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Phase equilibria in the oxidation of impure silicon nitride

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The normal impurities in hot-pressed Si_3N_4 fabricated with MgO as an additive include Ca, Fe, WC, and SiO_2. Within the bulk material the conditions are highly reducing, so the Fe and W will be in the reduced state. Thus the equilibrium oxide phases can be predicted from the CaO–MgO–SiO_2 phase diagram suitably modified by the solubility of the Si_3N_4 in the liquid phase. The presence of the Fe and W can lead to enhanced liquid formation on the surface, where the oxygen potential is higher. Only the nitrogen is capable of generating high internal pressures.

1. Introduction

Because of its useful mechanical properties and its chemical resistance silicon nitride, Si_3N_4, is of considerable interest as a high-temperature ceramic. Specifically, it is the prime candidate for a ceramic-containing gas turbine. Even if it cannot be used as a highly stressed rotating bucket material, it can still have important applications in stationary parts.

Two primary methods are used for producing dense bodies of Si_3N_4: reaction sintering, in which pressed silicon powder reacts with nitrogen gas, and hot-pressing of Si_3N_4 powder, where usually either MgO or Y_2O_3 is added to promote densification. The reaction-sintered material could be of high purity, whereas the hot-pressed material must contain the additive. In this hot-pressed material, WC is also normally present, arising from milling with carbide balls, and typically both Ca and Fe are also present to some degree.

The hot-pressed material also contains some oxygen, as SiO_2 or perhaps dissolved in the α-Si_3N_4 phase. The effectiveness of the hot-pressing additive is considered to result from the formation of a liquid phase composed of SiO_2, the additive and Si_3N_4.

In many applications the oxidation resistance of Si_3N_4 is of interest. Recently reported results indicate that the oxidation of the hot-pressed material can lead to blisters in the protective oxide and the formation of pits [1–3]. Such results are of concern, as this might lead to enhanced oxidation as well as mechanical degradation. The present study examines the thermodynamics of this material to determine what equilibrium phases should be present and what gas might be responsible for the blisters.

2. Oxidation of impure Si_3N_4 around 1400° C

The reaction that largely controls the possible products is, of course, the oxidation of the Si_3N_4,

$$Si_3N_4 + 3O_2 \rightarrow 3SiO_2 + 2N_2 \qquad (1)$$

The free energy of this reaction around this temperature is given* as

$$\Delta G\,(\text{calories}) = -467\,000 + 43.7T, \qquad (2)$$

such that

$$\frac{P_{N_2}^2}{P_{O_2}^3} = e^{(467\,000/T-43.7)/R}. \qquad (3)$$

At this stage we have no good idea what a reasonble pressure for nitrogen might be, but we will assume that it is 10 atm, which gives a partial

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*Unless otherwise noted the values for the thermodynamic functions were obtained from the National Physical Laboratory (England) through the Manlab Data (Cambridge, Mass.) system.

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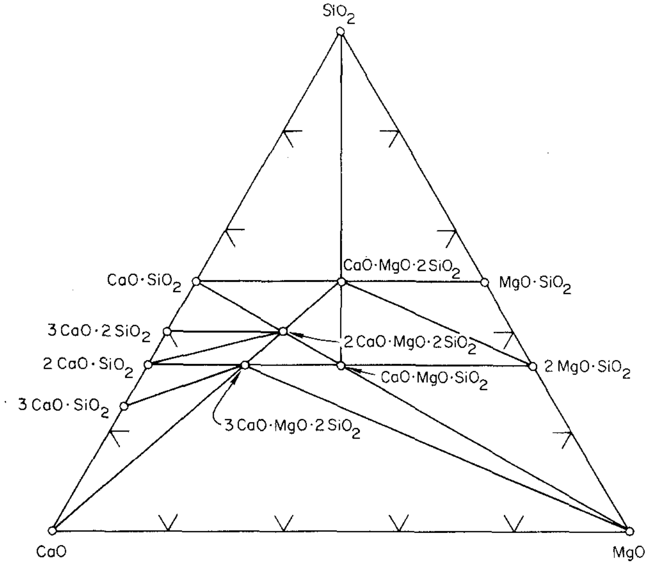

Figure 1 Phase equilibria in the $CaO{-}MgO{-}SiO_2$ system. Scale is in mole fraction.

pressure of oxygen of 1.5×10^{-17} atm at 1400° C. This value is such that the Ca and Mg will be fully oxidized and the W and Fe will be fully reduced. Varying the assumed pressure of nitrogen by a factor of 10 or so will not change these oxidation states. This condition exists in the bulk Si_3N_4; in the oxide layer the oxygen potential will be higher.

