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GRAIN BOUNDARY ENERGETICS IN NON-OXIDE CERAMICS.(U)
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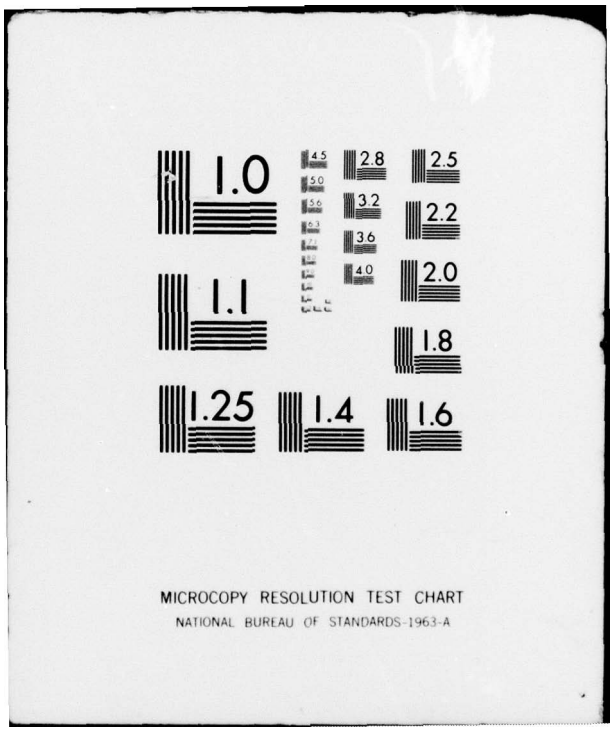
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(6) Grain Boundary Energetics in Non-Oxide Ceramics

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(10) A.H. Heuer and T.E. Mitchell

Department of Metallurgy and Materials Science

Case Western Reserve University

Cleveland, Ohio 44106

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Abstract

Research on "Grain Boundary Energetics in Non-Oxide Ceramics" has been conducted at CWRU since 1975 has concentrated on two specific areas--the $\beta \rightarrow \alpha$ transformation in polycrystalline SiC, and the nature of grain boundary phases in hot-pressed Si_3N_4 containing various densification aids.

The $\beta \rightarrow \alpha$ transformation in polycrystalline SiC is unusual in that it appears to occur in two stages. The first involves the growth of composite plates consisting of α-SiC plates sandwiched between recrystallized envelopes of β-SiC. This stage ends when the original polycrystalline β matrix is consumed. The second and more sluggish stages involves the thickening of the α plates within their β envelopes and requires repeated piecewise nucleation of α at the $\beta \rightarrow \alpha$ interface.

High resolution TEM has been used to show that commercial MgO-doped hot-pressed Si_3N_4 apparently contains a continuous grain boundary phase that is responsible for the poor high-temperature performance. Grain boundary microstructures have been characterized in polycrystalline Si_3N_4 containing Y_2O_3, ZrO_2, and $BeSiN_2$; the latter additive appears to be the most promising, since a continuous grain boundary film is not present.

Summary of Results

Research on "Grain Boundary Energetics in Non-Oxide Ceramics" was conducted by Professors A.H. Heuer and T.E. Mitchell of the Department of Metallurgy and Materials Science at Case Western Reserve University (CWRU) during the period 1 February, 1978 to 31 January, 1978. This section of the Final Technical Report summarizes the achievements of this work. The research began with two questions in mind: i) was the ratio of grain boundary to surface energies (γ_{GB}/γ_{SV}) too high in undoped SiC and other non-oxide ceramics to permit pressureless sintering to proceed to high sintered densities? and ii) what was the importance of dislocation creep relative to grain boundary sliding (GBS) creep during high temperature deformation in Si_3N_4? One important feature of the proposed work was the heavy reliance of transmission electron microscopy (TEM).

Both topics were attacked with vigor during the early stages of the research and qualitative answers to the two questions appeared rather quickly. The difficulty of sintering non-oxide ceramics is <u>not</u> due to a too high value of γ_{GB}/γ_{SV}, and hence a low value of the dihedral angle at a pore-grain boundary intersection, as the initial results showed that dihedral angles were $\geq 100^{\circ}$ in SiC. In the case of crept Si_3N_4 (samples obtained from Battelle Columbus Laboratories), the initial results suggested that GBS was much more dominant than dislocation creep in state-of-the-art, commercial (e.g. HS-130 and NC-132) hot-pressed Si_3N_4.

During the course of the TEM studies that led to these qualitative conclusions, two important questions suggested themselves for study and these became the main topics of research during the grant period. Each will be discussed in turn.

