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ON THE OXIDATION BEHAVIOUR OF MONOLITHIC TiB_2 AND Al_2O_3-TiB_2 AND Si_3N_4-TiB_2 COMPOSITES

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In view of the susceptibility of TiB_2 to oxidation, the thermal stability of monolithic TiB_2 and of Al_2O_3-30 vol% TiB_2 and Si_3N_4-20 vol% TiB_2 composites was investigated. The temperature at which TiB_2 ceramic starts to oxidize is about 400°C, oxidation kinetics being controlled by diffusion up to $T \approx 900$°C and in the first stage of the oxidation at 1000°C and 1100°C (up to 800 min and 500 min respectively), and by a linear law at higher temperatures and for longer periods.

Weight gains in the Al_2O_3-TiB_2 composite can be detected only at temperatures above ≈700°C and the rate governing step of the oxidation reaction is characterized by a one-dimensional diffusion mechanism at $T = 700$°C and $T = 800$°C and by two-dimensional diffusion at higher temperatures.

Concerning the Si_3N_4-TiB_2 composite, three different oxidation behaviours related to the temperature were observed, i.e. up to ≈1000°C the reaction detected regards only the second phase; at $\approx 1000 < T < \approx 1200$°C, the diffusion of O_2 or N_2 through an oxide layer is proposed as the rate-governing step; at $T > \approx 1200$°C, a linear kinetic indicates the formation of a non protective scale.

Keywords: monolithic TiB_2 and Al_2O_3-TiB_2 and Si_3N_4-TiB_2 composites, oxidation kinetics

Introduction

Titanium diboride has been studied extensively for its potential applications and it has received great attention because of its high melting point, hardness, electrical conductivity and wettability by molten Al [1 –3].

The addition of TiB_2 to an Al_2O_3 or Si_3N_4 matrix greatly increases hardness, strength and fracture toughness; in addition, these composites can be used as electrodes, wear parts, cutting tools, high temperature heaters and heat exchangers.

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In this respect the thermal stability of monolithic TiB_2, of Al_2O_3-TiB_2 and Si_3N_4-TiB_2 composites is an important property to evaluate, since in use they can be exposed to oxidizing environments.

Moreover, because of the propensity of titanium diboride to oxidize, the success of the composites in high temperature applications will depend on the extent to which the matrix can prevent the oxidation of TiB_2 particles [7–9].

The purpose of this study is to evaluate the thermal stability in air of TiB_2 and of oxide (Al_2O_3)- and non-oxide (Si_3N_4)-based composites containing TiB_2 as a secondary phase.

Thermal oxidation causes a net-weight gain which can be monitored using thermogravimetric analysis to determine the oxidation kinetics. On the basis of the morphological and structural characteristics of the oxidized surfaces and of the kinetic and thermodynamic parameters, an evaluation of the phenomenological processes involved was attempted.

Experimental procedure

Materials

Starting with a commercial TiB_2 powder (Starck, Grade F), dense TiB_2 ceramics were obtained through hot pressing at 1850°C for 60 min and at 30 MPa [3].

Al_2O_3-TiB_2 composites were produced by adding 30 vol% TiB_2 to Al_2O_3 (Alcoa A16 S. G.) and by hot pressing the mixture at 1600°C , 30 MPa for 30 min [10].

With regards to the Si_3N_4 composite, silicon nitride powders (Starck LC12) were wet mixed with the sintering aids (3 wt% Al_2O_3 and 8 wt% Y_2O_3) and then TiB_2 in 20 vol% amount was added. Dense samples were obtained by uniaxially hot pressing at 1750°C and 30 MPa.

Starting compositions, hot pressing conditions, the values of some microstructural parameters and mechanical properties of monolithic TiB_2 and of the composites have been reported elsewhere [3, 6, 10].

Oxidation tests

Short term oxidation tests (20–30 hours) were carried out in a static air atmosphere on samples diamond sawn from the hot pressed billets, then polished and cleaned. The weight gains were continuously recorded by a TG-DTA apparatus (P. L. Thermal Sciences, U. K.); oxidation temperatures ranged from 350° to 1400°C; the heating rate was 30 deg·min^{-1}.

