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FINAL SCIENTIFIC REPORT ON
A FUNDAMENTAL STUDY OF THE BONDING OF THERMAL BARRIER COATINGS

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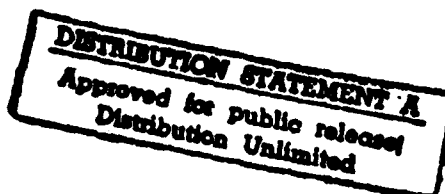
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16. SUPPLEMENTARY NOTATION			

1. INTRODUCTION

This report describes the progress and publications which have resulted from AFOSR support of our research on fundamental studies of the bonding of zirconia-yttria thermal barrier coatings to alumina-forming alloy bond coats on superalloys. This research has been directed by Professors T.E. Mitchell and A.H. Heuer with the active research being performed by Ms. S. Kraus (for her M.S. Thesis) and Dr. V. Lanteri (for his Ph.D. Thesis).

Two layer thermal barrier coatings are currently being developed for extending the performance of nickel base superalloy gas turbine engines. The best materials reported to date comprise a Ni-Cr-Al-Y bond coat and a Y_2O_3 partially stabilized ZrO_2 (Y-PSZ) thermal barrier coat. The Y level of both the bond coat and the thermal barrier coat have been studied empirically but the fundamental factors that govern optimization of the thermal barrier system are not well understood. Optimized systems perform remarkably well during high temperature exposure and thermal cycling but failure still tends to occur by radial cracking in the ceramic coat and circumferential cracking at the various metal/ceramic interfaces. ~~In the present study we have concentrated on~~ two fundamental aspects of the behavior: ^{as discussed} firstly, phase stability in the zirconia-yttria system itself, particularly the desirable tetragonal phase, and secondly, the nature of the important zirconia-alumina interface which forms during oxidation of the underlying bond coat. The results of this research are described briefly below and in the various Appendices. Section 6 lists our various publications deriving from AFOSR sponsorship.



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2. PHASE STABILITY IN YTTRIA PARTIALLY STABILIZED ZIRCONIA

The microstructure of the tetragonal phase in yttria partially stabilized zirconia (Y-PSZ) is very sensitive to cooling rates. With fast cooling rates a displacive, but non-martensitic, transformation occurs resulting in the formation of a tetragonal solid solution (t' -ZrO₂) with the same yttria content as the parent cubic phase (c -ZrO₂). The microstructure is characterized by the presence of antiphase domain boundaries (APB's) resulting from the loss of symmetry during the transformation, and by 90° twins formed mechanically to relieve the transformation strains.

With slow cooling rates, the equilibrium tetragonal solid solution (t -ZrO₂) starts to precipitate; at room temperature the material has a tweed-like microstructure. After lengthy annealings at high temperatures in the two phase field ($t + c$), t -ZrO₂ coarsens in a cubic matrix which can again undergo a displacive transformation upon cooling depending on its rate. t -ZrO₂ has a particular microstructure consisting of large colonies of twin related variants. Each colony is formed by stacking plates of two tetragonal variants sharing the same (101) habit plane, with their c -axes at about 90°. This microstructure effectively reduces the overall strain energy.

The tetragonal colonies can martensitically transform to monoclinic symmetry (m -ZrO₂) under the action of a propagating crack. There is no evidence of a t' -ZrO₂ to m -ZrO₂ transformation.

The colonies can also transform to an orthorhombic phase (o -ZrO₂) by a pure thin film effect. This transformation is also displacive and is characterized by the presence of APB's.

The difference in morphology and distribution of tetragonal

precipitates in the three major classes of PSZ (Mg-, Ca-, and Y-PSZ) is explained in terms of strain energy reduction using Khachaturyan's theory of structural transformations in solids.

3. STRUCTURE OF $\text{ZrO}_2/\text{Al}_2\text{O}_3$ INTERFACES

High resolution electron microscopy has been used to study the interfacial structures in ZrO_2 -toughened Al_2O_3 . The ZrO_2 exists as both inter- and intragranular particles, and the most informative images are of intragranular $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interfaces. The majority of these particles are spherical, but some are faceted, implying that there are low energy interfaces between the two materials. For spherical particles, both ledge-like structure and misfit dislocation-like structures accommodate the lattice misfit, depending on the orientation of the interface. The intergranular particle/matrix interfaces yielded little information, as there is a ubiquitous glassy phase which can, at times, obscure the interface boundary. Computer simulation is being used to interpret the structures: successful matches between experimental and computed images of the perfect Al_2O_3 matrix have been made and the technique is being extended to the interface. The results show that the interface is sharp, that there is no evidence for any interaction zone between the two oxides, but that the interfacial adhesion is still apparently strong.

4. RELEVANCE TO THERMAL BARRIER COATING BEHAVIOR

So far as phase stability is concerned, our results show quite clearly that compositions in the range of 6-8 wt.% yttria ought to consist of 100% tetragonal phase (t'). This phase is metastable but has been called non-transformable because the monoclinic phase does not form during cooling

to room temperature. It ought to remain stable during exposure to temperatures as high as 1200°C even during thermal cycling. In fact, our own observations and those of others show that the amount of monoclinic and cubic phases gradually increase during high temperature exposure and the monoclinic phase is a potential source of failure. The most likely reason for this is the non-uniformity of the powder compositions used for plasma spraying since powder containing less than about 4 wt.% yttria will transform to the monoclinic phase on cooling. Transmission electron microscope studies have shown that the microstructures observed in the plasma sprayed material are much the same as in the bulk material except for the variability in the microstructure which is produced by the inhomogeneous composition and the variation in cooling rate. Near to the bond coat the splats have a high cooling rate and so the resulting structure consists of very fine columnar grains of t' . Near the outer surface the cooling rate is much slower and so the grains are larger and contain the t' colonies and APB's already described in the bulk material. The structure is still stable to high temperature exposure and it is the compositional inhomogeneity which gives rise to problems with stability. If a powder with a uniform composition of 6-8 wt.% yttria were used, the resulting 100% tetragonal ceramic coat should be stable to high temperature exposure. These results were presented at the workshop on Thermal Barrier Coatings organized by NASA Lewis Research Center, May 20-21, 1985 and at a similar symposium organized by the American Vacuum Society in San Diego, April 7-11, 1986.

So far as the zirconia-alumina interface is concerned, we have shown that the interface is incoherent but that the incoherency is accommodated with step-like and dislocation-like structures at the atomic level. Such

an interface will form during high temperature exposure of the thermal barrier coating system, since the bond coat becomes oxidized by diffusion of oxygen through the ceramic coat. Electron microscopy observations on these interfaces show that they are quite adherent in much the same way as the interfaces observed by high resolution electron microscopy. In fact, we have found that the ceramic coat spalls off at the alumina-metal interface just as much as at the alumina zirconia interface. The main problem here seems to be to maintain a sufficient level of yttrium in the Ni-Cr-Al bond-coat so as to maintain adhesion at the alloy/alumina interface.

5. Prior AFOSR - Supported Research

As a matter of completeness, we include in Section 6 several publications completed during the current contract period which actually derives from previous AFOSR support to T.E. Mitchell and A.H. Heuer (Contract No. F49620-78C-0053). Both relate to oxidation issues relevant to advanced high temperature ceramics; one provides evidence that diffusion of oxygen through the passive silica film that forms on SiC cannot control the oxidation kinetics; the second reviews the use of "volatility" or "stability" diagrams, which are the most convenient way of representing available thermodynamic data relevant to oxidation of metals, alloys, and non-oxide ceramics and also evaporation of oxide ceramics.

16. PUBLICATIONS

1. V. Lanteri, A.H. Heuer and T.E. Mitchell, "Tetragonal Precipitation in the System Y_2O_3 - ZrO_2 ", in Proc. 41st Annual Meeting, Electron Microscopy Society of America, G.W. Bailey, ed., San Francisco Press, p. 58 (1983). - Appendix 1
2. S. Farmer, V. Lanteri, J. Hangan, T.E. Mitchell, and A.H. Heuer, "Ordered Defect Fluorite Compounds in ZrO_2 Alloys", in Electron Microscopy in Materials Science, W. Krakow, D.A. Smith and L.W. Hobbs, eds., North Holland, p. 357 (1984). - Appendix 2
3. V. Lanteri, A.H. Heuer and T.E. Mitchell, "Tetragonal Phase in the System Y_2O_3 - ZrO_2 ", in Advances in Ceramics, Vol. 12, Science and Technology of Zirconia II, The American Ceramic Society, Columbus, Ohio, p. 118-130, 1984. - Appendix 3
4. A.H. Heuer, S.P. Kraus-Lanteri, P.A. Labun, V. Lanteri, and T.E. Mitchell, "HREM Studies of Coherent and Incoherent Interfaces in ZrO_2 -Containing Ceramics: A Preliminary Account", Ultramicroscopy 18, 335-348 (1985). - Appendix 4
5. S. Kraus, "HREM Studies of Interfaces in ZrO_2/Al_2O_3 Ceramics", Proc. 43rd Annual Meeting, Electron Microscopy Society of America, G.W. Bailey, ed., San Francisco Press, p. 218-219 (1985). - Appendix 5
6. A.H. Heuer, S.P. Kraus-Lanteri, P.A. Labun, and T.E. Mitchell, "HREM of Incoherent ZrO_2/Al_2O_3 Interfaces", Inst. Phys. Conf. Ser. No. 78, EMAG '85, Adam Hilger, p. 519-522 (1985). - Appendix 6
7. S.P. Kraus-Lanteri, T.E. Mitchell and A.H. Heuer, "Structure of Incoherent ZrO_2/Al_2O_3 Interfaces", J. Amer. Ceram. Soc. 69, p. 256-258 (1986). - Appendix 7
8. V. Lanteri, T.E. Mitchell and A.H. Heuer, "The Morphology of Tetragonal Precipitates in Partially-Stabilized Zirconia", J. Amer. Ceram. Soc., in press (1986). - Appendix 8 (Abstract only)
9. A.H. Heuer, R. Chaim and V. Lanteri, "The Displacive Cubic-Tetragonal Transformation in ZrO_2 Alloys", submitted to Acta Met. (1986). - Appendix 9 (Abstract only)
10. D.M. Mieskowski, T.E. Mitchell and A.H. Heuer, "Bubble Formation in Oxide Scales on SiC", J. Am. Ceram. Soc., Vol. 67, No. 1, (1984). - Appendix 10
11. V.L.K. Lou, T.E. Mitchell and A.H. Heuer, "Review - Graphical Displays of the Thermodynamics of High-Temperature Gas-Solid Reactions and Their Application to Oxidation of Metals and Evaporation of Oxides", J. Am. Ceram. Soc., Vol. 68, No. 2, (1985). - Appendix 11

TETRAGONAL PRECIPITATION IN THE SYSTEM Y_2O_3 - ZrO_2

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INTRODUCTION: The major applications of partially stabilized zirconia (PSZ) concern materials in which the microstructures are in the two phase regions (cubic-tetragonal or cubic-monoclinic). The aim of this paper is to discuss the occurrence of tetragonal precipitation in yttria-PSZ. Despite the similarity with other doped zirconia alloys (Mg-PSZ, Ca-PSZ), the shape, the habit planes and mechanisms of precipitation are found to be different for Y-PSZ. Single crystals, obtained from skull melting, with composition 8wt%- Y_2O_3 were examined by transmission electron microscopy (TEM) and the tetragonal phase was imaged using standard dark field techniques.

AS RECEIVED MATERIALS. Because of the crystallography of the tetragonal phase (t - ZrO_2), which is obtained by slight displacements of the oxygen atoms from the fluorite type cubic phase (c - ZrO_2), there are three variants (the c -axis being along one of the $\langle 100 \rangle$ directions). Fig. 1 shows a $\{111\}$ diffraction pattern, where the two reciprocal lattices (c - ZrO_2 and t - ZrO_2) are indexed. The weakest spots, which are forbidden for the fluorite structure, are due only to the t - ZrO_2 resulting from the slightly distorted fluorite cell. In this particular orientation, $\{112\}$ spots were used to image the three variants of the t - ZrO_2 phase, as shown in the dark field micrographs of Fig. 2. Fig. 2a and 2b clearly show the three variants of precipitates which have $\{110\}$ habit planes and possess all the features of a diffusion-assisted transformation. Fig. 2c, which is obtained using the third $\{112\}$ tetragonal reflection, surprisingly shows a different microstructure. This t - ZrO_2 phase must be the non-transformable t' - ZrO_2 reported by Scott (1) in his non-equilibrium phase diagram, and by Miller, et al. (2) in plasma sprayed materials. It is believed that this material is a mixture of t - ZrO_2 and t' - ZrO_2 with very little cubic phase (as confirmed by x-ray diffraction).

AGED SPECIMENS. Fig. 3 consists of dark field micrographs of the same material, aged at 24 hours at 1600°C, imaged as in the case above by using the three tetragonal reflections in the $\{111\}$ orientation. It is seen that the t' - ZrO_2 occurs in large colonies of plates lying in $\{110\}$ planes. Each colony is indeed formed by two variants (different c -axes) with the same habit planes. This is shown in Figs. 3a and 3b in which one variant is imaged using one particular reflection, whereas the other variant within the same colony is imaged with another reflection.

CONCLUSIONS. Evidence of two tetragonal phases has been found: t - ZrO_2 is the usual tetragonal phase formed by a diffusion process, also encountered in polycrystalline sintered materials (3); and t' - ZrO_2 , which is believed to form via a diffusionless process, is unstable at high temperatures, and decomposes into t - ZrO_2 and c - ZrO_2 during annealing.(4)

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4. The authors thank the Naval Research Lab, Washington, D.C. for providing the single crystals. This research has been supported by AFOSR-82-0227.

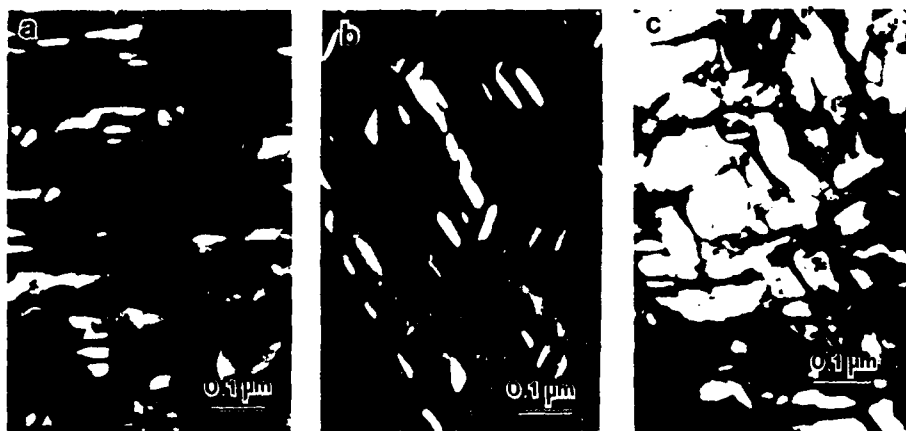


Fig. 2. Dark field micrographs of as received specimen
 a) $g = 112_t$ b) $g = 121_t$ c) $g = 211_t$

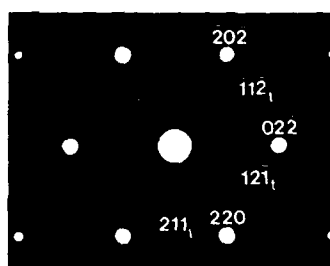


Fig. 1 $[111]$ Diffraction pattern

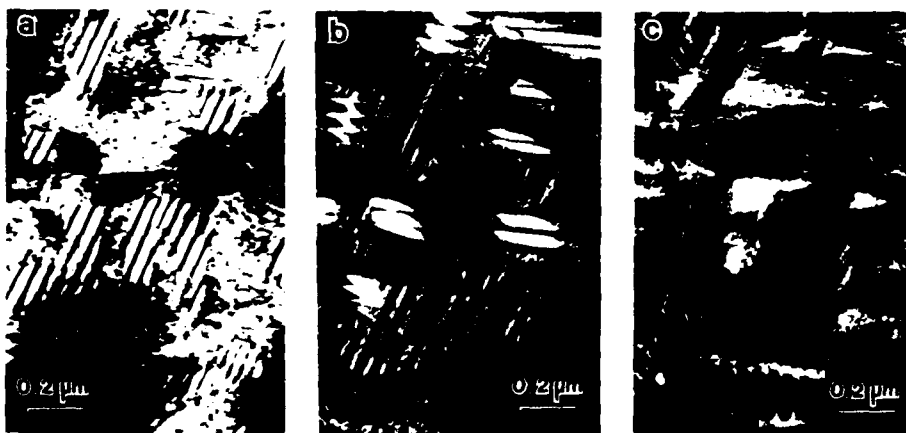


Fig. 3. Dark field micrographs of aged specimen at 1600°C for 24 hr.
 a) $g = 112_t$ b) $g = 121_t$ c) $g = 211_t$

S. Farmer, J. Hangan, V. Lanteri, T.E. Mitchell and A.E. Heuer, Case Western Reserve University, Department of Metallurgy and Materials Science, Cleveland Ohio 44106

ABSTRACT

Intermediate ordered-defect fluorite compounds are an important component of ZrO_2 alloys containing the aliovalent solutes MgO , CaO , or Y_2O_3 . These compounds also form in oxygen-deficient rare earth oxides and in other ternary oxides based on the fluorite structure, and can best be studied by TEM. Examples are given of such phases in the $MgO-ZrO_2$, $Y_2O_3-ZrO_2$, and $CaO-ZrO_2$ systems.

I. INTRODUCTION AND LITERATURE REVIEW

The high temperature cubic (c) polymorph of ZrO_2 with the fluorite structure (space group $Fm\bar{3}m$) transforms on cooling below $2370^\circ C$ to a tetragonally distorted fluorite-type structure (space group $P4_2/nmc$) (1). The subsequent tetragonal (t) $\rightarrow$ monoclinic (m) transformation (below $1000^\circ C$) can have untoward consequences in ZrO_2 -containing ceramics, and so considerable effort, extending over half a century (2), has been expended in "stabilizing" the cubic fluorite phase. For this purpose, MgO , CaO , Y_2O_3 , Sc_2O_3 , or any of a host of rare earth oxides are suitable; all show extensive solid solubility in ZrO_2 and act as "fluorite-stabilizers", in that they lower the temperature of the $c \rightarrow t$ transformation (3).

One consequence of the dissolution of considerable quantities of such aliovalent cation solutes is the generation of massive quantities of charge-compensating oxygen vacancies, one for each divalent cation or two trivalent cations. Dissolution of ZrN in ZrO_2 also stabilizes the c polymorph (4) and again produces one oxygen vacancy for every two nitrogen anions.

It has been recognized for some time (5) that the massive concentration of point defects thus engendered is not randomly distributed and non-interacting; rather, such systems exhibit significant short-range and long-range ordering (6), resulting in many cases in the formation of ordered defect-fluorite compounds.

The fluorite structure is also notable for its ability to accommodate non-stoichiometry, even in the absence of aliovalent solutes. For example, UO_{2-x} exists at high temperatures from $x=0.1$ on the hypostoichiometric side to $x=0.25$ on the hyperstoichiometric side of UO_2 (7). In rare earth oxides such as CeO_2 , PrO_2 , and TbO_2 , oxygen-deficiency is prevalent and results in a series of ordered fluorite superstructures (8), which are members of a homologous series M_nO_{2n-2} , with $n=7, 9, 10, 11$, and 12 . While all the superstructures are structurally related, only the $n=7$ example is isostructural in the Ce , Pr , and Tb systems. This M_7O_{12} structure is very common, and is the structural type for $Mg_2Zr_5O_{12}$, $Zr_3Sc_4O_{12}$, $Zr_4Y_4O_{12}$, and Zr_7O_{12} (and some of their HfO_2 analogues). (The crystal structure of this group of M_nO_{12} compounds was first determined for UY_6O_{12} (9), the isomorphous phase in which the cations are ordered.)

These M_7O_{12} structures are rhombohedral, all cations having either six or seven oxygen near neighbors. All the 6-coordinated cations lie along the 3-fold axis, forming so-called "Evan clusters" (one 6-coordinated cation and six 7-coordinated cation (Fig. 1)) which constitute infinite strings in the structure (10). However, not all members of the rare earth homologous series

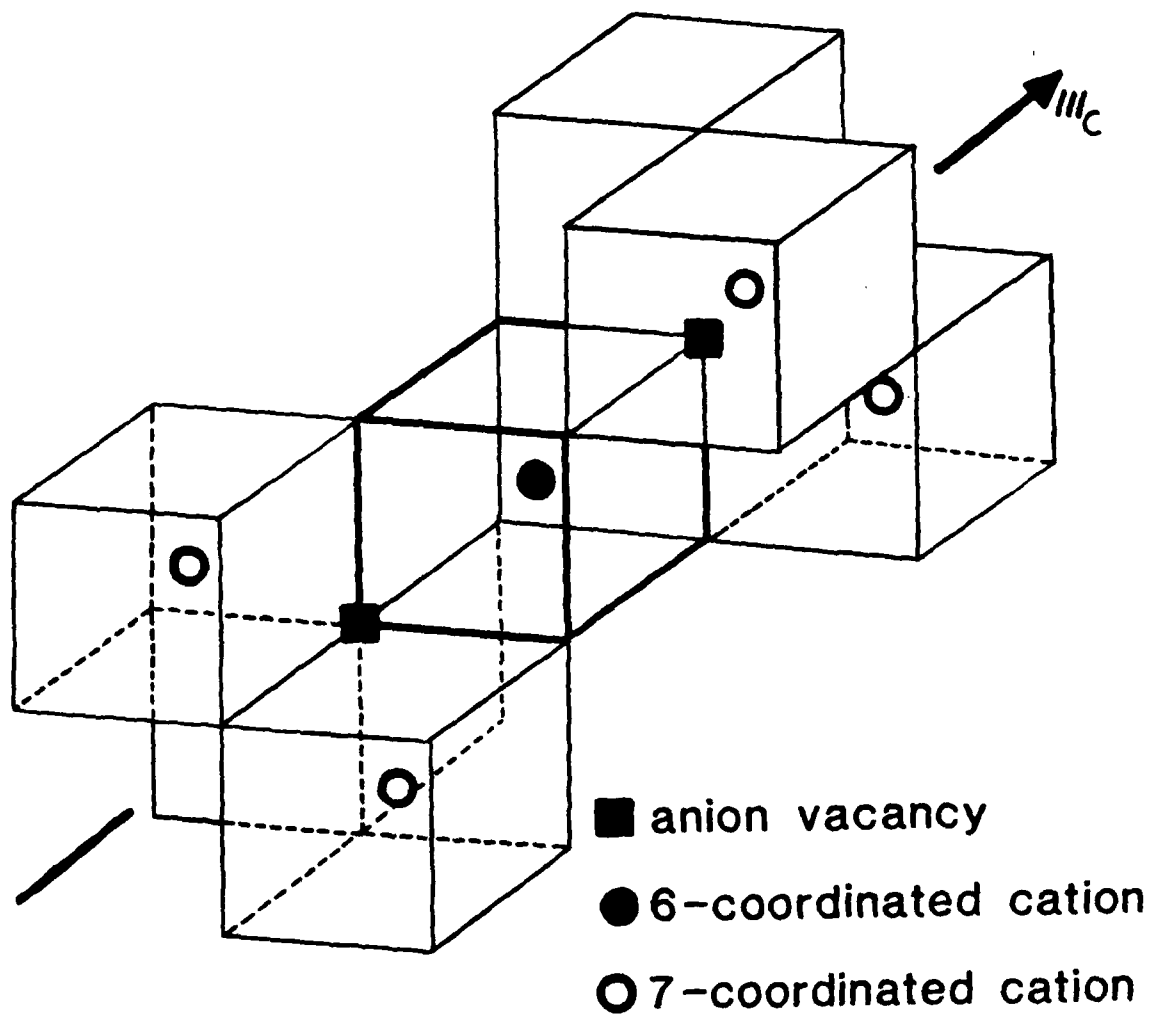


FIG. 1: Bevan cluster of one 6-coordinated cation, two oxygen vacancies, and six 7-coordinated cations. (Only four of the six 7-coordinated cations are indicated).

contain these strings of "Bevan clusters" along $\langle 111 \rangle_F$ directions; rather the oxygen deficiency is accommodated by the clusters aligning on $\{135\}$ planes along $\langle 211 \rangle_F$ directions (11); the $\{135\}$ planar spacing determines the stoichiometry, being every n th plane for M_2O_{2n-n} . It is of interest that infinite strings of 6-coordinated cations and two adjacent oxygen vacancies along all 3-fold axes are also found in the C-type rare earth sesquioxides (M_2O_3).

Although numerous intermediate phases have been identified in the binary rare earth oxides, isostructural phases are absent in most mixed rare earth oxide systems. This has been attributed to the sluggish diffusion in the cation sublattice, and the relatively low temperature of the order-disorder transformation so that equilibrium is rarely attained.

In the Sc_2O_3 - ZrO_2 and Sc_2O_3 - HfO_2 systems, three rhombohedral intermediate phases with disordered cations sublattices form (10). The ordered intermediate phases in the ZrN -, Y_2O_3 -, and MgO - ZrO_2 binaries are similar to those observed in the Sc_2O_3 - ZrO_2 system. In the CaO - ZrO_2 and CaO - HfO_2 binaries, the larger Ca ion causes a different packing of the 6-fold cations and the associated oxygen vacancies; three ordered phases form and all show some degree of cation order.

TEM has been an important, and in some cases an essential, tool in the study of these defect-fluorite oxides and oxynitrides, in part because the x-ray diffraction patterns are so similar, in part because of the incomplete "ordering" which is so common in these systems; and in part because the occurrence of these ordered compounds as fine precipitates requires a technique with good spatial resolution. It is this last advantage of TEM that has motivated our studies, in which the formation of these intermediate compounds as precipitate phases in c - ZrO_2 solid solutions alloyed with MgO , CaO , or Y_2O_3 , has been investigated. Our studies also have relevance to the understanding of the good mechanical properties of partially stabilized ZrO_2 's (PSZ's) (1).

II. The MgO - ZrO_2 System

There are no stable intermediate compounds in the currently accepted phase diagram for the MgO - ZrO_2 binary system (12). However, the existence of the compound $Mg_2Zr_5O_{12}$ (and its analogue in the MgO - HfO_2 system) was reported some years ago (13); as noted already, it is isostructural with $Zr_7O_8N_4$ and $Zr_3Sc_4O_{12}$.

The early literature (13, 14) suggested that $Mg_2Zr_5O_{12}$ could form from a c - ZrO_2 solid solution of the appropriate composition (28.57 m/o MgO) but decomposed to c - ZrO_2 and MgO below $1850^\circ C$. More recently, this compound has been formed as a precipitate phase in Mg -PSZ's containing 8-14 m/o MgO (15-17).

Our studies have focussed on two compositions, 8.1 and 11.3 m/o MgO , initially formed as a c - ZrO_2 solid solution and progressively decomposed (diffusionally) by annealing between 800 and $1100^\circ C$. Decomposition was found to be a sensitive function of previous thermal history.

