

TiN/Sialon Composites via in-situ Reaction Sintering

F. Hong, R. J. Lumby & M. H. Lewis

Centre for Advanced Materials Technology, Department of Physics, University of Warwick, Coventry CV4 7AL, UK

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Abstract

Titanium oxides can be totally converted to TiN which forms a second phase in TiN/Sialon composites via reaction sintering. The in-situ reaction-formed TiN has a unique network structure in the Sialon matrix, resulting in an increased electroconductivity compared with similar composites in which TiN is added directly as an inert dispersion.

Titanoxide können vollständig in TiN umgewandelt werden, das durch Reaktionssintern eine sekundäre Phase in TiN/Sialon-Composites bildet. Das in-situ reaktionsgebildete TiN besitzt eine einzigartige Netzwerkstruktur innerhalb der Sialon-Matrix, was zu einer erhöhten elektrischen Leitfähigkeit führt im Vergleich zu ähnlichen Composites, in denen TiN direkt als inerte Dispersion beigegeben wird.

Les oxydes de titane peuvent être complètement convertis en TiN, qui forme une seconde phase dans des composites TiN/Sialon par frittage-réaction. Le TiN formé par réaction in-situ a une structure de réseau tout-à-fait particulière dans la matière Sialon, ce qui conduit à une conductivité électrique plus élevée par rapport à des composites similaires, dans lesquels le TiN est ajouté directement, c'est-à-dire comme un dispersoïde inerte.

1 Introduction

The addition of dispersed particles, whiskers or platelets to ceramic matrices has been a common approach to enhancement of mechanical properties such as fracture toughness. However, for many systems the influence is generally small and an alternative reason for this approach is to improve electrical or thermal conductivity in previously insulating ceramics. In the case of an electrically non-conductive ceramic, the addition of a conduc-

tive second phase may confer sufficient conductivity to allow spark discharge machining and avoid some of the expense of diamond grinding in the preparation of components. Electroconductive ceramic composites involving highly conductive second phases such as TiN and TiB₂ in the matrices of Sialon and SiC are examples of such composites.^{1,2}

In general, most of the ceramic composites containing dispersed second phases result from a direct addition of the second phase. Densification is then achieved by either conventional ceramic sintering or hot pressing. Such materials can sometimes exhibit poor characteristics which result from an inadequate dispersion process and the lack of sinterability caused by the large volume fraction of inert dispersion required for conductivity. A preferable alternative is the in-situ formation of the second phase as a result of chemical reactions so that optimum properties can be obtained. The chemical reaction may be responsible for the production of the second phase only or it may synthesize both second phase and matrix simultaneously. For example, reactions are described between TiO₂ or TiC with B₄C to yield a fine dispersion of TiB₂ in a matrix of SiC.³ Earlier research in the Sialon system has demonstrated that TiO₂ may be reduced to TiN to supplement that present by direct addition.⁴

This paper describes the preparation and characterization of composites of TiN in a matrix of Sialon prepared by a complete reaction-sintering process. Powder charges of Ti₂O₃ or TiO₂ with Si₃N₄ and AlN were reacted to give TiN/Sialon composites which showed complete conversion and electrical conductivity at a lower volume fraction of TiN than by direct addition.

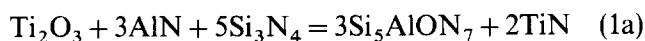
2 Experimental

Chemicals such as α -Si₃N₄ (grade SN-E10, UBE, Japan), AlN (grade C, H. C. Starck GmbH, FRG),

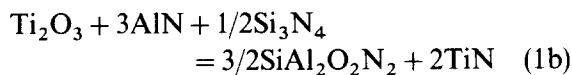
TiO₂ (grade GPR, BDH, UK) and Ti₂O₃ (grade Patinal, Alpha, FRG) were mixed in calculated proportion and micronized in a micronizing mill (McCrone Research Associates Ltd, UK) for 25 min in methanol. The powder mixtures were dried and uniaxially pressed under low pressure to form pellets of 25 mm diameter. The pellets were hot pressed in a graphite die at 1650°C in air for 1 h under a pressure of 20 MPa. Selected compositions were loaded in a dense Si₃N₄-lined graphite crucible and pressureless sintered at 1700°C in N₂ for 1 h with small silicate additions designed for liquid phase sintering. In both sintering processes the heating rate was in the range 10–30°C/min. The sintered samples were cut and polished for scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD). The electro-conductivity of the composites was measured using a four-probe method on specimens of size 4 × 4 × 24 mm.

