Combustion synthesis and subsequent sintering of titanium-matrix composites

A. CHRYSANTHOU*,†, Y. K. CHEN†, A. VIJAYAN†, J. O'SULLIVAN‡
Department of †Aerospace, Automotive and Mechanical Engineering and ‡Design Technology and Management, University of Hertfordshire, Hatfield, Herts AL10 9AB, UK

Titanium-matrix composites containing up to 50 wt% TiC particles were prepared by combustion synthesis using elemental powders. The products were subsequently sintered at 1160°C for various periods of time. SEM and X-ray diffraction were used to assess the changes that took place during the two stages of processing. Products of combustion synthesis containing in excess of 25%TiC contained large cracks as well as agglomerates of carbide particles that were undesirable from the point of view of reinforcing the metal. The carbide obtained by combustion synthesis had a higher carbon content than that expected according to the Ti-C equilibrium phase diagram, due to the non-equilibrium nature of the reaction. During the sintering stage, the carbide of non-equilibrium composition reacted with titanium to yield the carbide of equilibrium composition. The composition changes were investigated and their significance on the sintering process is discussed.
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1. Introduction

Titanium is a lightweight material with a strength to weight ratio superior to that of both steel and aluminium. For this reason, titanium has found a wide range of applications in the aerospace industry. Demands for improvements in mechanical properties and service temperatures have in recent years led to research in the development of titanium-matrix composites. Prospective uses of these materials include aircraft engine components [1, 2], automotive valves, wear-resistant parts like gears and tubing, sports equipment as well as military applications.

A number of problems have been identified that may restrict the development of titanium matrix composites. These problems include (i) the high reactivity of Ti with most ceramics, leading to instability of the reinforcement phase during processing and service and (ii) materials and processing costs. A number of studies have focused on using SiC as the reinforcement material in a titanium alloy matrix [3, 4]. However, titanium and SiC are chemically non-compatible and react together to form titanium silicides and TiC as can be verified by inspection of their Gibbs Free energy data. Similarly, B_4C will react with titanium to form titanium boride and TiC, while a titanium/TiB_2 combination will yield TiB. The choice of reinforcement in this study was TiC, which according to the Ti-TiC equilibrium phase diagram, coexists with Ti over a range of compositions [5].

Using vacuum plasma spraying, Dearnley and Roberts [4, 6] prepared titanium matrix composites reinforced with SiC, B_4C and TiB_2, all of which are thermodynamically unstable with the matrix. Although this technique may be useful in avoiding interfacial reactions during processing, the problem still exists that these reinforcements will react with Ti at high temperatures during service. SiC has also been used as a reinforcement of titanium-based composites that were prepared by shock wave consolidation [3]. A cold and hot isostatic pressing (CHIP) technique has been developed by Dynamet Technology Inc. [7]. This process can successfully reinforce Ti-6A1-4V alloys with up to 10 vol%TiC. An investigation has shown that this route is unable to successfully produce composites with 20 vol%TiC because of clustering of particles and porosity problems [8]. The capital investment costs are quite high and the process will be at a disadvantage when competing with more conventional techniques. Chen *et al.* [9] produced Ti-TiC composites by introducing graphite powder into molten titanium followed by casting. This led to the in-situ formation of TiC in the metal. This route has the advantage of being simple to operate and is capable of producing complex shaped components.

The objective of the work which is reported here was to produce Ti-TiC composites by means of combustion synthesis and to subsequently sinter these to near-net-shape products. The process involves ignition of an exothermic reaction where the evolution of heat raises the temperature of the reactants and is sufficient to self-propagate the reaction. Its advantages include a low energy requirement and short reaction times. It has also been reported that the products of combustion synthesis are more easily sintered than those obtained by conventional methods [10].

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*Author to whom all correspondence should be addressed.

