Destabilization behaviour of ceria-stabilized tetragonal zirconia polycrystals by sodium sulphate and vanadium oxide melts

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Thermal barrier coatings, generally zirconia and alumina ceramics, provide a thin insulating layer on critical combustion turbine components and reduce the underlying metal surface temperature to 150–200 °C. This is one way of improving gas turbine operation efficiency and the life of components. The chief sources of hot corrosion which cause destabilization of zirconia are sodium sulphate and vanadium oxide. Malik and Asrar [1] explained that gas turbines operating at sea and engines burning low-grade fossil fuel, such as heavy oil and residual coal, somehow form Na_2SO_4 and other alkali and alkaline-earth sulphates to cause hot corrosion. Heavy residual oil contains an appreciable amount of vanadium in the form of oil-soluble porphyrin complex along with sodium and sulphur compounds. It is suggested that V_2O_5 alkali-metal sulphides form low-melting compounds of the type Na_2VO_3 or $Na_2OV_2O_5$ which exert a fluxing action on metals or alloys and propagates hot corrosion.

Several investigators, namely McKee and Siemers [2], Hamilton and Nagelberg [3], Nagelbery [4] and David *et al.* [5], have reported the attack and destabilization of yttria-stabilized zirconia by molten sodium and vanadium salts, observed by Raman spectroscopy, X-ray diffraction and microstructural studies, showing the salt chemistry and destabilization of cubic/tetragonal (C/T) zirconia to monoclinic (M) phase. They showed that V_2O_5 reacts with Y_2O_3 to form YVO_4 and leads to the destabilization of zirconia ceramics. The sulphation behaviour of CeO_2- and Y_2O_3-stabilized ZrO_2 was studied by Jones *et al.* [6], who showed that CeO_2-stabilized ZrO_2 was superior to Y_2O_3-stabilized ZrO_2. The corrosion of CeO_2-stabilized ZrO_2 ceramics by $NaVO_3$ at 700–900 °C was reported by Jones and Williams [7], who explained that the molten $NaVO_3$ readily leached CeO_2 from ZrO_2 ceramic and destabilized it. In this letter we report the destabilization of 10, 12.5 and 15 mol% CeO_2-stabilized zirconia exposed to molten Na_2SO_4 and a mixture of $Na_2SO_4 + 2$ mol% V_2O_5, studied by X-ray diffraction (XRD) and scanning electron microscopy. The destabilization is predominant in the presence of V_2O_5 and is a function of the amount of CeO_2 stabilizer present in the zirconia ceramics.

Mixtures containing ZrO_2–10, 12.5 and 15 mol% CeO_2 were prepared by thorough mixing and grinding of oxide powders together with 2% poly(vinyl alcohol) binder, before pressing into bars of desired sizes at 10000 lb in.$^{-2}$ (69 MPa). The pressed samples were sintered in air atmosphere at 1500 °C for 5 h. The mechanical properties such as the modulus of rupture (MOR) and hardness of the samples were reported a previous letter [8]. The M-, T- and C-phases were identified using a Philips diffractometer (X-ray generator PW-1010, recorder PW-1051, CuK_α radiation), ground and polished samples being used for study of the microstructure by scanning electron microscopy (Jeol JSM-840A, Japan). The proportions of C-, T- and M-phases were estimated from the relative areas under the $(1 1 1)_M$, $(1 1 \bar{1})_M$ and $(1 1 1)_{T,C}$, and $(0 0 4)_T$, $(4 0 0)_T$ and $(4 0 0)_C$ profiles using the method of Garvie and Nicholson [9].

In corrosion experiments the samples were exposed to molten salts mixtures (Na_2SO_4 and 2 mol% $V_2O_5 + Na_2SO_4$) by placing them in a graphite crucible in an air atmosphere at 950 °C for 5–20 h exposure. XRD patterns were first obtained from the samples before salt exposure. After exposure to the molten salt the samples were quickly removed from the melt to avoid the deposition of a salt layer on the surface of the samples. The exposed ceramics were cleaned in an ultrasonic cleanser for 5 min using distilled water. XRD patterns were then obtained after the corrosion tests. A small portion of specimens as-sintered and after corrosion were used for microstructural studies.

