At small loads, cracks did not appear at each corner of every indentation. As the indentation load increased, the lateral cracks propagated through the surface and removed chips from the surface adjacent to the indentation print [16]. Typical patterns observed by confocal microscopy are shown in Fig. 4. The threshold load for the creation of radial crack varied between 0.05 and 0.10 N for all the specimens investigated, and chipping or spalling (subsurface outlines of laterals cracks) were found to occur at the side of the indentation above a critical load of about 1–2 N in all the materials. The total crack length, 4 l measured from the impression corner, as a function of the applied load, P, was linear, between 0.25 and 1 N as assumed for Palmqvist cracks [10]. For loads above 2 N the crack length was lower than the previous one. The deviation is related to the chipping corresponding to well-developed lateral cracks. The increase in lateral crack development is reflected in a decrease in the driving force for the radial cracks and corresponds to an apparent increase of the toughness [16–20]; the extent of lateral cracks decreases the constraint in the deformation zone and diminishes the residual field driving the radial cracks. The crack length, c, measured from the centre of the indentation, is plotted in Fig. 5 versus the logarithm of the applied load. A $P^{2/3}$ dependence is found corresponding to median or half penny radial crack models. The experimental data are in accordance with the Evans and Charles [21] straight line (Equation 1) plotted in Fig. 5, in spite of a Palmqvist geometry for the cracks under the surface and spalling for the higher loads. (K_{IC} is in MPa m$^{1/2}$ when P is in MN and c in m):

$$K_{\mathrm{IC}} = 0.0824 P c^{-3/2} \tag{1}$$

Shi and James [22], had an advantage in choosing large cracks for calculating K_{IC} because residual stresses very near the surface have a minor effect than for small cracks. However, in this work we are limited by the occurrence of chipping.

The variation of K_{IC} with the crack length (then the applied load) is shown in Fig. 6. The large scatter



(a)

(b)

(c)

Figure 4 Confocal micrographs showing radial cracks and chipping for applied loads: (a) 2 N; b) 10 N; and (c) 20 N.

of values is probably caused by the surface residual stresses in glass and the heterogeneity of the materials. In this figure, the values of K_{IC} calculated by means of both the Evans and Charles (Equation 1) and the Shetty *et al.* formula [23] (Equation 2):

$$K_{IC} = 0.0638 P d^{-1} l^{-1/2} \qquad (2)$$

respectively, for Median and Palmqvist cracks, are reported. It can be seen that the first values are lower than those obtained by Equation 2.

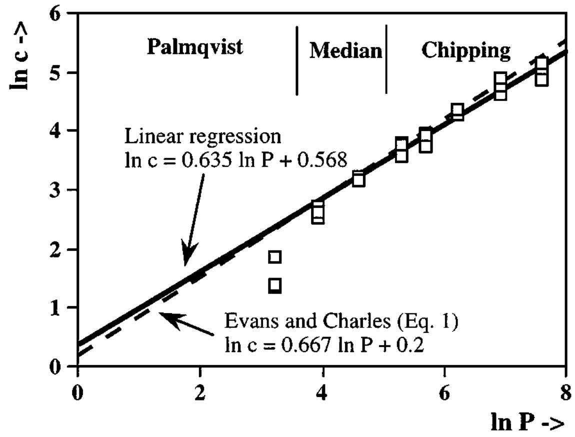


Figure 5 Variation of the crack length, c, versus the applied load, P.

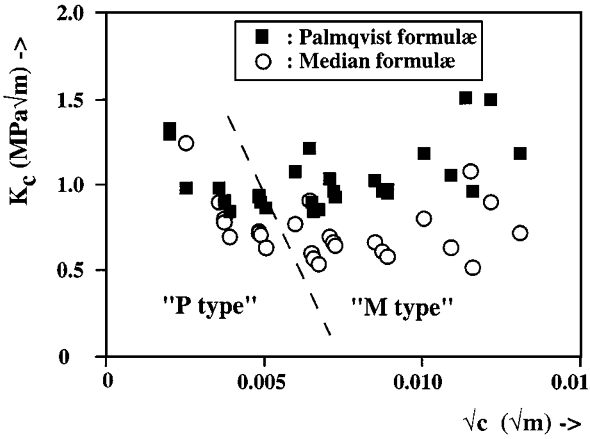


Figure 6 Fracture toughness as a function of the crack length.

