A new route for the synthesis of SiC–$MoSi_2$ ceramic composite materials

F. J. Narciso-Romero, A. Sepúlveda-Escribano and F. Rodríguez-Reinoso*

Departamento de Química Inorgánica, Universidad de Alicante, Aptdo. 99, E-03080 Alicante, Spain

SiC–$MoSi_2$ ceramic composite materials with controlled molybdenum content can be prepared by reaction of silicon with previously formed molybdenum carbide.

Reaction-bonded silicon carbides (RBSC) are fully dense engineering ceramics formed by the bonding together of silicon carbide powders with further silicon carbide produced *in situ* by chemical reaction between silicon and carbon.[1] Fabrication of RBSC involves the forming of a compact of silicon carbide, graphite and a polymeric binder by various standard formation routes such as extrusion and pressing. The compact is then heated in air to remove the binder and the resulting porous compact infiltrated with liquid silicon. The silicon rises through the porous material by capillary action, reacting with the graphite to form new silicon carbide which 'bonds' the material together. The final material consists of a matrix of SiC, with 10–55% silicon occupying the residual pore space. The presence of Si drastically reduces the mechanical properties of RBSC materials at temperatures higher than 1600 K (mp of Si = 1683 K). Thus, it would be interesting to find new processing routes for silicon carbide advanced ceramics yielding low residual free silicon contents. One possibility is the replacement of free silicon by a refractory metal disilicide;[2–4] in addition to their high melting points, a number of them have a brittle-to-ductile transition temperature at *ca.* 1300 K, and this phenomenon may allow them to act as a dispersed ductile phase at high temperatures. The main problem of the infiltration with Si–Mo alloys in the carbon preform is that the maximum percentage of Mo in the alloys must be only of the order of 5%; if this is higher, the melting point of the alloy is too high, and infiltration is impossible since the reaction between silicon and carbon is very fast and stops the infiltration. Here, we report the formation of a silicon carbide–molybdenum disilicide composite material from silicon, carbon and a molybdenum precursor salt. It is shown that molybdenum carbide is formed, in a first stage, at low temperature and then silicon reacts at higher temperature with both carbon and molybdenum carbide. The advantage of the method proposed here is based on the control of the content of Mo, which in this method may be higher (between 0 and 25 mass% of Mo) than in previous systems described in the literature.

The formation of molybdenum carbide has been studied by using graphite (from Merck), with a BET surface area (N_2, 77 K) of 2 m^2 g^{-1}, as the carbon source. Samples have been prepared by immersion of graphite in water–ethanol solutions of ammonium heptamolybdate (10 cm^3 of solution per gram of carbon) with the appropriate concentration to achieve molybdenum loadings of 5, 10 and 20 mass%, at room temperature. The excess of solvent was evaporated by gently heating to dryness while the slurry was magnetically stirred. The decomposition of the molybdenum precursor and the reaction of species formed by reaction with graphite in an inert atmosphere were followed by TG-DTA and mass spectrometry. A sample with 20 mass% Mo was treated in flowing nitrogen (100 cm^3 min^{-1}) at 1173 K for 2 h in a horizontal furnace and the phase composition of the resulting material was analysed by X-ray diffraction.

Fig. 1 shows the TG–DTA thermograms obtained when heating the 20% Mo–graphite sample in flowing helium, which are qualitatively similar to those obtained with samples having lower Mo content. Three endothermic peaks are observed in the 450–600 K temperature range, corresponding to the decomposition of the molybdenum precursor, as well as a mass loss due to the elimination of water and ammonia. The more important feature is a strong endothermic peak at 1140 K, accompanied by a sudden mass loss (*ca.* 10% in this case), which can be assigned to the reduction of molybdenum oxide (MoO_x at this stage, where x = 2 or 3) to metallic molybenum. The analysis of gases evolved during the heat treatments (Fig. 2) corroborates the water and ammonia evolution in the first stages of the treatment. At higher temperatures, *ca.* 1150 K, the gases evolved are comprised mainly of carbon monoxide produced during the reaction between molybdenum oxide and graphite. A small peak of CO_2 evolution can also be observed at lower temperatures, which can be assigned to the reduction of molybdenum oxide in close contact with graphite taking place before the bulk reaction. This behaviour has also been observed in other C–MO systems (M = metal).[5]

X-Ray diffraction analysis of the 20% Mo–graphite sample treated in flowing nitrogen at 1173 K for 2 h clearly shows the

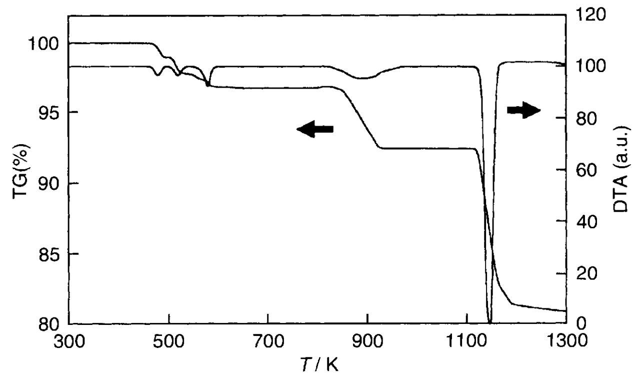

Fig. 1 TG–DTA curves of graphite containing 20% mass of Mo (m_0 = 10 mg, He flow, heating rate 10 K min^{-1})