Heat treatment of either composition (as a single phase solid solution) at $800^\circ C$ for one hour, followed by $1100^\circ C$ for 5 hours, induced growth of coherent t - ZrO_2 precipitates and precipitates of the ordered phase $Mg_2Zr_5O_{12}$ within the c - ZrO_2 matrix (Figs. 2a and b). The t - ZrO_2 phase actually nucleated and grew to ~ 5 nm on cooling from a previous heat treatment at $1800^\circ C$, during which the solid solution was homogenized; it further coarsened to 50-20 nm during the $800/1100^\circ C$ "aging". The equilibrium phases for these temperatures, m - ZrO_2 and MgO , are not much in evidence after such short

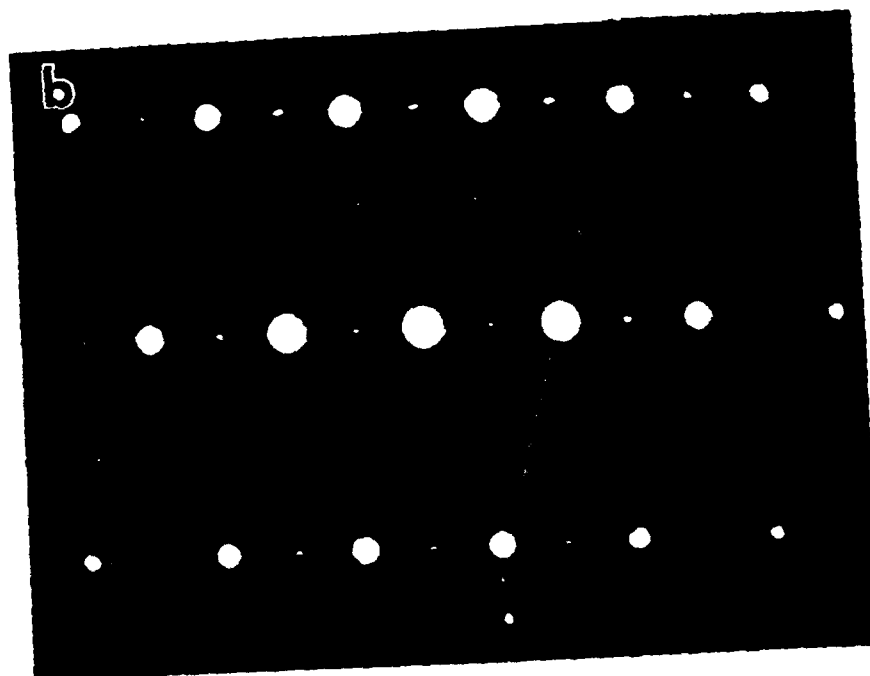
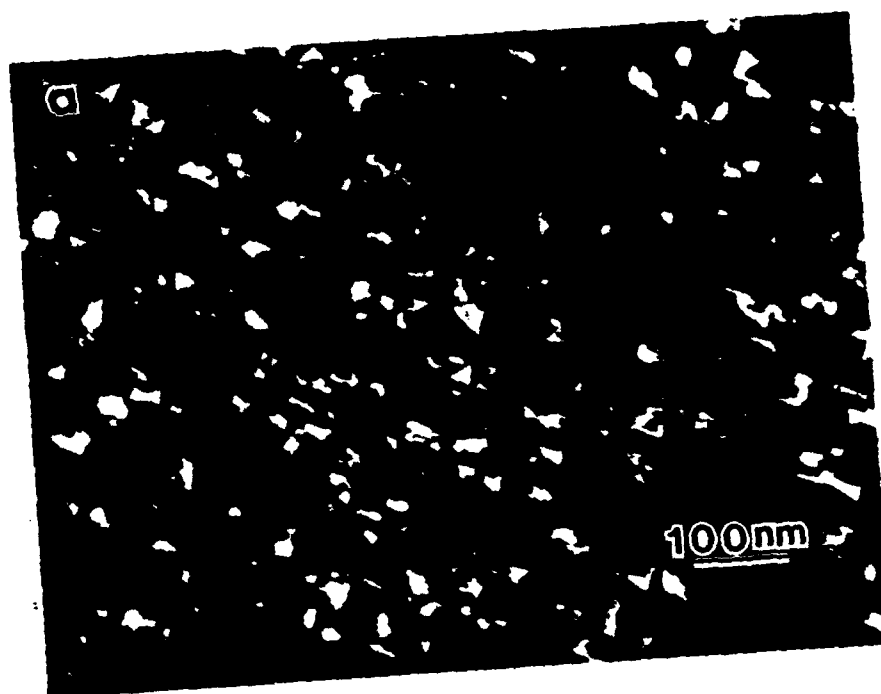


FIG. 2: $\text{Mg}_2\text{Zr}_5\text{O}_{12}$ precipitate in Mg-PSZ. (a) is a dark field image of a single precipitate variant in a c-ZrO_2 matrix and (b) is a $\langle 310 \rangle_F$ zone axis diffraction pattern. The most intense ("fundamental") reflections are from the c-ZrO_2 matrix, while the weakest reflections are from two variants of $\text{Mg}_2\text{Zr}_5\text{O}_{12}$. The arrowed reflections are due to t-ZrO_2 precipitates, which are out of contrast in (a).

aging times.

If the aging time at 1100°C is increased to 10 hours, the $\text{Mg}_2\text{Zr}_5\text{O}_{12}$ does not coarsen appreciably, but a good deal of m-ZrO_2 is found at grain boundaries of the polycrystalline Mg-PSZ. This grain boundary "phase" is actually a eutectoid decomposition product consisting of m-ZrO_2 plus MgO, which advances into the surrounding grains as a coupled growth product (Fig. 3), and consumes the c-ZrO_2 and its t-ZrO_2 and $\text{Mg}_2\text{Zr}_5\text{O}_{12}$ precipitates. The ordered compound $\text{Mg}_2\text{Zr}_5\text{O}_{12}$ is therefore clearly a metastable decomposition product, although it may have a region of stability at some other temperature on the equilibrium phase diagram.

The conditions under which the $\text{Mg}_2\text{Zr}_5\text{O}_{12}$ formed were quite specific--solution annealing at $T > 1600^\circ\text{C}$, followed by the 300/1100°C heat treatment. The lower temperature heat treatment is necessary to nucleate this phase; 300°C was usually used although 900°C was also found to be suitable. It was of interest that nucleation and growth of $\text{Mg}_2\text{Zr}_5\text{O}_{12}$ could be suppressed by an intermediate heat treatment. For example, prior heating at 1600°C for 1 hr, followed by furnace cooling, prevented the formation of $\text{Mg}_2\text{Zr}_5\text{O}_{12}$ during the 300/1100°C aging. If such material is subsequently given a second solution annealing of 2 hrs at 2100°C in an oxy-acetylene furnace, followed by rapid cooling (~ 5 min) to room temperature, aging at 1100°C leads to the ready formation of $\text{Mg}_2\text{Zr}_5\text{O}_{12}$ without the need for a lower temperature nucleation heat treatment. Similar behavior has previously been noted concerning the formation of ordered defect-fluorite phases in some rare earth oxide systems (12), in which a suitable quenched-in high temperature cation arrangement is necessary to permit nucleation of particular ordered phases.

III. The $\text{ZrO}_2\text{-Y}_2\text{O}_3$ System

Two intermediate ordered compounds are known in the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system, an M_7O_{12} compound at 40 m/o Y_2O_3 and an $\text{M}_{11}\text{O}_{20}$ phase at 75 m/o Y_2O_3 . The most recent phase diagrams for this system (19-21) suggest that the former phase should be ubiquitous in high ZrO_2 compositions. However, a number of TEM studies have been reported of technologically interesting compositions containing between 2 and 8 m/o Y_2O_3 (22, 23); only m , t , and c-ZrO_2 polymorphs have been reported. This is probably due to the low temperature of the eutectoid in this system.

Recently, however, we have found evidence of an unusual ordering reaction in a 6.3 m/o Y-PSZ (the composition was determined by calibrated EDS analysis) (24). This material is a commercial furnace tube; we presume it was fired at a temperature above 1500°C and cooled slowly to room temperature.

Most grains have t-symmetry but contain anti-phase domain boundaries (Fig. 4), a result of a diffusionless $\text{c} \rightarrow \text{t}$ transformation (1). Such microstructures are common in other $\text{Y}_2\text{O}_3\text{-ZrO}_2$ ceramics (23). Some t-ZrO_2 "colonies" are also present, each colony consisting of stacked plates sharing a {101} habit plane, alternate plates being twin-related (their c-axes are rotated by 90°). Such colonies are also common in $\text{Y}_2\text{O}_3\text{-ZrO}_2$ samples heat treated in the two-phase t plus c field (22, 25).

A few grains in this polycrystalline ceramic possessed a different structure, one not observed previously in any prior study of lower Y_2O_3 material. The fundamental reflections in SAD patterns (Fig. 5) show tetragonal symmetry, and satellite reflections are seen about each of the strong fundamental reflections. Very weak superlattice reflections are also visible in $\langle 111 \rangle_F$ orientations.

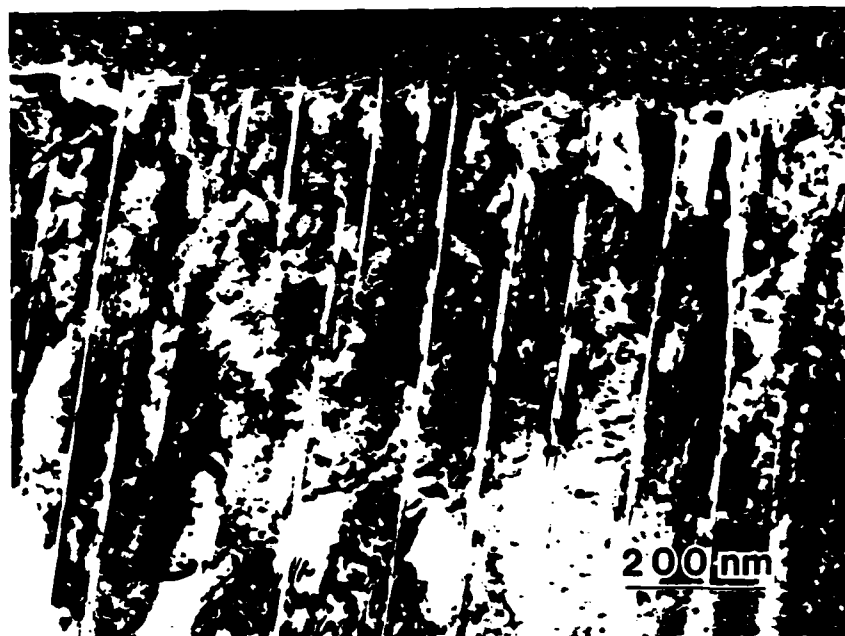


FIG. 3: Eutectoid decomposition product of m -ZrO₂ and MgO in Mg-PSZ. The grain being consumed is at the top of the micrograph.

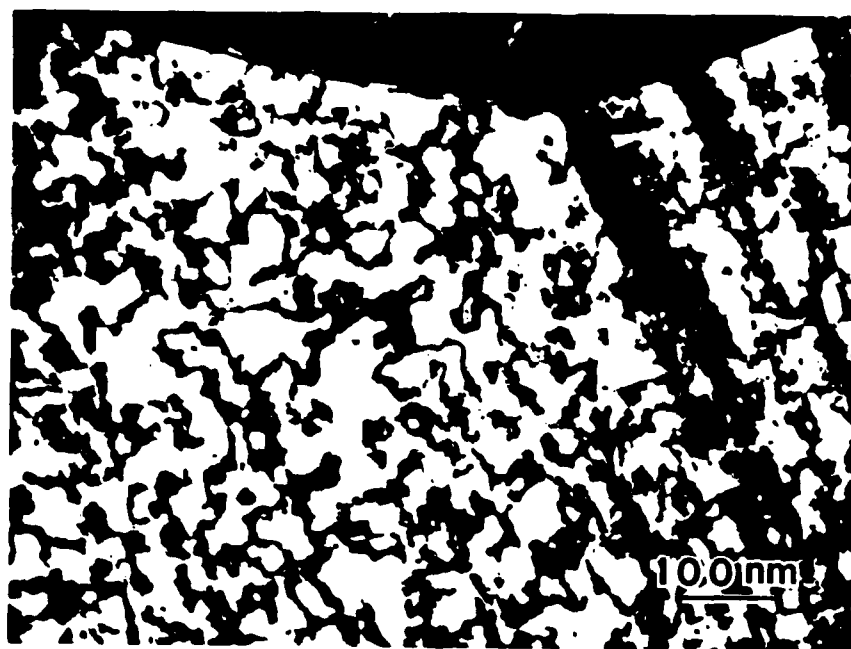


FIG. 4: Antiphase domain boundaries arising from a diffusionless but non-martensitic $c \rightarrow t$ transformation in 6.3 m/o Y-PSZ.

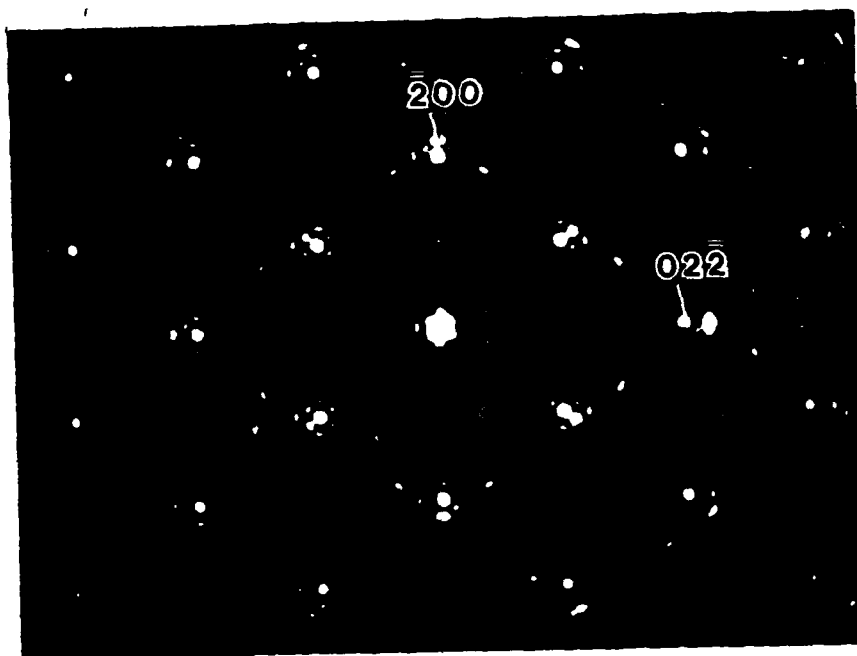


FIG. 5: $\langle 011 \rangle_F$ zone axis diffraction pattern of possible ordered phase in 6.3 m/o Y-PSZ.

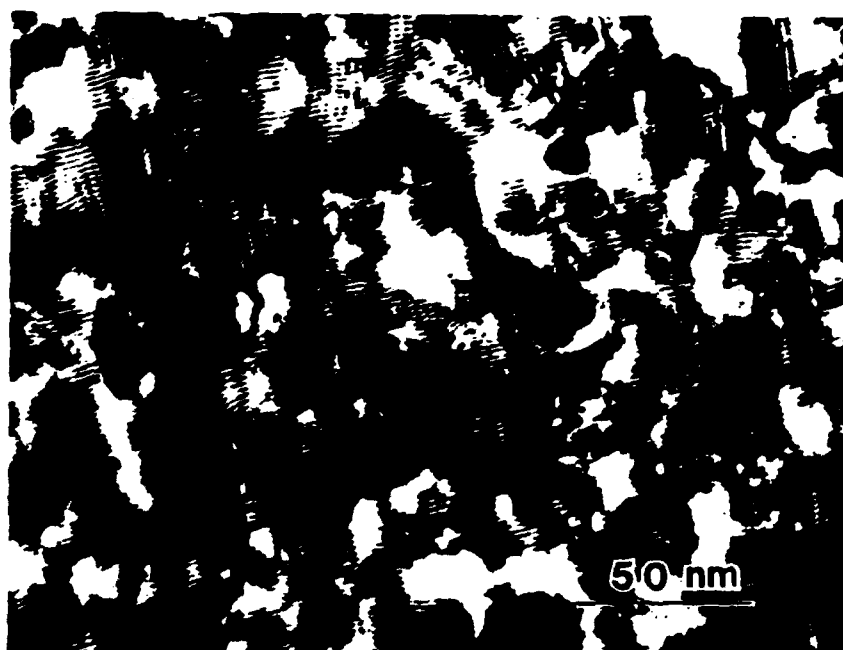
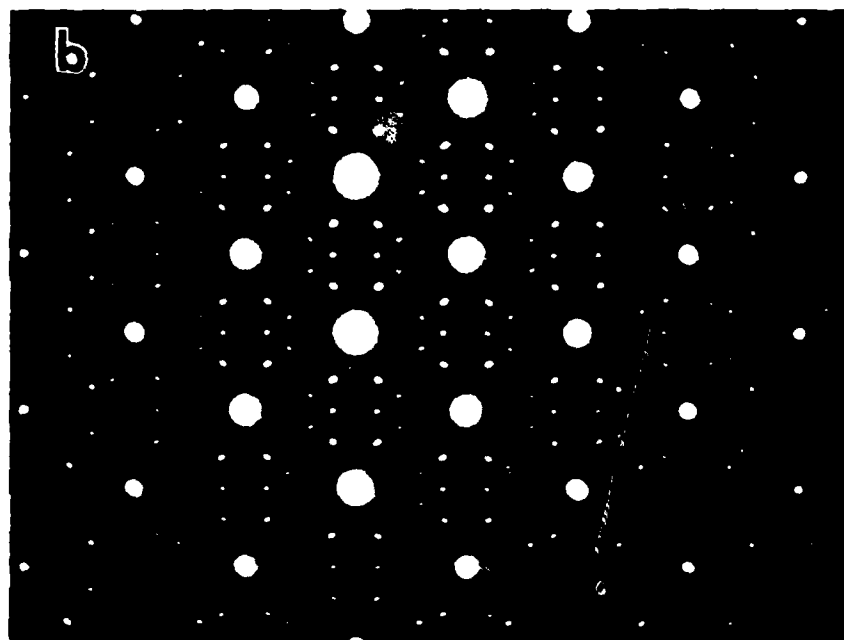
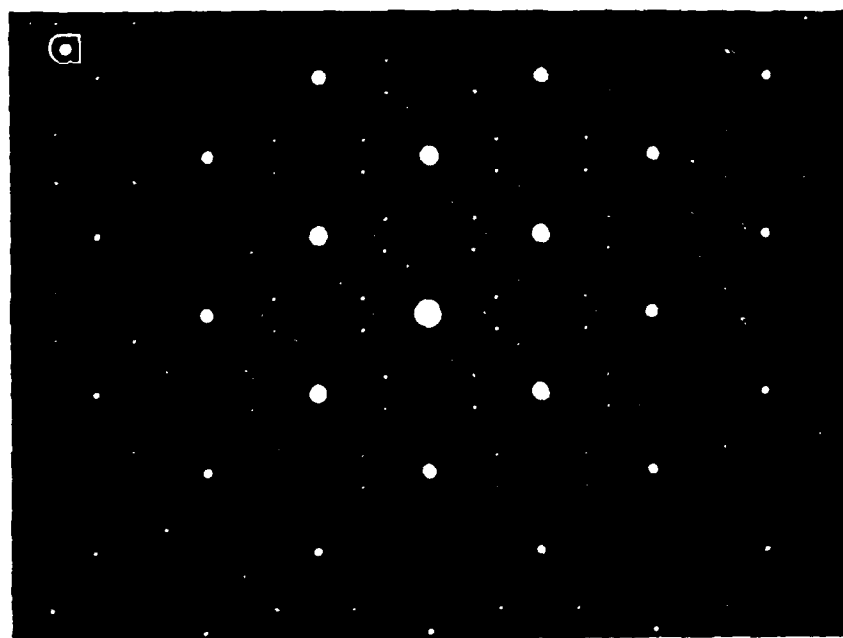


FIG. 6: Bright field image of 6.3 m/o Y-PSZ oriented to a $\langle 111 \rangle_F$ zone axis orientation.



— FIG. 7: $\langle 011 \rangle_F$ zone axis diffraction patterns of CaO-stabilized ZrO_2 containing (a) ϕ_1 precipitate (19 m/o CaO) and (b) ϕ_2 precipitates (21 m/o CaO).

precipitates in Figure 9 in compositions leaner in CaO than 20 m/o aged for long times (30).

The morphology of ϕ_2 precipitates in the CaO-rich crystals studied is shown in Figure 10. The ϕ_2 particles are equiaxed and exhibit higher coherency strains in bright field images (not shown here) than do ϕ_1 , in keeping with the notion that ϕ_1 is metastable (31) but nucleates readily. If this is correct, the assemblage c-ZrO₂ plus ϕ_2 must be only modestly more stable than the assemblage c-ZrO₂ plus ϕ_1 , which combined with the high coherency strains, renders ϕ_2 more difficult to nucleate than ϕ_1 .

ACKNOWLEDGMENT

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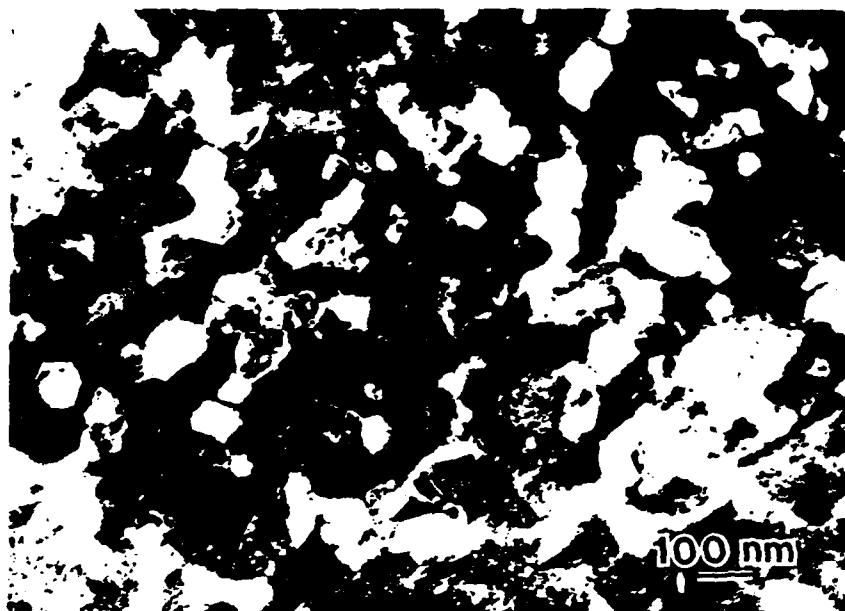


FIG. 9: Ø_1 precipitates in 19 m/o CaO-stabilized ZrO_2 aged 336 hours at 1200°C .



FIG. 10: Ø_2 precipitates in 21 m/o CaO-stabilized ZrO_2 aged 100 hours at 1200°C .

HREM STUDIES OF COHERENT AND INCOHERENT INTERFACES IN ZrO_2 -CONTAINING CERAMICS: A PRELIMINARY ACCOUNT

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HREM has been applied to the study of interfaces in various ZrO_2 -containing ceramics. In dispersion-toughened ceramics, such as ZrO_2 -toughened Al_2O_3 , fine ZrO_2 particles can be either *intra-* or *inter-* granular. *Intragranular* ZrO_2 particles form *incoherent* interfaces with their Al_2O_3 hosts, and such interfaces have been imaged by HREM. The interfaces between *inter-* granular ZrO_2 particles and Al_2O_3 grains are generally covered with a glassy phase, 1–3 nm in thickness, and evidence for this phase is also present in HREM images. If the ZrO_2 transforms from tetragonal to monoclinic symmetry during cooling from the fabrication temperature, it is generally twinned, and the *coherent* twin boundaries have also been imaged in HREM. Tetragonal precipitate colonies which occur on annealing certain ZrO_2 - Y_2O_3 alloys have also been studied. Each colony consists of alternating variants which are 90° twins. HREM shows that the twin boundaries are highly coherent with a slight tilt between the variants. The “matrix” between the tetragonal colonies is shown by optical diffraction analysis of the HREM images to have tetragonal rather than cubic symmetry, indicating the occurrence of a diffusionless cubic $\rightarrow$ tetragonal transformation.

1. Introduction

ZrO_2 -containing ceramics have attracted much attention in recent years because of their unusual mechanical and electrolytic properties [1,2]. Their considerable potential for high-technology structural applications derives from the phenomenon of *transformation toughening*. Briefly, ZrO_2 is polymorphic, the three polymorphs being shown in fig. 1 [3]. The high-temperature form is cubic and is isostructural with CaF_2 (fluorite structure). At temperatures below $\sim 2350^\circ\text{C}$ for pure ZrO_2 , or at temperatures considerably lower for ZrO_2 alloys, the cubic polymorph (*c*- ZrO_2) transforms to a tetragonally distorted version of the fluorite structure shown in fig. 1b (*t*- ZrO_2). At still lower temperatures, *t*- ZrO_2 transforms martensitically to the monoclinic structure shown in fig. 1c (*m*- ZrO_2). This martensitic *t* $\rightarrow$ *m* transformation is the origin of transformation toughening in ZrO_2 -containing ceramics, as will now be described.

In suitably fabricated ceramics, particularly if the *t*- ZrO_2 is present as fine particles, the start or M_s temperature of the martensitic transformation,

which is $\leq 1000^\circ\text{C}$ in pure bulk ZrO_2 , can be reduced to below room temperature, i.e., the *t*- ZrO_2 is retained metastably at room temperature. However, the *t* $\rightarrow$ *m* transformation can be induced by external stresses, for example, the stress field associated with a propagating crack. This stress-induced tetragonal-to-monoclinic transformation thus “shields” the crack tip from the applied stresses and is the origin of the improved strength and toughness of transformation-toughened ZrO_2 -containing ceramics.

It should be clear from this introduction that the type, amount, morphology and distribution of the ZrO_2 polymorphs within ZrO_2 -containing ceramics are of prime importance, and both homophase ($\text{ZrO}_2/\text{ZrO}_2$) and heterophase (ZrO_2 particle/non- ZrO_2 matrix) interfaces are of interest. In fact, such studies of interfaces in polycrystalline, polyphase ceramics are crucial for understanding the variety of diffusional and diffusionless transformations that are important when considering microstructural evolution during fabrication and performance during service. Inasmuch as HREM can play a vital role in understanding

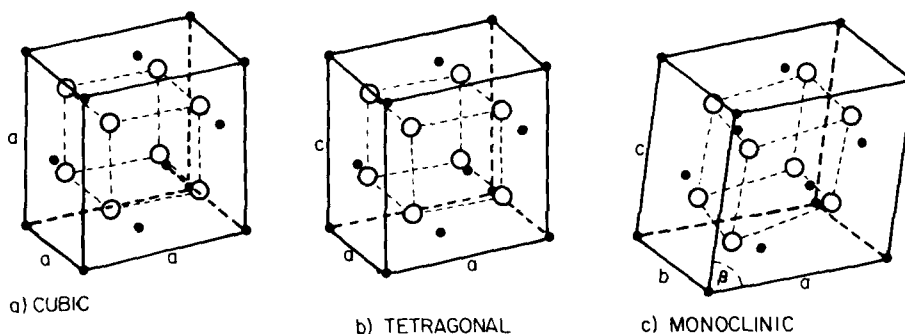


Fig. 1. Three polymorphs of ZrO_2 : (a) cubic phase; (b) tetragonal phase, $c/a \approx 1.02$; (c) monoclinic phase. The small filled spheres are Zr atoms, the large open spheres are oxygen.

these technologically important ceramics, we have begun a broad program using high-resolution electron microscopy to study interfaces in such ceramics.

2. Experimental procedures

15 vol% ZrO_2 -toughened Al_2O_3 (ZTA) specimens were obtained from Dr. N. Claussen (Max-Planck-Institut für Metallforschung, Stuttgart, Fed. Rep. of Germany). The starting powders were Alcoa A-16 Al_2O_3 and Magnesium Electron ARZ52 ZrO_2 . Processing consisted of attritor milling for 12 h, followed by hot pressing at 1550°C for 30 min; the density of the resulting ceramic was 99.5% of theoretical.

Single crystal skull-melted ZrO_2 -8 wt% Y_2O_3 was obtained from the Ceres Corporation. This material was then heat-treated for 50 h at 1600°C and furnace-cooled; Laue back-reflection photographs were used to orient the crystal to a $\langle 111 \rangle$ zone.

Both materials were prepared for TEM examination using standard techniques, i.e. diamond-wafering thin slices, grinding and polishing to approximately $50\text{ }\mu\text{m}$ thickness, followed by ion-beam thinning to electron transparency. A thin carbon coat was sputtered on one surface before insertion into a JEOL 200CX having a C_s of 1.1 mm and a point resolution of $\leq 0.24\text{ nm}$. An Intellect 200 image analysis system is used for

on-line image processing; Skarnulis' CELLS program [4] is available for image simulation.

3. Zirconia-toughened alumina

ZTA, an example of a wider class of dispersion-toughened ceramics, is one of the three useful types of ZrO_2 -containing ceramics. These materials typically contain 15 vol% ZrO_2 in a fine-grained Al_2O_3 matrix; the ZrO_2 can be *inter-* or *intragranular* and the propensity for undergoing the martensitic transformation depends markedly on the morphology of the ZrO_2 particles [5]. Furthermore, the stability of *t*- ZrO_2 , i.e. its resistance to undergoing the martensitic transformation, involves stress concentrations at interfaces. It now appears that nucleation of the *t* $\rightarrow$ *m* martensitic transformation is always stress-assisted [6], and the magnitude of these stresses is very sensitive to particle morphology [7]. Understanding of the *t* $\rightarrow$ *m* martensitic transformation depends on increased knowledge of the interface structure, and a variety of ZrO_2 - Al_2O_3 interfaces have been imaged with high-resolution electron microscopy.

