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A Ceramic Matrix Composite Obtained by Highly Exothermic Reaction

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Abstract

Ceramic–metal composites have been obtained by the highly exothermic reaction between an intermetallic, Al_2Zr, and an oxide, Nb_2O_5. The reaction has been studied for different conditions of time, temperature and furnace atmosphere. Samples have been prepared with different amounts of Al_2O_3, added as a diluent, to control the reaction. The resulting microstructure, characterized by X-ray diffraction, optical microscopy and electron microscopy, always shows a dendritic or globular phase of ZrO_2, a eutectic region of Al_2O_3 and ZrO_2, and large, predominantly metallic, inclusions consisting of niobium with associated niobium oxides.

Keramik–Metall-Verbundwerkstoffe wurden durch die äußerst exotherme Reaktion zwischen intermetallischem Al_2Zr und oxidischem Nb_2O_5 hergestellt. Die Reaktion wurde bei verschiedenen Zeiten, Temperaturen und Ofenatmosphären untersucht. Die Proben wurden zur Kontrolle der Reaktion mit verschiedenen Mengen an Al_2O_3 verdünnt. Die sich ergebenden Gefüge wurden mittels Röntgenbeugung, Lichtmikroskopie und Elektronenmikroskopie untersucht. Es zeigte sich in allen Proben eine dendritische oder globulare ZrO_2-Phase, ein eutektischer Bereich aus Al_2O_3 und ZrO_2 und große, vorwiegend metallische Einschlüsse aus Niob mit benachbarten Nioboxiden.

On a élaboré des composites céramique–métal par mise en oeuvre de la réaction hautement exothermique entre l'intermétallique Al_2Zr et l'oxyde Nb_2O_5. Cette réaction a été étudiée pour différentes conditions de température, de temps et d'atmosphère du four. On a préparé des échantillons présentant différentes teneurs en Al_2O_3, ajoutée comme diluant afin de contrôler la réaction. La microstructure finale obtenue, caractérisée par diffraction X et microscopies optique et électronique, présentait toujours une phase ZrO_2 dendritique ou globulaire, un domaine eutectique d'Al_2O_3 et ZrO_2 et des inclusions de grande taille majoritairement métalliques constituées de niobium, auxquelles étaient associées des oxydes de niobium.

1 Introduction

The fabrication of ceramics with improved toughness continues to be one of the most demanding

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research topics for materials scientists. Efforts have usually been directed to the production of components with smaller critical flaw size or of components with toughened microstructures, obtained by the addition of fibres, metallic phases or phases which allow transformation toughening. Progress has been made using all of these techniques, but an economic process has yet to be developed, and usually the materials continue to be sensitive to defects introduced during fabrication or use. An interesting alternative route involves the use of exothermic reactions, which have increasingly been used for the production of ceramics or ceramic–matrix composites having complex microstructures and improved toughness.[1–4] The reactions can be grouped into those involving a gas phase (for example reaction-bonded silicon nitride), those involving a liquid phase (metal infiltration), and self-sustaining reactions such as high-temperature syntheses (self-propagating high-temperature synthesis), which may include reaction sintering or exchange reactions.[1,2]

Methods involving self-sustaining reactions are in principle simple and cost-competitive, since the temperatures necessary for the process result from the heat liberated by the exothermic reactions. In a process with no control of the reaction the heat generated can be sufficient to melt the products completely and the resultant material is then formed by a conventional solidification process. However, if the reaction is not exothermic or is controlled by the addition of diluents, the maximum temperature can be reduced and the formation reaction takes place by solid-state diffusion. The ideal process to obtain a dense microstructure would then be by means of a self-sustained reaction controlled with diluent addition, or by partial oxidation of the reactants. This situation could then represent a variation of the method of reaction sintering, in which the control of microstructure is possible and which has produced interesting results. For example, in the production of reaction-bonded SiC[5,6] the pores are filled by the infiltration of molten silicon by capillary action, with a highly controlled reaction.[7] In work involving an exchange reaction an improved toughness of the resultant zirconia-containing composite was measured;[8] these and other studies represent a continuing interest in such solid-state reactions.[9–14] Highly exothermic reactions can produce microstructures equivalent to those obtained by reaction sintering, provided the reaction can be limited in such a manner as to produce this controlled reaction. Such work is the subject of the present paper.

