

SYNTHESIS OF A CERAMIC COMPOSITE

MATERIAL: SiC-(W,Mo)Si₂

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SUMMARY: The presence of residual silicon in RBSC pieces reduces their mechanical properties at temperatures higher than 1300 °C (mp of Si = 1410 °C). This work presents the study of the substitution of silicon by a refractory silicide (W,MoSi₂). The preparation variables have been the carbon source (activated carbon, graphite and coke), the particle size and the experimental conditions used. The best results were obtained when a coke of small particle size was used; in this case, even the preparation of pieces of only SiC-Coke (without using of silicide precursor) with no residual silicon was possible. The use of silicide precursor in the preforms allows the synthesis of SiC-(W,Mo)Si₂ pieces that have no residual silicon. In all cases the mechanical properties of pieces are enhanced when silicon is replaced by silicide.

KEYWORDS: Reactive Infiltration, SiC, WSi₂, MoSi₂, Composites

INTRODUCTION

In recent years, there has been an increasing demand for high performance ceramics and composite materials for high temperature aerospace applications. A number of these applications require materials with high strength and toughness, oxidation resistance, and high thermal conductivity at temperatures approaching 1400°C. Among several options, silicon carbide, silicon nitride and SiAlON are the most attractive materials because of their low density, combined with good mechanical properties and chemical stability at high temperatures [1-12].

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 a chemical reaction between silicon and carbon. Fabrication of RBSC involves the forming of a compact of silicon carbide, graphite and a polymeric binder by various standard polymer forming routes such as extrusion and pressing. The compact is then heated in air to remove the binder and the resulting porous compact is infiltrated with liquid silicon. The silicon raises through the porous material by capillary action, reacting with the graphite to form new silicon carbide which "bonds" the material together [13]. The final material consists of a matrix of SiC, with 10 to 55% silicon occupying the residual pore space. The presence of Si drastically reduces the mechanical properties of RBSC materials at temperatures higher than 1300°C (mp of Si = 1410°C). In addition, there are other critical issues in the fabrication of silicon carbide based ceramics which are mainly related to the fabrication of complex shapes, processing time, and temperature. A combination of these factors is the responsible for the high manufacturing cost of the final components [14].

In view of the above considerations, it would be interesting to find a new processing route for silicon carbide advanced ceramics with low residual free silicon content, complex shape capabilities, high strength and toughness, high thermal conductivity, good oxidation resistance, and that can be manufactured by a cost effective process. Several authors have studied the possibility of changing silicon by other refractory materials (silicides, carbides, nitrides and borides) by using two approaches: a) infiltration of the preforms with Si alloys (with Mo, Nb) to produce NbSi_2 and MoSi_2 [14,15], and b) infiltration of the preforms with silicon, but in this case the preforms are composed by SiC, graphite and other material such as ZrC or TiC, to produce the corresponding silicides [16]. Replacement of free silicon by a refractory metal disilicide has certain advantages. In addition to their high melting points, a number of these silicides have brittle-to-ductile transition temperatures around 1000°C . This phenomenon may allow them to act as dispersed ductile phase at high temperatures. These refractory metal disilicides may also provide toughening via dispersed particle toughening mechanisms [14,15,17].

The aim of the present work is to design a new method to introduce Mo and/or W in the carbon preform and to study the related reactions involved in this process, as a previous stage to the study of the kinetics of Si infiltration in these preforms to produce SiC-(Mo,W)Si₂ composites. In this way, the decomposition of metal precursor, and its reaction with a carbon carrier upon heating in an inert atmosphere, have been monitored by several techniques. Also, the phase composition of the materials resulting from these heat treatments has been determined. A second objective is the study of the kinetics of the silicon-carbon reaction, the control of which is of paramount importance in the reactive infiltration processing. Finally, the fabrication of pieces and the analysis of their properties was also studied.