The first example is shown in fig. 2. A roughly spherical *m*- ZrO_2 particle is completely enclosed within an Al_2O_3 grain. As has been discussed elsewhere [8], this morphology arises from "break-away" grain growth of Al_2O_3 grain boundaries during densification or extended high-temperature

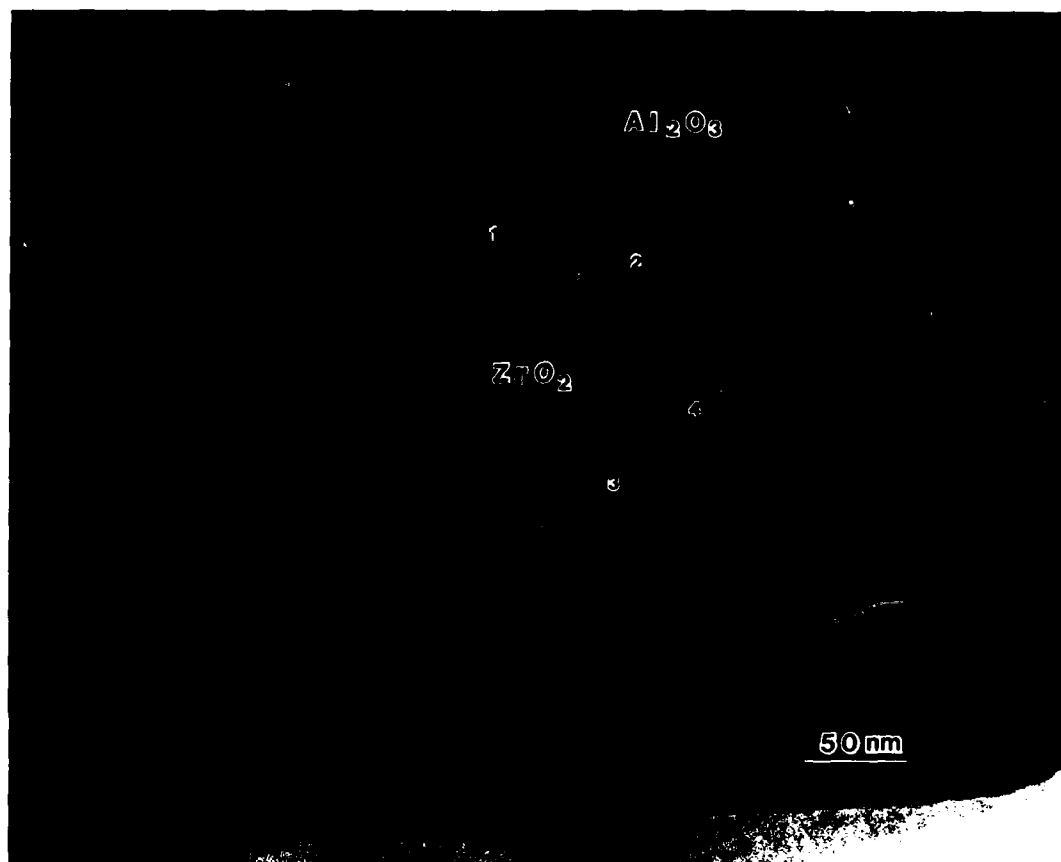


Fig. 2. Bright-field micrograph of intragranular ZrO_2 particle in Al_2O_3 grain.

annealing. While particles such as these are generally resistant to the martensitic transformation in bulk ceramics [5], foil preparation has been found to induce the $t \rightarrow m$ transformation, especially if, as in the present case, the ZrO_2 is free of any "stabilizer" solute. Thus, the ZrO_2 particle shown in fig. 2 has m symmetry, having transformed during foil preparation, and a conventional selected-area diffraction pattern of both the ZrO_2 particle and the Al_2O_3 matrix (not shown here) reveals the fortunate circumstance that the particle and matrix are oriented such that both are within a few degrees of a low-index zone axis orientation, [001] for ZrO_2 and [0001] for Al_2O_3 . Furthermore, the foil is of relatively uniform thickness over the

whole area of fig. 2, and could be imaged in HREM. A structure image of the ZrO_2 particle after tilting to the exact [001] orientation is shown in fig. 3, along with an image calculated by computer simulation. It is clear that the image matching in this particular instance is acceptable. We also hope to model the interfaces (at regions 1–4 in fig. 2 to be shown next), although such interface simulations have not yet been completed.

The particle–matrix interface is shown at higher resolution in fig. 4: the ZrO_2 is oriented exactly on the zone axis in fig. 4a, while the Al_2O_3 is oriented exactly on the zone axis in fig. 4b. The feature marked F in figs. 4a and 4b is a fault in the m - ZrO_2 which we have not yet analyzed. The

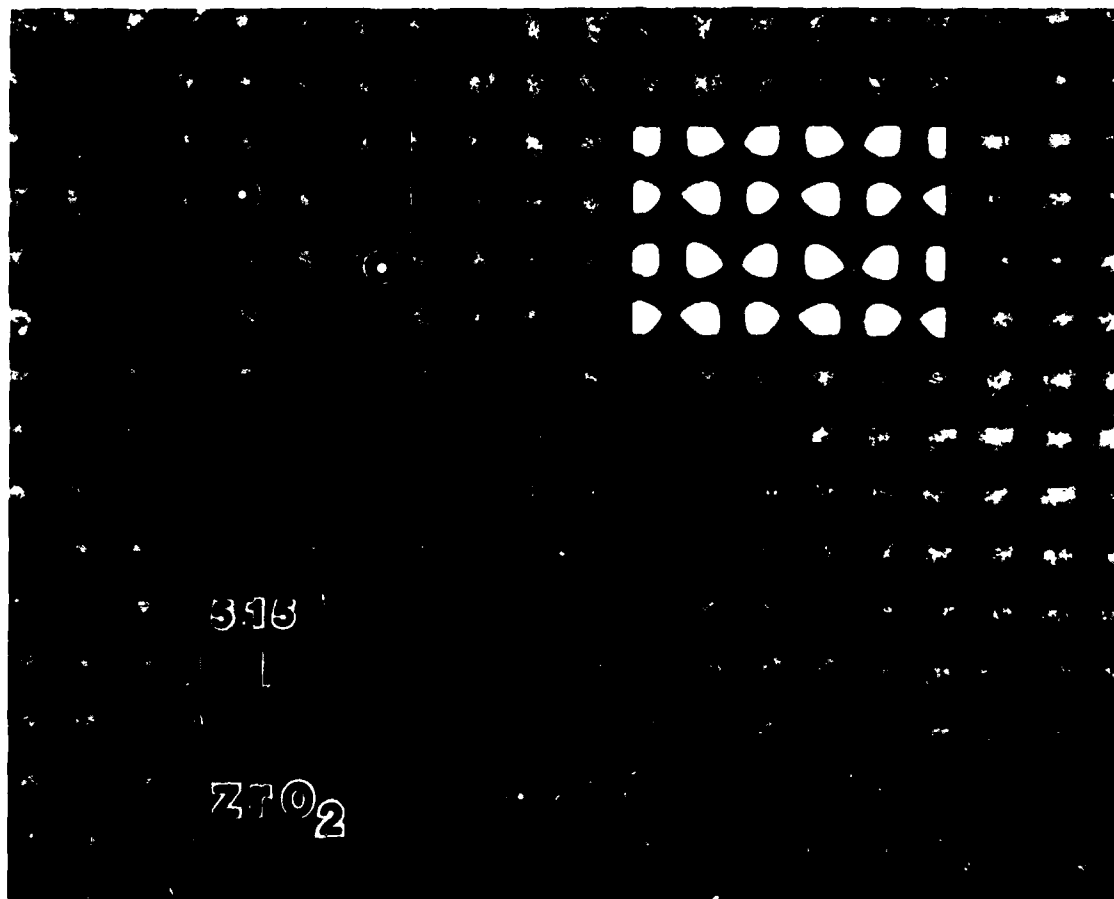


Fig. 3. High-resolution image of $[001]_m \text{ZrO}_2$, with calculated image match. The unit cell is shown.

features marked 1 and 2 in fig. 4a denote particular interface regions which are shown at higher magnifications in fig. 5. We believe that the interface is most nearly parallel to the electron beam in region 1 in fig. 5a, and expect that sensible image interpretation of the atomic structure of this interface will be possible. On the other hand, the region shown in fig. 5b is judged to be uninterpretable because the interface is inclined to the electron beam; no further analysis is being contemplated for this image.

Slight tilting brings the Al_2O_3 grain into its symmetry position, and fig. 6 shows two regions (marked 3 and 4) on the opposite side of the

faulted particle. Fig. 6a shows an area in which the interface is more or less parallel to the electron beam and for which we hope to provide suitable image simulations in the near future. Fig. 6b, on the other hand, shows a region of interface that is inclined to the electron beam and is judged unsuitable for further interpretation. Figs. 5a and 6a are remarkable in that they show the images extend right to the Al_2O_3 - ZrO_2 interface, and that this *incoherent* interphase interface appears to accommodate the two dissimilar lattices without undue difficulty.

With regard to transformation toughening, intergranular particles are preferred in ZrO_2 -

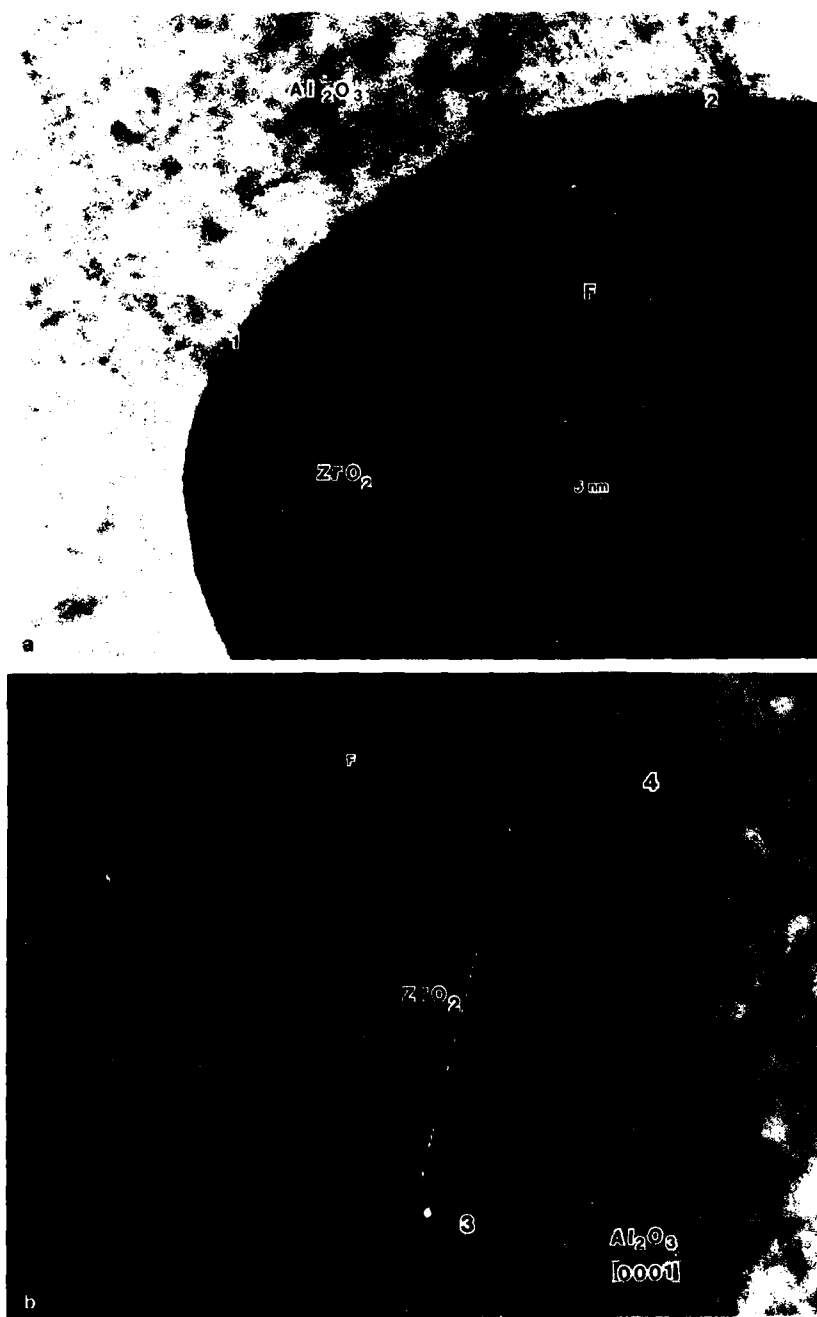


Fig. 4. (a) Higher-magnification micrograph of ZrO_2 particle in fig. 2 with interfacial regions 1 and 2 indicated. F is a fault in the particle. The foil is oriented so that ZrO_2 is exactly on the $[001]$ orientation. (b) ZrO_2 particle with interfacial regions 3 and 4 indicated. The foil is oriented so that Al_2O_3 is exactly on the $[0001]$ orientation.



Fig. 5. (a) High-resolution image of interfacial region 1. (b) High-resolution image of interfacial region 2.

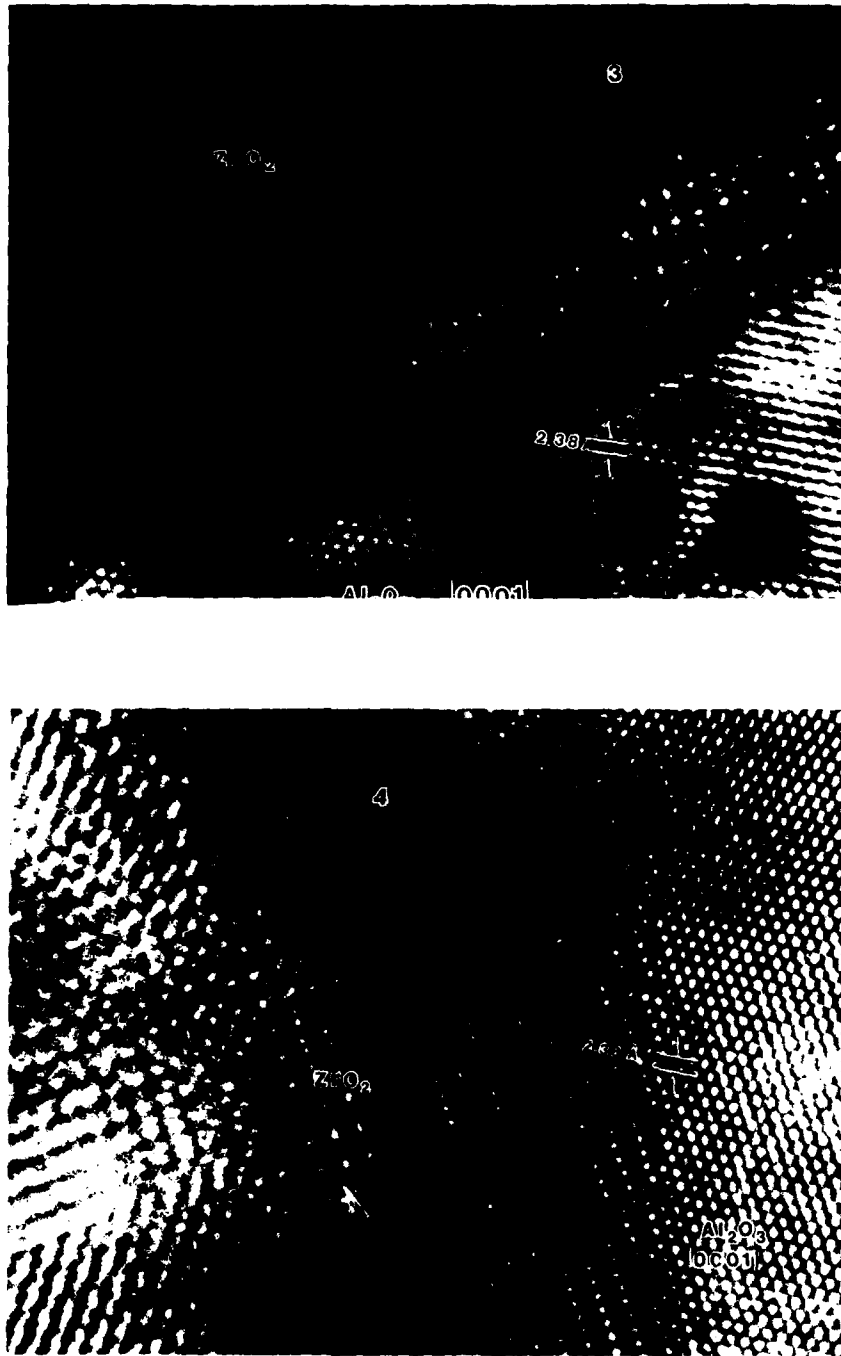


Fig. 6. (a) High-resolution image of interfacial region 3. (b) High-resolution image of interfacial region 4.

toughened Al_2O_3 , and the sample of figs. 2–6 in fact contains more inter- than intragranular particles. However, it should be mentioned that virtually all $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ grain boundaries and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ intergranular boundaries in this sample are coated with a thin film (1–3 nm) of a SiO_2 -containing amorphous phase (the SiO_2 impurity having been introduced during processing); such a grain boundary phase appears to be ubiquitous in all the ZrO_2 -toughened Al_2O_3 's studied to date. This glassy phase can best be imaged by forming a dark field image using diffuse inelastically scattered electrons. The glass is thus located at the bright regions in fig. 7 and the particular arrowed feature is glass along an Al_2O_3 – Al_2O_3 grain boundary. The presence of

such an amorphous phase at the Al_2O_3 – ZrO_2 interface does not detract from detailed HREM studies of the interfaces. A HREM image of a twinned m - ZrO_2 particle in this sample is shown in fig. 8. (This is not the same region as shown in fig. 7.) The ZrO_2 particle is extensively twinned, the twinning occurring during spontaneous transformation on cooling following fabrication. This twinning occurs to minimize the shape strain of the particle during the martensitic transformation, and is present in virtually all m - ZrO_2 particles, except those which have transformed in a thin foil, as in fig. 2.

The orientations of the two Al_2O_3 grains and the several twinned "domains" of the ZrO_2 particle were determined by taking optical diffracto-



Fig. 7. Diffuse dark-field micrograph of intergranular ZrO_2 in an Al_2O_3 matrix, showing glassy phase at grain boundaries. (The arrowed region is an $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ boundary.)

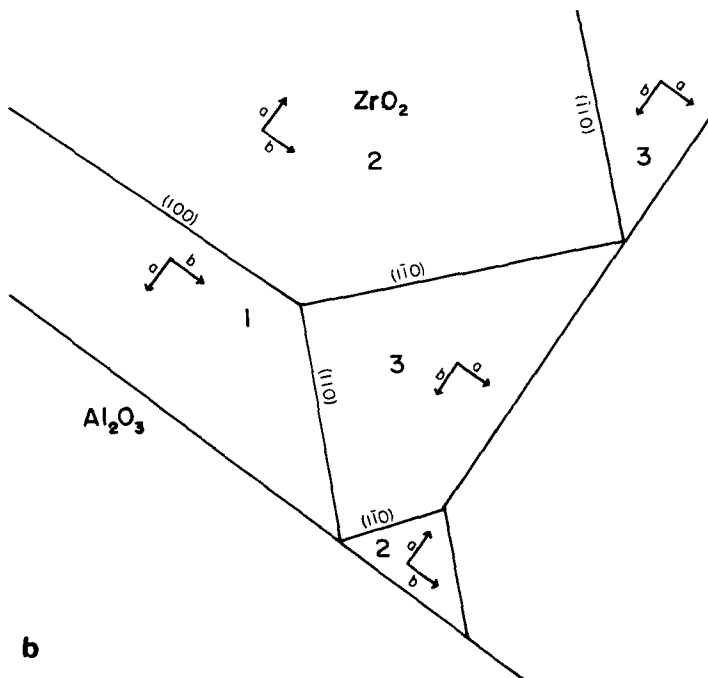
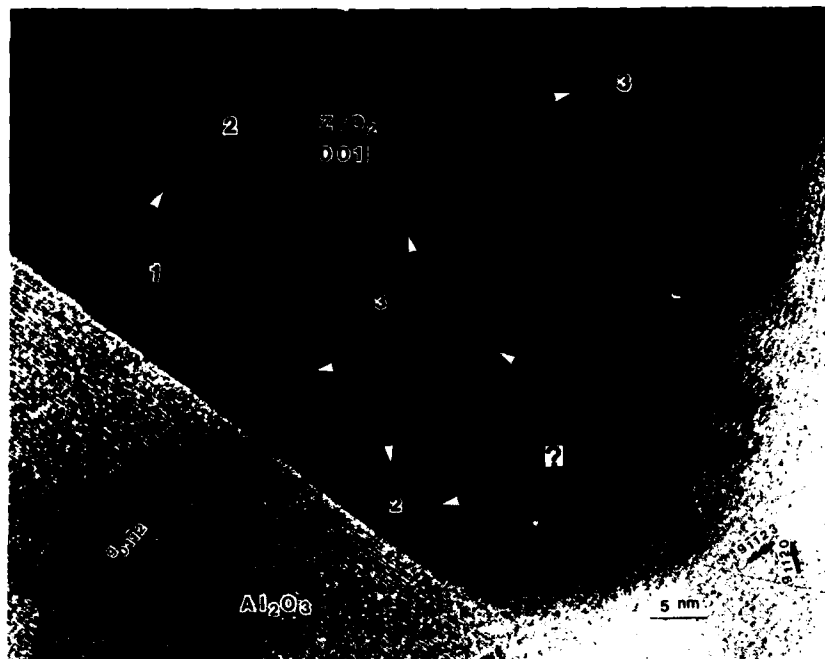


Fig. 8. (a) High-resolution image of intergranular ZrO_2 particle showing microtwins. The twin boundaries are arrowed, as is an $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ grain boundary. 1, 2, and 3 refer to specific twin orientations shown in (b); the question-mark is a region of serious overlap between the ZrO_2 and Al_2O_3 . (b) Diagram of (a) showing twin planes and orientations.

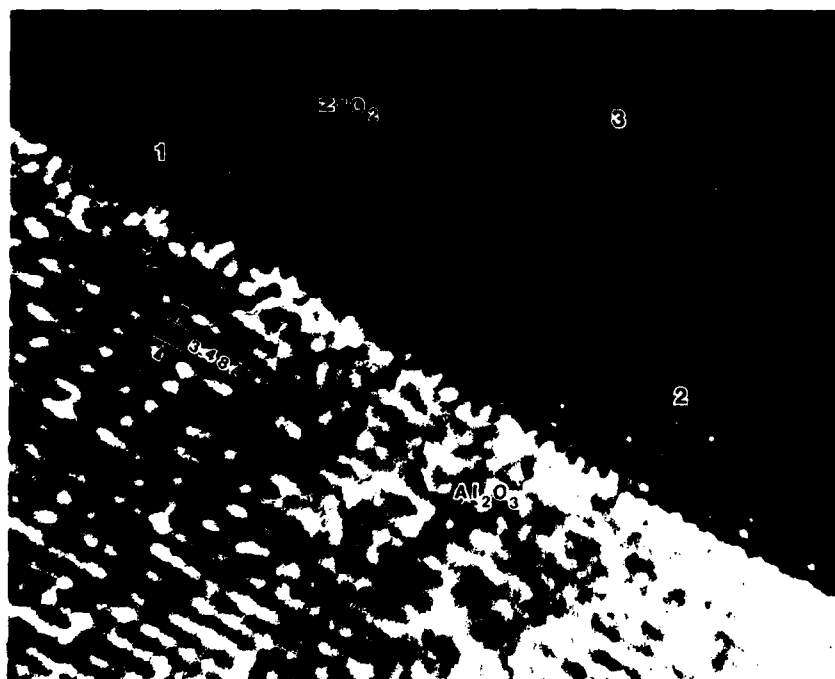


Fig. 9. High-resolution image of ZrO_2 particle in fig. 8a showing possible glassy phase at grain boundary. 1, 2, and 3 refer to the twin orientations shown in fig. 8b.

grams from fig. 8a, and yielded the results shown schematically in fig. 8b. The morphology of the twinned domains, as well as the existence of $(100)_m$, $(110)_m$, and $(\bar{1}\bar{1}0)_m$ twin boundaries, are identical to the results described by Van Tendeloo et al. in $\text{ZrO}_2\text{-ZrN}$ alloys [9].

The final figure for this section (fig. 9) shows the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ interface at high magnification. It is tempting to argue that the broad bright region between the Al_2O_3 and ZrO_2 is a manifestation of the amorphous phase believed to be present, but image simulation is clearly needed to resolve this point. Even lacking such image simulation, it is again remarkable that the features in the structure image extend virtually undisturbed to the incoherent interphase interface. (It is fortunate that the interface in this region of foil is essentially parallel to the electron beam.)

4. $\text{ZrO}_2\text{-Y}_2\text{O}_3$ alloys

$\text{ZrO}_2\text{-Y}_2\text{O}_3$ alloys represent a second major class of ZrO_2 -containing ceramics which have also been subject to significant commercial exploitation. Low Y_2O_3 -content (2–4 mol%) compositions in this system are in use as strong and tough wear-resistant ceramics [10]; medium Y_2O_3 -content (4–8 mol%) compositions find use as oxygen sensors in automotive application [11]; and single crystals containing ~ 10 mol% Y_2O_3 are used as imitation diamonds [12]. We have been studying phase equilibria at temperatures between 1300 and 1600°C in this system using a range of compositions between 3 and 9 mol% Y_2O_3 . Our strategy is to anneal various compositions for long times to allow the pro-eutectoid precipitation reaction to go to completion and to use analytical electron mi-

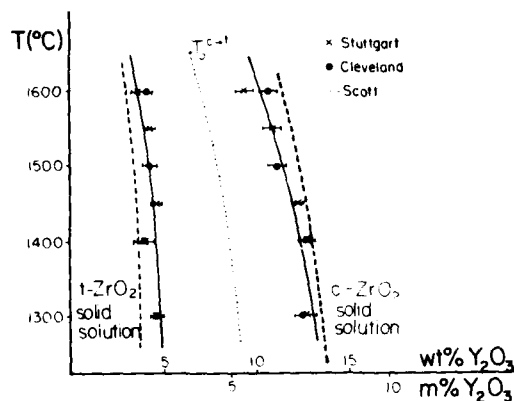
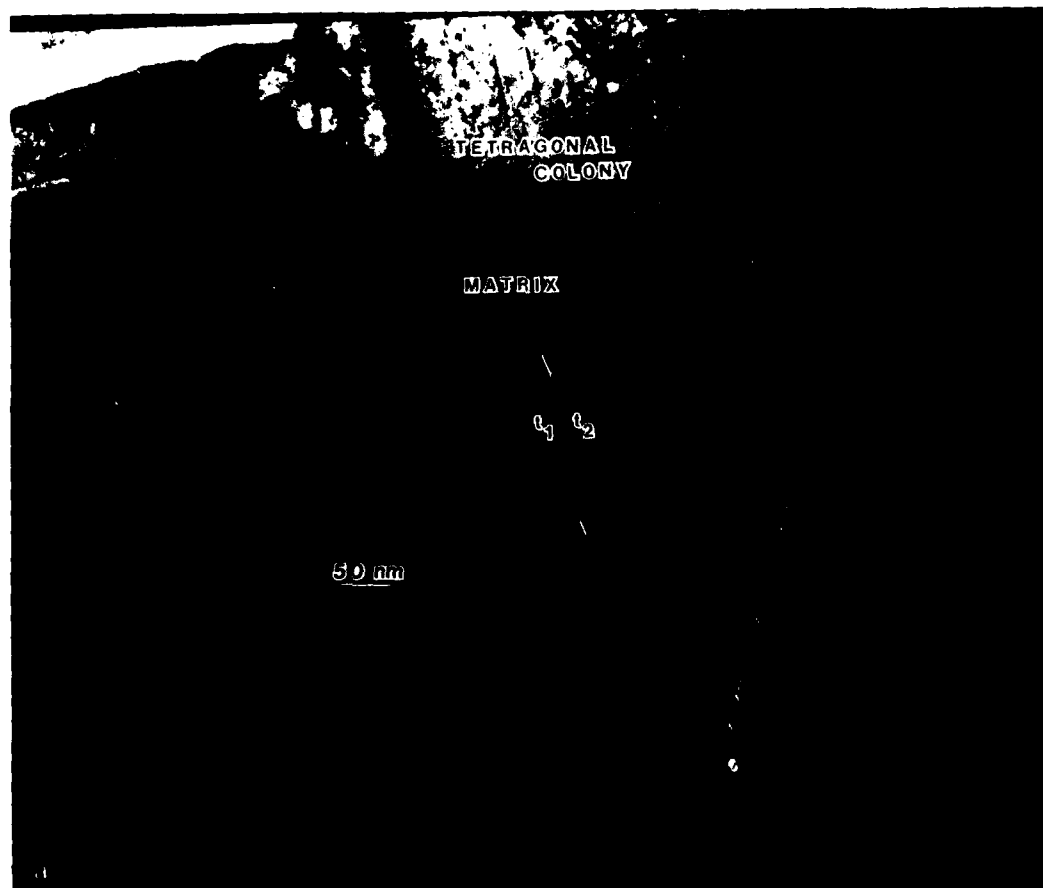


Fig. 10. ZrO₂-rich portion of the equilibrium phase diagram in the ZrO₂-Y₂O₃ system. The equilibrium compositions were determined by EDS methods.

croscopy to study the compositions of the coexisting *c* and *t* solid solutions (Y₂O₃ is very potent in stabilizing *t*-ZrO₂ and reducing *M_c* well below room temperature) [3]. The results of these AEM studies are shown in the partial phase diagram in fig. 10 [3]. For most compositions in the two-phase *t* + *c* solid solution phase field, the *t*-ZrO₂ occurs as twinned "colonies", whose structure will be discussed in the remainder of this paper. The colony structure is shown in fig. 11a; this micrograph is taken from a 4 mol% Y₂O₃ ZrO₂ single crystal oriented to an exact $\langle 111 \rangle$ matrix zone-axis orientation. Each colony contains two *t* variants, which are actually 90° twins (fig. 11b); this morphology occurs to minimize strain between the colony precipitates and the matrix. As will be discussed next, the matrix also has tetragonal sym-



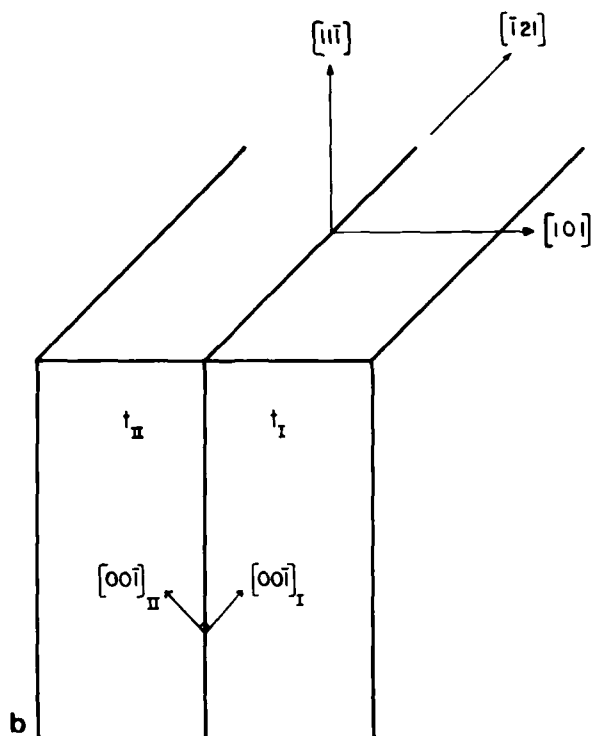


Fig. 11. (a) Tetragonal colony structure in ZrO_2 -4 mol% Y_2O_3 showing a typical interface of interest (arrowed). (b) Schematic diagram showing twin variant crystallography. (The interface is perpendicular to $[101]$.)

metry, having undergone a diffusionless $c \rightarrow t$ transformation on cooling from the annealing temperature [3]. The twinned colony structure of the t - ZrO_2 precipitates is very stable even during extended annealing; the number of twins per colony remains constant even as the colonies coarsen [13].