2. Experimental

Predetermined amounts of titanium and graphite powders were weighed out and pressed into pellets using a steel die. Samples of five different compositions were prepared containing 1.25%C, 2.5%C, 3.75%C, 5%C and 10%C by weight, in each case the balance being titanium. The expected amount of TiC reinforcement was 6.25%, 12.5%, 18.75%, 25% and 50% respectively. Thus, in all samples there was sufficient titanium present to not only react with the graphite, but to also form the matrix of the composite product. The total weight of each pellet was 1 g. The titanium powder that was used in the study was of 99.5% purity and had a particle size less than 20 μm, while the carbon had a particle size less than 44 μm. The compacted powder samples were placed in an alumina boat and inserted in the hot zone of a horizontal furnace at room temperature. The furnace was then evacuated by means of a vacuum pump and reactions were carried out in vacuum by heating each sample to ignition at a rate of 25°C per minute. A temperature-time response curve was obtained for each run by using a two-colour pyrometer together with a computerised acquisition system which could register as many as 500 readings per second. Following combustion, samples were subsequently sintered in the same furnace under vacuum conditions by heating at 1160°C for various periods of time. The products of combustion synthesis and of the sintering operation were analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and light microscopy. Porosity measurements were performed using the GENIAS 25 programme in order to monitor the densification of the samples.

3. Results and discussion

The reaction between titanium and graphite was observed to be self-propagating for all samples except for the Ti-1.25%C mixture. The reason for this particular composition not reacting in a self-propagating manner was the presence of a high amount of titanium that acted as a heat sink and absorbed some of the exothermic heat. Fig. 1 shows the ignition temperatures for all the reacting mixtures after preheating at a rate of 25°C · min^{-1}. Fig. 2 displays the temperature-time profile of the Ti-50%TiC sample and shows that the reaction reached a maximum temperature of 2352°C, 0.5 s after ignition.

Microscopic examination of the samples immediately after combustion synthesis indicated the
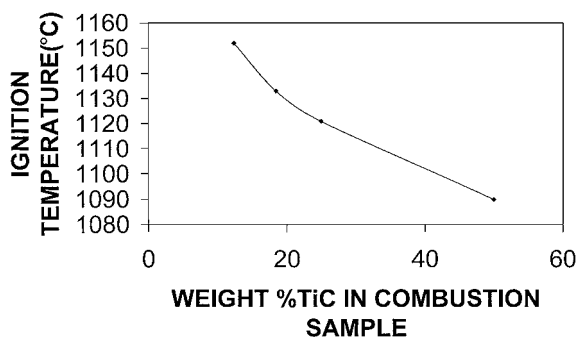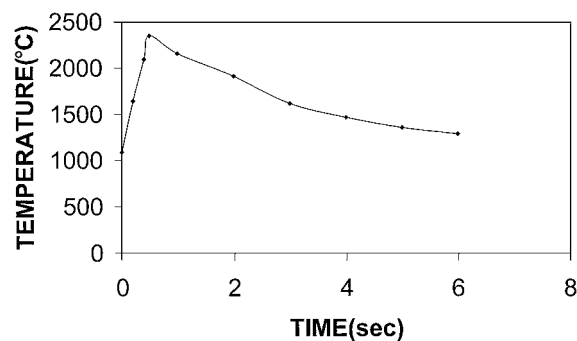
Figure 2 Temperature-time response curve for the combustion of a sample giving a Ti-50%TiC product.

formation and dispersion of fine TiC precipitates in a titanium metal matrix. The size of the TiC particles produced by the Ti-12.5%TiC sample ranged from roughly 2 μm to about 15 μm as presented in Fig. 3. Such a fine and uniform dispersion of carbide particles will probably act as an effective reinforcement for the matrix. The particle size range for the Ti-18.75%TiC sample was 3 μm to 22 μm, while the reaction of the Ti-25%TiC and Ti-50%TiC samples produced larger TiC particles as well as many TiC agglomerates that are undesirable from the point of view of reinforcing the metal.

The adiabatic temperature of the reaction can be calculated using the equation,

$$-\Delta H_{T_{ig}}^{\circ} = \int_{T_{ig}}^{T_{ad}} C_{p} \, dT$$

where, $\Delta H_{T_{ig}}$ = the enthalpy of the reaction at the ignition temperature, T_{ig} = the ignition temperature, T_{ad} = the adiabatic temperature, and C_{p} = the specific heat capacity of the products.