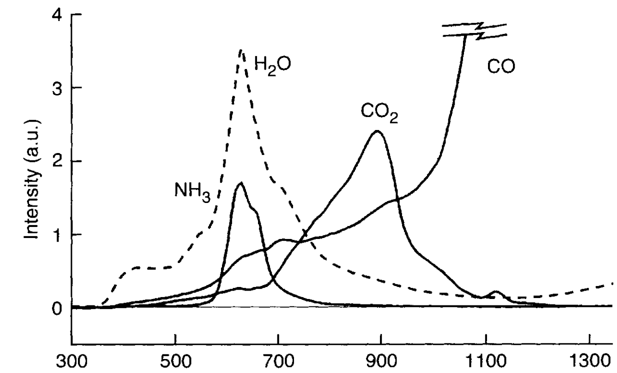

Fig. 2 Evolved gases produced by graphite containing 20% mass of Mo (m_0 = 100 mg, He flow, heating rate 10 K min^{-1})

formation of molybdenum carbide (α-Mo_2C). The enthalpy of the reaction [eqn. (1)], at 1173 K, obtained from differential

$$2\ MoO_3 + 7\ C \rightarrow Mo_2C + 6\ CO \quad (1)$$

thermal analysis experiments, was 173, 175 and 165 kJ mol^{-1} for samples with 5, 10 and 20 mass% Mo, respectively, in good agreement with the value calculated from thermodynamic data, 176 kJ mol^{-1}.

The kinetic analysis of the silicon–graphite reaction in the 1673–1723 K temperature range reveals that silicon carbide is readily formed from silicon and graphite at 1673 K. The reaction rate at 1723 K is much faster than at 1673 K, and this can be explained by bearing in mind that the melting point of silicon is 1685 K and thus, reaction at 1723 K is taking place between liquid silicon and graphite.

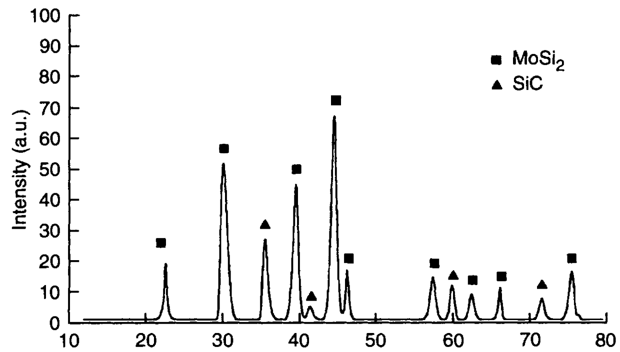

Fig. 3 X-Ray diffraction pattern of graphite with 20% mass of Mo and silicon after thermal treatment at 1723 K, for 5 h

Finally, silicon–graphite ammonium heptamolybdate mixtures with different molybdenum loadings (5 and 20 mass%) were heated in flowing argon (purity 99.999%, 100 cm^3 mm^{-1}) at 1723 K for 5 h. Fig. 3 shows the X-ray diffraction pattern of the material obtained for the mixture containing 20% molybdenum. The presence of both silicon carbide and molybdenum disilicide can be clearly seen. For shorter thermal treatments, small diffraction peaks of another silicide, Mo_5Si_3, can also be observed, this being probably produced at zones having a higher concentration of molybdenum; this product, however, disappears if the treatment is extended to 5 h or longer.

Since the reaction of graphite with molybdenum oxide to form Mo_2C already occurs at 1173 K, further reaction with solid silicon will initially produce SiC and $MoSi_2$ followed by the reaction at higher temperatures, of molten silicon with the unreacted graphite to produce more SiC. SiC and $MoSi_2$ formation takes place at 1500 K and the SiC thus formed exhibits a morphology which is different (more elongated) to that of the SiC produced in the second process.[6] The formation of the two SiC morphologies is governed by two different mechanisms, the first occurring by solid-state diffusion of carbon and silicon, the second by the solution of carbon into silicon, with SiC precipitation.[7]

References

1 J. Ness and T. F. Page, *J. Mater. Sci.*, 1986, **21**, 1377.
2 Y. M. Chiang, R. P. Messner and C. D. Terwilliger, *Mater. Sci. Eng. A*, 1991, **144**, 63.
3 M. Singh and D. R. Behrendt, *J. Mater. Res.*, 1994, **9**, 1701.
4 A. J. Whithead and T. F. Page, *J. Mater. Sci.*, 1992, **27**, 839.
5 D. Cazorla, J. P. Joly, A. Linares, C. Salinas and A. Marcilla, *J. Phys. Chem.*, 1991, **95**, 6611.
6 C. H. Henager and J. L. Brimhall, *Scripta Met. Mater.*, 1992, **26**, 585.
7 X. M. Xi and X. F. Yang, *J. Am. Ceram. Soc.*, 1996, **79**, 102.

Received, 22nd April 1996; Com. 6/02797K