The XRD patterns and percentage of phases of specimens containing 10, 12.5 and 15 mol% CeO_2, denoted by I, II and III, respectively, as-sintered and after corrosion with the molten salt mixture are shown in Fig. 1 and Table I. It is evident from the patterns of as-sintered specimens I, II and III that they contain predominantly T-phase. It was observed that no significant destabilization occurred in the amount of T-phase in specimens I, II and III which were exposed to molten Na_2SO_4 at 950 °C for 20 h, with T-phase destabilized into M-phase by 7, 3 and 0%, respectively. In all cases the specimens showed that a considerable reduction in intensities occurred after exposure to molten Na_2SO_4 salt. Specimen I, when exposed to the molten mixture of salts of $Na_2SO_4 + 2$ mol% V_2O_5 at 950 °C for 5 h, showed a substantial amount of M-phase (75%) and only 25% T-phase remained in the specimen, whereas specimens II and III which were exposed to
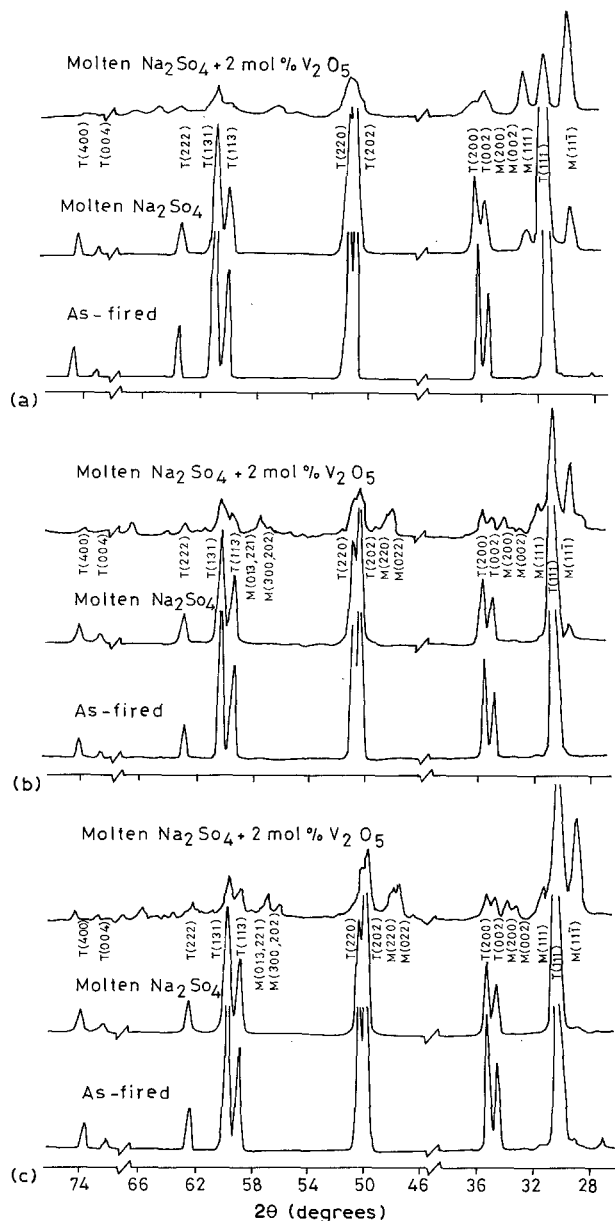
Figure 1 XRD profiles of CeO₂-stabilized tetragonal zirconia polycrystals showing the destabilization behaviour by sodium sulphate and vanadium oxides melts: (a) 10, (b) 12.5 and (c) 15 mol % CeO₂ (specimens I–III, respectively).

specimen containing 10 mol % CeO_2 had significant hardness, it is less corrosion resistant with molten salts.

The microstructure of the as-sintered specimen containing 15 mol % CeO_2 is shown in Fig. 2. It is clearly seen that the specimen contained predominantly T-phase, which was also supported by the XRD patterns. Fig. 3, a micrograph of the composition 15 mol % CeO_2 after corrosion with the molten mix of Na_2SO_4 + 2 mol % V_2O_5 at 950 °C for 5 h, shows a very different and irregular structure due to destabilization into M-phase. The micrograph shows corrosive action and leaching effects.