Exothermic reactions between an intermetallic and an oxide have been carried out with the objective of producing a ceramic–metal composite of improved toughness. The reaction

$$Al_2Zr + Nb_2O_5 \rightarrow ZrO_2 + Al_2O_3 + 2Nb$$

is of interest, since the resulting system can incorporate a variety of toughening mechanisms which are known to be operative in ceramic materials. These include plastic deformation of a metallic phase, transformation toughening due to ZrO_2, and crack deflection by fibres if Al_2O_3 fibres are added as a diluent to control the reaction.

2 Experimental procedure

The reactions were generated by heating pressed pellets of the intermetallic powder (Al_2Zr) and niobium oxide (Nb_2O_5) under predetermined conditions of time, temperature and furnace atmosphere.

The Al_2Zr intermetallic was produced by melting a stoichiometric mixture of metallic powders of aluminium and zirconium in an arc furnace. Aluminium was purchased in the powder form and the zirconium as a sheet which was hydrogen embrittled prior to ball-milling for conversion to a similar grain size to the aluminium. The intermetallic product of melting was characterized by X-ray diffraction and then ground to a maximum grain size of 37 μm.

The pellets for the reaction were prepared by mixing together powders of the intermetallic and of niobium oxide in appropriate proportions and by die pressing without binders under a pressure of 100 MPa. Alumina (A-16, Alcoa, Chemicals Division, Pittsburgh) was added to some samples as a diluent to inhibit the reaction, the amount varying from 5% to 60% by weight.

The reaction treatments were performed in the temperature range 700 to 1400°C under vacuum, in air and in an argon atmosphere with times varying from 1 to 4 h and with heating rates varying from 50 to 500°C/min.

The samples resulting from the reaction were analysed by X-ray diffraction, scanning electron microscopy (Hitachi S530), transmission electron microscopy (Jeol JEM 400FX and Philips CM12) and microprobe analyser (CAMECA CAMEBAX).

3 Results and discussion

Table 1 shows the conditions of the reaction treatments, the types of reaction observed, and the

Table 1. Treatment conditions, types of reaction observed and resulting phases

Atmosphere	*Sample*	*Al_2O_3 (wt%)*	*T (°C)*	*t (h)*	*Reaction*	*Resulting phases*
Vacuum	01	0	900	—	Violent	Nb, Nb_2O_5, Al_2O_3, ZrO_2
	31	0	1 400	1	Violent	Nb, Al_2O_3, ZrO_2
	32	5	1 400	1	Violent	Nb, Al_2O_3, ZrO_2
	33	0	750	—	Violent	Nb, Al_2O_3, ZrO_2
	L1	20	700	3	No reaction	Nb_2O_5, Al_2O_3, Al_2Zr
	L2	20	900	3	Controlled	Nb, Al_2O_3, ZrO_2
	L3	20	1 100	3	Controlled	Nb, Al_2O_3, ZrO_2
	L4	20	1 400	3	Controlled	Nb, Al_2O_3, ZrO_2
	X2	5	1 400	3, 5	Controlled	Nb, Al_2O_3, ZrO_2
	X5	0	1 400	4	Controlled	Nb, Al_2O_3, ZrO_2
Argon	09	0	900	2	No reaction	Nb_2O_5, Al_2O_3, Al_2Zr
	22	0	1 100	4, 5	Controlled	Nb, Al_2O_3, ZrO_2
	23	30	1 100	4, 5	Controlled	Nb, Al_2O_3, ZrO_2
Air (50°C/min)	03	0	900	1	Oxidation	Nb_2O_5, Al_2O_3, ZrO_2
	L6	20	900	3	Oxidation	Nb_2O_5, Al_2O_3, ZrO_2
	L7	20	1 100	3	Oxidation	Nb_2O_5, Al_2O_3, ZrO_2
Air (500°C/min)	53	0	1 100	—	Violent	Nb, Al_2O_3, ZrO_2
	54	0	1 100	—	Violent	Nb, Al_2O_3, ZrO_2
	55	0	1 100	—	Violent	Nb, Al_2O_3, ZrO_2

resulting phases which were identified by X-ray diffraction. The samples treated in vacuum and in argon were heated at a low rate, of the order of 50°C/min, and the samples treated in air were heated at increasing rates up to 500°C/min. The temperatures indicated in Table 1 are the final temperature of the furnace.