A HREM image of a twin variant interface is shown in fig. 12; this interface is similar to the one arrowed in fig. 11a, but of course was taken in a thinner region of the foil. It can be seen that the $(1\bar{1}0)$ planes are imaged in one t variant, while the $(2\bar{2}0)$ planes are imaged in its twin. This difference is believed to result from the very small tilt of one twin relative to the other, and would not occur were the c/a ratio exactly unity.

The origin of the colony stability is also apparent from fig. 12. The twin interface of fig. 12 (marked TB) can hardly be discerned; were it not for the slight tilt of the two twins, the twin

boundary might not be visible. The good atomic matching thus implied assures that the twin boundary energy is correspondingly low. Thus, interface energy in the twinned structure must always be less than the reduced strain energy between colony precipitate and matrix.

The HREM study has also helped resolve a question concerning the matrix crystallography. As first suggested by Scott [14], and as is discussed elsewhere [3,13,15], c - ZrO_2 alloys quenched from high temperature can undergo a displacive $c \rightarrow t$ transformation below a certain critical temperature, T_0 . (The variation in T_0 with composition is indicated by the dashed line in fig. 10 marked $T_0^{c \rightarrow t}$.) The equilibrium composition of the c - ZrO_2 matrix annealed at 1600°C is 6.0 mol% Y_2O_3 ; T_0 for this composition is $\sim 900^\circ\text{C}$. We thus expect both the matrix and the colonies of fig. 11 to have t symmetry, but to differ in Y_2O_3 content by a

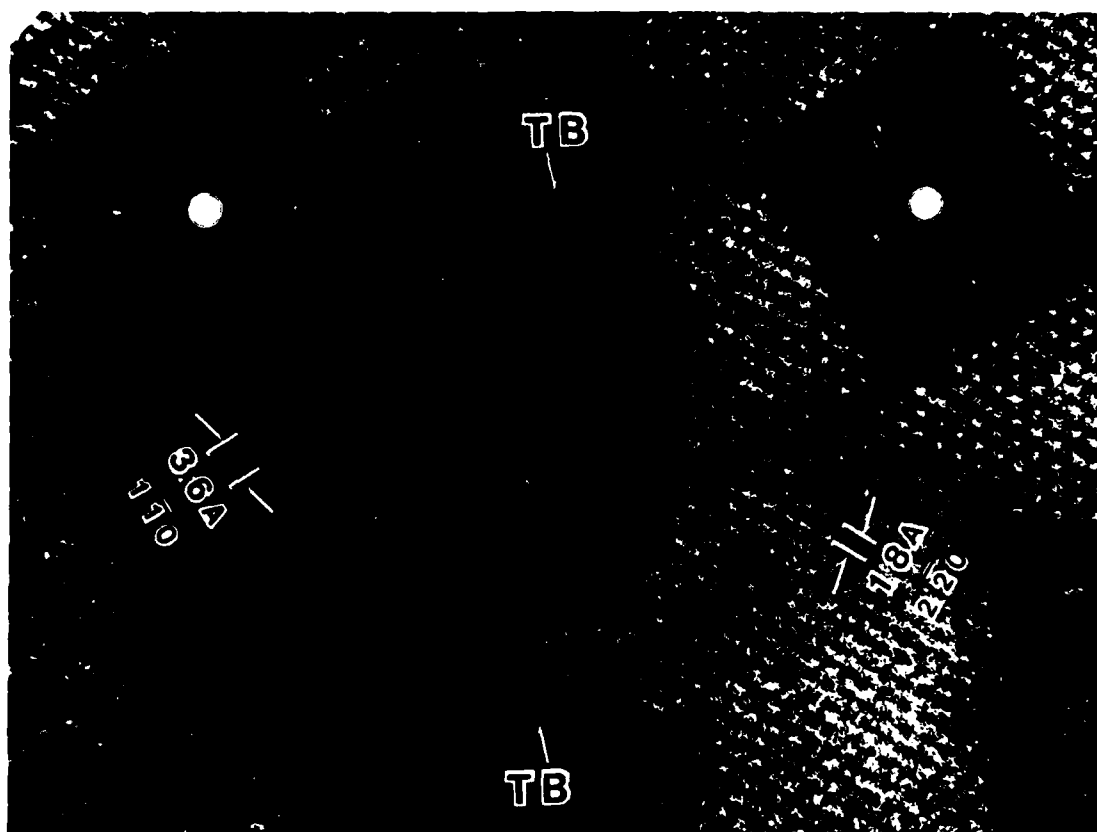


Fig. 12. High-resolution image of a coherent twin boundary (TB) between two tetragonal variants within the same colony. Optical diffractograms are shown as inserts.

factor of ~ 3 . This chemical difference has been confirmed by AEM [13]. However, the variation in lattice parameter with Y_2O_3 solute is too small in this system to give rise to any spot splitting in the *odd, odd, even* reflections unique to *t*- ZrO_2 in conventional large-area SAD patterns, and it is difficult to be certain that there is no contribution from the colonies in any SAD pattern taken only from the matrix.

Fig. 13 shows a high-resolution image of the matrix, along with two optical diffractograms taken from different regions of the image. The $\{220\}$

planes with 0.18 nm spacing imaged on the left portion of fig. 13 are consistent with either *c* or *t* symmetry. Slight bending of the foil has caused the adjacent area to be slightly off the exact orientation. In this region, (110) planes with 0.36 nm spacing are being imaged. (110) is a forbidden reflection for both *c*- ZrO_2 and *t*- ZrO_2 , but often occurs in *t*- ZrO_2 by double diffraction from (112) planes. In any event, this spacing in the optical diffraction pattern is unambiguous evidence that the matrix has undergone the *c* $\rightarrow$ *t* transformation.

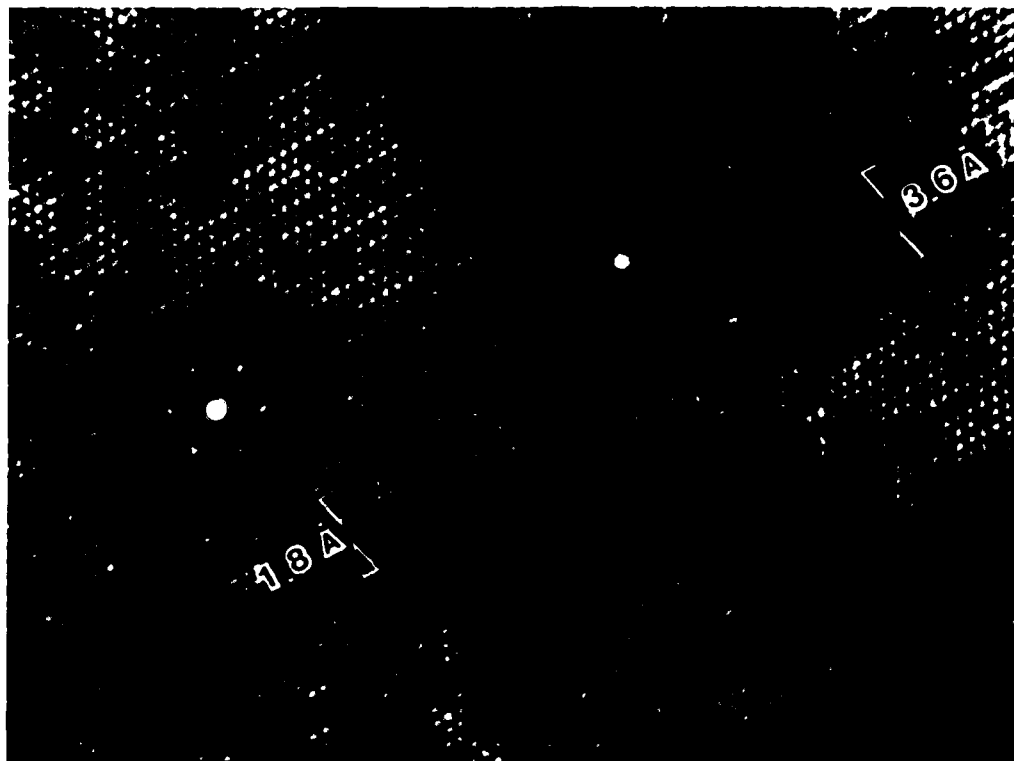


Fig. 13. High-resolution image and optical diffractograms of the matrix between two colonies.

Acknowledgments

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HREM STUDIES OF INTERFACES IN $\text{ZrO}_2/\text{Al}_2\text{O}_3$ CERAMICS

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Because of its unusual mechanical and electrolytic properties, zirconia (ZrO_2) finds a wide variety of uses, such as refractories, oxygen sensors, heaters and extrusion dies.^{1,2} ZrO_2 exists in three polymorphic forms; the high temperature phase is cubic and is isostructural with CaF_2 (fluorite); below 2350°C (in pure ZrO_2), a tetragonally-distorted version of the fluorite structure exists. At still lower temperature, the tetragonal form ($t\text{-ZrO}_2$) transforms martensitically to a monoclinic structure ($m\text{-ZrO}_2$). This $t \rightarrow m$ transformation gives rise to the phenomenon of transformation toughening in ZrO_2 -containing ceramics, and thus provides ceramics with potential for high technology structural applications.

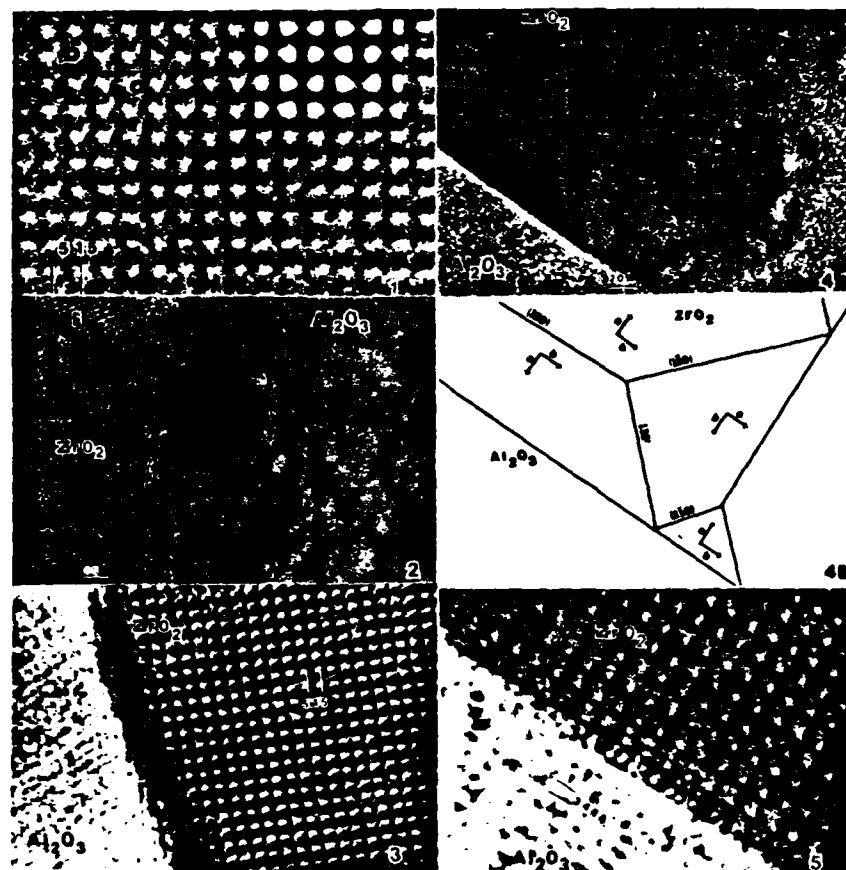
ZrO_2 -toughened Al_2O_3 (ZTA) is an example of a wide class of dispersion-toughened ceramics. These materials typically contain 15 vol.% ZrO_2 in a fine-grained Al_2O_3 matrix; the ZrO_2 is dispersed as both intra- and intergranular particles, and can have monoclinic or tetragonal symmetry. The propensity for undergoing the martensitic transformation depends markedly on the morphology of the ZrO_2 particles, and nucleation of transformation invariably occurs at the interface between ZrO_2 and Al_2O_3 . Since HREM can contribute vital information in helping to understand these interfaces, a variety of ZrO_2 -containing ceramics are being investigated on a JEOL 200CX high resolution microscope with a point resolution of 2.4 Å. This paper reports data obtained from a 15vol.% ZTA ceramic, sintered at 1600°C for four hours.

Since the ZrO_2 particles are randomly oriented, it was a fortunate circumstance to find a roughly spherical, intragranular particle, such that both particle and matrix were oriented within a few degrees of a low index zone; [001] for ZrO_2 and [0001] for Al_2O_3 . A high resolution image of the ZrO_2 particle tilted exactly to the [001] zone is shown in Fig. 1; the calculated image is inset. The particle has monoclinic symmetry, but is believed to have transformed during thin foil preparation. A high resolution image of the particle-matrix interface can be seen in Fig. 2; where the Al_2O_3 grain is tilted to the exact [0001] orientation. The feature marked F is a fault in the $m\text{-ZrO}_2$. Fig. 3 shows a higher magnification of the interface structure with the ZrO_2 exactly on zone. In this region, the interface is nearly parallel to the electron beam, and sensible image interpretation should be possible. (Calculated images are presently being produced using several interface models.) Interface images with the Al_2O_3 grain oriented on zone have also been obtained.

A high resolution image of a twinned, intergranular $m\text{-ZrO}_2$ particle is shown in Fig. 4A. The twinning occurs on transformation during cooling after fabrication, and minimizes the shape strain of the particle resulting from the martensitic transformation. Optical diffractograms of twins permitted determination of the twinned structure, which is shown schematically in Fig. 4B. Our results agree exactly with the findings of Van Tendeloo, et al. in $\text{ZrO}_2\text{-ZrN}$ alloys.⁵ It is believed that a thin (1-3 nm) glassy phase exists at the ZrO_2 particle- Al_2O_3 matrix interface (Fig. 5). However, image simulation is again needed to correctly interpret the interface structure and determine whether or not an amorphous phase is actually present. It is tempting, however, to suggest that the bright broad region at the interface is the amorphous phase.⁶

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6. This work is supported by the Air Force Grant No. AFSOR-82-0227. I thank my advisors A.H. Heuer and T.E. Mitchell for their guidance and P. Labun for her patience and support.



- Fig. 1--High resolution image of [001] ZrO_2 , with calculated image match. Unit cell is shown.
- Fig. 2--High resolution image of ZrO_2 - Al_2O_3 interface. Al_2O_3 is on [0001] zone, and F is fault in particle.
- Fig. 3--Higher magnification of interface structure. Interface is nearly parallel to electron beam.
- Fig. 4--(A)High resolution image of intergranular ZrO_2 particle showing microtwins. (B)Diagram showing twin planes and orientations.
- Fig. 5--High magnification image of ZrO_2 particle in Fig. 4A showing possible glassy phase at grain boundary.

Tetragonal Phase in the System $\text{ZrO}_2\text{-Y}_2\text{O}_3$

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Analytical electron microscopy has been used to obtain information on tetragonal (*t*) ZrO_2 in the system $\text{ZrO}_2\text{-Y}_2\text{O}_3$. Evidence of two tetragonal solid solutions (*t* and *t'*) has been found in single crystals obtained from skull melting. Of the two, *t'*- ZrO_2 has the higher Y_2O_3 content and has been described by previous workers as "nontransformable"; it is present in as-grown crystals but is metastable. After annealing at high temperatures (1600°C), *t'*- ZrO_2 decomposes into a mixture of the two equilibrium phases: a low- Y_2O_3 -content *t*- ZrO_2 and a high- Y_2O_3 -content cubic (*c*) phase, *c*- ZrO_2 . The *t*- ZrO_2 appears as precipitate colonies consisting of two twin-related variants in contact along the coherent {101} twin plane.

Precipitates of the high- ZrO_2 tetragonal distorted-fluorite phase in the system $\text{ZrO}_2\text{-Y}_2\text{O}_3$ appear to be quite different from those observed in other well-studied partially stabilized zirconias (Mg-PSZ, Ca-PSZ).¹⁻³ In this paper, we discuss the nature of the tetragonal phase in Y_2O_3 partially stabilized zirconia (Y-PSZ) single crystals. We note that three versions⁴⁻⁶ of the phase diagram exist, which differ in detail mainly at the high- ZrO_2 region; our work thus also sheds light on the subsolidus phase equilibria in this system.

Scott⁴ described a metastable "nontransformable" high- Y_2O_3 -content tetragonal ZrO_2 solid solution (*t*- ZrO_2), which he and other workers^{7,8} suggested formed from the cubic ZrO_2 solid solution (*c*- ZrO_2) via a displacive phase transformation; the nontransformability relates to its reluctance to undergo the stress-assisted martensitic transformation to monoclinic symmetry found in lower- Y_2O_3 -content *t*- ZrO_2 (Fig. 1). This form of nontransformable *t'*- ZrO_2 is widely encountered in plasma-sprayed Y-PSZ⁷⁻⁹ and may form only in nonequilibrium situations, as suggested by Scott. For example, *t'*- ZrO_2 was not found by Stubican et al.,⁵ who used reactive gels and powders in the experiments that led to their construction of the phase diagram for this system.

Virtually all prior studies of this nontransformable *t*- ZrO_2 have utilized X-ray studies of powders. One of the goals of this study has been the electron microscopy examination of this form of ZrO_2 in single crystals. According to Miller et al.,⁷ the nontransformable *t'*- ZrO_2 formed in plasma-sprayed Y-PSZ is unstable; if these materials are annealed in the two-phase (*t*- ZrO_2 + *c*- ZrO_2) phase field, *t*- ZrO_2 forms via a diffusion-controlled precipitation reaction and may subsequently transform martensitically to monoclinic symmetry on cooling.

Attention has been given in this work to a single composition (8 wt% Y_2O_3) in the two-phase field, which should be single phase with cubic symmetry at high temperatures but which, according to the experiments of Miller et al.,⁷ should transform to *t'*- ZrO_2 on cooling from high temperature. The stability of *t'*- ZrO_2

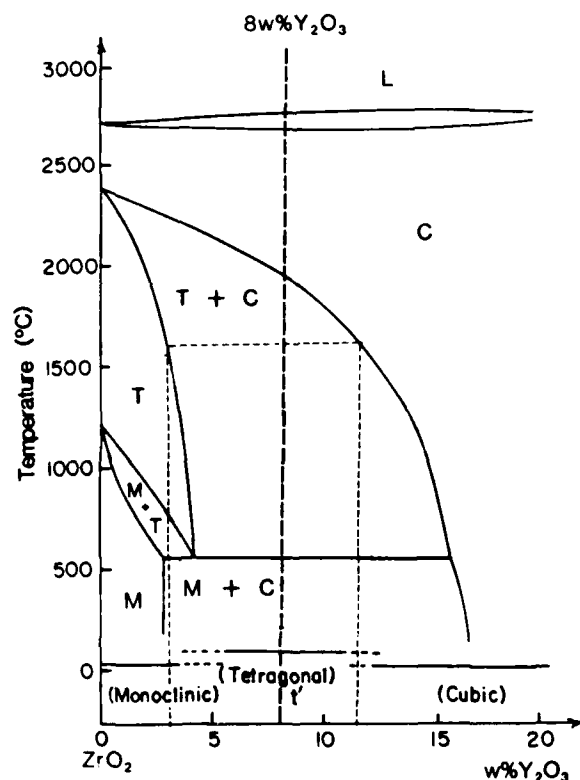


Fig. 1. Phase diagram of the ZrO₂-rich region of the system ZrO₂-Y₂O₃ (Ref. 4).

has been investigated with respect to annealing at high temperatures (1600°C), and the phases present after this heat treatment have been characterized.

Experimental Procedure

As mentioned above, the single-crystal sample used contained 8 wt% Y₂O₃ and was grown by skull melting.* The crystals were opaque and white, a physical appearance characteristic of nonreduced zirconia. For X-ray diffraction, the sample was crushed into fine powder in an agate mortar. Plates (1 by 10 by 10 mm) were annealed in air at 1600°C for 24, 50, and 100 h and quenched by removal from the furnace. The microstructure of the as-received and annealed specimens was characterized by analytical electron microscopy using a Philips EM400T microscope with standard dark-field techniques, supplemented by energy dispersive X-ray analysis (EDX).

Before proceeding to the results, it is appropriate to describe the techniques used to form dark-field images of *t*-ZrO₂. To distinguish this phase from *c*-ZrO₂,

*This crystal was furnished by NRL and manufactured by CERES Corp., Waltham, MA. For further information, see Ref. 10.

only certain foil orientations can be used, where reflections that are unique to the t phase are present. When transformation from c to t symmetry occurs in this system, whether by precipitation or via a displacive phase transformation, three t variants result, the t c axis being parallel to any of the three original $\langle 100 \rangle_c$ directions. To image all the t variants, the most convenient foil orientation is $\langle 111 \rangle$. Also, t -ZrO₂ can be described in terms of either a nonprimitive base-centered unit cell, which in fact is a slightly distorted version of the c fluorite unit cell, or a conventional primitive t unit cell.^{11,12} For convenience in this paper, the former C-centered t cell will be used for comparison with the fluorite cell of c -ZrO₂.

Results

Figure 2 is a typical $[\bar{1}11]$ diffraction pattern of the as-received material. The most intense ("fundamental") reflections are those allowed by both c - and t -ZrO₂, whereas the weaker reflections are due to the t phase and have the subscript t . For all $\{1\bar{1}2\}_t$ -type reflections to be present in a $[\bar{1}11]$ zone axis selected-area diffraction (SAD) pattern, three t variants must be present in the area of foil giving rise to the SAD, each variant giving rise to one $\{1\bar{1}2\}_t$ reflection.¹³ It is thus possible to image all the t variants in the dark field using the three $\{1\bar{1}2\}_t$ reflections (see below). X-ray diffraction performed on the as-received specimen showed that only a very small amount of c -ZrO₂ was present, indicating that the material contains almost 100% t -ZrO₂.

Figure 3 shows dark-field micrographs of the as-received material using the three $\{1\bar{1}2\}_t$ reflections just described. The t -ZrO₂ particles imaged in Fig. 3(a) appear to be precipitates ≈ 10 nm thick by ≈ 50 nm long, lying on two $\{101\}$ habit planes. The t -ZrO₂ precipitates in Y-PSZ thus appear to be different from t -ZrO₂.

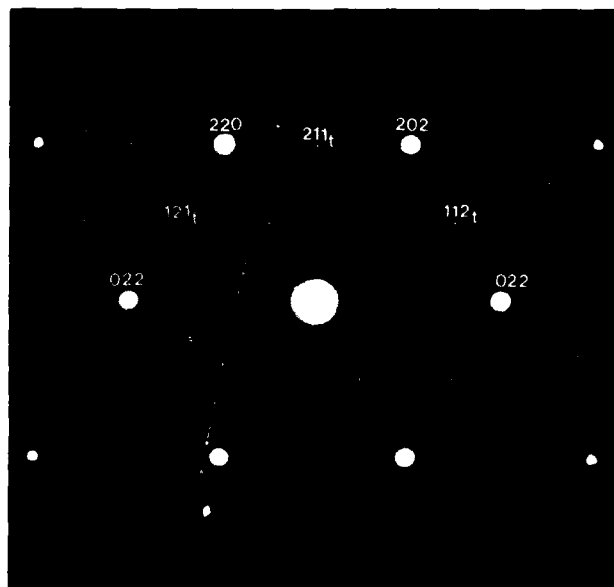


Fig. 2. Diffraction pattern, $[\bar{1}11]$ zone axis.

precipitates in Mg-PSZ, where the precipitate/matrix habit plane is invariably $\{100\}$, and Ca-PSZ, where the precipitates tend to be equiaxed. Figure 3(b) is obtained by using a second $\{1\bar{1}2\}_t$ reflection in the same area of the foil. A second tetragonal variant is imaged in this case and is also present as well-defined precipitates with a $\{101\}$ habit plane. The third $\{1\bar{1}2\}_t$ tetragonal reflection (Fig. 3(c)) gives rise to a different microstructure in the same area of the foil—the “matrix” in which the precipitates of Fig. 3(a) and (b), are contained. If the three micrographs are superimposed, all the foil area has been illuminated; it appears that the entire foil area has t symmetry, confirming the X-ray analysis.

It thus appears that the single crystal consists of a t matrix containing t precipitates! We believe that, during the slow cooling that is part of the skull-melting crystal-growth process, a high-temperature displacive transformation from c to t symmetry occurred, giving rise to the t' matrix structure of Fig. 3(c). The precipitates of Fig. 3(a) and (b) are believed to be low- Y_2O_3 t - ZrO_2 , which formed via a conventional diffusion-controlled reaction, either from the c phase or from the t' - ZrO_2 itself. The small amount of c - ZrO_2 indicated by the X-ray analysis was not detectable in the area of foil imaged in Fig. 3. It has been suggested^{14,15} that the $c \rightarrow t'$ displacive reaction should give rise to antiphase domain boundaries (APBs), which have been imaged by TEM by Bender and Lewis¹⁶ in 3 and 6 wt% Y-PSZ single crystals after laser irradiation, by Chaim et al.¹⁵ in a 12 wt% Y-PSZ polycrystal after suitable heat treatment, and by Michel et al.¹⁷ in 5.4 wt% single crystals. The arrowed features in Fig. 3(c) are also thought to be APBs arising from this transformation.

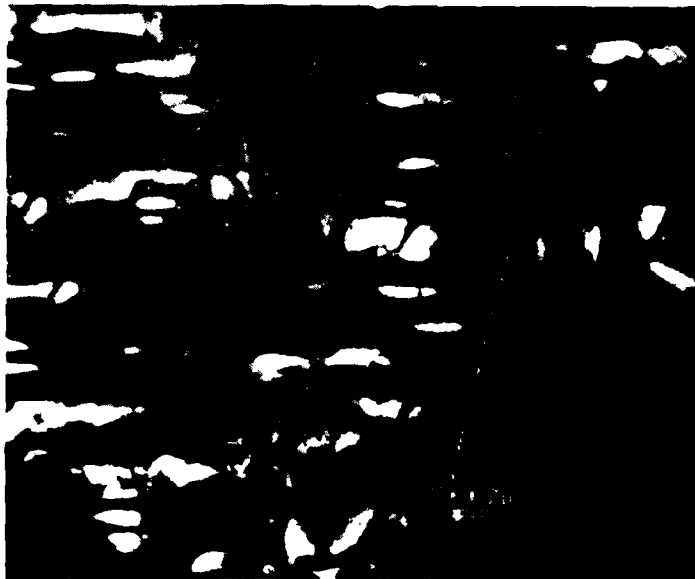
EDX analysis of the matrix of Fig. 3(c) showed a Y_2O_3 content of ≈ 8 wt%. If, as has been suggested, t - ZrO_2 is a precipitate that formed in a c or t' matrix, then it should have a lower Y_2O_3 content than the parent t' matrix (see Fig. 1). Unfortunately, the small size of the t - ZrO_2 precipitates and the difficulty of distinguishing the precipitates during conventional bright-field imaging prevent confirming this prediction by EDAX analysis. Therefore, we studied further decomposition of the t' matrix during high-temperature (1600°C) annealing, with the expectation that the precipitates would coarsen.

From the phase diagram (Fig. 1), t' - ZrO_2 should decompose into a low- Y_2O_3 t - ZrO_2 solid solution containing ≈ 3 wt% Y_2O_3 plus a c - ZrO_2 solid solution containing ~ 12 wt% Y_2O_3 . Dark-field micrographs of the same area of a foil, again obtained with the three $\{1\bar{1}2\}_t$ reflections, are shown in Fig. 4 from a specimen which had been aged 24 h at 1600°C. Figure 4(a) and (b) indicates that the t - ZrO_2 precipitates have grown at the expense of the t' matrix, the precipitates occurring in the form of large “colonies”; each colony actually consists of plates of two twin-related variants. The two variants have different c axes but share a habit plane, which is the coherent twin plane. Small colonies can actually be discerned at the arrowed region of Fig. 3(a); it is clear the colonies coarsen during annealing. The remaining t' - ZrO_2 is imaged in Fig. 4(c); notice that it is located at the periphery of the colonies and has a c axis different from that of the two variants constituting the colony. The t' - ZrO_2 is clearly a minor component, confirming that t' - ZrO_2 is unstable with respect to diffusion at high temperatures. We thus expect the decomposition products of t' - ZrO_2 to be a mixture of equilibrium phases, namely, c - ZrO_2 and the colonies of t - ZrO_2 . Such a microstructure can be seen in Fig. 5 from a specimen aged for 50 h at 1600°C. Figure 5(a) is a bright-field micrograph and shows coarse colonies set among c regions. Figure 5(b) is the corresponding dark-field micrograph, taken with a t reflection.