EXPERIMENTAL

Three carbon materials have been used for sample preparation: a) a powdered activated carbon (surface area of $1100\text{ m}^2/\text{g}$), obtained from olive stones by carbonization in flowing nitrogen and further activation with steam, b) powdered graphite with a surface area of $3,5\text{ m}^2/\text{g}$ supplied by Merck and c) premium coke of three different particle sizes (below $20\text{ }\mu\text{m}$, $20\text{-}63\text{ }\mu\text{m}$ and $63\text{-}100\text{ }\mu\text{m}$) supplied by The Carbide/Graphite Group Inc. Particle size of graphite and activated carbon corresponds with medium size coke. Three samples have been prepared with each precursor by impregnation with ethanolic solutions of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ and/or $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, with the adequate concentration to achieve metals loading of 5, 10 and 20 wt%. The carbonaceous material was immersed in the corresponding solution and the solvent was evaporated by gently heating up to dryness, while the slurry was magnetically stirred. The decomposition-reaction of the molybdenum precursor on the samples, upon heating in an inert atmosphere (flowing helium), has been followed by thermogravimetry (TG), differential thermal analysis (DTA) and Mass Spectrometry, with a heating rate of $10^\circ\text{C}/\text{min}$. Samples with 20 wt% Mo were treated in flowing nitrogen at 900°C for 2 h and the phase composition of the resulting material was analyzed by X-Ray Diffraction. To study the kinetics of the silicon carbon reaction, samples with only carbon and silicon were heated in Ar atmosphere at 1400 and 1450°C , for 1, 3, 5 and 10 hours, and the phase composition of the resulting material was analyzed by X-Ray Diffraction.

For the preparation of pieces, carbon samples impregnated with heptamolybdate were treated in flowing nitrogen at 900°C for 5 h, then the products were mixed with a phenolic resin and pelletized by extrusion. Pieces were carbonised in flowing nitrogen at 900°C for 2 h and then infiltrated with silicon in flowing Ar at 1400 and 1450°C during 30 min., 1 h and 5 h. Pieces were analyzed by Scanning Electron Microscopy (JSM 840, from JEOL) fitted with a Link QK 200 dispersive X-ray analyzer and by Reflecting Polarized-light Microscopy (Leica). Microhardness was determined with a Vickers hardness tester. Indentation was measured

using an optical head equipped with a vernier scale giving a potential accuracy in the measurements of $\pm 0.25 \mu\text{m}$. Pieces without molybdenum and/or tungsten were also prepared to compare the resulting materials.

RESULTS AND DISCUSSION

Mo-C. Reaction below 1000°C.

Figure 1 shows the temperature programmed desorption (TPD) profile of evolved gases obtained when heating sample 10% Mo-Coke under flowing helium.