3 Sintering Reactions and Microstructural Analysis

The β'-Sialon solid solution (Si_{6-z}Al₂O₂N_{8-z}, 0 < z < 4) is able to accommodate Al and O generated by the sintering reactions. To produce ceramics with increasing TiN content requires a proportional increase in titanium oxides and hence in the requirement for substitution of oxygen in the β'-phase. Hence, if the substitution level z = 1, the following reaction (1a) will give a stoichiometrically balanced Sialon composite containing 8.0 vol.% of TiN:

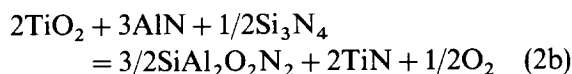
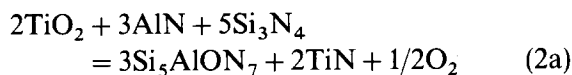


If z = 4, reaction (1b) will give 25.3 vol.% of TiN in the composite:



In a series of reactions in which z values vary from 0 to 4, the general formula of Sialon, Si_{6-z}Al₂O₂N_{8-z}, is maintained, while the ratio of TiN and Sialon phases is changed.

Alternatively, using the less expensive TiO₂ instead of Ti₂O₃, similar Sialon composites may be produced via reactions (2a) and (2b):



The excess oxygen may escape as a gaseous phase during the sintering or exist in the composites as a solid solution of TiN(O).

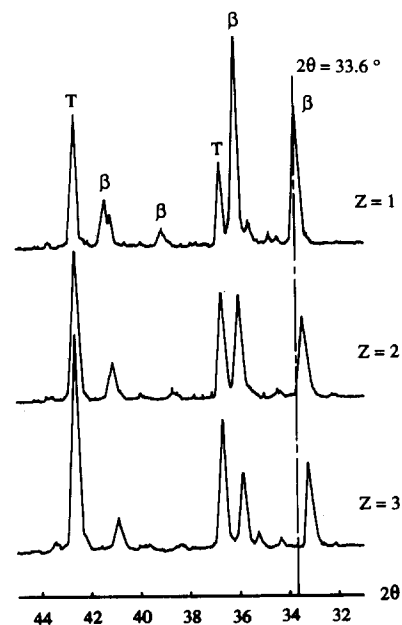
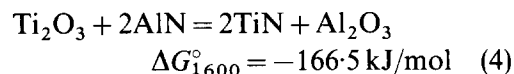
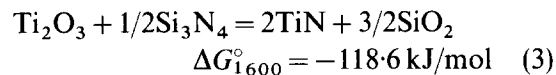


Fig. 1. XRD spectra showing the change in TiN/Sialon ratio and shift in β'-Sialon lattice space with increasing z value. β = β'-Sialon, T = TiN.

XRD of both reaction series 1 and 2, regardless of the different initial titanium oxides used, confirms that all of the proposed reactions occur as predicted to give the TiN phase in Sialon matrices. Figure 1 is an example of the series 2 reactions developed during hot pressing. As the z value of Sialon changes from 1 to 3, the ratio of TiN and Sialon changes accordingly, giving the variation of XRD intensities and a shift in β'-lattice spacing. All these composites have above 99.6% of the theoretical density, indicating that the sintering process is complete. The pressureless sintered samples have shown similar XRD results and 97% of the theoretical density, verifying that the difference in sintering method does not change the reactions.

Thermodynamic calculation suggests that in the reaction series 1 and 2 titanium oxide reacts with AlN in preference to Si₃N₄ to produce TiN and Al₂O₃. For example, in the reaction series 1, the free energies at 1600 K for the reactions between Ti₂O₃ and Si₃N₄ or AlN are shown in reactions (3) and (4):



During the first stage of sintering when the temperature is below 1400°C there is insufficient liquid phase in the system, especially in the hot-pressed sample to which none of the liquid sintering additions have been made, such that the reaction is based on a solid-state route. Once the temperature is raised above 1400°C a liquid phase starts to form, which consists mainly of SiO₂, Al₂O₃ and possibly