(a)



(b)



(c)

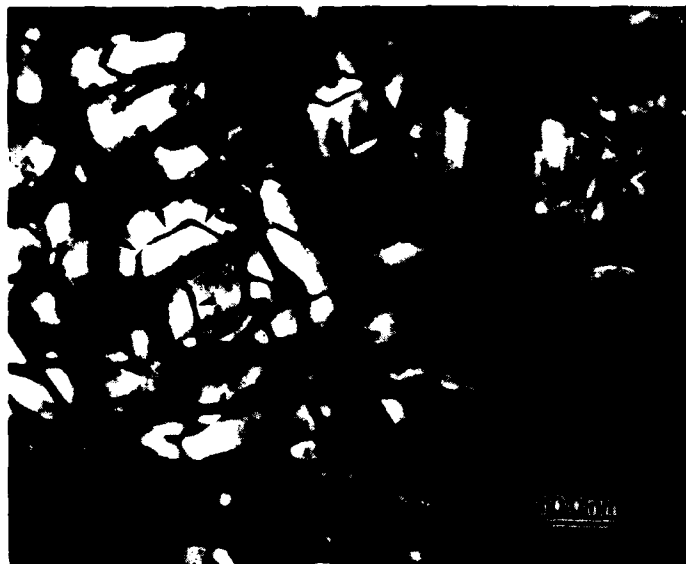


Fig. 3. Dark-field micrographs of as-received single crystal (8 wt% Y_2O_3). (a) $\mathbf{g} = \bar{1}1\bar{2}$, (b) $\mathbf{g} = 211$, and (c) $\mathbf{g} = 12\bar{1}$.

Microchemical EDX analysis was performed to compare the Y_2O_3 content of the colonies and the $c\text{-ZrO}_2$. The two spectra are compared in Fig. 6, where it is clear that the c phase is significantly richer in Y_2O_3 than are the t colonies. Quantification of these data revealed a Y_2O_3 content of 4.1 ± 0.1 and $10.6 \pm 0.1\%$ for the colonies and the $c\text{-ZrO}_2$, respectively, close to but not identical with the predictions of Scott's phase diagram (Fig. 1).

The twin relation of variants within the same colony is best illustrated in Fig. 7 from a specimen aged at 1600°C for 100 h; the same features as in Fig. 5 are present, and the coarsening of the tetragonal colonies has progressed further. The selected-area diffraction pattern from one colony shows that only two variants are present. The third variant, which in fact was the original $t'\text{-ZrO}_2$ in the starting material, is not contained in this area of foil. By imaging the colony with the two remaining $\{1\bar{1}2\}$ reflections, reverse contrast is observed, showing that the colony indeed contains two twin-related variants.

Discussion

This study has shown evidence of two tetragonal solid solutions, $t\text{-ZrO}_2$ and $t'\text{-ZrO}_2$. These two phases have a quite different microstructure and composition. In the as-received crystal, metastable bulky $t'\text{-ZrO}_2$ is present, while after annealing, the equilibrium $t\text{-ZrO}_2$ precipitates are in the form of colonies. The colony orientation appears to be closely related to the original orientation of the $t'\text{-ZrO}_2$. Within each colony, there are two twin-related variants, whose respective c axes

(a)



(b)



(c)



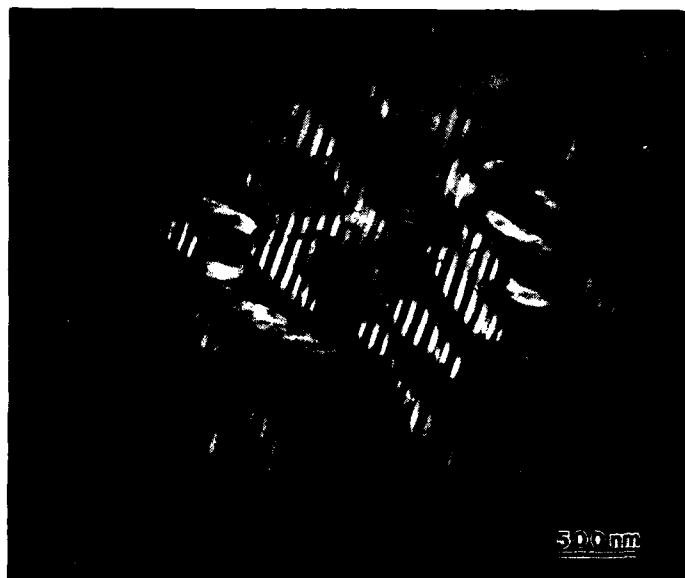
Fig. 4. Dark-field micrographs of specimen aged 24 h at 1600°C: (a) $g = \bar{1}1\bar{2}$, (b) $g = 211$, and (c) $g = 12\bar{1}$.

are along the a and b axes of the original t' -ZrO₂. These colonies have also been observed in polycrystalline sintered ceramics with the same Y₂O₃ content¹⁸ and in a 12 wt% Y₂O₃ polycrystal.¹⁵ (In the former material the tetragonal colonies nucleated and grew in a cubic matrix.) The formation of colonies at the expense of the t' matrix, and in c -ZrO₂ grains in a sintered ceramic, and their stability after lengthy annealing suggest that the twin interface within the colonies has an unusually low interfacial energy and that formation of colonies in both t' and c -ZrO₂ minimize lattice strain very effectively. In fact, as the habit plane of the colony is perpendicular to the a axis of t' -ZrO₂ and of c -ZrO₂, the "fit" between the t colony and its matrix is very similar in both situations.

Earlier workers also pointed out that t' -ZrO₂ is nontransformable, in the sense that it does not undergo the martensitic transformation to monoclinic symmetry even under stress (e.g., during grinding). However, the t colonies formed from t' -ZrO₂ are also quite stable in that no monoclinic phase was found by X-ray diffraction in crushed specimens that had been annealed for 50 h. This is quite different from what has been observed in other partially stabilized zirconias and is not well understood at this time.

Finally, it is interesting to provide a thermodynamic/kinetic rationale for the existence of two t -ZrO₂ solid solutions in this system. We assume that (i) c -ZrO₂ does form in 8 wt% materials from the melt, (ii) during cooling following skull melting, the cooling history is such that diffusional decomposition to c - and t -ZrO₂, which should occur at $T < 2000^\circ\text{C}$ (Fig. 1), does not occur, and (iii) the c -ZrO₂ undergoes a displacive transformation to tetragonal symmetry at some critical

(a)



(b)

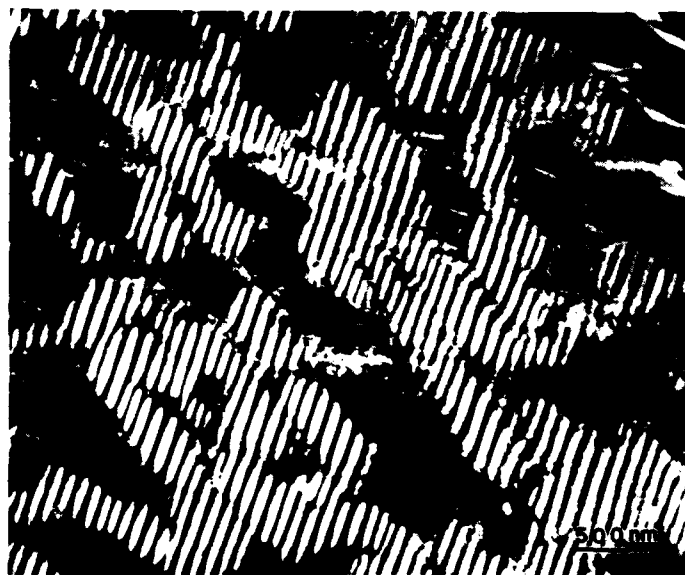


Fig. 5. Micrographs of specimen aged 50 h at 1600°C: (a) bright field and (b) dark field, $\mathbf{g} = \bar{1}12$.

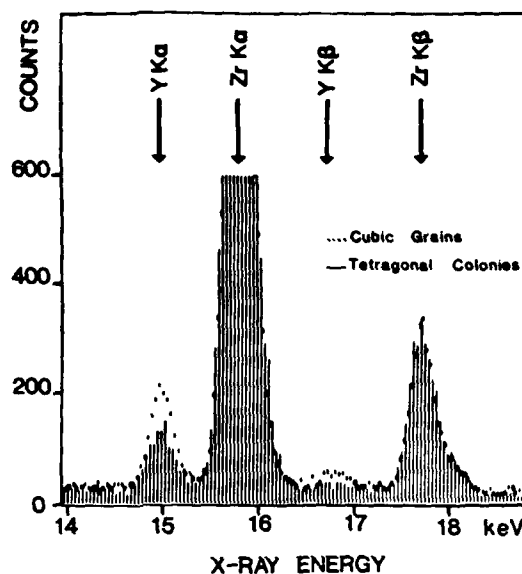


Fig. 6. Energy dispersive X-ray spectra of *c* matrix and *t* colonies.

temperature T_0 . Plausible free energy vs composition curves above and below T_0 are depicted in Fig. 8. Although a two-phase assemblage has the minimum free energy for an 8 wt% material for the situation depicted in Fig. 8(a), supersaturated *c*-ZrO₂ solid solution will persist until *t*-ZrO₂ of the equilibrium composition can be nucleated. If cooling below T_0 without nucleation of *t*-ZrO₂ occurs (Fig. 8(b)), a displacive transformation in an 8 wt% material from supersaturated *c*-ZrO₂ to supersaturated *t'*-ZrO₂ can occur and will lower the free energy from G_s to G_i ($\Delta G'$). The solid solution *t'*-ZrO₂ can further lower its energy by forming *t*-ZrO₂ of free energy G_t and *c*-ZrO₂ of free energy G_c for a further energy reduction of $\Delta G''$, but this will be a sluggish transformation, as considerable diffusion is required.

Further study is under way on the mechanism of the displacive *c* $\rightarrow$ *t'* transformation and on the variation of T_0 with composition. These experiments should also assist in determining the actual boundaries of the two-phase (*c*-ZrO₂ + *t*-ZrO₂) field by using EDX microchemical analysis of the equilibrium microstructures (*c*-ZrO₂ and colonies of *t*-ZrO₂).

Acknowledgments

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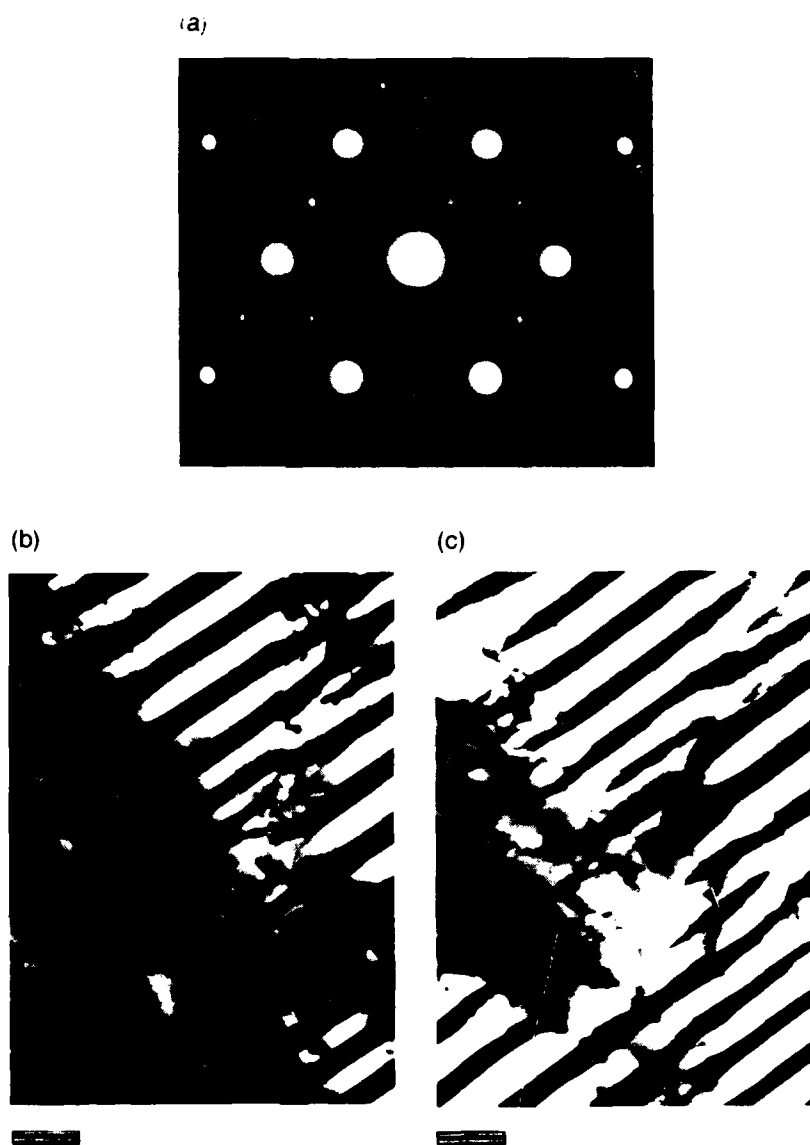


Fig. 7. Specimen aged 100 h at 1600°C: (a) SAD pattern, $[111]$ zone axis from one colony, (b) dark-field micrograph, $\mathbf{g} = 11\bar{2}$, and (c) dark-field micrograph, $\mathbf{g} = 211$. The arrows in (b) and (c) point to the same feature. Bar = 500 nm.

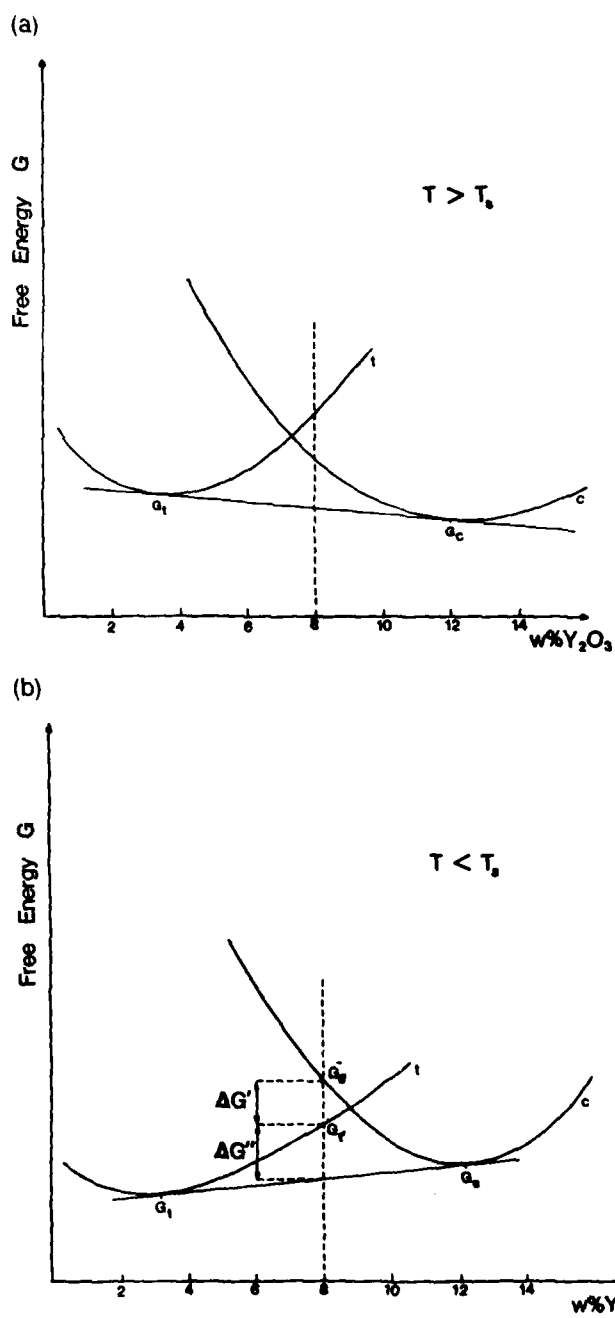


Fig. 8. Free energy vs composition curves: (a) above the critical temperature T_0 and (b) below the critical temperature T_0 .

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HREM of incoherent $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interfaces

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Introduction

Dispersion-toughened ceramics have received much attention in recent years due to their impressive mechanical properties. In particular, ZrO_2 additions to Al_2O_3 can increase the strength of the material to greater than 1 GPa (1). Typically, small amounts of ZrO_2 (≤ 30 vol.%) are dispersed in a fine-grained Al_2O_3 matrix; the ZrO_2 exists as both intragranular and intergranular, incoherent particles with either monoclinic (m) or tetragonal (t) symmetry. The enhanced strength and toughness arise from the phenomenon known as transformation toughening, involving the martensitic t- ZrO_2 to m- ZrO_2 transformation. Nucleation of the transformation invariably occurs at the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interface (2).

High resolution electron microscopy contributes vital information in helping to understand these interfaces. In the past, HREM has been performed on materials of known orientation containing coherent or semi-coherent interfaces. In polycrystalline ZrO_2 -toughened Al_2O_3 (ZTA), the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interface is not only incoherent but the particle and matrix are of random orientation. In spite of these adverse conditions, HREM is still possible, and yields interesting results.

Experimental procedure

As-sintered ZTA samples containing 3.8, 10, and 15 vol.% ZrO_2 were studied using HREM. Thin foils were prepared by conventional ion-milling techniques. After ion-milling, the thin foils received a short heat treatment (15 min. at 1200°C) to reverse any t $\rightarrow$ m transformation which may have occurred during foil preparation. Samples were examined in a JEOL 200CX transmission electron microscope fitted with a top entry $\pm 10^\circ$ tilting stage; the microscope has a C_s of 1.1 mm, and has a point-to-point resolution of 0.236 nm.

Results and discussion

In order to image the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interface successfully, each phase must be exactly on zone, while the interface should be parallel to the electron beam. Due to the random distribution of ZrO_2 particles, these conditions are difficult to meet; hundreds of particles were investigated, but few were in (or could be tilted to) the proper orientation.

Fig. 1a shows an intragranular, t- ZrO_2 particle from a 10 vol.% sample at low magnification. The Al_2O_3 matrix is oriented to the $[01\bar{1}1]$ zone, while a single set of $\{111\}$ planes is visible in the ZrO_2 , as it is about two degrees off its $\langle 110 \rangle$ zone. The $\{111\}$ ZrO_2 planes and $(0\bar{1}11)$ Al_2O_3 planes are misoriented by about five degrees; furthermore, the d-spacings of these two sets of planes differ significantly, 0.295 nm for $\{111\}$ ZrO_2 and 0.393 nm for $(0\bar{1}11)$ Al_2O_3 . In spite of this apparent

lattice mismatch, no microcracks or other gross distortions appear at the interface in these HREM images.

Quasi-periodic fringes give rise to some unusual contrast around the particle. At higher magnification (Fig. 1b), the periodicity of the fringes is seen to arise from every fourth Al_2O_3 plane (arrowed) stopping short at the interface, as compared to the three preceding planes. As the interface orientation changes, the periodicity changes from every fourth to every third Al_2O_3 plane. These arrowed planes are analogous to misfit dislocations commonly observed in semicoherent interfaces. As the orientation changes, so does the apparent configuration of misfit dislocations in the interface structure; they do not appear periodic in Fig. 1c, and are widely spaced in Fig. 1d.

At some orientations, the lattice mismatch is accommodated by a series of ledges one atomic plane in height (Fig. 1e). It is remarkable that features familiar from semicoherent interfaces, i.e. misfit dislocations and ledges, are also a feature of incoherent interfaces in the present system. This must arise in this instance, because the lattice mismatch is in fact small: four ErO (111) planes have a spacing of 1.180 nm, while three Al_2O_3 (011) planes are spaced 1.179 nm.

Near the interface in the ErO particle, some structure images including planes with half of the (111) planar spacing can be discerned. It is believed that the strains arising from the thermal expansion mismatch of the two materials have bent the ErO lattice into a favorable orientation for imaging the (111) planes. This can be seen most clearly in Fig. 1e.

The majority of the intragranular ErO particles in the 10 vol.% material are spherical, but some faceted particles are also present (Fig. 2a). The facetting suggests the existence of a low energy interface between Al_2O_3 and ErO . The Al_2O_3 grain is exactly oriented to the (1010) zone, but the Moiré fringes in the particle unfortunately indicate that the ErO overlaps the Al_2O_3 . The ErO orientation was determined using optical diffractometry, which showed that (200) planes from t-ErO were parallel to (1110) Al_2O_3 planes. Fig. 1f shows that the basal planes of Al_2O_3 are also parallel to the facet. Muerolles, et al. (3) have studied Al_2O_3 - ErO (Y_2O_3) eutectics and found the following planes of t-ErO and Al_2O_3 to be parallel: t-ErO // (0001), (100) // (1110), (010) // (0110); the corresponding directions were also parallel. For the particular faceted particle in Fig. 2b, (200) is parallel to (1110).

Image simulations using Keefe's SHRII (Simulated High Resolution Lattice Imaging) program (4) are currently being performed with various models to obtain a match with experimental images, and thus determine the interface structure. Our strategy is to first create a sharp interface with the ideal ErO and Al_2O_3 structures in the observed (random) orientation, and then to relax the atomic positions to best fit the observed images. To date, the perfect lattices of Al_2O_3 in the [100] and [110] zones have been successfully simulated.

Summary

Incoherent $\text{ErO}/\text{Al}_2\text{O}_3$ interfaces can be successfully imaged with HREM. Lattice mismatch is accommodated by a combination of misfit dislocations and ledges, analogous to those found in semicoherent precipitates. Low energy orientations also exist between ErO and Al_2O_3 , as attested to by presence of faceted particles.

Acknowledgment

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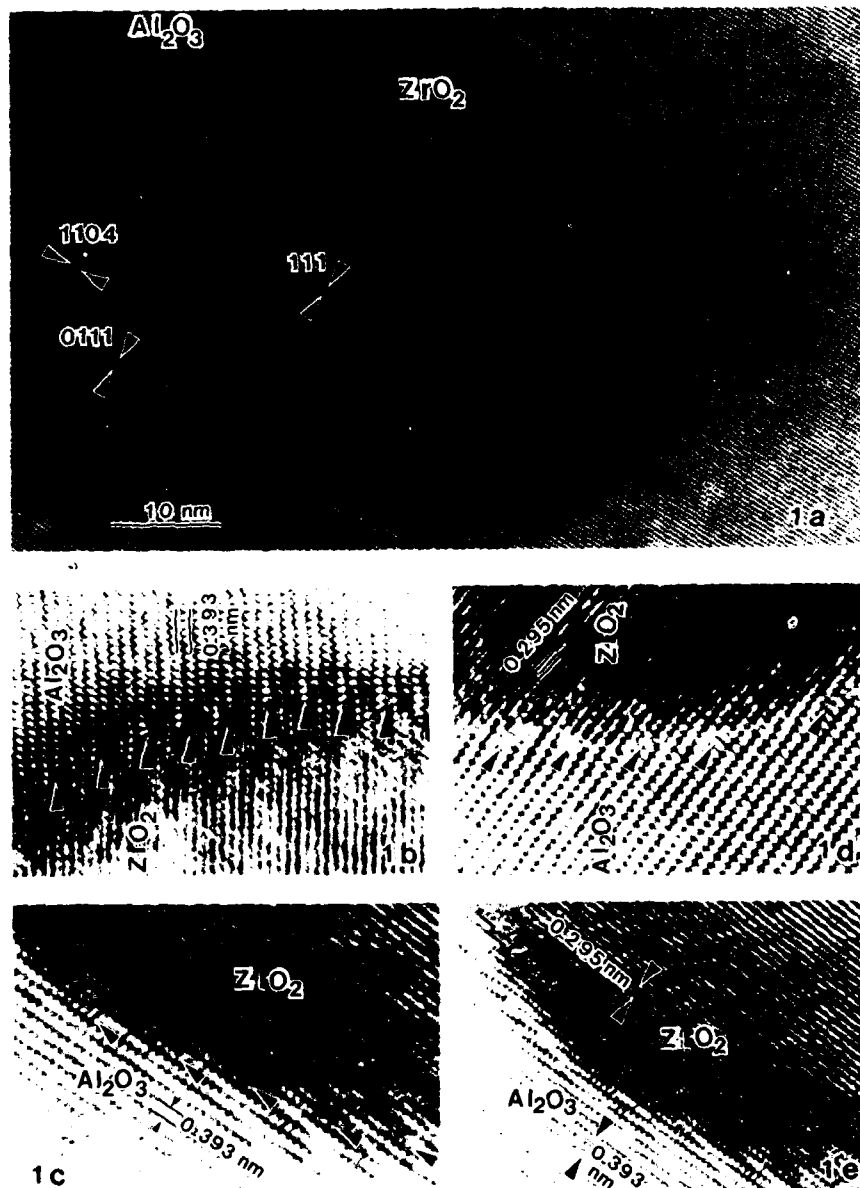


Fig. 1 (a) Intragranular, t - ZrO_2 particle with higher magnification images of various areas (b-e). See text for details.

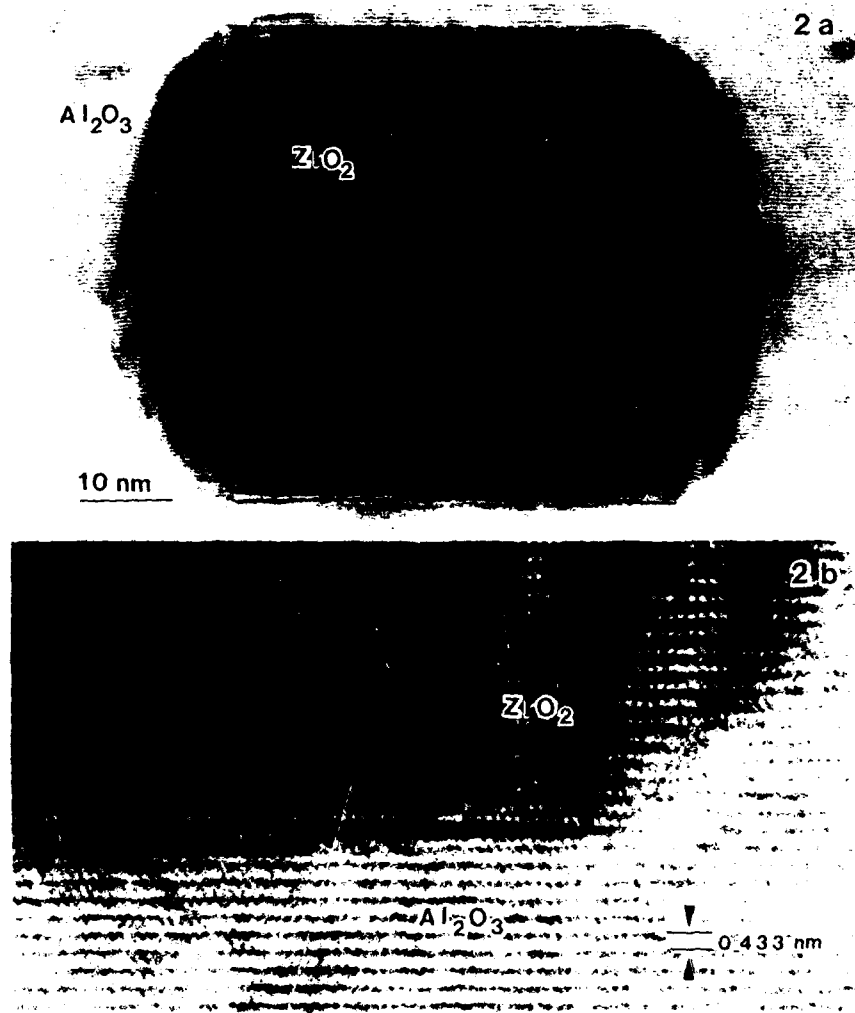


Fig. 2 (a) Intragranular faceted t - ZrO_2 particle. (b) Note Al_2O_3 basal planes parallel to facet.

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Structure of Incoherent $\text{ZrO}_2/\text{Al}_2\text{O}_3$ Interfaces

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High-resolution electron microscopy was used to image incoherent $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interfaces in ZrO_2 -toughened Al_2O_3 containing intragranular ZrO_2 . These particles are generally spherical but are sometimes faceted. High-resolution electron micrographs provide atomic-level information on the interfacial structure. For spherical particles, both ledgeline images and misfit dislocation-like images accommodated the lattice misfit, depending on the orientation of the interface, while faceted particles imply at least one low-energy $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interface.