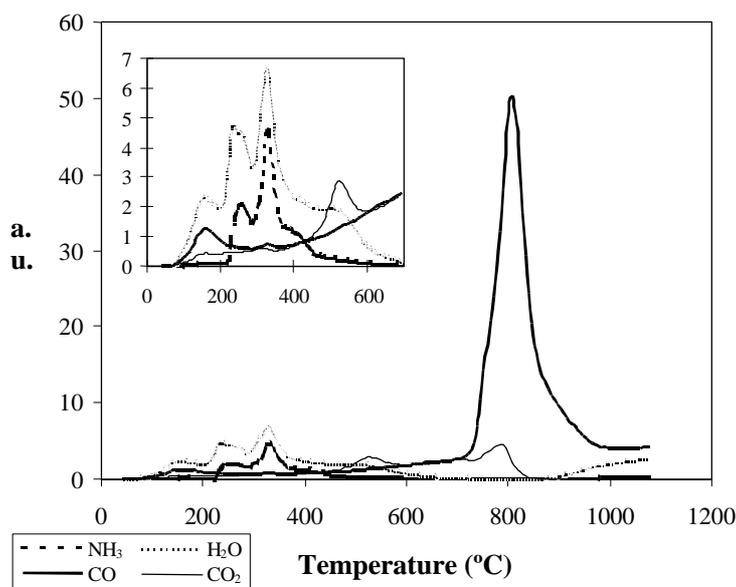


Figure 1. TPD-MS of 10% Mo-Coke under flowing helium

The four TPD peaks observed at lower temperatures correspond with endothermic peaks observed by TG-DTA. The first peak corresponds to the elimination of crystallization water and the elimination of oxygen complexes formed in the process of impregnation when drying the sample in an oven at 110 °C. After the elimination of water, the molybdate complex is decomposed by elimination of NH_3 and H_2O in two steps, that correspond with two different coordination spheres; similar results are observed in other salts such as $\text{CuSO}_4 \cdot 10\text{H}_2\text{O}$ [18]. The final product obtained after this process is molybdenum oxide. At higher temperatures, about 800 °C, the gas evolved contains mainly carbon monoxide, which is produced in the reaction between molybdenum oxide and coke. Similar results are obtained when activated carbon or graphite are used as carbon source. In the case of activated carbon, the temperature at which the reduction takes place is greatly reduced; the endothermic peak appears at 750 °C and the gas evolved is again mainly CO, along with a very small amount of carbon dioxide. Before the large evolution of CO, a small evolution of CO_2 can be observed in some samples. We believe that this evolution corresponds to the reaction between carbon and molybdenum oxide that are in close contact, which takes place before the bulk reaction. This is corroborated by similar results obtained with other C-MeO systems, such as C-CaO [19]. The reaction between the tungsten precursor and the carbon material is less complex and no peaks have been observed below 700 °C. Only one peak appears at 950 °C, corresponding to the evolution of carbon monoxide.

Figure 2 shows the XRD pattern of sample 10% Mo-Coke treated under flowing nitrogen at 900 °C for 2 h. It can be clearly seen that molybdenum carbide (actually, α -Mo₂C) has been formed upon reaction of molybdenum oxide under the experimental conditions used. In the case of the tungsten precursor it is necessary to increase the temperature up to 1000 °C to complete the reaction, and the carbide produced is WC.

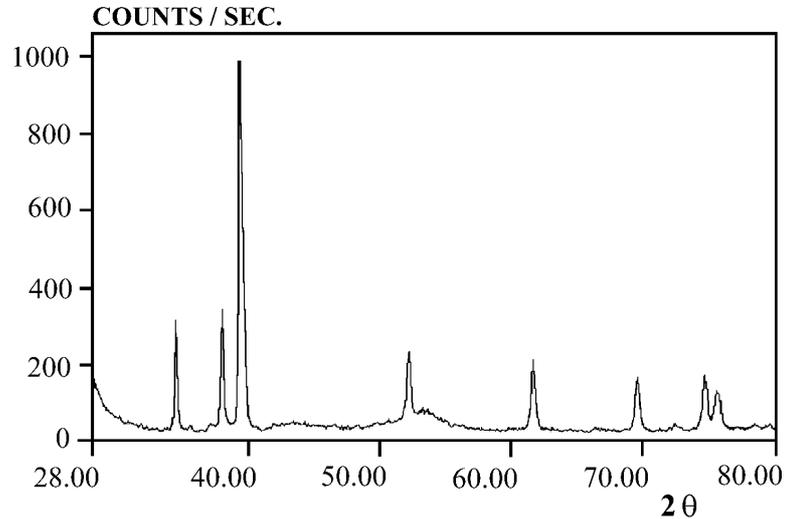


Figure 2. XRD pattern of sample 10% Mo-Coke treated under flowing nitrogen at 900 °C for 2 hours. All peaks correspond to Mo₂C.

Si-C. Reaction at 1000-1500°C.

Figure 3 shows the DRX pattern of a silicon-coke sample treated in Ar at 1450 °C for 5h. The diffraction peaks of the β -SiC phase can be observed, but neither elemental silicon nor carbon were detected in any of the diffracted X-Ray intensity versus scattering angle plots. Thus, the reaction completely transformed the starting materials. Also the typical diffraction peak ($2\theta=35$) associated with the defects of stacking observed when this SiC is obtained by carbothermal reaction between SiO₂ and C [20] at similar temperatures, is not observed in these experiments.