Thermodynamic calculations using the ignition temperature data recorded during the study indicate that at least some partial melting of the titanium will take place during combustion. This was confirmed by microscopic examination in Fig. 3 which showed that the titanium particles partially melted and joined together to create a continuous metallic matrix. From the Ti-C equilibrium phase diagram [5], titanium is expected to melt at a eutectic temperature of 1645°C, as the addition of carbon lowers the melting point of the metal. All products showed some degree of porosity that increased with increasing carbon in the starting material. The presence of porosity in the products of combustion synthesis is normally associated with the explosive nature of the reaction, the evolution of adsorbed gases or volatile impurities and with the volume change in going from reactants to products. During the present study, almost all the pores were surrounded by TiC particles that dispersed in the matrix. This observation indicated that the porous areas were occupied by the graphite prior to reaction with titanium. Judging from the nature of the temperature-time plot in Fig. 2, there was not sufficient time during the reaction for the molten titanium to enter and fill up the pores that were formed during the formation of TiC.
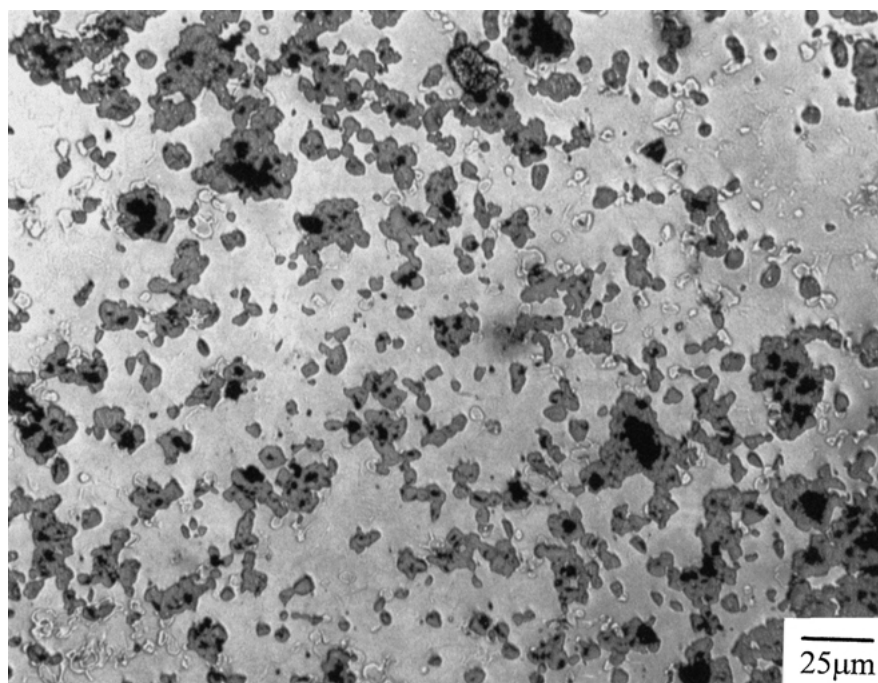
Figure 1 Plot of ignition temperature against composition.

Figure 3 Microstructure of a Ti-12.5%TiC sample immediately after combustion synthesis (light microscopy).
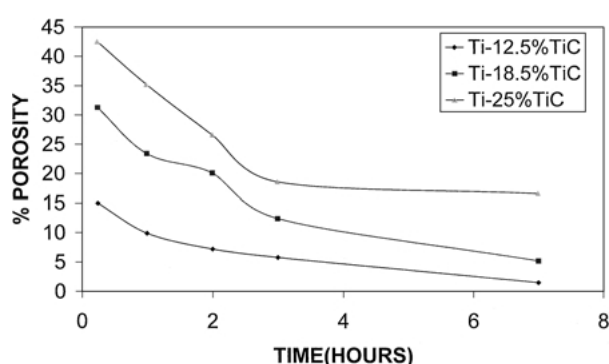

Figure 4 Plot of % porosity with sintering time for samples Ti-12.5%TiC, Ti-18.75%TiC and Ti-25%TiC.

The effect of sintering time at $1160°C$ on the densification of the composite products of combustion synthesis is presented in Fig. 4. It is evident that the higher the porosity following combustion, the longer the time required for full densification. It is also interesting to note that almost full densification can be achieved after about 7 hrs at a relatively low temperature of $1160°C$. The samples containing in excess of 25%TiC developed large cracks immediately after combustion. Even after sintering for 24 hrs it was not possible fill up and eliminate these cracks. The large amount of porosity displayed in Fig. 4 for the Ti-25%TiC sample after 7 hrs corresponds mainly to the remaining void regions created by the cracks.