The calculation of the partial pressure of CO and CO_2 from the oxidation of the WC is straightforward, using the above pressure of oxygen. At 1400° C, the pressure of CO is 0.06 atm; the pressure of CO_2 is less. Thus, while the presence of CO and CO_2 may be important in vapour-phase transport, they contribute much less to the internal pressure than nitrogen.

The upper pressure limit for SiO can be calculated by means of the reaction

$$SiO_2 + Si \rightarrow 2SiO, \tag{4}$$

which has a free energy change of

$$\Delta G \text{ (calories)} = 150\,000 - 70.0T. \tag{5}$$

This gives the partial pressure of SiO as

$$P^2_{\mathrm{SiO}} = e^{-(150\,000/T - 70)/R}, \tag{6}$$

assuming unit activity for Si; yielding a value of 0.007 atm at 1400° C. This result would apply to the reaction-bonded material, which contains free silicon, but for the hot-pressed material the activity of the silicon is much lower, so the magnitude of the SiO pressure is always low. Again, SiO might be important in vapour transport.

Because the Ca and Mg are fully oxidized, the equilibrium oxide phases can be ascertained from the $CaO{-}MgO{-}SiO_2$ phase diagram. Fig. 1 has been adapted from material in the standard source [4]. This diagram represents the stable high-temperature crystalline phases. Some of the phases are known to have a considerable solid solution range, primarily the interchanging of the Ca and Mg, but we have not tried to represent this. The diagram is characterized by three-phase equilibria as indicated by the triangles. The lines are, in fact, narrow two-phase fields.

The liability of having CaO present in the sample is shown by an examination of the solidification surface for this system (Fig. 2). Here the intersections of this surface are plotted over the region of interest, and the temperatures (°C) at the junctions are given. Whereas, according to our present understanding, a liquid phase during hot-pressing is essential for high densification, the presence of a liquid phase at the test temperatures materially reduces the strength. Thus, the presence of CaO, even in small amounts, may produce a liquid phase at 1400° C or below. Even in the pure $MgO{-}SiO_2$ system, a liquid starts to form at 1543° C unless the mole ratio of MgO to SiO_2 is at least 2.

The phase relations are somewhat complicated by the presence of a silicon oxynitride, Si_2ON_2, which is known to be stable in the Si–N–O system. However, using the free energy data of Blegen [5] we find that this phase is unstable in the presence of MgO; it reacts to form an Mg sili-

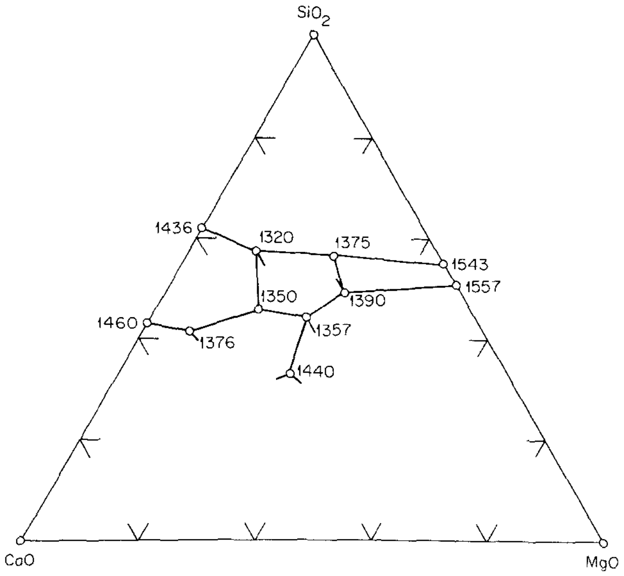

Figure 2 Partial solidification surface for the CaO–MgO–SiO_2 system showing the eutectic valleys and the freezing points (° C) at the junctions.

cate and Si_3N_4. The unresolved question of whether or not α-Si_3N_4 contains oxygen is not a complication because this phase always transforms to the beta form under hot-pressing conditions [6].

As we have already indicated, the Fe and W should be reduced, forming metallic iron and WC or perhaps a mixed carbide and an Fe–W alloy. Some of the Fe and W would be present as the oxide dissolved in any liquid phase that might be present, but we are not presently able to estimate the amount. Any appreciable amounts in the liquid would reduce the temperature at which the liquid disappears.