I. Introduction

ZIRCONIA-TOUGHENED alumina (ZTA) is the most important member of the wide class of ZrO_2 -containing dispersion-toughened ceramics.¹ Such materials typically consist of modest amounts of ZrO_2 (up to 30 vol%) dispersed in a fine-grained Al_2O_3 matrix. The ZrO_2 particles can have tetragonal (*t*) or monoclinic (*m*) symmetry, are incoherent with the Al_2O_3 matrix, and can be either intergranular or intragranular (Fig. 1).

In the present paper, we will show high-resolution electron micrographs which provide information on the nature of the incoherent $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interfaces on an atomic level, particularly for intragranular ZrO_2 particles. Intergranular $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interfaces appear to be wetted by an amorphous grain-boundary phase;² these interfaces have also been imaged by high-resolution electron microscopy (HREM), but these results will be reported elsewhere.³

II. Experimental Procedure

ZTA samples containing 3.8, 10, and 15 vol% ZrO_2 have been studied using HREM; the fabrication or provenance of the samples is described elsewhere.² All microscopy was performed in a transmission electron microscope* dedicated to HREM and fitted with a top entry $\pm 10^\circ$ tilting stage; the TEM pole piece has a *C*, (spherical aberration constant) of 1.1 mm. This microscope routinely provides point-to-point resolution down to 0.236 nm.

Thin-foil HREM samples were prepared by ion beam thinning

using conventional means, except that the thinned foils were annealed at 1200°C for 15 min before HREM examination. This annealing induced the (reverse) *m* $\rightarrow$ *t* transformation in particles in which the (forward) *t* $\rightarrow$ *m* transformation had occurred during foil preparation, a common occurrence in ZTA. (A preliminary report showing micrographs of an *m*- $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interface, in which such a *t* $\rightarrow$ *m* transformation had occurred in an intragranular ZrO_2 particle during thin-foil preparation, has been published elsewhere.⁴)

Before describing our results, we note that imaging conditions for HREM are very stringent. Firstly, the foil must be very thin, ≤ 20 to 30 nm. Secondly, both the ZrO_2 particle and the Al_2O_3 matrix have to be oriented such that a low index zone axis for both phases is exactly (or nearly) parallel to the electron beam. Because the ZrO_2 particles in these dispersion-toughened ceramics are randomly oriented with respect to their Al_2O_3 matrices, this requirement is very difficult to satisfy, particularly as the interface itself should also be parallel to the electron beam. Of the more than 100 ZrO_2 particles examined to date, only a handful satisfied these difficult constraints. In this paper, we report images of two intragranular $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interfaces from which useful structural information can be obtained.

Thirdly, it is customary to take a through-focus series of images at various amounts of defocus, as the optimum defocus to achieve maximum structural information in the final image (the so-called Scherzer defocus) is difficult to know *a priori*.⁵ Finally, unambiguous image interpretation requires exact image matching between computed (simulated) and experimental images, starting with assumed structural models and known microscope parameters (amount of defocus, *C*, etc.). While acceptable image matching for defect-free ZrO_2 or Al_2O_3 is straightforward (we have used both Skarmulis' CELLS program⁶ and O'Keefe's SHRLI program⁷ for this), modeling of the interface is much more difficult; this topic is currently a subject of much attention in our group. Because of the lack of computed interface images, our conclusions about interface structure must be considered tentative at this time.

III. Results and Discussion

Two ZrO_2 intragranular particles, one nearly spherical and one faceted, that satisfied the stringent HREM requirements are shown in Figs. 2(A) and (B), respectively. We discuss the spherical particle first.

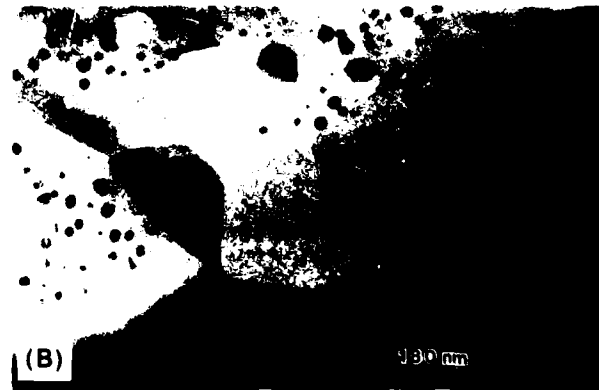


Fig. 1. Typical microstructure of ZrO_2 -toughened Al_2O_3 showing (A) intergranular and (B) intragranular ZrO_2 particles; a few particles are arrowed.

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*Model 200CX, JEOL USA Inc., Peabody, MA.

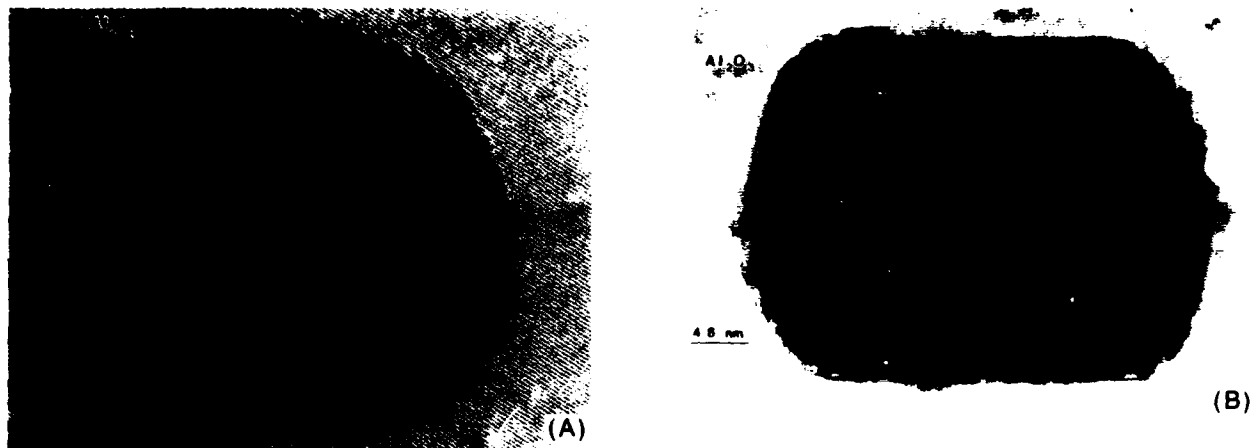


Fig. 2. (A) Intragranular ZrO_2 particle; a single set of (111) planes is visible in ZrO_2 , while Al_2O_3 matrix is exactly oriented to $[3\bar{1}2\bar{1}]$ zone. (B) Faceted ZrO_2 particle in Al_2O_3 matrix, which is oriented exactly to $[10\bar{1}0]$ zone; note Moiré fringes in ZrO_2 particle.

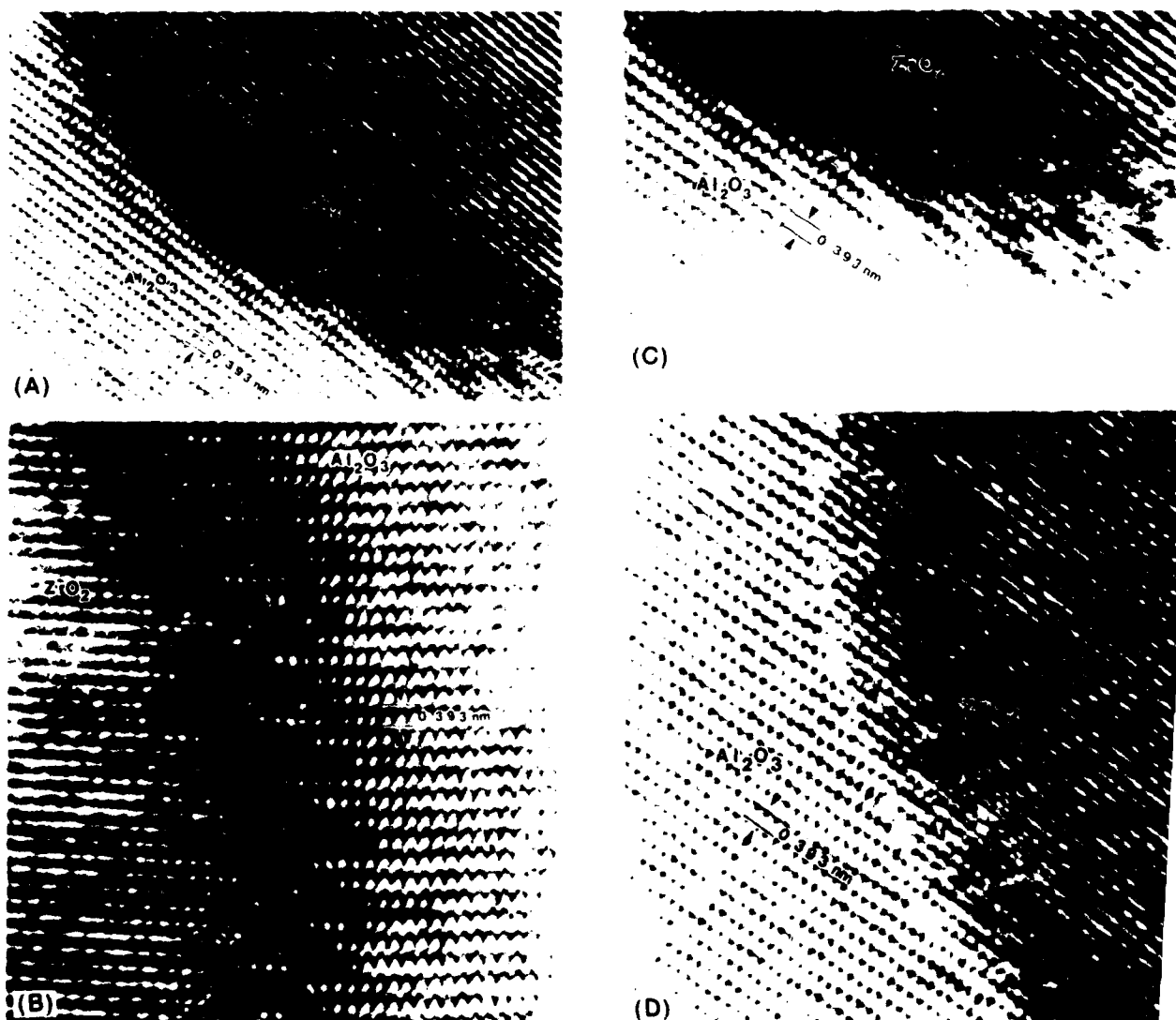


Fig. 3. Higher magnifications of various areas of Fig. 2(A). (A) Lattice mismatch accommodated by a series of ledges. (B) Periodicity changes at interface from every fourth Al_2O_3 plane stopping short of interface (arrowed) to every third one. (C) Lattice mismatch accommodated by misfit dislocation. (D) Interface which appears smooth; sighting along atomic planes reveals misfit dislocations.

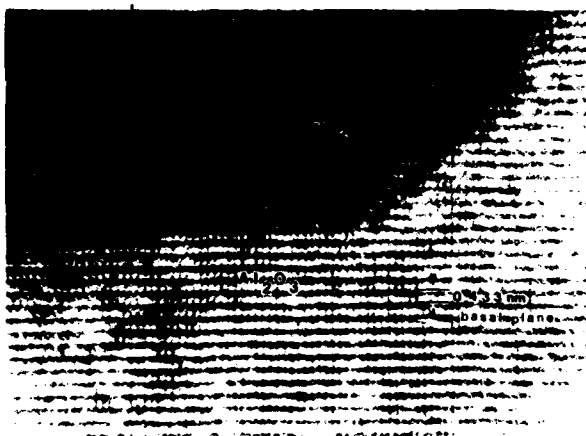


Fig. 4. Higher magnification of Fig. 2(B); Al_2O_3 basal plane (d spacing of 0.433 nm) is parallel to ZrO_2 facet.

As seen in the low-magnification micrograph of Fig. 2(A), the Al_2O_3 matrix is oriented exactly to the $[3\bar{1}21]$ zone axis and $(0\bar{1}11)$ and $(1\bar{1}04)$ planes can be discerned. On the other hand, the ZrO_2 particle, which has t symmetry, has only a single set of (111) planes visible, as the closest zone axis $[110]$ is tilted by a few degrees to the electron beam. The (111) ZrO_2 planes are misoriented by $\approx 5^\circ$ from the $(0\bar{1}11)$ Al_2O_3 planes; furthermore, the d spacings for these two sets of planes differ significantly, 0.295 nm for (111) ZrO_2 and 0.393 nm for $(0\bar{1}11)$ Al_2O_3 . In spite of this marked lattice mismatch, no microcracks or other gross distortions appear in the HREM image of the interface.

Various regions of the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interface are shown at higher magnification in Fig. 3. In the region shown in Fig. 3(A), the lattice mismatch between the two phases appears to be accommodated by a series of ledges, each one atomic plane high; such ledges are commonplace in semicoherent interfaces, as can occur between a precipitate and its matrix, but it is somewhat surprising to see them in the incoherent interface in Fig. 3(A).

Al_2O_3 and $t\text{-ZrO}_2$ have significantly different thermal expansion coefficients (7×10^{-6} to 8×10^{-6} and 9×10^{-6} to $11 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, respectively, depending on orientation), and thermoelastic strains between 0.2% and 0.4% are expected, assuming the system was stress free during sintering and stress relief mechanisms are inoperable below $\approx 1000^\circ\text{C}$. (Thermal strains of this order have been detected by Rühle and Kriven⁸ using HVEM techniques.)

Evidence for such strain is also available in the image of Fig. 3(A). As noted above, the $t\text{-ZrO}_2$ is tilted $\approx 2^\circ$ off its $[110]$ zone axis such that only one set of (111) planes is being imaged. Near the interface, however, one set of (222) planes, with half the spacing of the (111) set, is visible, as well as an apparent structure image. We believe that the lattice bending due to these thermal expansion mismatch strains has tilted the lattice toward the $[110]$ zone axis so that the (222) planes are apparent, but computer simulation is necessary to confirm this interpretation.

Figure 3(B) shows another region of the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interface, which accommodates the lattice mismatch without any apparent use of ledges. This region of the interface exhibits a type of periodic quasi-fringe contrast in the low-magnification image of Fig. 2(A). At higher magnification this periodic contrast (at the top of Fig. 3(B)) is seen to be due to every fourth Al_2O_3 plane (arrowed) extending less far into the interface than its neighboring planes. As

the interface orientation changes, so does the period of the interface structure, so that near the center of Fig. 3(B), it is every third Al_2O_3 plane which stops short of the interface.

This periodic contrast has some similarities to misfit dislocations which can also exist in semicoherent interfaces to accommodate lattice mismatch; this type of mismatch accommodation is certainly in evidence in the region of interface shown in Fig. 3(C), although there are also ledge-like regions in conjunction with the dislocation-like regions in this micrograph. Finally, Fig. 3(D) shows a region of the interface which is apparently smooth and free of ledges; however, viewing along the planes of the images reveals the presence of periodic misfit dislocations. It appears that for this incoherent $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interface, the lattice mismatch is accommodated by a combination of ledges and misfit dislocations, depending on interface orientation.

A higher-magnification image of the faceted interface of Fig. 2(B) is shown in Fig. 4. As noted in this figure, the facet plane is parallel to the basal plane of Al_2O_3 , and this orientation of $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interface must have a lower interfacial energy than any of the interface orientations of Fig. 3. Unfortunately, as will now be discussed, we have been unable so far to specify the ZrO_2 orientation that leads to this low-energy interface.

It is common in HREM to determine the crystal orientation of the material under study by taking an optical diffraction pattern of the image, using a laser diffractometer; and the crystal orientations shown in Fig. 3 were determined in this way. The Moiré fringes visible in Fig. 4 indicate that this is not possible with this image; in spite of the fact that this region of foil appeared to be quite thin (≤ 20 nm), the ZrO_2 particle apparently does not go through the foil and must be overlaid with some of the Al_2O_3 matrix. In fact, this suggests the existence of still another low-energy faceted $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interface, in this case parallel to the $(10\bar{1}0)$ foil plane of Fig. 4. We are presently seeking other examples of faceted $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interfaces in which the ZrO_2 extends through both the top and bottom of the foil so that the interface orientation can be specified exactly.

IV. Conclusion

HREM can be used to image incoherent $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interfaces in ZTA. Both spherical and faceted ZrO_2 particles occur in ZTA; in the spherical particles, the mechanism of lattice accommodation of the two phases is a combination of ledges and misfit dislocations which depends on interface orientation.

The occurrence of faceted particles implies the existence of low-energy $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interfaces. Although we are not yet able to specify the ZrO_2 orientation that leads to the low-energy interfaces, both basal (0001) and prism plane $\{11\bar{2}0\}$ Al_2O_3 orientations appear to be present.

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TEF

MORPHOLOGY OF TETRAGONAL PRECIPITATES

IN PARTIALLY-STABILIZED ZrO_2

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ABSTRACT

Tetragonal(t) ZrO_2 precipitates in Mg-, Ca-, and Y- partially stabilized ZrO_2 (Mg-PSZ, Ca-PSZ, Y-PSZ) have different habit planes and different morphologies. These differences arise because of differences in lattice parameters of precipitate and cubic (c) ZrO_2 matrix in the three systems. The approximate {001} habit plane and oblate spheroid precipitate morphology observed in Mg-PSZ are explained in terms of anisotropic elasticity using the theory of Khachaturyan. The aspect ratio of ~ 5 of these particles is used to calculate a c/t interfacial energy of $\sim 0.15 \text{ Jm}^{-2}$.

The aligned equiaxed precipitates observed in Ca-PSZ and the twinned colonies observed in Y-PSZ can also be explained using this theory and arise from interactions between strain fields during coarsening; the aligned particles in Ca-PSZ may actually represent an intermediate state before the formation of colonies in this system.

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THE DISPLACIVE CUBIC $\rightarrow$ TETRAGONAL TRANSFORMATION
IN ZrO_2 ALLOYS

by

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ABSTRACT

A displacive but non-martensitic cubic (c) to tetragonal (t) phase transformation is ubiquitous in ZrO_2 - Y_2O_3 alloys containing from ~4 to ~13 wt% Y_2O_3 . The microstructures of the transformed phase are characterized by the presence of anti-phase domain boundaries (APB's), similar to those present in ordered alloys, and in fine-grained polycrystals, by {101} twins. The latter are interpreted as mechanical deformation twins, which relieve the strains arising from the (small) tetragonality of the product phase and the (small) molar volume change accompanying transformation.

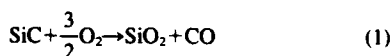
Bubble Formation in Oxide Scales on SiC

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The oxidation of α -SiC single crystals and sintered α - and β -SiC polycrystals has been investigated at elevated temperatures. Bubble formation is commonly observed in oxide scales on polycrystalline SiC but is rarely found on single-crystal scales; bubbles result from the preferential oxidation of C inclusions, which are abundant in SiC polycrystals. The absence of bubbles on single crystals in fact implies that diffusion of the gaseous species formed on oxidation, CO (or possibly SiO), controls the rate of oxidation of SiC.

SILICON carbide, along with other Si-containing nonoxide ceramics, has been studied extensively in recent years because of its potential application as a high-temperature structural material; oxidation resistance is of major importance in these applications. In the temperature range 1200° to 1400°C and at times <100 h,¹⁻⁷ passive oxidation of SiC follows a parabolic rate law. In the early stages of oxidation the oxide scale is primarily amorphous SiO₂, but at longer times devitrification to cristobalite occurs. During passive oxidation, SiC and O₂ react according to



which is believed to occur at the SiC/SiO₂ interface as the result of the inward diffusion of oxygen through the scale.⁷⁻⁹

Bubble formation in the scale, which has been observed by several researchers using scanning electron and optical microscopy, has been attributed to CO evolution at the SiC/SiO₂ interface.^{4,6,10,11} In the present research, bubble formation has been studied in greater detail by examining and comparing oxide scales on both single-crystal and polycrystalline SiC.

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EXPERIMENTAL PROCEDURE AND RESULTS

The materials studied included single-crystal α -SiC¹ and sintered polycrystalline α -² and β -³ SiC. The surfaces of the samples were polished on polishing paper⁴ using, successively, 30-, 15-, 6-, and 1- μ m diamond paste. Cleaning after polishing included a 1-h soak in a 20% HF solution to remove residual SiO₂ from the specimen surface. Specimens were oxidized in alumina boats in air or oxygen.

Comparison of the oxide scales formed on single-crystal and polycrystalline SiC showed that extensive bubble formation occurred only on the SiC polycrystals. Figure 1 is a scanning electron micrograph of the oxide formed on a sintered specimen and shows bubbles ranging in size from 1 to 4 μ m. Bubbles on specimens oxidized for longer times or at higher temperatures were larger, up to 20 μ m in diameter.

We believe that bubble formation arises from inclusions, which are common in both types of polycrystalline SiC we have studied, but rare in SiC single crystals. Figure 2 shows pits on the surface of an α -SiC polycrystal after removal of

the oxide scale, whereas Fig. 3 shows inclusions of quite similar size on a polished but unoxidized sample of this material. The sample of Fig. 3 contained 4.8×10^4 inclusions/mm²; for comparison, a sample oxidized at 1200°C contained 4.8×10^4 pits/mm², whereas samples oxidized at 1300° and 1400°C contained 3.8×10^4 and 4.4×10^4 pits/mm², respectively. The inclusions in Fig. 3 were analyzed using X-ray energy dispersive spectroscopy on the scanning electron microscope, but only Si was detected; we therefore assume they are C inclusions, as reported by other workers (e.g. Ref. 12). We do not think that these inclusions acted as preferred nucleation sites for bubble formation, since the scale on a single crystal, which was deliberately pitted by "polishing" with 30- μ m diamond paste, followed by 6-, 3-, and 1- μ m pastes, was also bubble-free.

Bubbles were not particularly abundant at short oxidation periods, i.e. for scale thicknesses <0.3 μ m. Of course, C inclusions that intersect the free surface, such as those in Fig. 3, oxidized immediately after specimens were inserted into the oxidation furnace and did not give rise to bubbles. The absence of bubbles in thin scales implies that subsurface inclusions which are exposed by the progressive oxidation to the inward-growing scale do not give rise to bubbles until a critical thickness is reached. This observation permits inferences about gaseous diffusion through the scale. The flow rate, F , of a gas (in m³/s at 0°C and 10⁵ Pa (1 atm) pressure per unit area of scale of thickness, x) is given by

$$F = \frac{K(p_2 - p_1)}{x} \quad (2)$$

where K is the permeation constant (in m²/s), p_1 the external pressure, and p_2 the gas pressure at the SiC/scale interface. (K is actually the product of D , the diffusivity, and S , the solubility of the diffusing species in the scale.) The formation of bubbles clearly requires buildup of gas at the interface, and the critical scale thickness at which bubbles become abundant ($\approx 0.3 \mu$ m) must be determined by K for silica glass for the gaseous species formed on oxidation of the inclusions.

Previous investigators^{4,6,7,11} observed

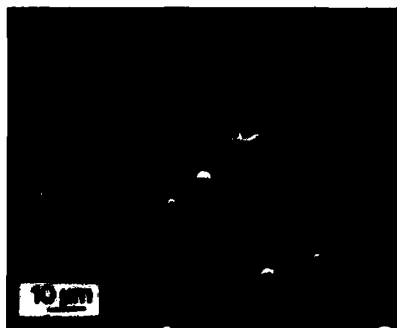


Fig. 1. Bubbles on oxide scale on β -SiC polycrystal (sample oxidized for 12.9 h at 1300°C in 10⁵ Pa dry O₂; scale thickness $\approx 0.5 \mu$ m).



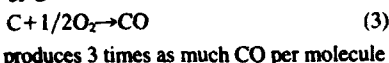
Fig. 2. Surface of α -SiC polycrystal after removal of 1.1- μ m oxide scale by dissolution in HF (sample oxidized for 81.3 h at 1200°C in 10⁵ Pa dry O₂).



Fig. 3. Polished and unoxidized surface of sample of Fig. 2.

bubbles on polycrystalline SiC and thought that they resulted from the evolution of CO at the SiC/SiO₂ interface during oxidation—they apparently believed that CO could not diffuse readily through the scale and would, as a result, be released to the atmosphere in the form of bubbles. The lack of bubbles on single-crystal SiC shows that this argument is not correct and that diffusion of CO (and possibly SiO) has a K value large enough to prevent bubble formation. In fact, bubble formation resulting from oxidation of C inclusions in SiC polycrystals, its absence on SiC single crystals, and the superior oxidation resistance of SiC compared to Si (which also oxidizes by inward diffusion of oxygen) all imply that the rate of oxidation of SiC is controlled by the outward diffusion of CO (or SiO) and not by the inward diffusion of O₂. This behavior must be related to subtle details of the diffusion processes, since both CO and O₂ are linear molecules with similar interatomic distances (C–O, 0.1128 nm; O–O, 0.1208 nm).¹³ Actually, the possibility that the rate-controlling species is SiO rather than CO cannot be excluded at this time (the interatomic distance of SiO is 0.1509 nm¹³).

The CO generated by oxidation of the C inclusions must be produced at a rate sufficiently high that discrete bubbles form. This no doubt occurs because the oxidation of C



of O₂ diffusing through the scale as does the oxidation of SiC (cf. Eqs. (1) and (3)). Bubble formation will occur when the pressure at the substrate/scale interface is sufficient to overcome the ambient pressure and the force exerted by the surface energy of the oxide, i.e.

$$p_2 = p_1 + \frac{2\gamma}{r} \quad (4)$$

where γ is the surface energy of the oxide scale (assumed to be 0.3 J/m² for SiO₂¹⁴) and r the bubble radius. The bubbles observed on polycrystalline SiC range in size from ≈ 1 to ≈ 20 μm , and the corresponding bubble pressures therefore range from ≈ 1.3 to $\approx 7 \times 10^5$ Pa.

CONCLUSIONS

The permeability coefficients for the gaseous oxidation products formed during passive oxidation of SiC, CO, and possibly SiO are sufficiently high that bubble formation is not observed during oxidation of single-crystal SiC; diffusion of one of these gaseous species must be the rate-controlling step during oxidation. Carbon inclusions in polycrystalline SiC, however, give rise to quantities of CO large enough that bubbles can form. The smallest such bubbles are ≈ 1 μm in diameter and contain gas at $\approx 7 \times 10^5$ Pa pressure.

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REVIEW — Graphical Displays of the Thermodynamics of High-Temperature Gas-Solid Reactions and Their Application to Oxidation of Metals and Evaporation of Oxides

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The construction and utility of volatility diagrams — isothermal plots showing the partial pressures of two gaseous species in equilibrium with the several condensed phases possible in a system — are demonstrated for simple oxides with reference to the Mg-O, Al-O, and Si-O systems and compared with Ellingham-type representations of these same data. Both types of diagrams are useful for providing a condensed format for a great deal of thermodynamic information. Their use is illustrated by analyzing the oxidation of Mg, Al, and Si and the volatilization of MgO, Al₂O₃, and SiO₂ in both neutral and reducing gases.

I. Introduction

THERMODYNAMIC data on many oxides, nitrides, carbides, and other high-temperature ceramics are readily available. Extensive compilations of such data are found in the Appendix of Kubaschewski's Metallurgical Thermochemistry,¹ the Metals Handbook,² the JANAF Tables,³ and the Thermodynamical Properties of Inorganic Substances.⁴ This information is essential for understanding high-temperature processing and high-temperature service of these ceramics, as well as the native metals from which they are made, but the data can be overwhelming. In the V-O system for example, the JANAF Tables report on the four states of vanadium metal and 10 different forms of oxides, and it is virtually impossible to use these data in practice without further calculation. Thus, when one is investigating the thermodynamics of a particular system, the question often is not whether the relevant data are available, but how to utilize the data.

Lengthy calculations can always be done on the dozen or more reactions that are possible in each system. This is not only inconvenient but often unsatisfactory, because in a complex system where many compounds exist, it is pertinent to have an overview of the relations between them, and formulae and calculations alone are generally unsatisfactory for this purpose. The best approach is often by graphical representation. The Ellingham or Richardson diagram is one example of the value of graphical representation. One single Ellingham diagram contains more information on metals and their oxides than pages of tabulated thermodynamic free

energies. In fact, this diagram contains full data on the oxidation/reduction behavior of solid oxides in all types of environments and at all temperatures and has proved to be indispensable to large numbers of users. Pourbaix diagrams are of similar usefulness to corrosion scientists. As will be discussed below it is possible to extend the utility of Ellingham diagrams to include data on volatilization of oxides.

High-temperature materials engineers are often confronted with gas-solid reactions of various types — oxidation, reduction, evaporation, etc. For example, gas-solid reactions are currently of considerable interest in nitride ceramics, in that these materials are much less stable than the traditional oxide ceramics, and N₂ evolution may be unavoidable during high-temperature processing or service. For more familiar ceramics, many oxides are sintered in H₂ or CO/CO₂ environments so that reactions involving volatile sub-oxides are important. The loss of dopants at high temperatures and the contamination of ceramic wares by impurities are further examples.

