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Short communication

Synthesis of ternary molybdenum carbosilicide

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Abstract

Dense compacts of $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$ have been prepared by reactive hot pressing of a mixture of elemental powders of Mo, Si and C. Synthesis temperatures and soaking times have been optimized for obtaining pure $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$. The hardness of pure sample is 14.7 GPa.

Keywords: A. Hot pressing; Synthesis; Molybdenum carbosilicide

1. Introduction

Molybdenum carbosilicide, $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$, a Nowotny phase, [1] is the only ternary phase in the Mo–Si–C system, as identified by Nowotny et al. [2] It belongs to a class of compounds of the general formula $M_{\leqslant 5}Si_3C_{\leqslant 1}$ where M = Zr, Nb, Mn or Mo, [1] has a melting point of about 2100 °C [3], and crystallizes in a hexagonal structure ($D8_8$) [1,4]. Its crystallographic formula may be written as $Mo^{I}_3Mo^{II}_{\leqslant 2}Si_3C_{\leqslant 1}$ where C atoms occupy partially the octahedral sites formed by Mo^{I} atoms. It is proposed [3] that $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$ could not only be a reinforcement second phase but also a new matrix phase for composites based on Mo–Si–C systems. Shobu and coworkers have used $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$ as infiltrants to produce composites with SiC. [5–7]

Preparation of $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$ as a single-phase product is reported to be difficult owing to the small stability region in the phase diagram [8,9]. Suzuki and Niihara have prepared $Mo_{4.8}Si_3C_{0.6}$ as a single phase by reactive hot pressing of elemental powders at 30 MPa and 1500 °C for 1–2 h [3]. Parthe and Jeitschko have prepared a compound of this composition starting from Mo, Si and C powders by hot pressing and annealing at 1600 °C for 12 h in a vacuum furnace [1]. We attempted to synthesize single phase $Mo_{4.8}Si_3C_{0.6}$ in a shorter duration of time by reactive hot pressing of elemental powders at 26 MPa and temperatures ranging from 1600 to 1750 °C in argon atmosphere and succeeded in obtaining a nearly single-phase product at 1700 °C in a time, as low as 8 min.

2. Experimental

Compounds of the nominal composition $Mo_{4.8}Si_3C_{0.6}$ have been prepared starting from stoichiometric amounts of elemental Mo powder (Aldrich, 99%), silicon powder (Aldrich, 99%) and carbon soot (home made), taken according to the equation

$$4.8Mo + 3Si + 0.6C \rightarrow Mo_{4.8}Si_3C_{0.6} \quad (1)$$

The powders were mixed together and hot pressed in a BN coated graphite die (12 mm i.d.) at 26 MPa for 8–30 min in an argon atmosphere at temperatures ranging from 1600 to 1750 °C. After the synthesis, the pellets were polished with 1 μm diamond paste and characterized by powder x-ray diffraction (Cu K_α, Philips Powder Diffractometer), density measurement (Archimedes principle), scanning electron microscopy (Jeol JSM-5600 LV Scanning Electron Microscope) and Vickers hardness measurement (Shimadzu HMV-2000 micro hardness tester).

3. Results and discussion

In all the preparations, $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$ is the observed major phase confirming the X-ray diffraction pattern reported in the literature [1,4,10]. The small amounts of

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impurity phases are Mo_5Si_3, Mo_2C and some unidentified phases. Table 1 lists the phases present in these preparations.

For the samples prepared at 1600 and 1650 °C, the amount of the impurity phase, Mo_5Si_3, is comparatively large. At 1700 °C, Mo_5Si_3 is absent. This indicates that during the reaction Mo and Si react to form Mo_5Si_3 first, which then reacts with Si and C to form $Mo_{4.8}Si_3C_{0.6}$. However, when the preparation temperature is raised to 1750 °C Mo_5Si_3 forms again, probably due to the decomposition of $Mo_{4.8}Si_3C_{0.6}$. It seems that a temperature of 1700 °C is ideal for short-duration synthesis. Fig. 1 shows the XRD patterns of samples prepared at various temperatures with a fixed soaking time of 15 min.

To find the effect of soaking time, we carried out synthesis experiments at 1700 °C by using different soaking times (Fig. 2). Nearly single phase $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$ is formed at this temperature with a soaking time of just 8 min (Fig. 2a). For this sample only one impurity-line at $2\theta = 39.4°$, which corresponds to 100% line of Mo_2C, is present. Therefore, under these synthesis conditions it is possible to obtain nearly single phase $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$. Fig. 3 shows the SEM image of this sample. At higher soaking times, the amount of Mo_2C increases. Suzuki and Niihara [3] have observed the formation of Mo_2C in their preparations when the Si-content in the starting mixture was slightly less than that required for single-phase formation. Therefore, formation of Mo_2C in our preparations may be due to the volatilization of a small amount of Si from the reaction mixture during high-temperature treatment.