β→α Transformation in Polycrystalline SiC

Polycrystalline β-SiC (i.e. the cubic polymorph) tranforms upon annealing at temperatures above ∿1800°C to the α form--α being the collective designation of a large number of polytypes with hexagonal or rhombohedral symmetry, all based on different stacking sequences of the basic Si-C double layer. The mechanism of this transformation is of considerable technological importance since the α transformation product invariably appears as large platelets which degrade the mechanical properties. A noteworthy and unique feature of the β→α transformation in polycrystalline SiC is the fact that these α plates are "sandwiched" between "sheaths" or "envelopes" of recrystallized β-SiC.

It appears that transformation occurs in two conceptually-distinguishable stages: the first involves the growth of these composite plates until the original polycrystalline matrix is completely consumed, and the second (and much more sluggish) stage is the thickening of the α plates within their β sheaths.

This unusual morphology of the reaction product and unusual transformation sequence arises from the fact that the interface between the α plate and the β sheath involves parallel close packed planes in both phases ($\{111\}_\beta \parallel (0001)_\alpha$) and the resulting interfacial energy appears to be several orders of magnitude less than high angle β/β or α/α grain boundaries or randomly-oriented β/α interface boundaries. The sluggishness of the final stages of the β→α transformation follows directly from the very low energy of the ($\{111\}_\beta/(0001)_\alpha$) coherent interface and the subsequent need for repeated piecewise nucleation of α--an α nucleus can propagate rapidly parallel to the β/α interface but cannot grow easily perpendicular to this interface.

The first stage of the transformation is discussed in papers 2 and 3 in Table I, which is a list of publications arising from this research, while the final stage is treated in paper 4. In addition, the microstructure of sintered polycrystalline α-SiC (produced by Carborundum Co.) with respect to the polytypes and impurity phases present has been characterized by TEM and the results are being written up for publication (paper 5 in Table I.)

Grain Boundary Phase(s) in Si_3N_4

The presence of a continuous grain boundary film in hot-pressed Si_3N_4 has been suspected since the discovery more than 5 years ago that serious (and unacceptable) loss in strength took place at ~1400°C. While the notion that this weakening resulted from softening and flow of a MgO-containing (presumably silicate) phase present because of the MgO added to permit liquid-phase densification during hot pressing, direct micrographic evidence of this phase was not available in commerical materials, in spite of the prior TEM work addressed to this point. As discussed in papers 1 and 6 in Table I, both HS-130 and NC-132 appear to have a continuous grain boundary phase (in addition to measureable amounts of Si_2N_2O, WC, SiC, etc.) but its detection is quite difficult--in electron transmission, the plane of the grain boundary must be accurately parallel to the electron beam and the two grains on either side of the boundary must be oriented such that both are strongly diffracting. Our recent work has involved characterizing microstructures of Si_3N_4 fabricated using densification aids other than MgO and will now be summarized.

In order to improve the creep and oxidation resistance of hot-pressed Si_3N_4, a number of additives have been used in place of MgO as densification

TABLE I

Publications and Dissertations resulting from research on

"Grain Boundary Energetics in Non-Oxide Ceramics"

Publications

1 "Lattice Resolution Studies of Engineering Ceramics: SiC and Si_3N_4", A.H. Heuer, L.K.V. Lou, L.U. Ogbuji and T.E. Mitchell, J. de Micro. et de Spec. Electron, 2 (475-480) (1977).

2 "The β→α Transformation in Polycrystalline Silicon Carbide (SiC): I - Microstructural Aspects", A.H. Heuer, G.A. Fryburg L.U. Ogbuji, T.E. Mitchell and S. Shinozaki, in press, J. Amer. Cer. Soc.

3 "The β→α Transformation in Polycrystalline Silicon Carbide (SiC): II - Interfacial Energetics", T.E. Mitchell, L.U. Ogbuji and A.H. Heuer, in press, J. Amer. Cer. Soc.

4 "The β→α Transformation in Polycrystalline Silicon Carbide (SiC): III - Final Stages", L.U. Ogbuji, A.H. Heuer and T.E. Mitchell, in preparation.

5 "Electron Microscopical Characterization of Sintered α-SiC", L.U. Ogbuji, T.E. Mitchell and A.H. Heuer, in preparation.

6 "Impurity Phases in Hot-Pressed MgO-doped Si_3N_4", L.K.V. Lou, T.E. Mitchell and A.H. Heuer, in press, J. Amer. Cer. Soc.

7 "Grain Boundary Structures in Si_3N_4 Fabricated with Y_2O_3, ZrO_2 and $BeSiN_2$ Additives", K.K.V. Lou, A.H. Heuer and T.E. Mitchell, in preparation.

8 "Microstructural Changes in Si_3N_4 During High Temperature Annealing", L.K.V. Lou, T.E. Mitchell and A.H. Heuer, in preparation.