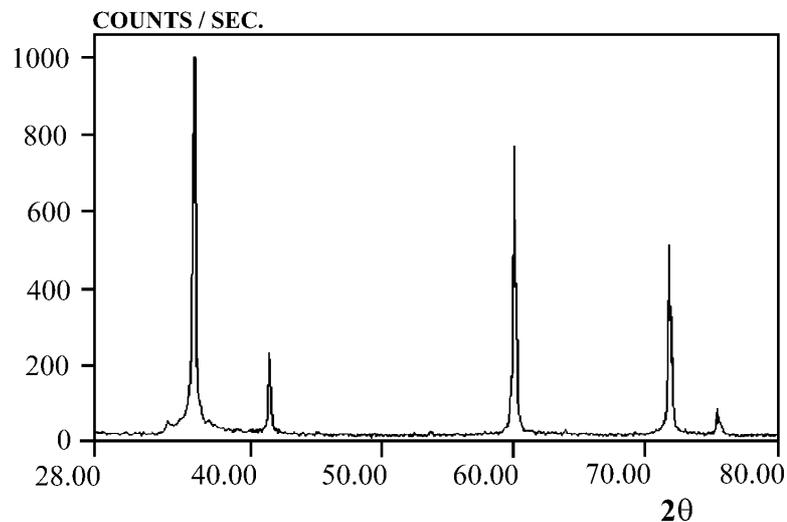


Figure 3. XRD pattern of sample 1:1 Si-Coke treated in Ar at 1450 °C for 5 hours. All peaks correspond to β -SiC.

Figure 4 shows the yield in SiC as a function of time for coke of three particle sizes, graphite and activated carbon at 1350 and 1400 °C. The rate of reaction at 1450 °C is very fast as compared with 1350 and 1400 °C because the melting point of Si is 1410 °C, and the liquid-solid reaction is faster than the solid-solid reaction (1450 °C); at this temperature all carbons are fully reacted in 30 minutes. One factor of great importance in the rate of reaction is the particle size: smaller particles react faster than larger particles. The knowledge of the rate of reaction is very important because if it is very fast it can inhibit the infiltration process.

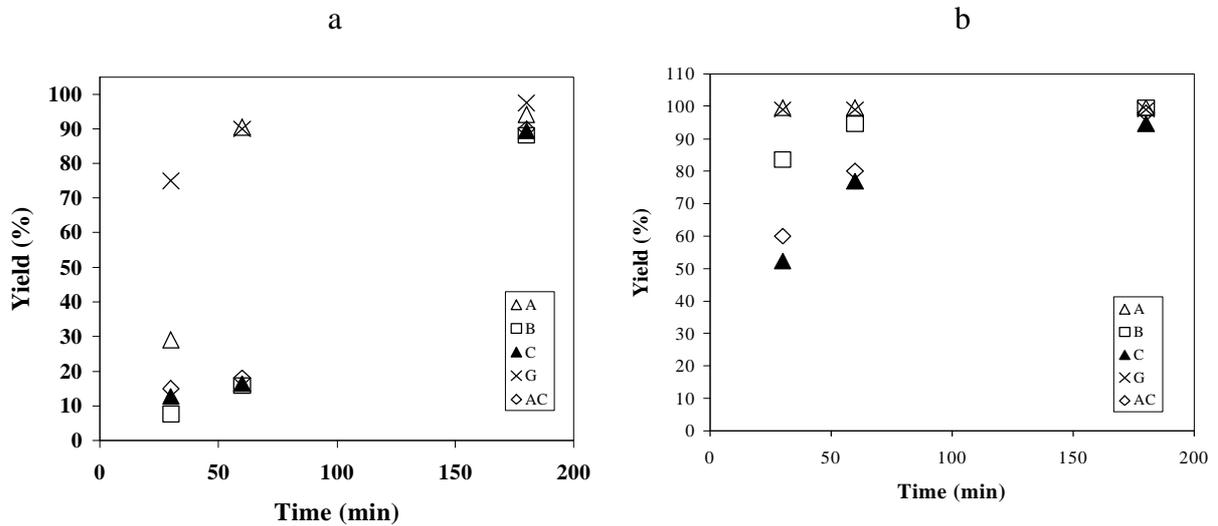


Figure 4. Yield in SiC as a function of time. The carbon sources are: A, fine coke, B, medium coke, C, large coke, G, graphite and AC, activated carbon. The temperatures of reaction are: a) 1350 °C and b) 1400 °C.