The XRD data indicated the formation of TiC as a result of the combustion reactions. By reference to the Ti-C equilibrium phase diagram [5], TiC in equilibrium with titanium at $1160°C$ has a C:Ti atomic ratio of about 1:2, that is, it forms non-stoichiometric TiC which is deficient in carbon. The carbide still retains its face-centred cubic crystal structure and contains vacant carbon sites in the lattice. The TiC composition

obtained from the combustion reactions was deduced by lattice parameter measurements that showed that the carbide that was formed was richer in carbon compared to the composition expected under equilibrium conditions. For example, for the Ti-25%TiC sample immediately after combustion the carbide composition was TiC_x where $x = 0.65$. This difference in the TiC composition with the equilibrium value occurred because of the nature of the combustion reaction which was extremely fast and did not allow sufficient time for the products to equilibrate. Observation of the XRD data showed a progressive increase in the value of the TiC scattering angles as sintering progressed. In addition, new and distinct XRD peaks emerged at slightly higher scattering angles near the TiC peaks, effectively converting the original TiC peaks into doublets. The scattering angles for these new peaks were approximately the same for all the samples and remained constant with sintering time. The lattice parameter of the face-centred cubic crystal structure based on these new peaks was approximately 4.2975 Å. Using the lattice parameter data as a function of TiC composition that have been compiled by Storms [11], it was observed that the new peaks at higher scattering angles represented the non-stoichiometric TiC with a C:Ti ratio of approximately 1:2, that is, the TiC composition which is expected in equilibrium with titanium metal. For the sake of simplicity this will be referred to as the carbide of composition $TiC_{0.5}$. Fig. 5a, b and c show how the (311) diffraction peak of TiC_{1-x} changes with sintering time at $1160°C$ for the Ti-25%TiC sample. Fig. 5a presents the (311) diffraction peak for TiC_x $(x = 0.65)$ which was formed by combustion synthesis. Sintering for about 2 hrs has led to the appearance of a new diffraction peak which represents the $TiC_{0.5}$ composition, while the scattering angle for the original peak has increased slightly as presented in Fig. 5b. It is

RELATIVE INTENSITY (%)

120
100
80
60
40
20
0

71   72   73   74   75

SCATTERING ANGLE

(a)

RELATIVE INTENSITY (%)

90
80
70
60
50
40
30
20
10
0

71   72   73   74   75

SCATTERING ANGLE

(b)

RELATIVE INTENSITY(%)

120
100
80
60
40
20
0

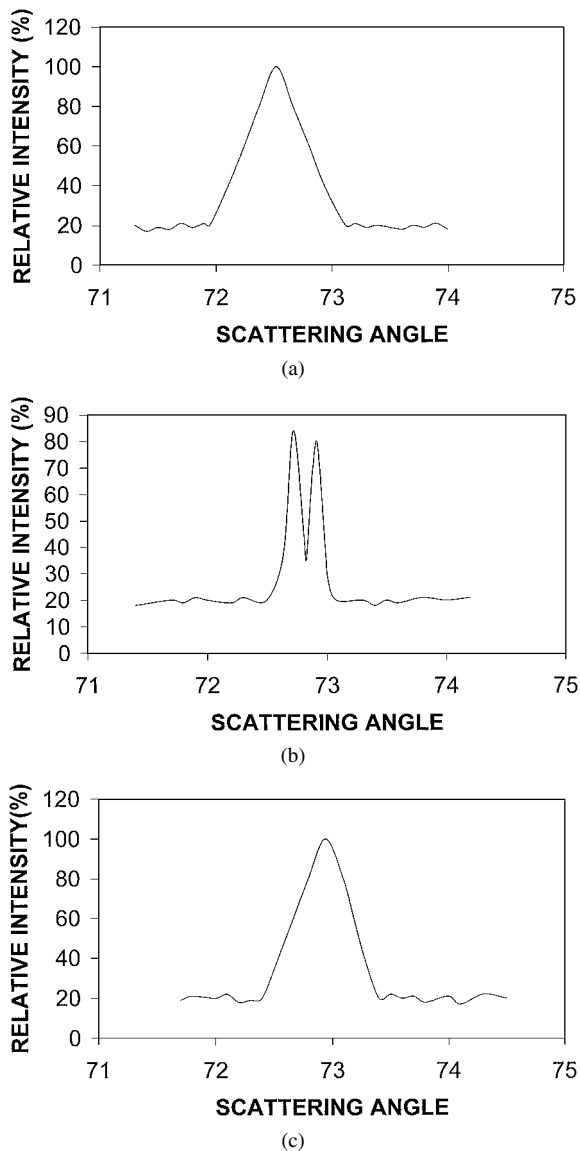71   72   73   74   75

SCATTERING ANGLE

(c)