Four distinct forms of behaviour were observed after the treatments:

(i) no reaction;
(ii) violent exchange reaction;
(iii) controlled exchange reaction; and
(iv) oxidation of the intermetallic.

Samples treated under argon atmosphere or in vacuum and at temperatures below 900°C did not react, suggesting that an ignition temperature above this temperature is required to start the reaction. In fact, for most samples which reacted, the ignition temperature was measured and always found to be in the region of 900°C.

Samples containing a low amount or no diluent heated under vacuum and samples heated in air with high heating rates and the furnace temperature above the ignition temperature always showed a self-sustaining, violent reduction/exchange reaction with a rapid increase in temperature immediately after reaching the ignition temperature. The reaction resulted in the formation of the expected phases, with two oxides, Al_2O_3 and ZrO_2, and one metallic phase, Nb. For the conditions outlined the samples lost their original shape, since the rise in temperature was sufficient to melt the products completely. Thermodynamic calculations[15] estimated the maximum temperature of the reaction to be around 2700°C for the stoichiometric mixtures heated to the ignition temperature. The reaction can be self-sustaining, leading to complete melting unless some form of diluent is added to absorb heat and control the maximum temperature rise of the sample. The exceptions to this behaviour were samples X2 and X5, where violent reaction was probably prevented by the partial oxidation of the intermetallic phase during heating at low rates (50°C/min).

Samples with high volume fractions of diluent, or samples heated under conditions which could partially oxidize the intermetallic phase, showed a controlled reaction, probably because the pre-oxidation inhibited the triggering of the reaction in the self-sustaining mode. For such cases there was no significant sudden increase in temperature and the samples maintained their original shape, independent of the localized fusion of the product phases. These were found to be the expected phases, Al_2O_3, ZrO_2 and Nb. The effect of pre-oxidation of the intermetallic was also confirmed by the result of sample 33. This sample, which was prepared under controlled conditions in a glove box and which was then protected by toluene while being transferred to the vacuum furnace, showed a violent reaction at 750°C, which is considerably lower than the normal ignition temperature of approximately 900°C exhibited by all the other samples.

Finally, the samples heated in air with low heating rates always showed complete oxidation of the intermetallic, resulting in the presence of three oxide phases, Nb_2O_5, Al_2O_3 and ZrO_2, in the product.

All samples which reacted as expected, that is with the reduction of the niobium oxide, showed a complex microstructure, formed basically by the phases Al_2O_3, ZrO_2 and metallic Nb. These were identified by X-ray diffraction and by microanalysis in a CAMECA microprobe. The X-ray diffraction results occasionally showed peaks of low intensity which could not be identified and could well be due to small amounts of metastable phases formed as a result of the rapid solidification.

Figure 1 shows a SEM micrograph of sample 31, which had undergone a violent reaction, probably with total fusion of the products. The microstructure is typical of most samples which underwent the exchange reaction; a metallic phase is distributed in a ceramic matrix formed by a dendritic or spheroidal phase together with a lamellar eutectic. The metallic region was observed to occur in two different morphologies, either spread over large areas of the sample, as in Fig. 1, or as large spheroidal inclusions surrounded by the ceramic phases, as observed in sample 33 shown in Fig. 2. The predominantly metallic areas are formed of two distinct phases, one of pure Nb and the other of niobium oxide or niobium sub-oxides. The oxide phases were identified by microanalysis in all samples, but could not be detected by X-ray diffraction, except in the case of sample 01.

Figure 3 is a SEM micrograph of sample 32 showing details of the ceramic matrix. The Al_2O_3 added as diluent in this sample could not be identified in the microstructure, a further indication of the very high temperatures reached during the reaction.