Si-Mo-C Reaction.

Figure 5 shows the XRD pattern of the sample treated in Ar at 1450 °C for 5h, with 20 wt% molybdenum. This figure shows the sample with the highest content of MoSi₂, where the diffraction peaks of another molybdenum silicide (Mo₅Si₃) can be appreciated; this compound is produced in zones with a high content of Mo, but it disappears if the thermal treatment is extended to 10 hours. In the case of lower Mo content (10%) in the original sample, Mo₅Si₃ is not observed. In the experiment performed with tungsten only WSi₂ was obtained.

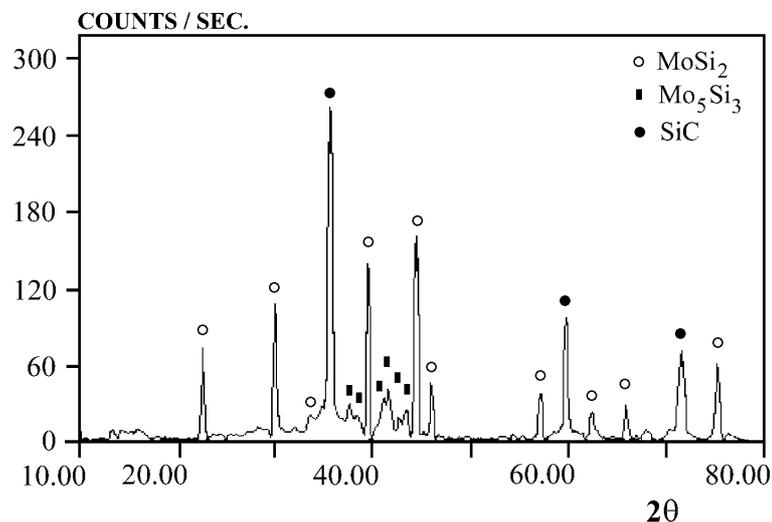


Figure 5. XRD pattern of sample 20% Mo-Graphite treated in Ar at 1450 °C for 5 h.

Figure 6 shows the evolution of the different compounds obtained at 1300 and 1450 °C from the mixture of coke (medium size), silicon and precursor (10 wt%). It can be observed that the metallic disilicide is obtained at temperatures below 1300 °C, because the yield is constant in every experiment and corresponds with the theoretical value. The reaction between silicon and carbon takes place faster at higher temperatures, as it was expected, and the reaction is completed in 5 hours. Some other experiments were performed in which the metal content and the temperature were modified, and it can be concluded from them that the reaction between silicon and metallic carbide starts at 1100 °C for tungsten and at 1200 °C for molybdenum, and that Mo_5Si_3 can be obtained only when the metal content is higher than 20%. No equivalent product with W has been detected. Similar results have been obtained by Hojo *et al.* working with powders [21,22], but they used silica as silicon source. Furthermore, they obtained W_5Si_3 when the reaction was carried out between discs of WC, silica and carbon. Martinelli *et al* [10], in their experiments with two discs of Mo and SiC, obtained Mo_5Si_3 , and only obtained the disilicide when the reaction took place during long time. We can conclude that there was a problem of diffusion in the reaction of WC or MoC with silicon. In our case, the WC is obtained at 1000 °C and the reaction with silicon starts at 1100 °C. Since additionally the carbide obtained is a finely divided powder, there is no diffusion problems and WSi_2 is directly formed. Selected experiments using both precursors simultaneously were performed, only (Mo, W) Si_2 -CSi being detected.