Based on the above results, it can therefore be concluded that destabilization is predominant in the case of molten salt containing small amounts of V_2O_5. This destabilization may be due to leaching of
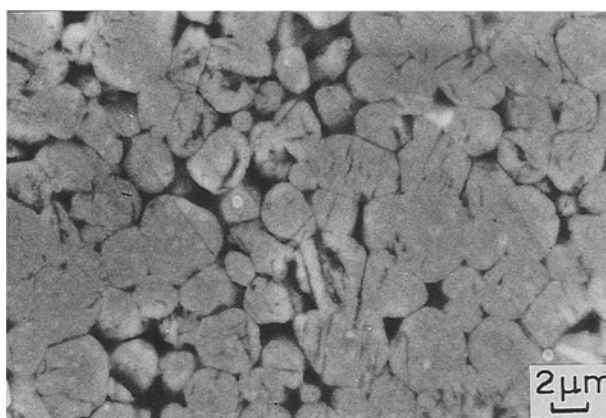

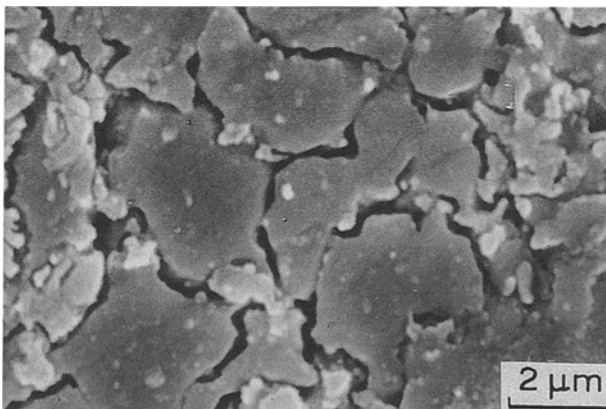Figure 2 SEM micrograph of specimen III as-sintered.

Figure 3 SEM micrograph of specimen III after 5 h corrosion in the molten mix Na_2SO_4 + 2 mol % V_2O_5.

molten mixtures of Na_2SO_4 + 2 mol % V_2O_5 at 950 °C for 5 h showed the destabilization of T-phase into M-phase by 25 and 15% respectively. Specimens I, II and III which were exposed for 10 h to mixed molten salts become brittle, perhaps due to the substantial amount of M-phase formed. Although in earlier work [8] we showed that the

TABLE I Corrosion conditions and corresponding phases

Conditions		Phases (%)					
		Specimen					
		I		II		III	
Molten salt at 950 °C	Time (h)	M	T	M	T	M	T
As-sintered		2	98	1	99	2	98
Na_2SO_4	20	7	93	3	97	1	99
Na_2SO_4 + 2 mol % V_2O_5	5	75	25	25	75	10	90

CeO$_2$ stabilizer from the zirconia ceramics and formation of CeVO$_4$/CeVO$_3$ which forms below 1000 °C. The destabilizing process increases with increasing time and decreasing ceria content.

References

1. A. U. MALIK and N. ASRAR, *Sci. Rep.* **20** (1983) 508.
2. D. W. McKEE and P. A. SIEMERS, *Thin Solid Films* **73** (1980) 439.
3. J. C. HAMILTON and A. S. NAGELBERY, *J. Amer. Ceram. Soc.* **67** (1984) 686.
4. A. S. NAGELBERY, *J. Electrochem. Soc.* **132** (1985) 2502.
5. W. S. DAVID, W. HARTD and C. B. CARTER, *J. Amer. Ceram. Soc.* **71** (1988) 992.
6. R. L. JONES, S. R. JONES and C. E. WILLIAMS, *J. Electrochem. Soc.* **132** (1985) 1495.
7. R. L. JONES and C. E. WILLIAMS, *Surf. Coating Technol.* **32** (1987) 349.
8. S. A. MUQTADER, B. R. RAO and S. G. SAMDANI, *J. Mater. Sci. Lett.* **9** (1990) 1075.
9. R. C. GARVIE and P. S. NICHOLSON, *J. Amer. Ceram. Soc.* **55** (1972) 303.