Figure 5 XRD pattern showing the evolution of the (311) TiC diffraction peak with sintering time for a Ti-25%TiC sample: (a) just after combustion synthesis, (b) sintering time of 2 hrs, and (c) sintering time of 7 hrs.

evident that titanium and the TiC_x ($x = 0.65$) composition have reacted to yield TiC of two different compositions, TiC_x ($x = 0.58$) and $TiC_{0.5}$. After about 7 hrs of sintering the only (311) diffraction peak that is observed in Fig. 5c represents the equilibrium composition $TiC_{0.5}$. Microscopic examination using SEM revealed a composition contrast within TiC particles as shown in Fig. 6 which is representative of a sample containing 25%TiC after 2 hrs of sintering. Chemical composition analysis for carbon was carried out using energy dispersive X-ray spectroscopy. For the composite sample which is presented in the SEM micrograph in Fig. 6, the chemical analysis revealed two distinct regions of different carbide compositions. This observation is in agreement with the XRD results. The lighter areas in the micrograph had a lower carbon content than the darker areas. The lighter regions had a composition of 65.5 at%Ti and 34.49 at%C which is close to the composition of non-stoichiometric TiC that is expected in equilibrium with titanium. The darker TiC areas contained a higher amount of carbon and on the basis of

energy dispersive X-ray spectroscopy represented the carbide of composition TiC_x (x is approximately 0.58 which is in good agreement with the XRD data). The compositional changes that took place during the sintering process were dictated by the Ti/TiC equilibrium. The non-equilibrium nature of the products of the combustion reactions and their subsequent need to equilibrate acted as a driving force for the sintering process at $1160°C$. The overall reaction that took place during sintering can be described by the equation,

$$Ti + 0.5/x\ TiC_x \rightarrow 0.5/x Ti + TiC_{0.5}$$
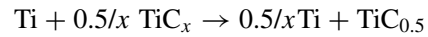
Equilibration of the carbide composition took place either by the solid diffusion of carbon into the titanium followed by reaction between the two or by the diffusion of titanium into the carbide. The former is the most likely reaction mechanism since the diffusion of carbon into titanium is faster than the diffusion of titanium into TiC. The reaction is expected to lead to a small increase in the particle size of the carbide. Based on a theoretical calculation, carbide particles of diameter of 15 μm will increase in diameter by only about 2 μm which is an insignificant increase. At the same time, a slight increase in the titanium lattice parameter was observed. The amount of carbon that dissolved into the titanium matrix during the combustion reaction was probably lower than the equilibrium value. As a result, further carbon dissolution into the titanium matrix took place, indicating that during sintering the matrix was also equilibrating simultaneously with the carbide.