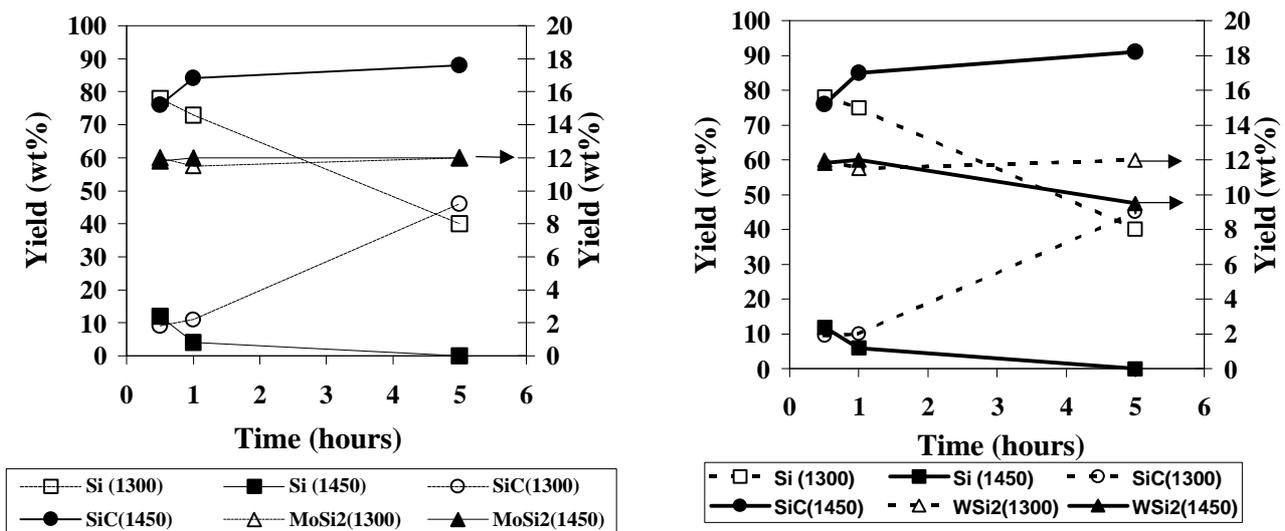


Figure 6. Evolution of products as a function of time at 1300 and 1450 °C (10% of Metal).

Study of the pieces.

The pieces obtained present great differences depending on the carbon source employed in the preparation process. Pieces made using active carbon show very high porosity. This high porosity makes them unable to be used as structural material. On the other hand, pieces made from graphite present so low porosity that they break when infiltrated with silicon. The high reactivity of graphite originates a very fast expansion that results excessive for the mechanical resistance of the material. Best results are obtained with pieces made by employing coke as carbon source.

Properties of pieces made from coke depend on temperature, reaction time and particle size. Pieces made from small particles present a more homogeneous microstructure, lower porosity and better mechanical properties than pieces made from larger particles. Temperature and reaction time have similar influence: high temperatures and long reaction times produce pieces with better properties. In pieces made without molybdenum precursor different microstructures were obtained when changing these factors. It could be possible to obtain

pieces without residual silicon using small and medium size particles. Figure 7 shows micrographs of pieces made without the molybdenum precursor by using different coke size but the same conditions in temperature and reaction time. Great differences between the microstructures of these pieces can be observed. Microstructure of the piece made employing fine coke is more homogeneous, has lower residual silicon and lower proportion of unreacted coke. The presence of two different SiC types can also be detected. These SiC phases can be better appreciated in pieces made using large size coke. These different SiC phases are epitaxial and fine grained: epitaxial when phase grows over coke particles; fine grained when crystallized without nucleation [23].