3. Discussion

Computer programs are available to calculate complex equilibria based upon the minimization of the total free energy. One such program, SOLGASMIX, originally written by Eriksson [7] and modified by Besmann [8], was used in the present work. However, once we recognized that the equilibrium oxygen potential within the bulk Si_3N_4 was sufficiently low to be highly reducing to Fe and W, the present problem resolved basically to an examination of the CaO–MgO–SiO_2 ternary system. An additional factor that is important here is that the free energy of reaction between two oxides to form a mixed oxide is typically much smaller in magnitude than the free energy of formation of the pure oxides. This is true even for a reaction between a highly acid and a highly basic oxide, specifically SiO_2 and CaO. Thus, when the oxygen potential is much too low to oxidize the Fe or W, then the somewhat more stable phases in the presence of SiO_2 (Fe and W silicates) also will not form. As the oxygen potential increases in the outside film a point will be reached where these phases are stable.

The amount of liquid and solid phases in the bulk of the hot-pressed Si_3N_4 under equilibrium condition should be quantitatively predictable from the CaO–MgO–SiO_2 phase diagrams. Published results appear to be in reasonable agreement with this [9–11]. In particular, it has been recognized that the CaO is particularly effective in promoting liquid formation. Even in the absence of CaO, the MgO-to-SiO_2 ratio must be 2 to eliminate the formation of a liquid just above 1500° C. For a given SiO_2 content, the amount of Mg-bearing phases in the final product can be minimized while the above ratio is maintained by using Mg_3N_2 or $MgSiN_2$ in place of MgO [12, 13].

The above result is somewhat complicated by the Si_3N_4 which is soluble in the liquid. A liquid phase which was retained from 1700° C did, on ageing 24 h at 1350° C, form $MgSiO_3$ and Si_2N_2O which indicates that the Si_3N_4 was soluble in the liquid [14, 15]. More recently it has been found that 10 wt% Si_3N_4 is soluble in a SiO_2–MgO liquid mixture at 1700° C [16]. The nitride in the solution will complicate the phase relations but it should be noted that the onset of rapid densification during hot pressing coincides approximately with the minimum melting point in the MgO–SiO_2 system [14]. This matter is under current investigation [17].

It has been demonstrated that the presence of the nitride in the MgO–SiO_2 liquid materially increases its stability which is the reason why a vitreous phase is readily retained in the hot-pressed Si_3N_4 [16]. Undoubtedly, this is in part the result of the increase in viscosity because of the strong covalent bonding of the nitride. That the liquid phase will decompose has been noted above and also in [18] and the probable importance of this on the mechanical properties has been noted [19]. However, it appears that much work remains to be done in this area. As a related matter it was noted that these high nitride glasses might in themselves be of interest [16].

Very recently it has been reported [20] that very thin non-crystalline films may exist between the grains in hot-pressed Si_3N_4. While such films could have remained after the hot-pressing, they also could have formed on cooling by the rejection of some components that were sparingly soluble in the nitride phase. Should this be so, then they are more or less intrinsic to the system, although subject to modification by cooling rate and ageing.

As indicated above, most of the Fe and W would be in a reduced state inside the Si_3N_4, but because of the entropy of mixing, some would be present in any liquid phase, necessarily reducing the freezing point. At present we are not in a position to estimate the amount of this solubility or the melting point depression. Experimental results [11] indicate that Fe is much less detrimental to the strength than is CaO. As the oxygen potential increases in the film, the Fe and W will oxidize and most likely form a silicate, or, if the temperature is high enough, they will be present in the liquid, thus increasing the amount of liquid and depressing its freezing point. Whether or not the presence of an external liquid film will degrade the mechanical properties is conjectural, but results have been obtained that the liquid does enhance the oxidation rate, as would be expected [2]. Thus, it is not at present known if Fe and W pose a significant liability inside the bulk material, but for service conditions where a liquid is present on the surface their presence can be viewed only as detrimental.

It has been reported [1] that during oxidation the Mg and Ca tend to concentrate on the surface. While this might appear to be an unexpected result at first glance, it is understandable since there is a driving force if the interior phases are not the highest silicates, the phases that would be stable in the surface film because of the excess SiO_2 present. The presence of a liquid phase would also provide a driving force for this migration, since this liquid would be rich in SiO_2. This migration and the onset of liquid formation may well give complex oxidation kinetics, as observed [2], but it is surely not rate controlling as has been suggested [21].

As our analysis has shown, the only gas that can generate a high pressure is nitrogen. Lacking specific information about the permeability of the nitrogen through the film, we cannot estimate the actual pressure.

4. Conclusions

(1) We have shown that in large measure the formation of a liquid phase in bulk hot-pressed Si_3N_4 can be analysed by an inspection of the CaO–MgO–SiO_2 phase diagram. The result of this examination is in general agreement with the many observations that relate to the presence of such a liquid phase.