Equilibrium studies of the Ti-C system have reported the existence of only one carbide, TiC with a B1(or NaC1) crystal structure [5]. Fig. 5a and b show discrete and separate reflections for TiC_x and $TiC_{0.5}$. This seems to suggest the existence of a separate Ti_2C phase that is distinct from non-stoichiometric TiC because a continuous range of homogeneity would produce broadened reflections instead. Two recent studies involving combustion synthesis or sintering of TiC-reinforced titanium-matrix composites, have claimed the existence of a distinct Ti_2C phase [12, 13]. Wanjara *et al.* [12] who sintered Ti-6%A1-4%V and TiC powder mixtures between $1000°C$ and $1500°C$ reported an interfacial reaction product of Ti_2C. Using lattice parameter measurements from neutron diffraction analysis as well as quantitative analysis from low voltage field emission gun scanning electron microscopy they concluded that the reaction product was stoichiometric Ti_2C with a B1 crystal structure. Ranganath and Subrahmanyam [13] who produced TiC-reinforced titanium-matrix composites also claimed the formation of a similar Ti_2C phase. The XRD observations of the present study are very similar to those reported by Wanjara *et al.* [12]. From the previous as well as the present study, it is not clear whether the Ti_2C phase, if it exists at all, is the result of ordering. However, there is one other factor that must not be neglected and that is the established fact that during heating, TiC can pick up oxygen to form titanium oxycarbides [11]. Therefore, before any conclusive evidence for the existence or otherwise, of Ti_2C is accepted, an accurate oxygen analysis is also necessary.
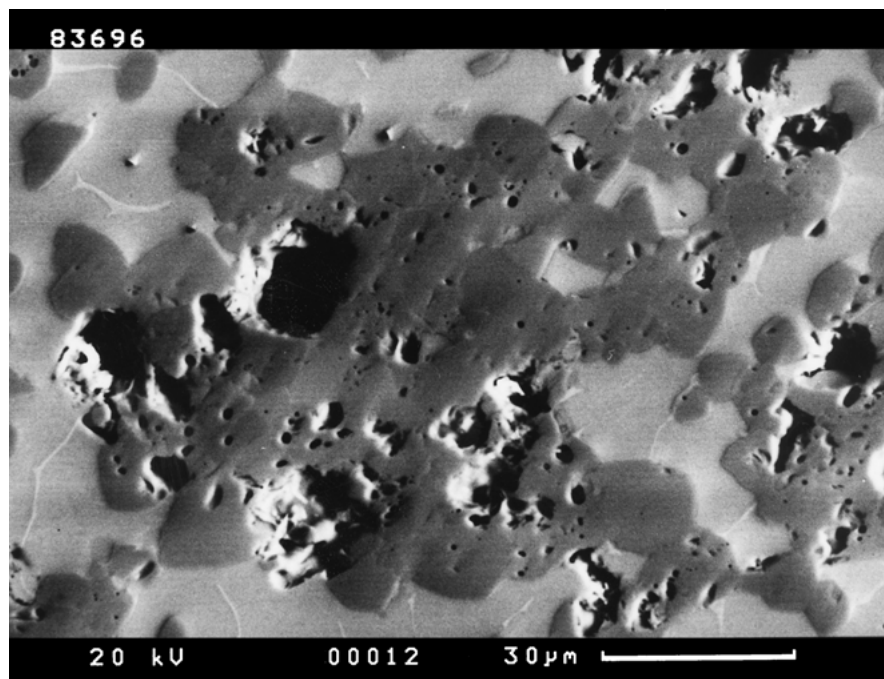
Figure 6 SEM micrograph of a Ti-25%TiC sample after 2 hrs of sintering showing the variation in composition of TiC (light grey represents carbide of composition $TiC_{0.5}$; dark grey represents carbide of composition $TiC_{0.58}$).

The evidence presented by the study is inconclusive and perhaps a reassessment of the relationships in the Ti-C system is necessary.

4. Conclusions

The study has shown that the combustion synthesis of Ti-TiC composites by reaction of elemental powders is possible for product samples containing in excess of 12.5%TiC. The products are highly porous and need to be sintered after combustion to produce near-net-shape components. Sintering at 1160°C resulted into dense products after about 7 hrs. The sintering route involved reaction of the carbide of non-equilibrium composition with the titanium matrix to produce the carbide composition that is expected under equilibrium conditions. The non-equilibrium nature of the carbide after combustion acted as a driving force for the sintering process.

References

1. R. HOLMES and C. SILGMAN, *Flight-Vehicle Mater.* **1** (1994) 307.
2. P. S. GRANT, *Mater. World* **5** (1997) 77.
3. T. CHRISTMAN, K. HEADY and T. VREELAND, *Scripta Metall. Mater.* **25** (1991) 631.
4. P. A. DEARNLEY and K. A. ROBERTS, in CHEMECA '90, Australasian Chemical Engineering Conference, 1990, p. 477.
5. E. K. STORMS, "The Refractory Carbides" (Academic Press, 1967) p. 3.
6. P. A. DEARNLEY and K. A. ROBERTS, *Powder Met.* **34** (1991) 112.
7. S. RANGANATH, *J. Mater. Sci.* **32** (1997) 1.
8. J. K. SHANG and R. O. RITCHIE, *Scripta Metall. Mater.* **24** (1990) 1691.
9. J. CHEN, Z. GENG and B. A. CHIN, "High Temperature Ordered Intermetallics III," *Mater. Res. Soc. Symp. Proc.* **133** (1989) 447.
10. O. R. BERGMAN and J. BARRINGTON, *J. Amer. Ceram. Soc.* **49** (1966) 502.
11. E. K. STORMS, "The Refractory Carbides" (Academic Press, 1967) p. 8.
12. P. WANJARA, R. A. L. DREW, J. ROOT and S. YUE, *Acta Mater.* **48** (2000) 1443.
13. S. RANGANATH and J. SUBRAHMANYAM, *Metall. Mater. Trans.* A **27** (1995) 237.