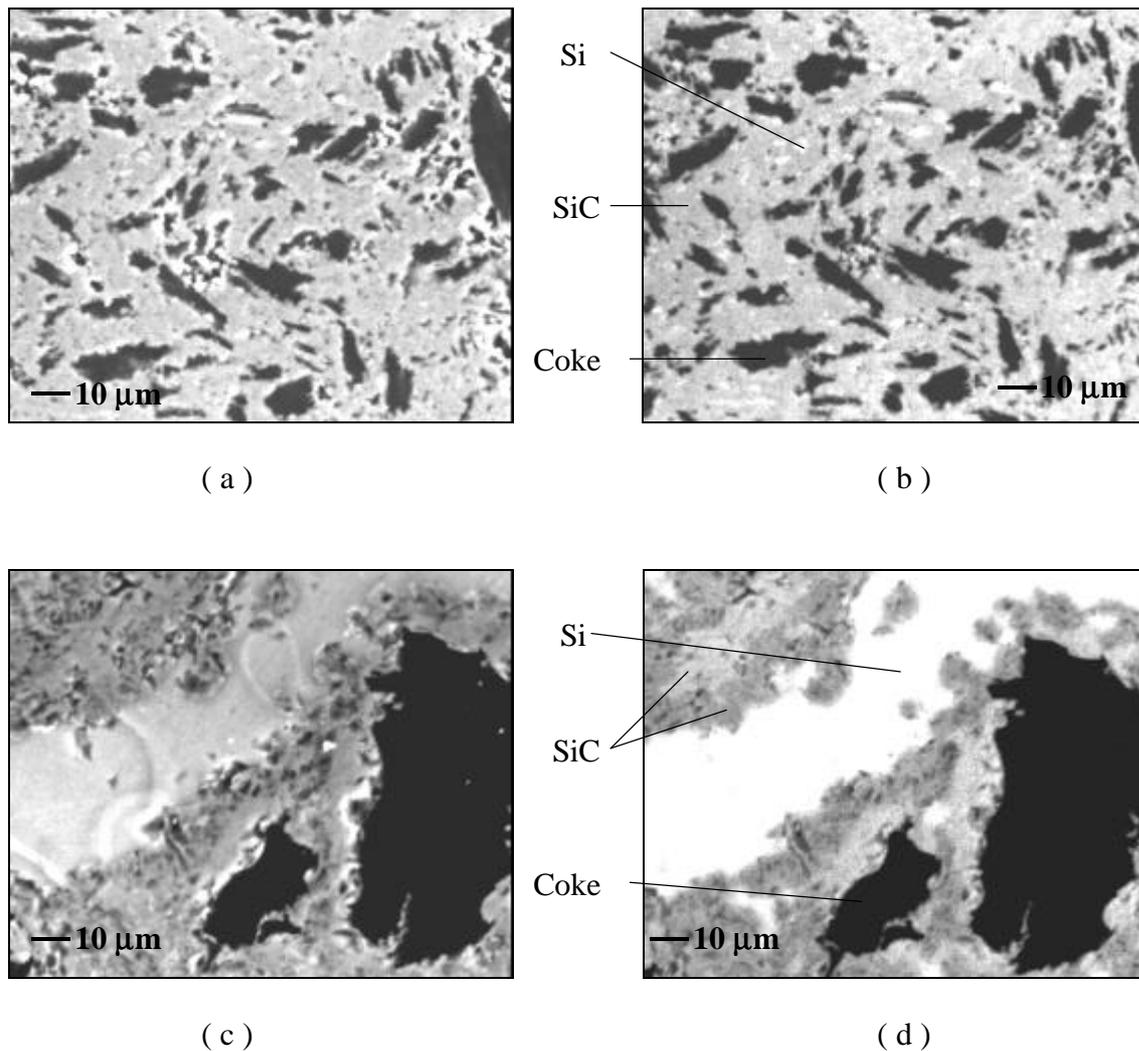


Figure 7. Micrographs of RBSC pieces made employing different sizes of coke. Experimental conditions: 1400 °C, 30 minutes. Micrographs a) and b) are of a piece made using fine coke, c) and d) are of a piece made using large sized coke. Micrographs a) and c) are made by SEM, b) and d) by BSEM

Residual silicon is only detected in pieces made using large size coke, at low temperature and short reaction time and, even in this case, the amount of residual silicon is lower than the amount present in pieces made under the same conditions but without employing the metallic precursor.

The mechanical properties of the pieces have a strong dependence on the particle size, reaction time and temperature used in their preparation but, in all cases, are highly enhanced when residual silicon is replaced by silicide.