The standard Ellingham-type diagram can be helpful in some cases, but alternate representations are also useful. In particular, we have found that "volatility" diagrams are appropriate for dealing with high-temperature ceramics when more than one gaseous species is involved. Volatility diagrams are isothermal plots showing the partial pressures of two gaseous species in equilibrium with the various condensed phases possible in the system. They permit ready understanding of the high-temperature chemistry and allow appropriate processing and service conditions to be specified. Wagner⁵ used them in his study of the volatilization of SiO and SiO₂ and Blegan.⁶ Colguhoun, Wild, Grievson, and Jack,⁷ Gulbransen and Jansson,^{8,9} and Singhal¹⁰ used them to define stable phase fields in the Si-O-N and Si-O-C systems. The intent of this paper is to promote the use of this type of construction in ceramic applications and also to explore new ways of simplifying and clarifying the existing construction method. Three new construction features to be introduced are the *isomolar line*, the *isobaric lines*, and the *constant H₂O/H₂ (or CO₂/CO) lines*. This paper is devoted to three simple oxides — MgO, Al₂O₃, and SiO₂; further papers will deal with the Si-O-N system and with ternary oxides, transition-metal oxides, and refractory metal oxides.

The new construction features and additional relevant data, in particular, the partial pressure of dominant metal vapor species, can be plotted on conventional Ellingham-type diagrams, and this graphical representation will be contrasted and compared with volatility diagrams. We also note that manipulation of the thermodynamic information we are treating can be handled by some of the

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Table I. Reactions in Mg-O, Al-O, and Si-O Systems Needed for Plotting Volatility Diagrams

Equation No.	Reaction	log K (1900 K)
1*	$2\text{MgO}(c) \rightarrow 2\text{Mg}(l) + \text{O}_2$	-21.32
2*	$\text{Mg}(l) \rightarrow \text{Mg}(g)$	1.28
3	$2\text{MgO}(c) \rightarrow 2\text{Mg}(g) + \text{O}_2$	-18.75
4*	$2\text{Mg}(l) + \text{O}_2 \rightarrow 2\text{MgO}(g)$	7.12
5	$\text{MgO}(c) \rightarrow \text{MgO}(g)$	-7.10
6	$\text{Al}_2\text{O}_3(c) \rightarrow 2\text{Al}(l) + \frac{3}{2}\text{O}_2$	-29.36
7	$\text{Al}(l) \rightarrow \text{Al}(g)$	-2.55
8	$\text{Al}_2\text{O}_3(c) \rightarrow 2\text{Al}(g) + \frac{3}{2}\text{O}_2$	-34.46
9	$4\text{Al}(l) + \text{O}_2 \rightarrow 2\text{Al}_2\text{O}(g)$	14.44
10	$\text{Al}_2\text{O}_3(c) \rightarrow \text{Al}_2\text{O}(g) + \text{O}_2$	-22.14
11	$\text{Al}_2\text{O}_3(c) + 4\text{Al}(l) \rightarrow 3\text{Al}_2\text{O}(g)$	-7.69
12	$2\text{Al}(l) + \text{O}_2 \rightarrow 2\text{AlO}(g)$	2.90
13	$2\text{Al}_2\text{O}_3(c) \rightarrow 4\text{AlO}(g) + \text{O}_2$	-52.91
14	$\text{Al}_2\text{O}_3(c) + \text{Al}(l) \rightarrow 3\text{AlO}(g)$	-25.00
15	$\text{Al}(l) + \text{O}_2 \rightarrow \text{AlO}_2(g)$	5.16
16	$2\text{Al}_2\text{O}_3(c) + \text{O}_2 \rightarrow 4\text{AlO}_2(g)$	-38.09
17	$2\text{Al}_2\text{O}_3(c) \rightarrow 3\text{AlO}_2(g) + \text{Al}(l)$	-43.25
18	$\text{SiO}_2(l) \rightarrow \text{Si}(l) + \text{O}_2$	-15.68
19	$\text{Si}(l) \rightarrow \text{Si}(g)$	-4.92
20	$\text{SiO}_2(l) \rightarrow \text{Si}(g) + \text{O}_2$	-20.60
21	$2\text{Si}(l) + \text{O}_2 \rightarrow 2\text{SiO}(g)$	13.86
22	$2\text{SiO}_2(l) \rightarrow 2\text{SiO}(g) + \text{O}_2$	-17.50
23	$\text{SiO}_2(l) + \text{Si}(l) \rightarrow 2\text{SiO}(g)$	-1.82
24	$\text{Si}(l) + \text{O}_2 \rightarrow \text{SiO}_2(g)$	8.29
25	$\text{SiO}_2(l) \rightarrow \text{SiO}_2(g)$	-7.30

*Note that 1900 K is above the boiling point of Mg.

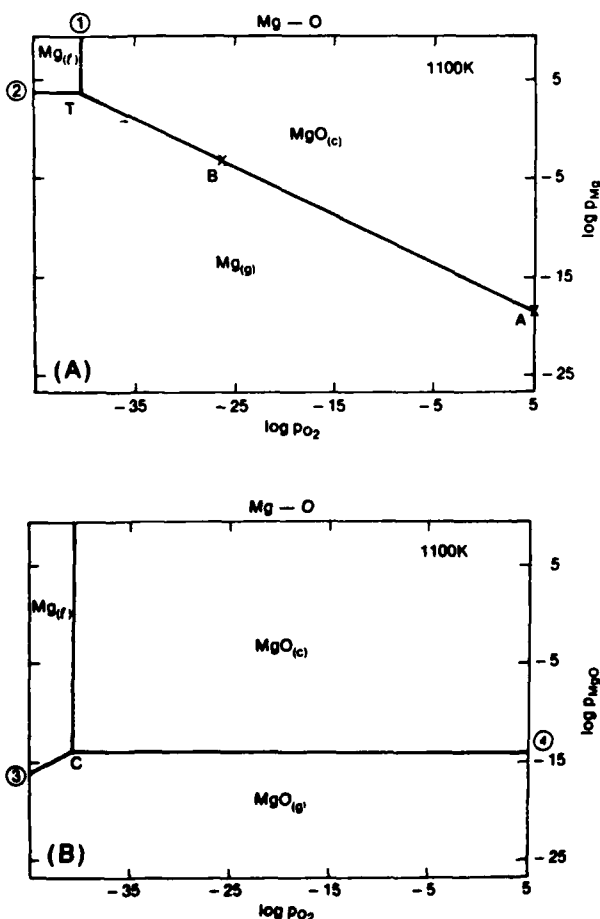


Fig. 1. (A) Volatility diagram for the Mg-O system at 1100 K for case when only Mg(g) is considered. In this and all other figures, pressures are given in Pa (1 atm = 1.013 × 10⁵ Pa). (B) Volatility diagram as per (A) but with MgO(g) considered.

computer programs now extant, e.g., SOLGASMIX.¹¹ However, graphical techniques have some advantages and our intention in this paper is to emphasize the ease of handling these data graphically using only the JANAF Tables. Before beginning our discussion, we note that, whether a computer program or a graphical display is used, there is always the danger of missing important species. *Caveat emptor!*

II. Data Base—Gaseous and Nongaseous Phases

Three common oxide systems will be dealt with here—Mg-O, Al-O, and Si-O. The thermodynamic data appropriate for these systems are tabulated in the JANAF Tables. In the Mg-O system, they are Mg (reference state), Mg(c),^{*} Mg(l), Mg(g), Mg⁺(g), MgO(c), MgO(l), and MgO(g); in the Al-O system, they are Al (reference state), Al(c), Al(l), Al(g), Al⁺(g), AlO(g), AlO⁺(g), AlO₂(g), AlO₂⁺(g), Al₂O(g), Al₂O₂(g), α-Al₂O₃(c), γ-Al₂O₃(c), and Al₂O₃(l); and in the Si-O system, they are Si (reference state), Si(c), Si(l), Si(g), Si₂(g), Si₂⁺(g), SiO(g), quartz SiO₂(c), cristobalite SiO₂(c), SiO₂(l), and SiO₂(g). For the temperature range of interest, all three metals and SiO₂ are in the liquid state, and one can reduce the condensed phases to Mg(l), Al(l), Si(l), MgO(c), α-Al₂O₃(c), and SiO₂(l). Furthermore one can reduce the number of gaseous species to be considered, as many of them have very low vapor pressures. Thus, one can eliminate all the charged radicals as well as dimeric and trimeric compounds for their influences are exerted by their monomeric counterparts. The gaseous phases that need to be considered are Mg(g), MgO(g), Al(g), AlO(g), Al₂O(g), Si(g), SiO(g), and SiO₂(g).

Even with this reduced number of species in each system, a large number of reactions have to be considered. Volatility diagrams are useful when reactions involving at least one condensed species and no more than one volatile species (except oxygen) are considered: reactions involving only gases are neglected. Table I is a tabulation of the 25 various reactions in these systems needed for the diagrams; for convenience, log K values at 1900 K are also given. All can be represented in standard thermodynamic form, i.e.

$$\Delta G = RT \ln K \quad (K = \prod p_i^{a_i} / \prod p_j^{a_j})$$

where P stands for product, R for Reactant, a for activity, and n for integer.

III. Construction and Utilization of Volatility Diagrams

(1) The Mg-O System

(A) Construction: Volatility diagrams for oxides are always constructed with log p_{O2} as the abscissa and log p_M or log p_{MO} as the ordinate. At 1100 K, equilibrium constants for Eqs. (1) to (5) in Table I can be either taken directly from the JANAF Tables or calculated from data given in these tables. Equation (1), which describes the oxidation of Mg to MgO, has an equilibrium constant of 10^{-45.6} and, as it is independent of p_{Mg}, is shown in Fig. 1(A) as vertical line 1-T that separates the Mg(l) and MgO(c) phase fields. Similarly Eq. (2), the evaporation of liquid Mg, is independent of p_{O2} and is shown as the horizontal line 2-T. Equation (3) describes the evaporation of MgO to form Mg(g) and O₂; as it involves both p_{Mg} and p_{O2}, it is plotted in Fig. 1(A) as the sloping line T-A with a gradient of -1/2. The intersection of these three lines, T, indicates the minimum p_{O2} needed to prevent reduction of MgO(c) and the maximum p_{Mg} possible in the system. At 1100 K the minimum log p_{O2} is -40.6 (Pa) and the maximum log p_{Mg} is 3.8 (Pa). The significance of the sloping line is that p_{Mg} decreases with increasing p_{O2}; thus, in an ambient pressure of 10⁵ Pa (1 atm) of oxygen (point A), volatilization of MgO is unlikely because of the very low equilibrium partial pressure of Mg, 10⁻¹⁴ Pa.

Normally, weight loss due to evaporation in a high-temperature experiment is important only if the vapor pressure of the evapo-

*The suffix c stands for crystal, l for liquid, and g for gas.

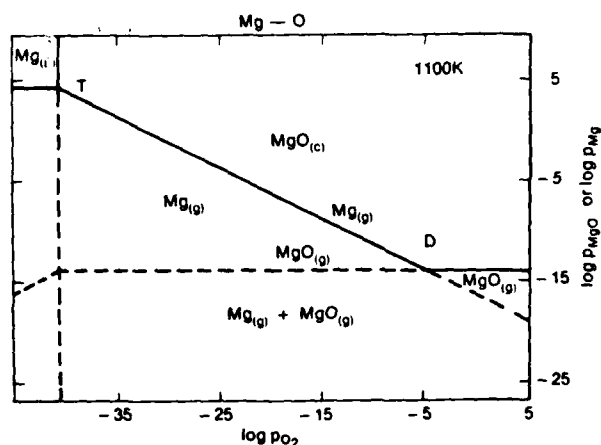


Fig. 2. Volatility diagram for the Mg-O system at 1100 K.

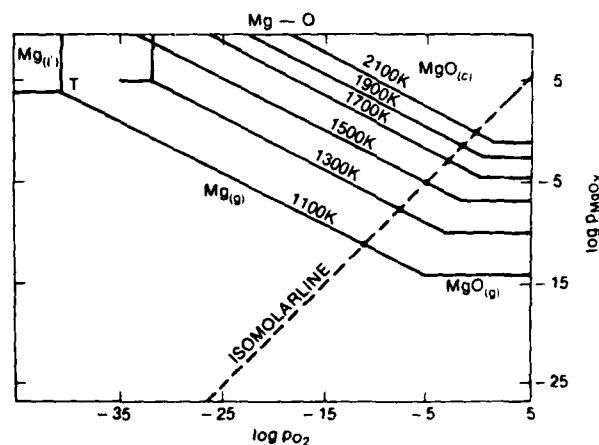


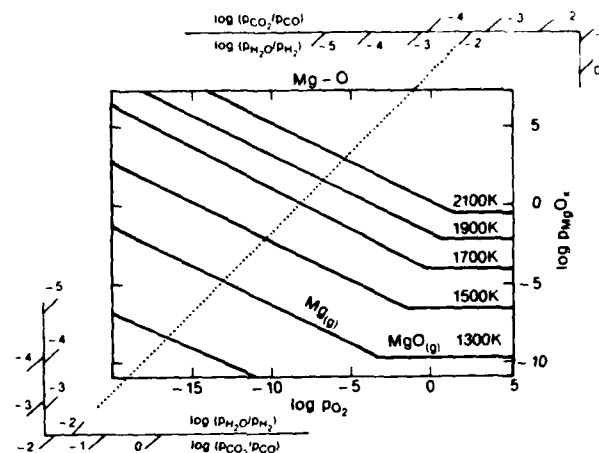
Fig. 3. Master volatility diagram for the Mg-O system from 1100 to 2100 K; isomolar line is defined in text.

rating species is higher than 10^{-3} Pa. Point B in Fig. 1(A) corresponds to this arbitrary condition, and a decrease in p_{O_2} beyond this point will result in significant weight loss.

A similar diagram can be constructed for MgO vapor by utilizing Eqs. (1), (4), and (5), as shown in Fig. 1(B) where $\log p_{MgO}$ is plotted on the ordinate instead of $\log p_{Mg}$. Equation (4) is an alternative oxidation reaction and depends on both p_{MgO} and p_{O_2} ; it is shown as the sloping line 3-C with a gradient of $+1/2$; Eq. (5), which describes the evaporation of MgO vapor over solid MgO, is independent of p_{O_2} and constant at 10^{-14} Pa (line C-4). The next step in the construction is to combine Figs. 1(A) and (B) into one diagram and to discard unimportant lines, as shown in Fig. 2. In the approximation we use, only the solid lines are important in this figure because the dashed lines represent species with smaller vapor pressures; we henceforth refer to these solid lines as maximum equilibrium pressure lines for obvious reasons. The intersection D, which we shall call the major vapor transition point, delineates the field where the major vapor species changes; to its right, it is MgO vapor and to its left, it is Mg vapor. It is easy to construct a number of such simple isothermal volatility diagrams which can be combined into a master diagram covering the temperature range of interest. Figure 3 is such a diagram for the Mg-O system and contains all the vital thermodynamic data on volatilization reactions between 1100 and 2100 K.

(B) *Evaporation of MgO in Vacuum and Inert Gases and the Use of the Isomolar Line:* When $MgO(g)$ is the major species, i.e., at values of p_{O_2} to the right of point D, the vapor pressure of MgO in a closed system will be constant; the evaporation of MgO to $MgO(g)$ (reaction 5) does not depend on p_{O_2} . However, if the p_{O_2} is reduced, the principal vapor species will change to $Mg(g)$ and the vapor pressure will increase following the line T-D in Fig. 2.

However, there is one other important fact of such an experiment that must be considered, the *mass balance criterion*. When 1 mol of $MgO(c)$ undergoes evaporation via Eq. (3), 1 mol of $Mg(g)$ and $1/2$ mol of O_2 are produced. Assuming ideal gas behavior and equal diffusivity of all gaseous species, the mass balance criterion stipulates that $p_{Mg} = 2p_{O_2}$ or $\log p_{Mg} = \log p_{O_2} + \log 2$. This relation is shown in Fig. 3 as the dashed line. We henceforth refer to it as an *isomolar line* and its gradient is always 1. At the point of intersection of the isomolar line with a maximum equilibrium pressure line, both the mass balance criterion and the thermochemistry are satisfied. The predicted equilibrium vapor pressures above crystalline MgO at 1900 K, for example, are $p_{Mg} = 0.1$ Pa and $p_{O_2} = 0.05$ Pa. Other isomolar points are also indicated by filled circles. Conceptually, when an MgO crystal dissociates into Mg vapor and O_2 , the respective partial pressures are controlled in a fixed ratio by the equilibrium constant. The isomolar line defines the maximum p_{Mg} over $MgO(c)$ in a

Fig. 4. Volatility diagram for Mg-O system with H_2O/H_2 and CO_2/CO nomographs included.

nonreactive environment and sets a limit to the valid portion of the volatility diagram; only conditions to the right of this line are attainable.

(C) *Evaporation of MgO in Reducing Gases and the Use of the Isobaric Lines:* It is well-known that reducing gases can cause severe weight loss of MgO at high temperatures; volatility diagrams can predict the vapor pressures of various gaseous species involved in the high-temperature reactions. In fact the isomolar point at any particular temperature is no longer applicable as the Mg vapor pressure is much higher with a reactive gas. For example, in the case of hydrogen with an H_2O to H_2 ratio of 10^{-2} , the JANAF Tables predict that $\log p_{O_2}$ at 1900 K will be -6.7 (Pa), and according to Fig. 3 the corresponding $\log p_{Mg}$ is 1.5 (Pa). The calculation can be repeated for other temperatures, and the argument presented in the Appendix shows that for a specific H_2O to H_2 ratio, the equilibrium p_{O_2} and p_{Mg} for various temperatures fall on a single straight line; the dotted line in Fig. 4 is constructed for an H_2O to H_2 ratio of 10^{-2} . As can be seen in this figure, a nomographic-type construction is possible: a straight edge can be placed on any desired H_2O to H_2 (or CO_2 to CO) ratio so that the equilibrium p_{O_2} above MgO can be determined at any temperature. The effect of moisture in the ambient is easily predicted from Fig. 4. At 1900 K, for example, if the H_2O to H_2 ratio changes from 10^{-2} to 10^{-1} , $\log p_{Mg}$ increases from 1.5 to 2.5 (Pa) and the

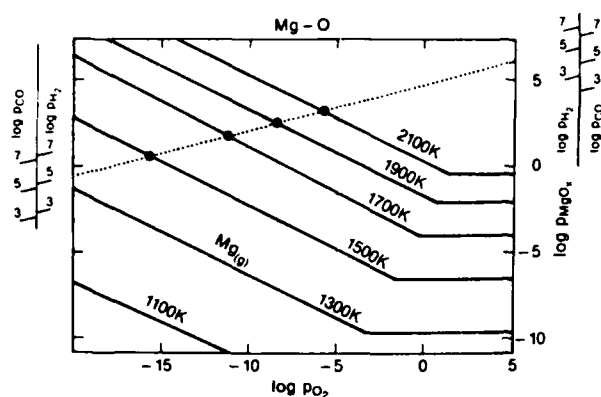


Fig. 5. Volatility diagram for the Mg-O system with isobaric line (dotted) included.

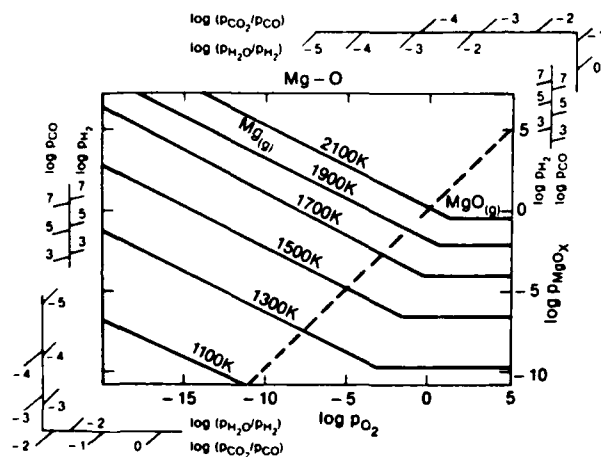
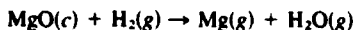


Fig. 6. Complete volatility diagram for the Mg-O system.

evaporation rate should likewise increase.

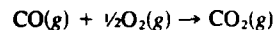
At first sight, p_{Mg} can increase up to the point T where $Mg(l)$ and $MgO(c)$ are in equilibrium with $MgO(g)$. However, such a direct interpretation of the volatility diagram must be modified to take cognizance of the mass balance. The reaction between MgO and H_2 is



and using the same assumption we made earlier, for every mole of Mg vapor produced, 1 mol of H_2O vapor is also produced. As in the case of the nonreactive environment, the volatilization reaction creates its own environment. One can calculate the equilibrium p_{Mg} and p_{H_2O} for this reaction by making the simple assumption that $p_{Mg} = p_{H_2O}$. At 1900 K in 10^5 Pa of dry H_2 , for example, the vapor pressure of H_2O or Mg is $10^{2.2}$ Pa. We refer to this point as the *isobaric point*; it is shown in Fig. 5 as a filled circle and indicates the maximum Mg vapor pressure allowed for any p_{H_2} at one particular temperature.

The Appendix also shows that the isobaric points at constant p_{H_2} and various temperatures should fall on a straight line, the *isobaric line*, as can be seen in Fig. 5. In fact, as shown in this figure, the best way of representation is to include additional scales on the ordinates, i.e., to create another nomograph; the position of an isobaric point can be determined by placing a straightedge across the diagram for the particular H_2 pressure of interest. The effect of CO can be determined on a similar basis by using the

corresponding CO scales, which are derived from the reaction



Thus, the final volatility diagram for MgO is shown in Fig. 6. The range of validity of the diagram for nonreactive ambients is to the right of the isomolar line. For reducing environments, H_2/H_2O or CO/CO_2 , the CO or H_2 nomograph is used for any particular pressure to define the validity of the volatility diagram—for any temperature, to the right of the intersection of a straight line connecting the CO or H_2 scales and the maximum equilibrium pressure line. For a given H_2O to H_2 or CO_2 to CO ratio, the appropriate scales are used to determine the equilibrium pressure on the maximum equilibrium pressure line. It is clear that all available thermodynamic information has been included in Fig. 6 in a compact and useful form.

Two additional points concerning the nomographic construction should be noted. Firstly, there is the question of volatile hydroxides and in this case $Mg(OH)_2(g)$ is the most volatile (OH)-containing species. However, our calculations based on values tabulated in the JANAF Tables suggest that it is a minor species under normal pressures and H_2O to H_2 ratios of less than 10^{-2} . Therefore, in Fig. 6, the highest $\log H_2O/H_2$ value on the scale is -2 . Actually, this is not a particularly severe limitation. A p_{H_2O} to p_H ratio of 10^{-2} corresponds to a dew point of $+7^\circ C$, and $Mg(OH)_2$ formation therefore requires injection of steam into the system. Under conditions where $Mg(OH)_2$ does form, a completely different type of volatility diagram is required. Normally hydroxides are important only at high p_{H_2O} and low temperature.

With regard to the CO_2/CO scale, the limitation here is sooting of carbon, and the condition for that in the present temperature range is a CO_2 to CO ratio of about 10^{-4} . Again this is reflected in Fig. 6, where the minimum value on the $\log CO_2/CO$ scale is -4 .

(D) *Use of Ellingham-Type Diagrams:* A useful alternative to the volatility diagram is to plot the data on the standard Ellingham-type diagram.¹ Clearly, either form will suffice since volatility diagrams are plots of equilibrium p_{O_2} vs equilibrium p_{MO} , for various temperatures, while the Ellingham-type diagrams have equilibrium p_{O_2} and T as the abscissa and ordinate, respectively, for various p_{MO} values. Such a diagram for the $Mg-O$ system is constructed in Fig. 7, where in accord with standard practice, the temperature is given in $^\circ C$ rather than K and the abscissa is actually $RT \ln p_{O_2}$. The nomographic constructions for p_{O_2} , H_2O to H_2 ratio, and CO_2 to CO ratio scales are well-known and will not be discussed. The data usually included in the Ellingham diagram define the oxidation of Mg to solid MgO , which are plotted as lines 1 and 3. The former represents the oxidation of solid or liquid Mg and the latter the oxidation of 10^5 Pa of Mg vapor; M is the melting point of Mg . Solid MgO is stable only above these lines, and the intersection of the two lines, B , is the boiling point of Mg . The vapor pressure of Mg over condensed Mg (Eq. (2)) at various temperatures is shown as a series of vertical lines (below line 1); lines corresponding to $>10^5$ Pa Mg pressure are not drawn. The vapor pressure of Mg over solid MgO plots as a series of sloping lines which are appropriately labeled in Fig. 7. Finally, the vaporization of MgO via Eq. (5) is shown as a series of vertical lines at the top of the diagram, line 4 corresponding to $p_{Mg} = 10$ Pa. Line 5 is the locus of the points marked D on Fig. 2 and denotes, for a given p_{Mg} , the p_{O_2}/T conditions where the major vapor species changes from Mg vapor (below the line) to MgO vapor (above the line).

At any p_{O_2} , the relevant p_{Mg} or p_{MgO} pressure can be obtained by noting which isobar passes through the intersection of the line between that p_{O_2} and point O on the left-hand vernier of the nomograph at a given T . (For example, p_{Mg} is 10 Pa at $1800^\circ C$ at $p_{O_2} = 10^{-2.5}$ Pa.) In any H_2O/H_2 (or CO_2/CO) mixture, a straightedge is placed between H (or C) on the vernier and the relevant gas mixture and likewise gives the p_{MgO} pressure as a function of temperature.

As in the volatility diagram, the valid regions of the Ellingham diagram can be determined using the mass balance criterion. In

¹This was pointed out by a reviewer of an earlier version of this paper.

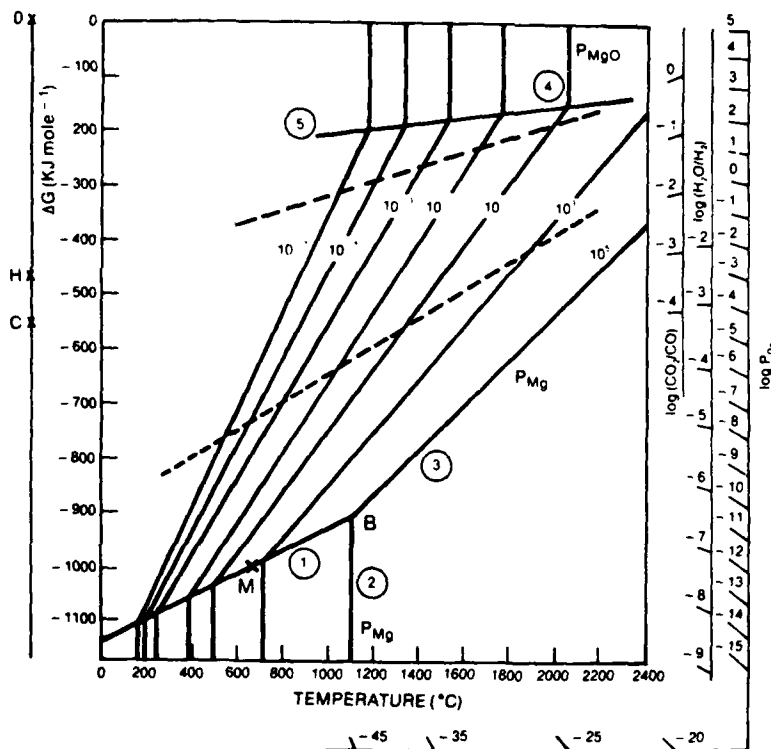


Fig. 7. Ellingham-type diagram for the Mg-O system.

vacuum or inert gases, p_{Mg} has to be equal to or less than $2p_{O_2}$ and such a condition is shown by the long-dashed isomolar line; the diagram is only valid above this line. In practice, for a given temperature, say 2000°C, the maximum Mg vapor pressure is found by noting which isobar intersects the point where the isomolar line crosses 2000°C; in addition, placing a straightedge through this point and point O on the vernier yields the minimum p_{O_2} as $10^{0.5}$ Pa.

The isobaric lines are constructed in a similar way, by noting that the limiting condition is $p_{Mg} < p_{H_2O}$. At 10^5 Pa H_2 , for example, the isobaric line is constructed (the short-dashed line in Fig. 7) by noting the temperature at which a straight line between the H vernier and a series of H_2O to H_2 ratios intersects the appropriate p_{Mg} isobar; the isobaric point for $p_{H_2O} = 10^1$ Pa is at 1900°C; for 10 Pa it is 1350°C; for 10^{-1} Pa it is 1050°C, etc. The diagram is only valid above the short-dashed line in such an atmosphere.