Microanalysis of the ceramic matrix showed for all samples that the eutectic region was formed predominantly of Al_2O_3 and ZrO_2, and that the dendritic or spheroidal phase was formed exclusively of ZrO_2.

The composition of the eutectic was different in samples resulting from the violent reaction as

Fig. 1. SEM micrograph of sample 31 which reacted in a violent mode. Region marked 1 is representative of the predominantly metallic inclusions, formed by Nb and niobium sub-oxides; region marked 2 is representative of the ZrO_2 dendrites; and region marked 3 is representative of the Al_2–ZrO_2 eutectic.

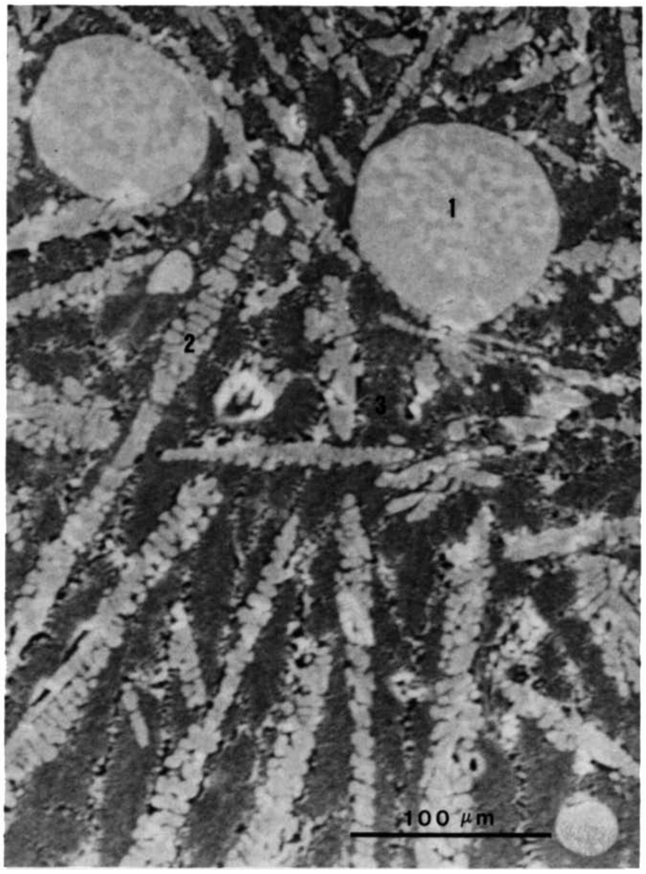

Fig. 2. SEM micrograph of sample 33 with the predominantly metallic inclusions (marked 1) surrounded by the ceramic phases: dendrites of ZrO_2 (marked 2) and the Al_2O_3–ZrO_2 eutectic (marked 3).

compared to samples which had reacted in a controlled mode. However, within each of these two groups, the composition did not vary greatly; violent reactions resulted in eutectic compositions of approximately 62 wt% Al_2O_3, 36 wt% ZrO_2 and 2 wt% Nb, whereas controlled reactions resulted in eutectics with approximately 43 wt% Al_2O_3 and 57 wt% ZrO_2, with no indication of niobium. Considering the high cooling rates which the samples experience after the violent reaction and the ternary or quaternary systems involved, the eutectic compositions obtained for the Al_2O_3–ZrO_2 system[16] are quite reasonable. In the case of controlled reactions somewhat larger discrepancies would be expected, since the temperature does not rise high enough to homogenize the alloy.

The niobium which appeared in the eutectic region could be identified as small inclusions between the two colonies of eutectics, suggesting that it had not melted completely, as occurred when there was metal segregation. However, a metallic niobium phase which had degenerated to form an individual lamella of the eutectic could also be observed.

Although the individual lamellae of the eutectic could not be analysed in the CAMECA microprobe, they could be identified by atomic number contrast in the SEM micrographs and also could be characterized by EDS analyses using a very small spot size in the STEM mode on the Philips microscope. Figure 4 is an example of the eutectic region of sample 33 imaged in the TEM mode, showing in detail the Al_2O_3 and ZrO_2 lamellae, appearing as bright and dark areas respectively.