From Equation 1, the fracture toughness was found to be near 0.85 MPa $m^{1/2}$ for all the glasses investigated, which is comparable to that of most commercial glasses lies.

4. Discussion

The quantification of adhesion between the coating and the substrate is a very important problem which affects the mechanical properties of laminate structures. The interfaces between the metallic bounding layer and the glass coating were investigated by the indentation technique. When indentation were made at the interface, the interface stayed intact. No cracks developed along the interface, but cracks propagated in the glass coating indicating a stronger interface. Fig. 7 shows the cracks propagation in the coating after an indentation made at the interface. Further, we used the technique proposed by Zhang and Lewandowski [24]. Microindentations at loads ranging from 0.1 to 20 N were made in the glass material near the interface. The cracks produced by the indenter propagated in glass and stopped at the interface. The fact that no debonding was found is an indication that the glass coating is weaker than the interface. Strong adhesion between the glass and the iron substrate is probably promoted more by phosphorus diffusion than by oxide development at the interface.

It is well accepted that stresses near the interface depend on the difference in the thermal expansion

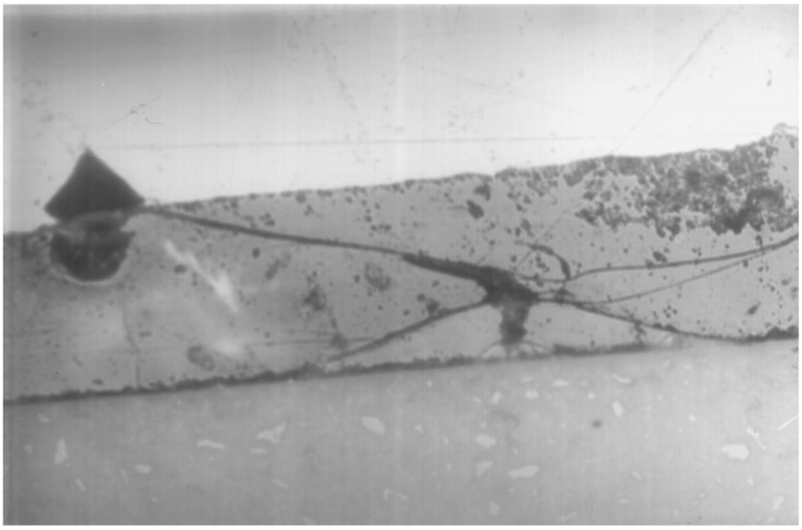


Figure 7 Optical micrograph showing crack propagation for indentation made at the interface between metal substrate and glass coating.

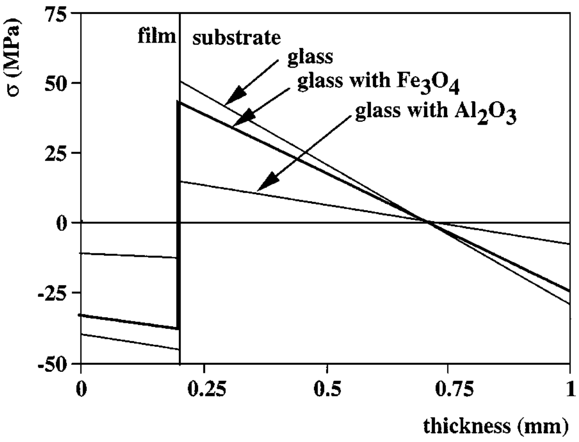


Figure 8 Residual stress profile in relation with the microstructure.

coefficient between glass and metal. As glasses are weaker in tension than in compression, compressive residual stresses yield better mechanical properties.

A method was first proposed by Timoshenko [25] to calculate the average stresses, resulting from the difference of thermal expansion coefficients in the case of a sandwich formed by two materials. But generally, several material layers are formed on the substrate, and this method has to be extended [26] keeping the same assumptions (stress origin, no material yielding, stratified materials). Here, the glass is considered as liquid if the temperature is greater than T_g with $T_g = 420\,^\circ\text{C}$ and $\Delta T = T_g - T_{\text{amb}} = 400\,^\circ\text{C}$. The generalized "bimetallic strip method" [26] applied to our glass coatings gives the results shown in Fig. 8. The stresses in the films are compressive, and the values that we obtained are probably greater than the real ones because only two materials were considered (glass and iron). In fact, a bond layer was created. As a consequence, the stresses obtained by this model is overvalued because of the decrease resulting from the gradient of expansion coefficient in the intermediate interphases. When a transition layer is formed between the substrate and the coating, the stress at the interface can be reduced and the bond strength may reach a high value [27].