The surface of the oxidized samples was analyzed by X-ray Diffraction (Rigaku Corporation), Scanning Electron Microscopy (Autoscan, ETEC, USA),

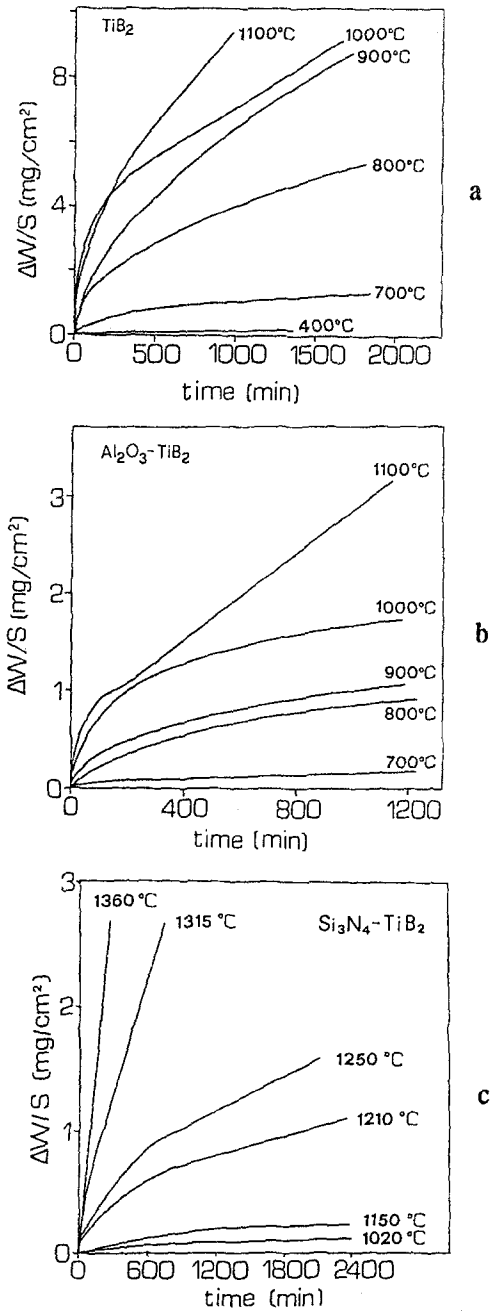

Fig. 1 Isothermal weight gain at various temperatures for: *a*) TiB_2; *b*) Al_2O_3-TiB_2; *c*) Si_3N_4-TiB_2

including Back-scattered electron imaging and Energy-Dispersive Spectroscopy (Philips, EDAX PV 9100).

Results and discussion

Under isothermal conditions, weight gains (DW/S, where DW is the weight gain and S is the surface of the sample) were detected starting at about 400°C for TiB_2 (Fig. 1a), at about 700°C for Al_2O_3-TiB_2 (Fig. 1b) and at about 800°C for Si_3N_4-TiB_2 (Fig. 1c).