The different globular morphology observed in the ZrO_2 phase is shown in Fig. 5, which is a SEM micrograph of sample 01. This characteristic was observed in sample 01, where the presence of Nb_2O_5 suggested that the reaction occurred at relatively low temperature; where the samples were of small dimensions, the faster solidification rate then prevented formation of the dendritic morphology.

Figure 6 shows SEM micrographs of sample X5. This microstructure is typical of all samples which reacted in the controlled mode. The microstructure indicates the occurrence of localized fusion of the products, which, with the consequent contraction on solidification, resulted in a porous sample. However, in the areas where the reaction occurred, the microstructure is dense, and is formed mainly of the Al_2O_3–ZrO_2 eutectic. As previously discussed, this contained more ZrO_2 than would be expected for

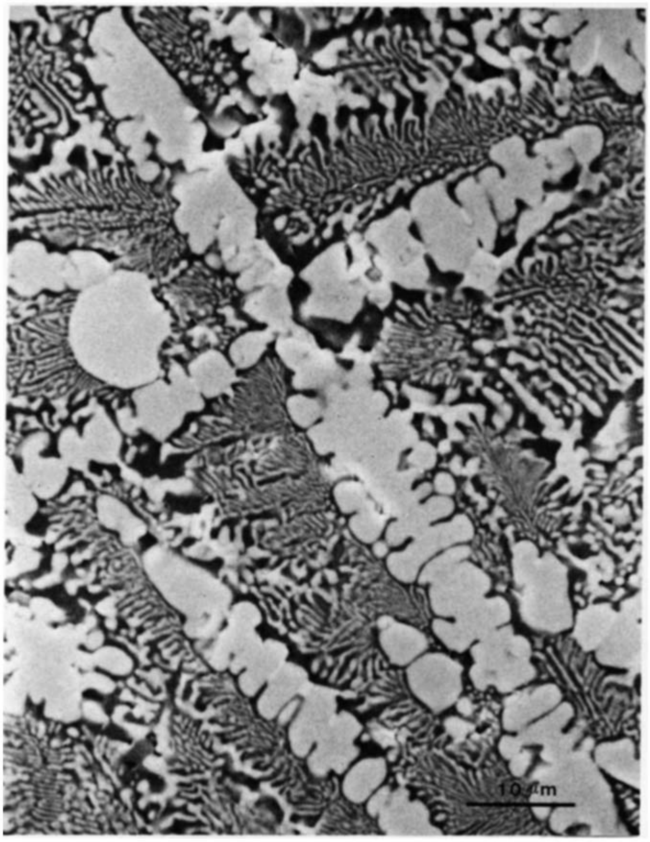

Fig. 3. Detail of the ZrO_2 dendrites and Al_2O_3–ZrO_2 eutectic observed in sample 32.