Figure 8 shows the evolution of hardness as a function of applied load for six samples of three different particle size and different experimental conditions, with and without molybdenum silicide precursor. The effect produced by the substitution of silicon by silicide can be clearly appreciated: pieces with molybdenum silicide show lower change of hardness with applied load and this hardness is higher than for pieces without silicide. Hardness obtained (measured at load=500 g) goes from 17 GPa (for pieces made from large size coke at low temperature and short reaction time) to more than 30 GPa (for pieces made using fine coke at high temperature and long reaction time). The effect produced by the substitution of silicon by WSi_2 is similar to the obtained by molybdenum: the hardness increases to 34 GPa in the best case (for pieces made using fine coke, high temperature and long reaction time).

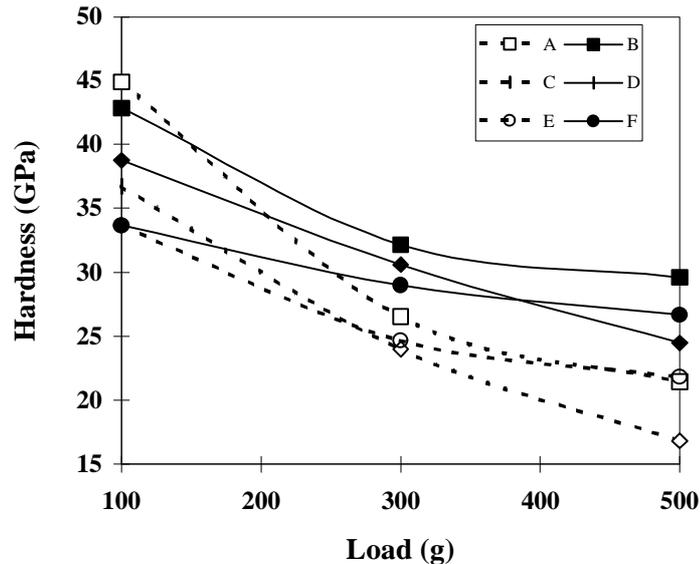


Figure 8. Hardness as a function of applied load for six pieces. Pieces A and B are made of fine coke at 1450 °C for 30 minutes; C and D are made of large coke at 1400 °C for 30 minutes, E and F are made of medium coke at 1450 °C for 5 hours. Pieces A, C and E are made without molybdenum silicide precursor; B, D and F are made using it.

Indentation fracture toughness (IFT) tests were also performed. The cracks used for the IFT measurements were the traces of median/radial cracks which propagated from the corners of high load (9.81 N) Vickers indentations. The IFT expression of Anstis *et al.* [24] was used to obtain values of K_{Ic} . For the composite materials K_{Ic} is over 7 MPa m^{1/2}, but is a little higher for (Mo,W)Si₂-SiC. The fracture toughness for these composite materials is two times higher than that reported for monolithic SiC [14,15]. Room-temperature flexural strength of the reaction formed silicon carbide materials described above were determined using the three-point bend technique. The average value of flexural strength for three samples was 225 MPa (for pieces made using fine coke at high temperature and long reaction time), and for composite materials in the same condition are 250 MPa. The non reacted carbon decreases the mechanical properties, but at the same time increase the thermal conductivity and the wear resistance.

CONCLUSIONS

Three carbon sources for preparation of SiC-MoSi₂ composites have been studied (coke, active carbon and graphite), better results being obtained with coke.

The particle size employed in the preparation of pieces has great importance. Small particle size yields the best results in this research, making it possible the preparation of pieces with better mechanical properties at lower temperatures and shorter reaction times than needed for larger particles.

The impregnation of the carbon source with ammonium heptamolybdate and its conversion into Mo₂C by thermal treatment allows to make pieces of SiC-MoSi₂ without free silicon. In all cases, mechanical properties of pieces are enhanced when silicon is replaced by silicide. A very important conclusion obtained in this research is that a careful selection of the carbon source, particle size and experimental conditions allows to make RBSC pieces that present no residual silicon even without the use of silicide precursors.

ACKNOWLEDGEMENTS.

Partial support from the CICYT (project MAT96-1048) is gratefully acknowledged.

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