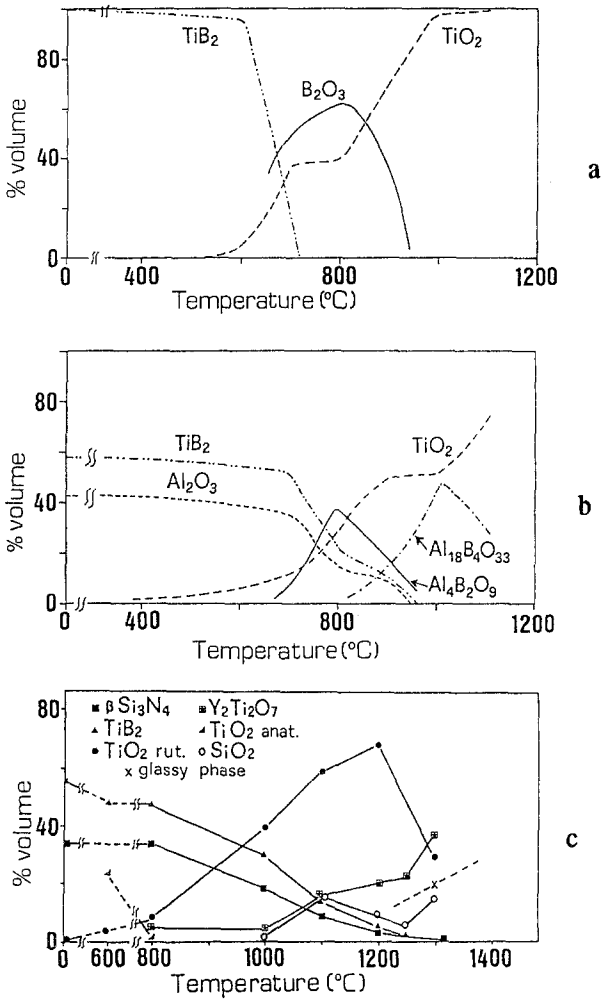

Fig. 2 Semiquantitative X-ray analysis of the oxidized surfaces showing the crystal phase content: *a*) TiB_2; *b*) Al_2O_3-TiB_2; *c*) Si_3N_4-TiB_2

a) Structure and morphology of the oxidized surfaces

The evolution of the crystalline phases content for the oxidized samples as derived from semiquantitative XRD analysis are shown in Fig. 2a, b, c for TiB_2, Al_2O_3-TiB_2 and Si_3N_4-TiB_2 respectively. The presence of crystalline TiO_2 was detected at temperatures higher than ≈700°C in Al_2O_3-TiB_2 and ≈400°C in TiB_2. The oxide scale in monolithic TiB_2 samples is also formed by crystalline B_2O_3 at $T = 700°–800°C$. However at $T > ≈800°C$ only highly textured TiO_2 crystals are detectable (Fig. 2a). The morphology of the crystals are shown in Fig. 3a.

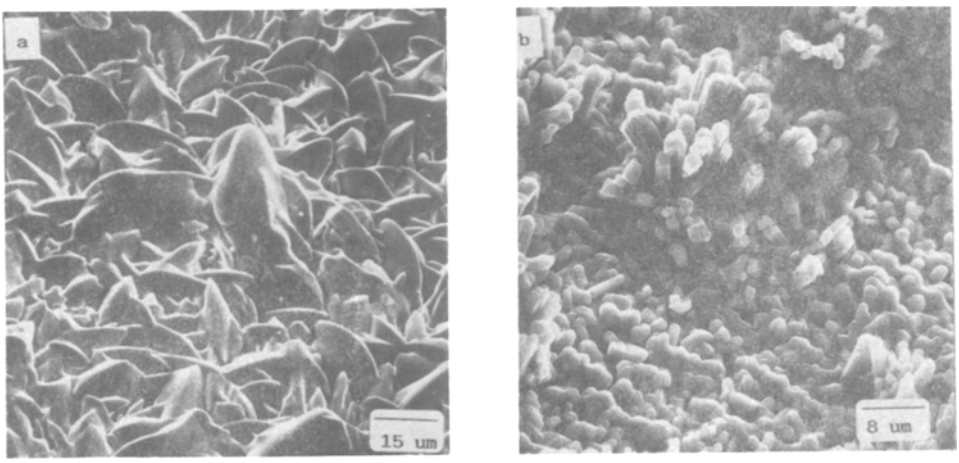

Fig. 3 Microstructure of the oxidized surfaces at 1000°C of: *a*) TiB_2; *b*) Al_2O_3-TiB_2

On the oxidized surface of Al_2O_3-TiB_2, the amount of rutile rapidly increases at $T > 700°C$. Moreover two aluminium borate phases: $Al_4B_2O_9$ at $700°C \leq T \leq 900°C$ and $Al_{18}B_4O_{33}$ at $T > 900°C$, were observed in Al_2O_3-TiB_2 (Fig. 2b). Figure 3b shows the microstructure of the Al_2O_3-TiB_2 oxidized surface at 1000°C characterized by TiO_2 crystals forming a thick oxide scale.

In the silicon nitride-based composites, up to ≈ 1000°C only the second phase undergoes an oxidation reaction and certain amount of rutile is observed at $T \geq 700°C$. At $T > ≈ 1000°C$, where the Si_3N_4 matrix is also involved in the oxidation reaction producing mainly SiO_2 and yttrium silicates, some reactions take place on the oxide scale among SiO_2, TiO_2 and Y-silicates. These reactions produce on the oxide scale after cooling the formation of $Y_2Ti_2O_7$, glassy silicate phase, crystalline SiO_2 and TiO_2. Figures 4–6 show the evolution of the surface morphology with the oxidation temperature.