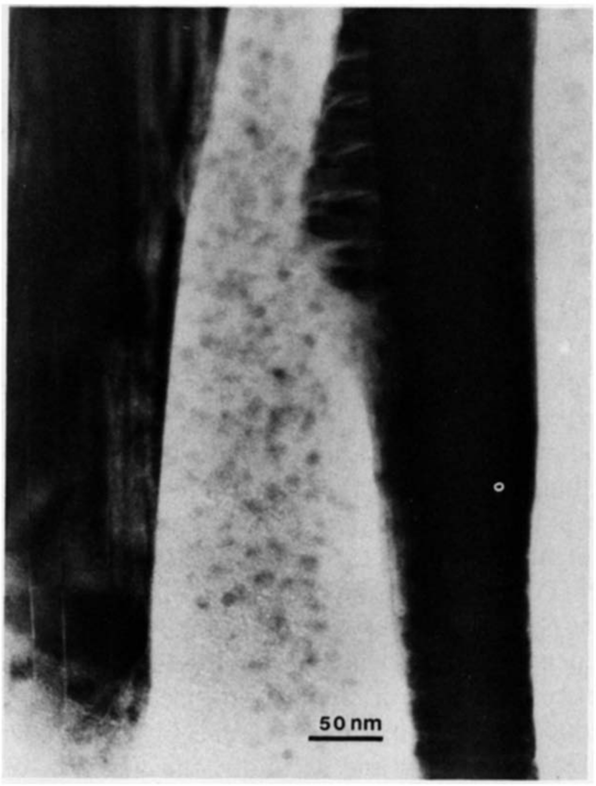

Fig. 4. TEM image of a eutectic region of sample 33; the dark lamella is formed of ZrO_2 and the bright lamella is formed of Al_2O_3.

Fig. 5. SEM micrograph showing a globular morphology of the ZrO_2 phase observed in sample 01. Again, marks 1, 2 and 3 are representative of the predominantly metallic region, ZrO_2 dendrites and Al_2O_3–ZrO_2 eutectic, respectively.

this system under equilibrium conditions. Although no dendrites of ZrO_2 nor large metallic areas were observed, the ZrO_2 and the Nb phases could be identified by microprobe analysis in the regions surrounding the eutectic phases.

4 Conclusions

Highly exothermic reaction between the intermetallic, Al_2Zr, and Nb_2O_5 has been used to obtain composites having a complex microstructure containing two ceramic phases and one metallic phase. Two types of reaction have been observed, one violent with complete fusion of the products and the other controlled with partial fusion of the products. The occurrence of each type of reaction was strongly dependent on two factors: firstly, the competition between oxidation of the intermetallic and the reduction of the oxide before reaching the temperature of reaction; and secondly, the addition of a diluent to absorb the heat generated by the reaction. The microstructures resulting from the violent reaction showed a dendritic or globular phase of ZrO_2, a eutectic region formed basically of Al_2O_3 and ZrO_2, and large, predominantly metallic, inclusions formed by Nb associated with niobium oxides. These same phases were also observed in the microstructures resulting from controlled reactions. A different morphology was associated with the ZrO_2 and the Nb phases, despite the formation of the Al_2O_3–ZrO_2 eutectic.

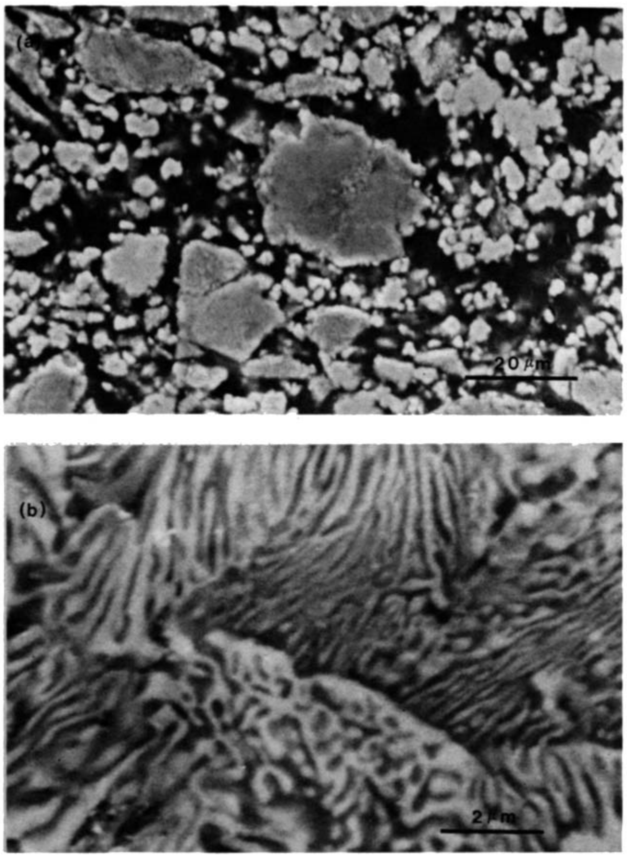

Fig. 6. (a) SEM micrograph of sample X5, representative of all samples which reacted in a controlled mode. (b) Detail of the Al_2O_3–ZrO_2 eutectic.

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