5. Conclusions

Two chemical compositions and heat treatments have been investigated for metaphosphate glasses. The above results show clearly that the coefficient of thermal expansion strongly depends on the chemical composition. On the other hand, the fracture toughness of the bulk specimens are nearly the same. From the above results some remarks and conclusion can be made:

(i) Because the occurrence of chipping and the crack morphology, the fracture toughness must be calculated only with applied loads near 1 N.

(ii) The fracture toughness of the coating depends on the residual stresses. The stress extrapolated to a zero load is near 0.85 MPa $m^{1/2}$.

(iii) Residual stresses depend on the coefficient of thermal expansion as a consequence of the chemical composition and the curing time of the metaphosphate glass.

(iv) Good adhesion is obtained when the indentation crack propagation occurs preferentially through the glass coating rather than through the interface. It is demonstrated for the chosen chemical composition.

(v) Adhesion of metaphosphate glasses is promoted on metallic substrates when interphases with intermediate coefficients of thermal expansion are generated.

References

1. E. J. GRIFFITH, "Phosphate Fiber" (Plenum Press, NY, 1995).
2. R. C. ROPP, "Inorganic Polymeric Glasses" (Elsevier, Amsterdam, 1992).
3. F. BARBIEUX, Thesis, Université de Technologie de Compiègne, 1996.
4. P. VAST, *J. Chim. Phys.* **IV** (1993) 1393.
5. M. DRAOUI, P. VAST and G. PALAVIT, *Rev. Chim. Miné.* **22** (1985) 256.
6. P. VAST, F. BARBIEUX and F. GOMEZ, *Verre* **2**(3) (1996) 3.
7. B. DEFFONTAINES, Thesis, Université des Sciences et Technologies, Lille, 1992.
8. F. FRÖHLICH, P. GRAU and G. GRELLMANN, *Phys. Stat. Solidi.* **42** (1977) 79.
9. A. IOST and R. BIGOT, *J. Mater. Sci.* **31** (1996) 3573.

10. S. PALMQVIST, Translation BISI No. 1865, January 1961, of *Jernkontorets Annaler* **141**(5) (1957) 300.
11. R. F. COOK and G. M. PHARR, *J. Amer. Ceram. Soc.* **73** (1990) 787.
12. Z. ZHANG, N. SOGA and K. HIRAO, *J. Mater. Sci.* **30** (1995) 6359.
13. C. B. PONTON and R. D. RAWLINGS, *Mater. Sci. Technol.* **5** (1989) 961.
14. M. T. LAUGIER, *J. Mater. Sci. Lett.* **6** (1987) 355.
15. M. TANAKA, *J. Mater. Sci.* **31** (1996) 749.
16. R. F. COOK, E. G. LINIGER, R. W. STEINBRECH and F. DEUERLER, *J. Amer. Ceram. Soc.* **77**(2) (1994) 303.
17. R. F. COOK and E. G. LINIGER, *J. Mater. Sci.* **27** (1992) 4751.
18. R. F. COOK, M. R. PASCUCCI and W. H. RHODES, *J. Amer. Ceram. Soc.* **73**(7) (1980) 1873.
19. S. M. SMITH and R. O. SCATTERGOOD, *ibid.* **75**(2) (1992) 305.
20. *Idem.*, *ibid.* **75**(9) (1992) 2593.
21. A. G. EVANS and E. A. CHARLES, *ibid.* **59** (1976) 371.
22. W. SHI and P. F. JAMES, *J. Mater. Sci.* **29** (1994) 824.
23. D. K. SHETTY, I. G. WRIGHT, P. N. MINCER and A. H. CLAUER, *ibid.* **20** (1985) 1873.
24. J. ZHANG and J. J. LEWANDOWSKI, *ibid.* **29** (1994) 4022.
25. S. TIMOSHENKO, “Strength of Materials” (Van Nostrand East West Press, 1958).
26. R. BIGOT, Thesis, Université des Sciences et Technologies, Lille, 1996.
27. Y. YANG, Z. LIU, C. LUO and Y. CHUANG, *Surf. Coat. Technol.* **89** (1997) 97.

Received 29 July
and accepted 23 December 1998