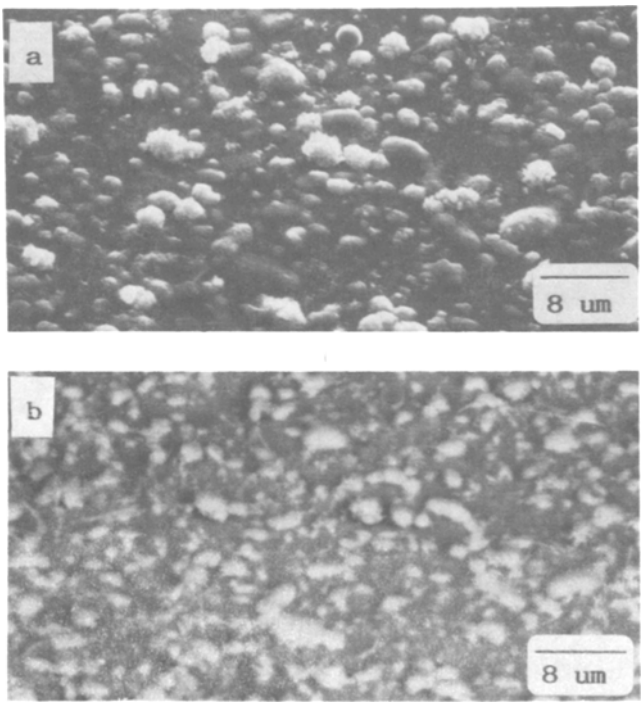

Fig. 4 Microstructure of the surfaces of Si_3N_4-TiB_2 oxidized at 820°C: *a*) morphology; *b*) back-scattered electron image

b) Oxidation kinetics and mechanisms

It is well known that TiB_2 oxidizes according to the chemical reaction:

$$TiB_2 + 5/2O_2 \rightarrow TiO_2 + B_2O_3 \qquad (1)$$

Crystalline B_2O_3 has been observed in monolithic TiB_2 after oxidation at $T = 700°C$ and $T \approx 800°C$.

In Al_2O_3-TiB_2, following the reaction (1), further reactions occur:

$$B_2O_3 + 2Al_2O_3 \rightarrow Al_4B_2O_9 \qquad \text{at } T < \approx 900°C$$

$$2B_2O_3 + 9Al_2O_3 \rightarrow Al_{18}B_4O_{33} \qquad \text{at } T > \approx 900°C$$

In Si_3N_4-TiB_2 composites, the main chemical reactions involved (following reaction 1) are:

$$B_2O_3 + 3O_2 + Si_3N_4 \rightarrow B_2O_3{\cdot}SiO_2 \text{ (glass)} + 2SiO_2 + 2N_2$$

minor reaction:

$$2TiO_2 + 2Y^{3+} + 3O^{2-} \rightarrow Y_2Ti_2O_7$$

Monolithic TiB_2

The set of curves in Fig. 1a may be fitted using two kinetic models:

1) diffusion-controlled kinetics $(DW/S)^2 = kt$, where k is the oxidation rate constant, valid up to $T \approx 900°C$ for the entire isothermal run; at 1000°C up to about 800 min, and at 1100°C up to ≈ 500 min;

2) linear behaviour $(DW/S \approx kt)$ for longer periods at 1000°C and 1100°C. In this case the large volume expansion that occurs during the reaction $TiB_2 \rightarrow TiO_2$ may cause cracking on the oxide layer, resulting in an increase in the active area for oxidation and in a heterogeneous diffusion in the barrier layer.