(2) This analysis shows, for example, that for the pure MgO–SiO_2 system the minimum melting point is about 1540° C, and this is further raised if the MgO-to-SiO_2 ratio is greater than 2. The presence of CaO substantially reduces the temperature required to form a liquid.

(3) The known solubility of Si_3N_4 in the liquid phase will modify these results to some extent. Specifically, this will increase the amount of the liquid phase.

(4) It is known that the presence of the Si_3N_4 in the solution increases its stability and its viscosity, leading to the retention of a vitreous phase under normal conditions.

(5) The presence of an unstable vitreous phase unquestionably can lead to important modifications of the properties by subsequent heat-treatment. Specifically, the substantial reduction of the vitreous phase by crystallization should materially increase the creep resistance.

(6) Very thin glass films have been observed between the Si_3N_4 grains. Since the amount of material is so small, this phase may have originated from the rejection of substances that are sparingly soluble in the nitride phase.

(7) Our analysis shows that the Fe and W would be highly reduced in the bulk nitride such that

they would have only small (but unknown) solubilities in the liquid phase. However, in the scale, where the oxygen potential is higher, they would oxidize and help to form a liquid. Thus a surface film containing a liquid is possible even though no liquid need be present in the interior.

(8) The only gas likely to form high pressures within this material is nitrogen.

(9) The migration of the Mg and Ca from the interior to the surface film is due to the formation of higher silicates and/or a liquid phase at the surface.

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References

1. S. C. SINGHAL, "Ceramics for High Performance Applications", edited by J. J. Burke, A. E. Gorum and R. N. Katz (Brook Hill, Chestnut Hill, Mass., 1975) p. 533.
2. W. C. TRIPP and H. C. GRAHAM, *J. Amer. Ceram. Soc.* **59** (1976) 399.
3. J. RUBIN, Ceradyne Corp., Discussion at the ARPA/NAVSEA Ceramic Gas Turbine Development Review Meeting, Castine, Maine, 1–4 August (1977).
4. E. M. LEVIN, C.R.B. ROBBINS and H. F. McMURDIE, "Phase Diagram for Ceramists" (American Ceramic Society, Columbus, Ohio, 1964).
5. K. BLEGEN, "Special Ceramics", Vol. 6, edited by P. Popper (British Ceramic Research Association, Stoke-on-Trent, UK, 1975) p. 223.
6. K. H. JACK, *J. Mater. Sci.* **11** (1976) 1135.
7. G. ERIKSSON, *Chem. Script.* 8 (1975) 100.
8. T. M. BESMANN, Oak Ridge National Laboratory, Oak Ridge, Tenn., Report ORNL/TM-5775 (1977).
9. F. F. LANGE and J. L. ISKOE, "Ceramics for High Performance Applications", edited by J. J. Burke, A. E. Gorum and R. N. Katz (Brook Hill, Chestnut Hill, Mass., 1975) p. 223.
10. J. A. MANGELS, *ibid*, p. 195.
11. J. L. ISKOE, F. F. LANGE and E. S. DIAZ, *J. Mater. Sci.* **11** (1976) 908.
12. G. R. TERWILLIGER and F. F. LANGE, *J. Amer. Ceram. Soc.* **57** (1974) 25.
13. S. WILD, P. GRIEVESON and K. H. JACK, "Special Ceramics", Vol. 5, edited by P. Popper (British Ceramic Research Association, Stoke-on-Trent, UK, 1972) p. 289.
14. S. WILD, P. GRIEVESON, K. H. JACK and M. J. LATIMER, *ibid*, p. 377.
15. K. H. JACK, "Ceramics for High Performance Applications", edited by J. J. Burke, A. E. Gorum and R. N. Katz (Brook Hill, Chestnut Hill, Mass., 1975) p. 265.
16. *Idem*, "High Temperature Chemistry of Inorganic and Ceramic Materials", edited by F. P. Glasser and P. E. Potter (Chemical Society, London, 1977) p. 204.
17. S. NUNN, H. HOHNKE, L. J. GAUCKLER and T. Y. TIEN, presented at American Ceramic Society Meeting, Detroit, Mich., 6–11 May (1978).
18. S. HAMPSHIRE, A.W.J.M. RAE and K. H. JACK, *ibid.*
19. F. F. LANGE, Discussion, "Special Ceramics", Vol 5, edited by P. Popper (British Ceramic Research Association, Stoke-on-Trent, UK, 1972) p. 382.
20. V.L.K. LOU, A. H. HEUER and T. E. MITCHELL, presented at American Ceramic Society Meeting, Hyannis, Mass., 25–28 September (1977).
21. S. C. SINGHAL, *J. Mater Sci.* **11** (1976) 500.

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