(2) The Al-O System

(A) Construction: The JANAF Tables list 15 metallic and oxide phases in this system, of which six are relevant to the present discussion—Al(l), α -Al₂O₃(c), Al(g), Al₂O(g), AlO(g), and AlO₂(g). The 1900 K isothermal section is chosen to demonstrate the construction. The vertical line in Fig. 8 represents the oxidation of Al(l) to α -Al₂O₃(c) (Eq. (6) in Table I) and the logarithmic value of the equilibrium constant is -29.4, from which $\log p_{O_2}$ is deduced to be -14.6 (Pa). The four lines to the left of this vertical line represent the vapor pressures of the four vapor species over metallic aluminum, namely Al(g), Al₂O(g), AlO(g), and AlO₂(g), corresponding to the chemical reactions described by Eqs. (7), (9), (12), and (15). The gradients of these lines can be determined from the ratio between oxygen and the volatile species, such that for Eq. (7) it is 0, for Eq. (9) it is $\frac{1}{2}$, for Eq. (12) it is $\frac{1}{2}$, and for Eq. (15) it is 1. To the right of the vertical line, the four lines represent vapor pressures of the same four species over α -Al₂O₃ and the corresponding reactions are described by Eqs. (8), (10), (13), and (16), for which the corresponding gradients are $-\frac{3}{4}$, -1, $-\frac{1}{4}$, and $\frac{1}{4}$. For each volatile species, the lines intersect on the vertical line to form a "triple" point where Al(l) and Al₂O₃(c) are in equilibrium with a gaseous species;

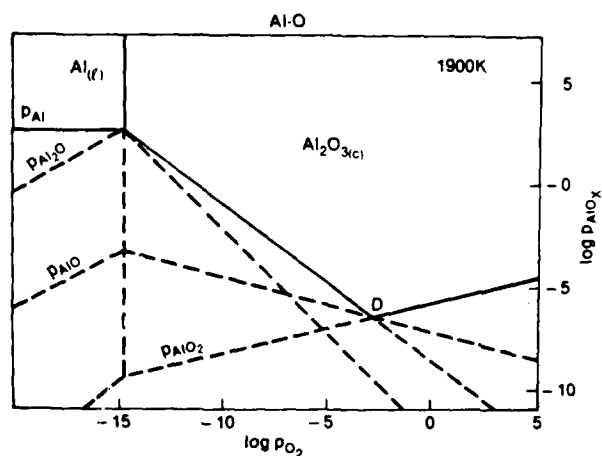


Fig. 8. Volatility diagram for the Al-O system at 1900 K.

in cases where the gases are more reduced than Al₂O₃, i.e., Al(g), Al₂O(g), and AlO(g), the triple points indicate the maximum possible vapor pressure of these gaseous species. These can be calculated according to Eqs. (7), (11), and (14), and their logarithmic values are 3.4, 3.4, and -3.3 (Pa). For AlO₂(g), which is more oxidized than Al₂O₃, the triple point does not represent the maximum vapor pressure, as it continues to increase in the oxide phase field (the reaction at this triple point is Eq. (17)). For practical purposes, the important lines in this diagram are the solid lines which show the vapor pressures of the most volatile species. It is apparent that under the most reducing conditions, the major vapor species is Al vapor but under more oxidizing conditions, i.e., to the right of D in Fig. 8, it is AlO₂(g). By use of this simplified construction, the 1700 and 2100 K sections are added in Fig. 9.

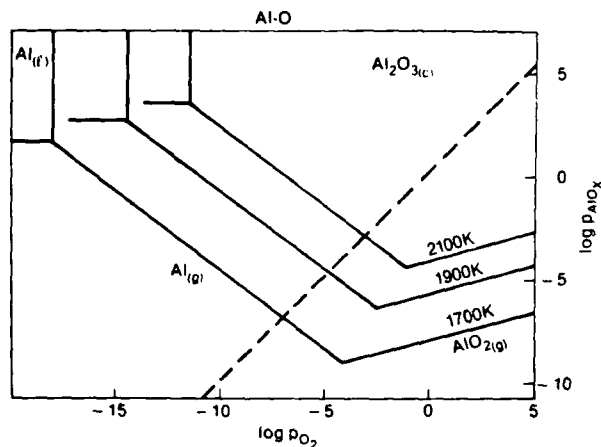


Fig. 9. Master volatility diagram for the Al-O system from 1700 to 2100 K.

(B) *Vacuum and Inert Gases:* The next step in the construction is to put in the isomolar points by considering the decomposition reaction



and the corresponding isomolar lines ($\log p_{\text{O}_2} = \log p_{\text{Al}} + \log \frac{3}{4}$ — the dashed line in Fig. 9). From the intersections one can predict the maximum vapor pressures of Al(g) and oxygen over $\alpha\text{-Al}_2\text{O}_3$ in a nonreactive system; for example at 1900 K, $\log p_{\text{Al}} = -4.8$ (Pa) and $\log p_{\text{O}_2} = -5.0$ (Pa). We stress again that the significance of the isomolar line is to define the valid portion of the diagram such that only the area to its right is accessible in nonreactive ambients.

(C) *H₂ and CO:* The nomographic construction of the iso-

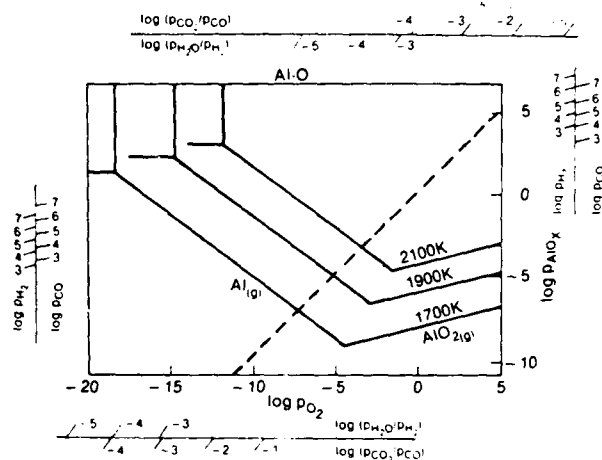
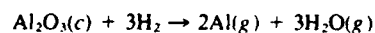


Fig. 10. Complete volatility diagram for the Al-O system.

baric lines in Fig. 10 is similar to that in the Mg-O system except that isobaric points are calculated according to the mass balance criterion $p_{\text{H}_2\text{O}} = \frac{1}{2}p_{\text{Al}}$ which follows from the reaction



The intersections with the maximum equilibrium pressure lines indicate the maximum vapor pressures at various temperatures; for example, at 10^5 Pa of dry hydrogen at 1900 K, $\log p_{\text{Al}}$ cannot exceed 0.3 (Pa). As with the Mg-O diagram, the CO scale is also included in the diagram. The constant $\text{H}_2\text{O}/\text{H}_2$ and CO_2/CO lines are likewise included and p_{Al} under various ratios of these gases can be readily determined. The range of these scales are again limited by reasons explained previously; for the $\text{H}_2\text{O}/\text{H}_2$ scale, the upper limit is 10^{-3} (dew point of -20°C) and for the CO_2/CO scale

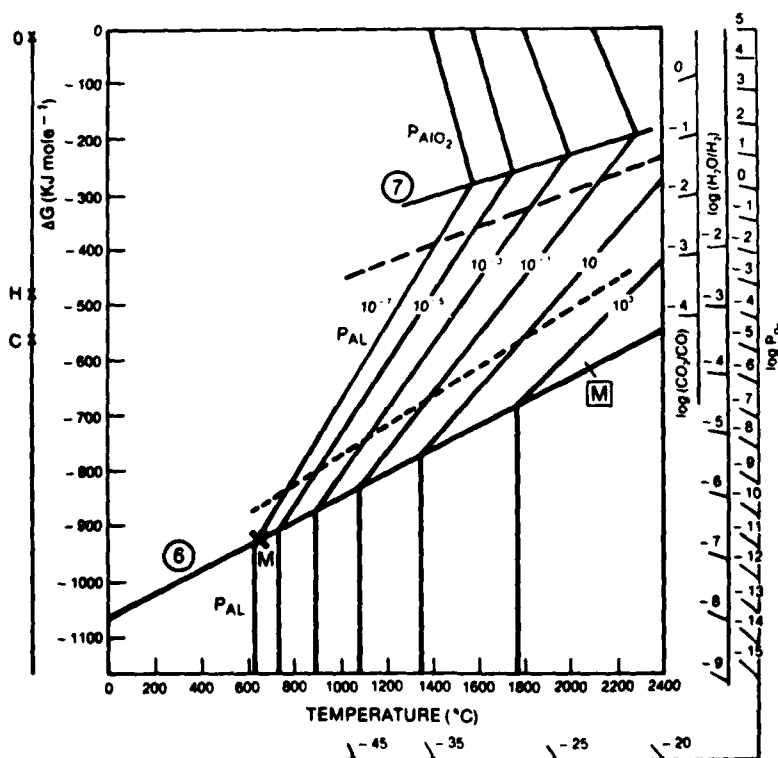


Fig. 11. Ellingham-type diagram for the Al-O system.

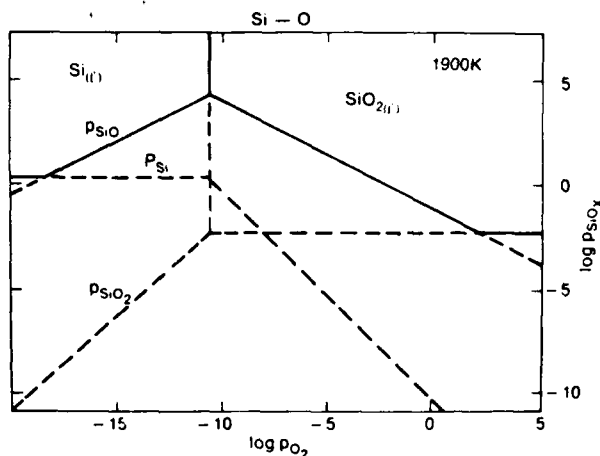


Fig. 12. Volatility diagram for the Si-O system at 1900 K.

the lower limit is 10^{-4} . It should again be cautioned that the region of validity for any H_2 or CO pressure is to the right of the corresponding isobaric line.

(D) *Ellingham Diagram*: The Ellingham-type compilation of the thermodynamic data for the Al-O system is shown in Fig. 11 and differs from Fig. 7 mainly in the vapor species found at high p_{O_2} 's; the constant p_{AlO_2} lines slope to the left and the transition from p_{Al} to p_{AlO_2} as the principal vapor species is shown as the line marked 7. Line 6 delineates the transition from Al (solid or liquid) to Al_2O_3 (solid or liquid) as the condensed phase, with M and $\bar{M}$ being the conventional symbols for the melting points of the metal and oxide, respectively.

(3) The Si-O System

(A) *Construction of the Diagram*: The important phases in this system are $Si(l)$, $SiO_2(l)$, $Si(g)$, $SiO(g)$, and $SiO_2(g)$. By use of values listed in the JANAF Tables, the 1900 K volatility diagram is shown in Fig. 12. The vertical line represents the oxidation of Si to SiO_2 (Eq. (18)), the three lines to its left describe the vapor pressures of $Si(g)$, $SiO(g)$, and $SiO_2(g)$ over $Si(l)$, according to Eqs. (19), (21), and (24), respectively, and the three lines to its right describe the vapor pressures over $SiO_2(l)$, according to Eqs. (20), (22), and (25). The most volatile species is $SiO(g)$, whereas $Si(g)$ and $SiO_2(g)$ are relatively unimportant except at low and high p_{O_2} , respectively, where they become the major vapor species.

The rest of the construction is identical with the previous two systems and only a brief description will be given here. Firstly, in Fig. 13, the 1700 and 2100 K isothermal sections are included and the isomolar line, which satisfies the mass balance conditions of Eq. (22), is also drawn. As before, this line delineates the valid region of the diagram when the system is under a non-reactive environment. In hydrogen, Fig. 14 is drawn to accommodate the mass balance corresponding to the SiO_2 - H_2 reactions: $SiO_2(l) + H_2 \rightarrow SiO(g) + H_2O(g)$. The maximum $SiO(g)$ vapor pressure is a function of the hydrogen pressure, and for example at 1900 K and $p_{H_2} = 10^3$ Pa, $\log p_{SiO}$ cannot exceed +2.6 (Pa). Isobaric points for other temperatures and pressures can be determined from Fig. 14. The valid portion of the diagram is to the right of the corresponding isobaric line, where p_{SiO} is determined by the H_2O to H_2 ratio of the environment. Similarly, in CO_2/CO mixtures, p_{SiO} can be determined from the diagram by using the corresponding CO_2/CO scale and the valid region of this scale is defined as before.

The Ellingham-type compilation of the data is included in Fig. 15. Line 8 delineates the transition from Si to SiO_2 as the condensed phase, and lines 9 and 10 show, respectively, transitions from SiO to SiO_2 and from Si to SiO as the principal vapor species.

(B) *Active Oxidation*: The Si-O system is unique in that

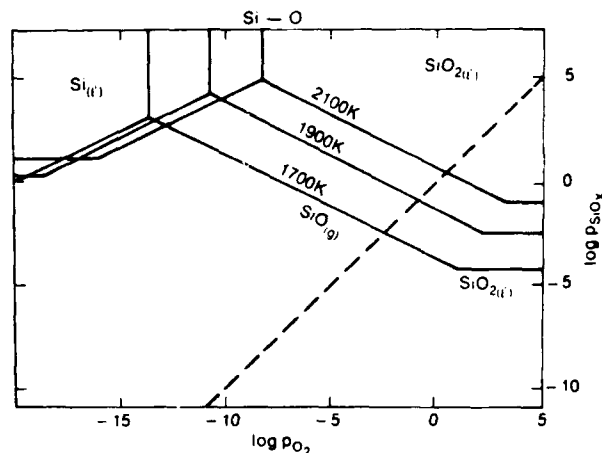


Fig. 13. Master volatility diagram for the Si-O system from 1700 to 2100 K.

over a large range of p_{O_2} 's, the sub-oxide (SiO) is the most important species over silicon. This differs from the Mg-O and Al-O systems where the metallic vapors $Mg(g)$ and $Al(g)$ predominate at low p_{O_2} 's. As a result, active oxidation of Si by the formation of SiO is important and has been well studied.^{5,8} The physical phenomenon of active oxidation involves weight loss, while passive oxidation involves weight gain as a protective oxide film grows. The active-passive transition is defined as the p_{O_2} at which further evaporation of SiO is prevented by the formation of a passive SiO_2 film. This point was first emphasized by Wagner⁵; here, we show the utility of volatility diagrams in dealing with the active-passive transition. Our approach is essentially that pioneered by Wagner,⁵ except that we ignore possible differences in the diffusivity of various species in the vapor phase.

Consider inserting a piece of Si into a furnace which contains some molecular oxygen. Two oxidation reactions are possible:



The volatility diagram is useful in differentiating active and passive oxidation and defining the active-passive transition. Figure 16(A) shows a schematic view of the active oxidation process. Oxygen molecules diffuse through a stagnant layer at the gas/solid interface and react with Si to form SiO molecules, which then diffuse away from this interfacial layer into the ambient. According to the

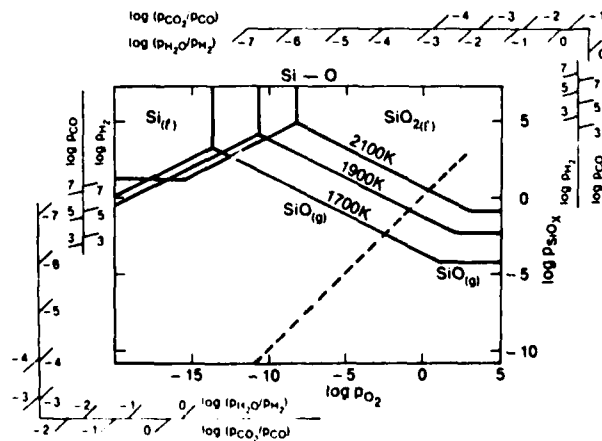


Fig. 14. Complete volatility diagram for the Si-O system.

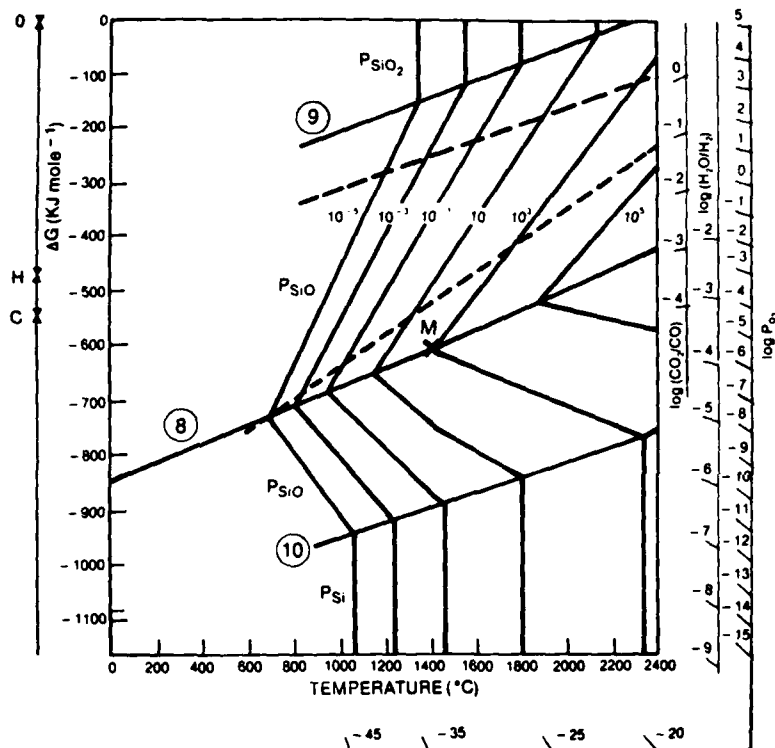


Fig. 15. Ellingham-type diagram for the Si-O system.

JANAF Tables, the equilibrium constant for Eq. (21a) at 1700 K is $\approx 10^{16}$. Thus, one can make the assumption that all the oxygen molecules arriving at this interface from the ambient are converted into $\text{SiO}(g)$. Based on this and the assumption that oxygen molecules arrive and SiO molecules depart at the same rate, active oxidation involves the generation of two SiO molecules for each oxygen molecule arriving at the Si surface. Therefore, at the interface $p_{\text{SiO}} = 2p_{\text{O}_2}$ in the ambient. (This condition is in fact the same as for the isomolar line.) For example, at 1700 K, if the ambient p_{O_2} is 10^{-15} Pa, then the p_{SiO} generated at the interface is 2×10^{-15} Pa. According to Fig. 17, this is many orders of magnitude lower than the equilibrium $p_{\text{SiO}} \approx 10^3$ Pa (point *a*)—and hence $\text{SiO}(g)$ should not condense. If the p_{O_2} is increased, the p_{SiO} will increase accordingly; at $p_{\text{O}_2} = 10^{-12}$ Pa (point *b*) for example, the system should be in the SiO_2 phase field; however, active oxidation will continue because the p_{SiO} is still far below the critical condensation value of $\approx 10^3$ Pa at this point. As the p_{O_2} is further increased, p_{SiO} approaches the critical value and SiO_2 smoke can form away from the interface (Fig. 16(B)). This active $\rightarrow$ active + smoke transition in fact occurs at the isomolar point (*c*). If p_{O_2} is further increased to 5×10^2 Pa, p_{SiO} is 10^3 Pa. This latter pressure will have exceeded the maximum equilibrium pressure defined by point *T*, and SiO_2 will begin to condense on the silicon surface. Beyond this point, a passive SiO_2 film will form, $\log p_{\text{SiO}}$ will drop from 10^3 Pa at point *T* to 10^{-4} Pa (point *d*), and weight loss will effectively cease. This is passive oxidation and is shown schematically in Fig. 16(C). The active-passive transition, although defined in terms of p_{O_2} , is determined by SiO vapor pressure: p_{O_2} at the active-passive transition $= \frac{1}{2}p_{\text{SiO}}$ at point *T*.

One can put forward similar arguments for a hydrogen environment. Unlike the previous case, however, the oxygen carrier is H_2O . Two oxidation reactions are possible:

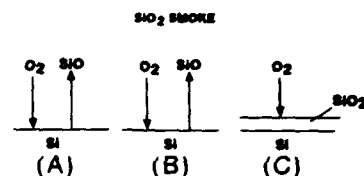
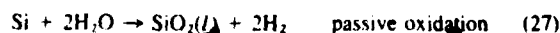


Fig. 16. Schematic view of active and passive oxidation of silicon; see text for discussion.

The method of construction of the $\text{H}_2\text{O}/\text{H}_2$ nomograph enables the direct determination of the corresponding p_{O_2} . For example, a point *b* in Fig. 17, $\log p_{\text{O}_2} = -12$ (Pa) and the corresponding H_2/O ratio is 10^{-4} , as is determined by noting the intersection of the $\text{H}_2\text{O}/\text{H}_2$ scale of a line through point *b*. One can assume, as in the previous case, that all the H_2O molecules are consumed by reaction (26) to form $\text{SiO}(g)$ and a simple relation— p_{SiO} at the interface $= p_{\text{H}_2\text{O}}$ in the ambient—is maintained. (This in fact is the condition for the isobaric lines.) Inserting a piece of Si into furnace containing $\text{H}_2\text{O}/\text{H}_2$ at a ratio of 10^{-4} at $p_{\text{H}_2} = 10^5$ Pa will generate 10 Pa of $\text{SiO}(g)$, and as this is below the critical condensation value of $p_{\text{SiO}} = 10^3$ Pa at point *T*, active oxidation will occur. With increasing H_2O to H_2 ratios, SiO_2 smoke will form when the ratio exceeds 10^{-3} (the condition at the isobaric point *e* on Fig. 17 the active-passive transition occurs when the ratio is 10^{-2} , as the SiO pressure at the triple point is then realized. At this condition p_{SiO} will drop from 10^3 Pa (point *T*) to 1 Pa; this pressure (point *d* on Fig. 17) is determined by the intersection of the 10^{-2} point on the $\text{H}_2\text{O}/\text{H}_2$ scale with the maximum equilibrium pressure line. The difference between molecular O_2 and $\text{H}_2\text{O}/\text{H}_2$, $T \rightarrow d$ as $T \rightarrow f$, respectively, is caused only by the thermodynamics of the $\text{H}_2\text{O}/\text{H}_2$ equilibrium. In the latter case, the active-passive transition occurs when $p_{\text{H}_2\text{O}}$ in the ambient $= p_{\text{SiO}}$ at point *T* and the system must change to point *f*.

IV. Summary and Conclusions

Volatilization reactions in a metal-oxygen system in nonreacting or reducing environments can be fully understood using either volatility diagrams or Ellingham-type diagrams. Three pairs of such diagrams are shown in this paper, Figs. 6 and 7 for the Mg system, Figs. 10 and 11 for the Al-O system, and Figs. 14 and 15 for the Si-O system. The construction of these diagrams is somewhat more involved than the classical Ellingham diagram but is as simple from an application viewpoint. Use does, however, require some understanding of the significance of the isomolar line.

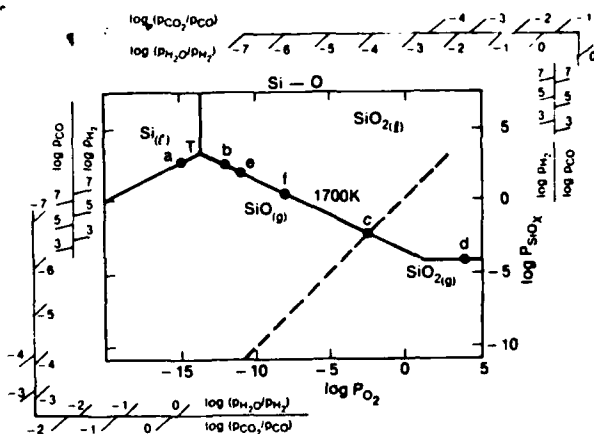


Fig. 17. Volatility diagram for the Si-O system at 1700 K. Points a-f refer to discussion in text on active and passive oxidation of Si.

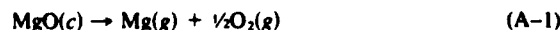
in neutral ambients and the isobaric lines in reducing ambients, in order to identify the valid portions of the diagrams—in fact, these *iso* lines are the principal original contributions of this paper.

The question of the relative merit of the volatility diagrams vs the Ellingham-type diagrams is interesting. On the one hand, the latter is more widely used in general, because of the convenient representation of the data, but volatility diagrams are popular with high-temperature scientists interested in gas-solid reactions because the species of interest, MO , gas, is plotted as one of the axes. Secondly, their use makes it easier to decide which vapor species in gas-solid reactions are important and to delineate valid regions of the p_{O_2} - p_{MO} fields, and in this way are a useful intermediate step in constructing an Ellingham-type diagram. Thirdly, they are much more useful than Ellingham-type diagrams when dealing with solid solutions, oxycarbides, and oxynitrides, as will be discussed in future papers. Fourthly, it is a simple matter to compare the volatility of different oxides at a single temperature by noting the p_{M} or p_{MO} , where the isomolar line intersects the maximum equilibrium pressure line (Fig. 18). Thus, it is easy to see that Al_2O_3 is the least volatile and MgO the most volatile of the three oxides considered, in accord with common laboratory experience; furthermore, it is easy to see why all three of the oxides under consideration cannot easily be reduced to their elements—in all cases, access to the conditions where metal, solid or liquid oxide, and gaseous species can coexist requires very high pressures of reducing gases.

Finally, it is convenient to use volatility diagrams to determine the transition from active to passive oxidation, which occurs in those systems where a volatile MO species predominates, as in the Si-O system.

APPENDIX

The constant dew point lines can be shown to plot as straight lines in volatility diagrams using the following derivation. The important reactions here are



and



The equilibrium constants for these reactions can be expressed in terms of the partial pressures as well as the entropies and enthalpies of these reactions:

$$\log K_1 = \log \frac{p_{\text{Mg}} p_{\text{O}_2}^{1/2}}{a_{\text{MgO}}} = -\frac{\Delta H_1}{2.3RT} + \frac{\Delta S_1}{2.3R} \quad (\text{A-3})$$

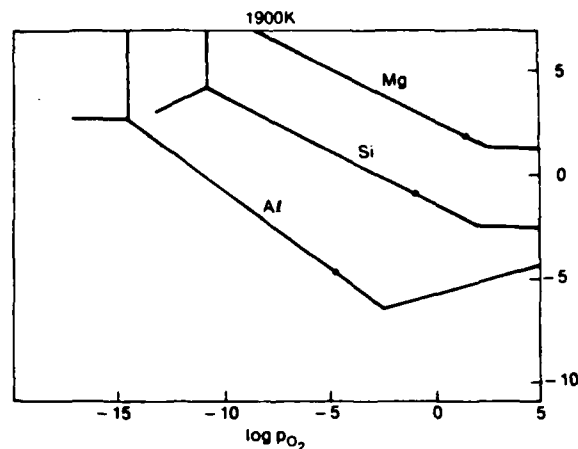


Fig. 18. Comparison of volatility diagrams for the Mg-O, Al-O, and Si systems at 1900 K.

$$\log K_2 = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{O}_2}^{1/2}} = -\frac{\Delta H_2}{2.3RT} + \frac{\Delta S_2}{2.3R} \quad (\text{A-4})$$

By rearranging Eqs. (A-3) and (A-4) one can eliminate T , and assuming a_{MgO} to be unity, we find

$$\frac{1}{\Delta H_2} \left[\frac{\Delta S_2}{2.3R} - \log \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{O}_2}^{1/2}} \right] = \frac{1}{\Delta H_1} \left[\frac{\Delta S_1}{2.3R} - \log (p_{\text{O}_2}^{1/2} p_{\text{Mg}}) \right]$$

which can be simplified to the temperature-independent form

$$A \log p_{\text{Mg}} + B \log p_{\text{O}_2} + C \log \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} + D = 0 \quad (\text{A-5})$$

where

$$A = 1/\Delta H_1$$

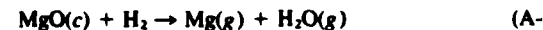
$$B = \frac{1}{2}[(1/\Delta H_1) + (1/\Delta H_2)]$$

$$C = -(1/\Delta H_2)$$

$$D = (1/2.3R)[(\Delta S_2/\Delta H_2) - (\Delta S_1/\Delta H_1)]$$

According to this equation, at constant $\text{H}_2\text{O}/\text{H}_2$, $\log p_{\text{Mg}}$ decreases linearly with $\log p_{\text{O}_2}$.

Similarly the relation between $\log p_{\text{O}_2}$ and $\log p_{\text{Mg}}$ (or $\log p_{\text{H}_2}$) as depicted by the isobaric lines will be derived here. The two important reactions are water formation and magnesia reduction by hydrogen.



The equilibrium constants are

$$\log K_6 = \log \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{O}_2}^{1/2}} = -\frac{\Delta H_6}{2.3RT} + \frac{\Delta S_6}{2.3R} \quad (\text{A-8})$$

$$\log K_7 = \log \frac{p_{\text{Mg}} p_{\text{H}_2\text{O}}}{a_{\text{MgO}} p_{\text{H}_2}} = -\frac{\Delta H_7}{2.3RT} + \frac{\Delta S_7}{2.3R} \quad (\text{A-9})$$

But $p_{\text{Mg}} = p_{\text{H}_2\text{O}}$ according to the mass balance criterion and assuming $a_{\text{MgO}} = 1$, Eq. (A-9) becomes

$$\log K_7 = \log \frac{p_{\text{Mg}}^2}{p_{\text{H}_2}} = -\frac{\Delta H_7}{2.3RT} + \frac{\Delta S_7}{2.3R} \quad (\text{A-10})$$

By rearranging Eqs. (A-8) and (A-10) and eliminating T , one can again derive an expression which is independent of temperature:

$$A \log p_{\text{O}_2} + B \log p_{\text{Mg}} + C \log p_{\text{H}_2} + D = 0 \quad (\text{A-11})$$

where

$$A = 1/2\Delta H_0$$

$$B = (1/\Delta H_0) + (2/\Delta H_7)$$

$$C = -(1/\Delta H_7) + (1/\Delta H_0)$$

$$D = (1/2.3R)(S_0/\Delta H_0) - (S_7/\Delta H_7)$$

According to Eq. (A-10), at constant p_{H_2} , $\log p_{H_2}$ decreases linearly with $\log p_{O_2}$.

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