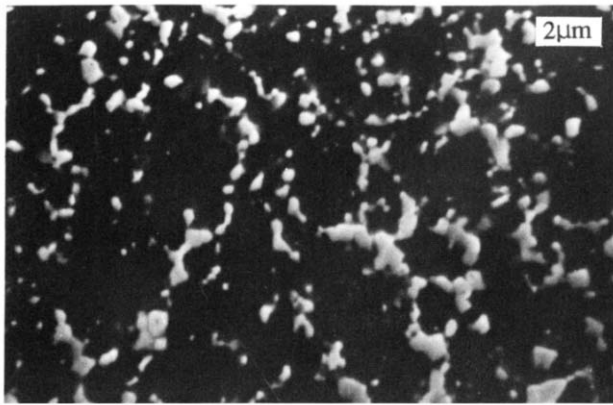
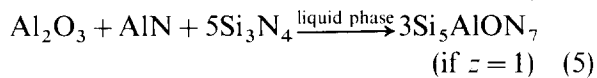


Fig. 2. Network structure of reaction-sintered TiN particles in a Sialon matrix.

TiO₂ or Ti₂O₃. SiO₂ is introduced by Si₃N₄ as a surface impurity as well as Al₂O₃ on AlN. Following liquid-phase formation, chemical reactions are accelerated and the β-Sialon phase is produced via a solution-precipitation mechanism in parallel with the TiN formation exemplified by



Scanning electron microscopy (Fig. 2) shows the microstructure of such a reaction-sintered TiN/Sialon composite at the z value of 3. The reaction-formed TiN particle size is in the range of $\sim 0.5 \mu\text{m}$. These fine particles tend to form around the relatively large β-Sialon grains, resulting in a network structure projecting along β-Sialon grain boundaries. This preferred distribution of the fine TiN particles forms TiN interconnections throughout the composite structure. However, this network structure is not observed in composites formed by direct addition, in which the TiN particles are isolated in the matrix.

4 Electroconductivity

Figure 3 shows a comparison of the electroconductivity between TiN/Sialon composites made by direct addition and in-situ reaction. The superior conductivity shown by the reaction-sintered TiN/Sialon provides evidence of the interconnected TiN network structure already described. In composites produced by direct TiN addition the electroconductive phase, in randomly distributed particulate form, has to exceed $\sim 30 \text{ vol.}\%$ in order to make conductive paths. In contrast, in this reaction-sintered composite the network structure requires only about $20 \text{ vol.}\%$ of TiN, which is equivalent to an addition of $\sim 30 \text{ wt}\%$ of TiO₂, to make the composite substantially electroconductive.

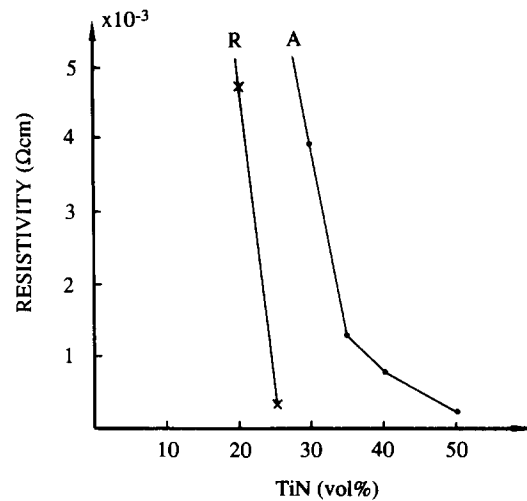


Fig. 3. Comparison of the electroresistivity between TiN/Sialon composites made by direct addition and in-situ reactions. A = Directly added,¹ R = reaction-sintered.

5 Conclusion

In comparison with ceramic-ceramic composites in which the second phase is added directly, prior to the sintering, an alternative reaction-sintering route has been demonstrated which produces electroconductivity with a relatively low volume fraction of conducting phase. In the TiN/Sialon systems a series of redox reactions have been successfully used to convert titanium oxides into titanium nitrides, whereas the matrix Sialon remains stoichiometrically balanced and sintered to high density. In general, β'-Sialon can act as a reservoir for oxygen released by redox reactions involving different types of reducible metal oxide. These principles have been extended to alternative redox reactions involving different transition metal compounds, such as the borides, and will be described in later publications.

Acknowledgements

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