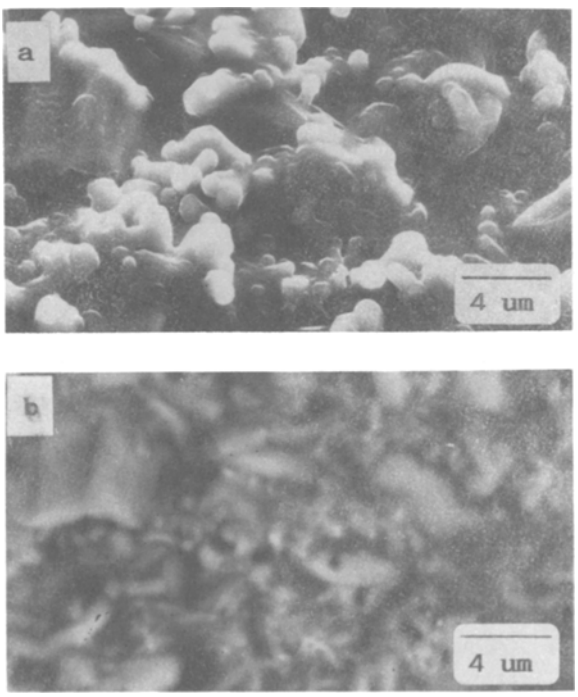

Fig. 5 Microstructure of the surfaces of Si_3N_4-TiB_2 oxidized at 1020°C: *a*) morphology; *b*) back-scattered electron image

Al_2O_3-TiB_2 composite

The thermal stability of this material is directly related to the oxidation of the dispersoid particles, which are present on the surface and/or connected to the surface through open porosity channels. The weight gain curves (Fig. 1b) indicate

diffusion-controlled kinetic, i.e. one-dimensional diffusion $(DW/S)^2 \approx kt$, at $T = 700^{\circ}C$ and $800^{\circ}C$, and two-dimensional diffusion $(1-\alpha)\cdot\ln(1-\alpha+\alpha) = kt$ (where α is supposed equal to $(DW/S)_{(t)}/(DW/S)_{(max)}$ and it is used as a mathematical artifice in order to define the kinetic relationship) at $T \geq 900^{\circ}C$. Actually the two-dimensional diffusion equation elaborated on the basis of a model for cylindrical particles can justifiably be proposed to explain the phenomenologies in our system, as it shows the development of needle-like and rod-shaped particles starting from $700^{\circ}C$, when the volume of the products is different from that of the reactants. Moreover, this second oxidation regime corresponds approximately to the temperature ($\approx 900^{\circ}C$) that allows the formation of a continuous oxide scale.

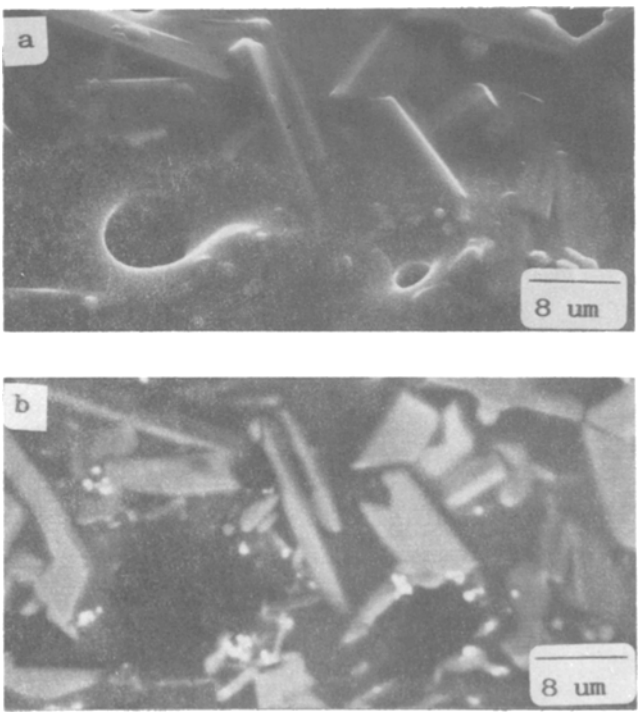

Fig. 6 Microstructure of the surfaces of Si_3N_4-TiB_2 oxidized at 1210°C: *a*) morphology; *b*) back-scattered electron image

The oxidation curve $T = 1100^{\circ}C$ presents a discontinuous trend around $T = 200^{\circ}C$ that could be attributed to a changing in the oxidation mechanism from a parabolic behaviour to a linear one caused by the breaking of the continuous oxide scale formed during the initial stage of the oxidation reaction.

Si_3N_4-TiB_2

From the analysis of the plots in Fig. 1c, three different oxidation regimes can be identified: at low ($< \approx 1000°C$), intermediate ($\approx 1000 < T < \approx 1200°C$) and high ($> \approx 1200°C$) temperature.