Dissertation

1 "The Mechanism of the β→α Phase Transformation in Silicon Carbide: An Electron Microscope Study", L.U. Ogbuji, M.S. Thesis (1977).

aids--Y_2O_3, Ce_2O_3, ZrO_2 and $BeSiN_2$--and all have been successful in allowing fully-dense bodies to be produced which showed some improvements in properties. Y_2O_3 and Ce_2O_3 have been chosen in an attempt to produce a more refractory glass phase (Y_2O_3 also has the possibility of improving oxidation resistance by forming a stable silicate second phase ($Y_{10}Si_7O_{23}N_4$ in the Si_3N_4-Y_2O_3-SiO_2 system)). ZrO_2 has been used in an attempt to improve the toughness while $BeSiN_2$ was used with the hope of vitiating the glassy second phase--it is possible to incorporate the additive (subsequent to densification) as a solid solution in Si_3N_4. Without going into the details of recent findings by other workers, the importance of the microstructure of these bodies cannot be dismissed and in particular, the grain boundary structures, which control high temperature behavior, are of paramount interest.

Our recent results are summarized in Table II and will be amplified by the following comments:

1) The stable oxy-nitride in NCX-34 is a yittrium-silicate-oxy-nitride (silicon oxy-nitride is stable in the MgO and ZrO_2 systems, which implies that Mg- and Zr- silicate - oxy-nitrides do not exist.) The presence of large amounts of glassy phases in the G.E. and AMMRAC samples was unexpected, as stable oxy-nitrides are known to exist in both systems.

2) As has already been discussed, Si_3N_4 bodies fabricated with MgO have a continuous grain boundary film between Si_3N_4/Si_3N_4, Si_3N_4/Si_2N_2O and Si_2N_2O/Si_2N_2O grains, but the grain boundary film in NCX 34 is apparently restricted to $Si_3N_4/Y_{10}Si_4O_{23}N_4$ interfaces. In the Si_3N_4-ZrO_2 samples, the grain boundary film is thicker and very extensive, which is probably caused by the low purity starting powders in this body.

TABLE II

	Additive	Phases found in T.E.M. Nitride	Oxynitride	Oxide	SiC	WC	Grain Boundary Film
Norton HS 110 HS 130 NC 132	5 w/o MgO	βSi_3N_4	Si_2N_2O	---	✓	✓	Continuous Film
Norton NCX 34	8 w/o Y_2O_3	βSi_3N_4	$Y_{10}Si_7O_{23}N_4$	---	✓	---	Some
(Max Planck Inst.) N. Claussen	18% ZrO_2	βSi_3N_4	Si_2N_2O	ZrO_2	✓		?
G. Gazza (AMMRC)	10 w/o Y_2O_3	βSi_3N_4	---Glass---				
S. Prochaska (G.E.)	7 w/o $BeSiN_2$	βSi_3N_4	Much Glass at Triple Points				Very little

3) The G.E. samples offer the most encouraging results. They were fabricated by hot-pressing at 1850°C or sintering at 2000°C under 80 atmospheres of nitrogen. Despite the presence of a large amount of glass at triple points, this glass did not penetrate into the grain boundaries. Among the many grain boundaries investigated, we have only succeeded in finding one grain boundary which was wet by this second phase, and even in this case, the apparent thickness of the film was very thin (less than 10 Å). Recent experiments by Drs. Greskovich and Prochazka at G.E. have shown that these materials have excellent properties, i.e. they retain 70% of their room temperature strength at 1500°C and also exhibit excellent oxidation resistance, a result attributable to the high purity of the starting powders. These good high temperature properties are consistent with our observations of the grain boundary structures. These results, as well as summaries of recent studies of microstructural changes occurring in MgO-doped Si_3N_4 upon high temperature (~2000°C) annealing, are presently being written up for publication papers (7 and 8 in Table I).

Personnel

The work on SiC described above has constituted the graduate work of Mr. Linus Ogbuji. He has already obtained an M.S. degree based on some of the results and portions of his Ph.D. thesis will consist the remainder of his SiC work. The research on Si_3N_4 has been performed by several post-doctoral research fellows, Drs. B.J. Pletka, G. Das and L.K.V. Lou, with the bulk of the work being performed by Dr. Lou.

Extensive interactions have been maintained with many other workers also studying non-oxide ceramics. These include (in alphabetical order) Drs. Ashbrook(NASA-Lewis), Clake (Rockwell International), Clausen (Max Planck Institute, Stuttgart, W. Germany), Frieman (Naval Research Laboratory),

Graham (Wright-Patterson Air Force Base), Greskovich (G.E.), Prochaska (G.E.), Shinozaki (Ford), Smeltzer (Battelle Labs, Columbus) and Smoak (Carborundum).

Final Comments

The authors would finally like to acknowledge AFOSR, particularly the contract monitor, Major Simmons, for providing the unfettered support for basic studies that have such obvious technological evidence.

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Phase Transformation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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BETA TO ALPHA

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