1) In the low-temperature range ($< \approx 1000°C$) the thermal stability of the composites does not involve Si_3N_4, therefore it is affected only by the reaction of $TiB_2 \rightarrow TiO_2$, with an evident bulking on every TiB_2 starting particle (Fig. 4a). At $T > \approx 800°C$ a more enhanced reaction of TiB_2 to TiO_2 rutile gives rise also to a further reaction of TiO_2 with the secondary phase (Y-silicate) producing some $Y_2Ti_2O_7$ needle like crystals as shown in back scattered electron image in Fig. 4b, SiO_2 (from a slight oxidation of Si_3N_4) also forms.

2) In the range $\approx 1000 < T < \approx 1200°C$, the thermal stability of the composite is dependent on the oxidation of both the matrix and the second phase, particularly at $T > \approx 1100°C$. Weight gain against time could fit the parabolic law and it could stand for a fairly protective action of the oxide scale. The surface of the oxidized sample is completely covered by a scale of TiO_2 crystals as shown in Fig. 5a. A large amount of SiO_2 and $Y_2Ti_2O_7$ form as a result of the oxidation of Si_3N_4 and of the diffusion of Y from the bulk to the reaction interface [11]. The morphology of these oxidation products are highlight by the back-scattered image in Fig. 5b.

3) At $T > \approx 1200°C$, weight gains after an initial parabolic stage tend to fit linear kinetics. Boric glassy phase forms in enhanced amounts and increases the

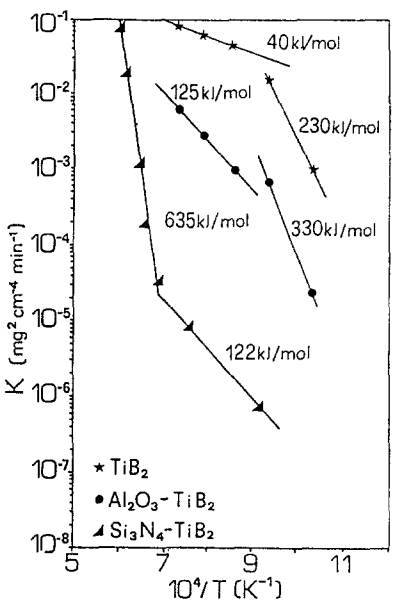

Fig. 7 Arrhenius plot of oxidation rate constants of TiB_2, Al_2O_3-TiB_2 and Si_3N_4-TiB_2

oxidation rate of Si_3N_4. As the Si_3N_4 matrix oxidizes, additional TiB_2 particles are encountered and oxidized; these provide more boron to flux the Si_3N_4 matrix. The fluid borosilicate glass allows oxygen to penetrate deeply into the body of the composite, which leads to additional attack of both TiB_2 and Si_3N_4. The oxide scale at $T > \approx 1200^\circ C$ does not protect the bulk from further oxidation and the linear kinetics are detected.

The Arrhenius plot of oxidation rate constants k against temperature are shown in Fig. 7.

For TiB_2, where diffusion-controlled mechanisms were found to be valid, the apparent activation energy is, at $T < 900^\circ C$, $E_a \approx 230$ kJ/mol and at $T > 900^\circ C$, $E_a \approx 40$ kJ/mol.

For Al_2O_3-TiB_2, at $T < 900^\circ C$ (parabolic kinetics), $E_a \approx 330$ kJ/mol and at $T > 900^\circ C$, (two-dimensional-diffusion regime), $E_a \approx 125$ kJ/mol.

For Si_3N_4-TiB_2, the main feature is a net change in the slope at $T \approx 1100^\circ C$ (the temperature at which oxidation of Si_3N_4 is massive). At $800 < T < 1100^\circ C$ the apparent activation energy E_a results ≈ 120 kJ/mol, a value that has been previously found for the diffusion of oxygen through silica or glassy silicates. In this case the diffusion of O_2 or N_2 through a complex layer (with TiO_2, SiO_2, $Y_2Ti_2O_7$ and glassy silicates) could be proposed as the rate limiting process.

At $T > \approx 1100^\circ C$, E_a results ≈ 630 kJ/mol, about the same value determined for the baseline Si_3N_4 constituting the matrix of the composite [11]. With regard to this baseline silicon nitride, the diffusion of additives and impurities cations across the grain boundary phase channels to the reaction interface has been indicated as the governing step for oxidation [11]. In the case of the composites, an evident decrease in the oxidation resistance is associated with the presence of TiB_2. At temperatures $> \approx 1100^\circ C$, the compositional and microstructural characteristics of the surface of Si_3N_4-TiB_2 composites result in a very complex system that makes the investigation of the reaction mechanisms difficult. They depend on the relative migration velocities of all the mobile participants across a particulary complex and inhomogeneous barrier layer and on the reactions that are sensitive to the local concentration of the various reacting species. Variation of thermodynamic parameters and oxidation products are associated with modification of the composition, the viscosity and morphology of the secondary phases and of the oxide scale.

Conclusions

The use of thermogravimetric analysis for the weight change during oxidation of TiB_2, and of the composites Al_2O_3-TiB_2 and Si_3N_4-TiB_2, combined with the analysis of the reaction products, allows the determination of kinetics and thermodynamic parameters of the process and the identification of the rate-control-

ling step. This can be used to suggest phenomenological models for the processes involved.

The oxidation of monolithic TiB_2 and of composites containing TiB_2 results in different behaviours and mechanisms depending on the temperature and time.

For TiB_2:

1) In the range $400^\circ \leq T \leq 900^\circ C$ and in the first stage of the oxidation at 1000° and $1100^\circ C$, the reaction is governed by a diffusion mechanism and crystalline TiO_2 and B_2O_3 are detected on the oxide scale.

2) During isothermal treatments at 1000° and $1100^\circ C$, longer than 8 and 13 hours respectively, the increase in the active area for oxidation causes a mechanism governed by a linear law, the oxide scale being composed only of highly textured TiO_2 crystals.

For Al_2O_3-TiB_2:

1) In the temperature range from about 700° to about $900^\circ C$ a one-dimensional diffusion mechanism characterizes the rate governing step of the oxidation reaction. TiO_2 (rutile) and $Al_4B_2O_9$ are the crystalline phases observed on the oxidized surfaces.

2) At $T > \approx 900^\circ C$ two-dimensional diffusion can be identified as the rate-governing step and the oxide scale is composed of highly oriented TiO_2 and $Al_{18}B_4O_{33}$.

For Si_3N_4-TiB_2:

1) Up to $T \approx 1000^\circ C$ only the reaction of TiB_2 to TiO_2 and B_2O_3 is observed.

2) At $\approx 1000^\circ < T < \approx 1200^\circ C$ the rate limiting step could be the diffusion of O_2 or N_2 through a TiO_2-rich silicatic layer.

3) At $T > \approx 1200^\circ C$ a linear kinetic indicates the formation of a non-protective scale, which is very thick and whose morphology signifies a very fluid phase (may be a boric glass) that increases the oxidation rate of both TiB_2 and Si_3N_4.

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Zusammenfassung — Im Hinblick auf die Neigung von TiB_2 zur Oxidation wurde die thermische Stabilität von monolytischem TiB_2 und der Gemische Al_2O_3-30Vol% TiB_2 sowie Si_3N_4-20Vol% TiB_2 untersucht. Die Temperatur, bei der TiB_2 Keramik beginnt zu oxidieren, liegt bei 400°C, die Oxidationskinetik wird bis zu T=900°C und im ersten Schritt der Oxidation bei 1000° bzw. 1100°C (bis zu 800 bzw. 500 min) durch Diffusion beherrscht, bei höheren Temperaturen und längeren Zeitabschnitten durch ein lineares Gesetz.
Eine Gewichtszunahme kann bei Al_2O_3-TiB_2-Gemischen nur bei Temperaturen oberhalb etwa 700°C beobachtet werden und der geschwindigkeitsbestimmende Schritt der Oxidationsreaktion ist bei T=700°C bzw. T=800°C durch einen eindimensionalen, bei höheren Temperaturen durch einen zweidimensionalen Diffusionsmechanismus charakterisiert.
Bezüglich des Si_3N_4-TiB_2-Gemisches wurden in Abhängigkeit von der Temperatur drei verschiedene Oxidationsverhalten beobachtet: bis etwa 1000°C betrifft die Reaktion nur die zweite Phase; bei Temperaturen zwischen 1000° und 1200°C wird die Diffusion von O_2 oder N_2 durch eine Oxidschicht als geschwindigkeitsbestimmender Schritt vorgeschlagen; bei Temperaturen oberhalb 1200°C zeigt eine lineare Kinetik die Bildung einer nichtschützenden dünnen Schicht