Table 1 also includes densities of the compacts obtained. We find that the highest density is obtained when the preparation is carried out at 1700 °C for 15 min. The Vickers hardness value for the pure sample, as indicated in Table 1, is 14.7 GPa. These values are higher than those reported by Suzuki and Niihara [3] (11.0–12.6 GPa for monolithic $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$). When the

Table 1
Impurity phases, density and hardness values of $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$ prepared under different conditions

Soaking temperature, °C	Soaking time, min	A[a]	B[a]	C[a]	Density, g/cm^3	Hv, GPa
1600	15	16	–	–	7.63	14.8
1650	15	15	24	–	7.12	12.3
1700	8	–	4	–	7.74	14.7
1700	15	–	6	5	7.79	13.8
1700	30	–	9	–	7.64	16.4
1750	15	12	–	–	7.59	18.0

[a] $A = 100*I_{60}$ (Mo_5Si_3)/I_{100} ($Mo_{4.8}Si_3C_{0.6}$), $B = 100*I_{100}$ (Mo_2C)/I_{100} $Mo_{4.8}Si_3C_{0.6}$) $C = 100*I_{100}$ (unidentified phase)/I_{100} ($Mo_{4.8}Si_3C_{0.6}$).

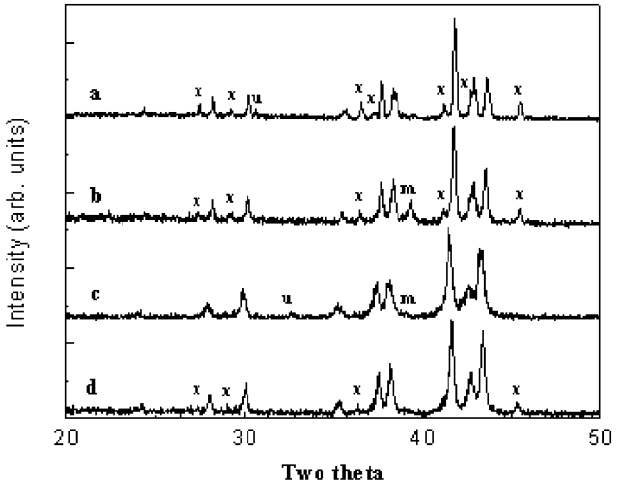

Fig. 1. X-ray powder patterns of $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$ samples prepared at (a) 1600, (b) 1650, (c) 1700 and (d) 1750 °C, with a fixed soaking time of 15 min. ($x = Mo_5Si_3$, $m = Mo_2C$, u = unidentified phase.)

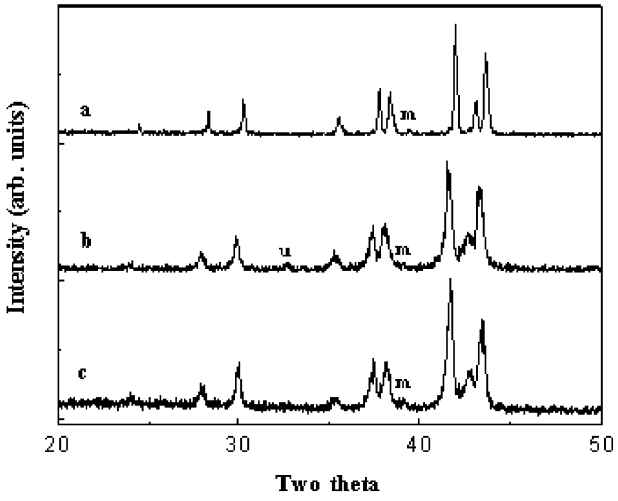

Fig. 2. X-ray powder patterns of $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$ samples prepared at 1700 °C with soaking times of (a) 8 min, (b) 15 min and (c) 30 min. ($m = Mo_2C$, u = unidentified phase.)

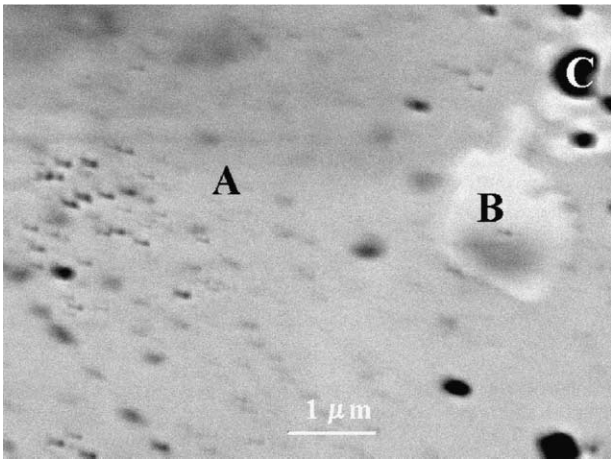

Fig. 3. Scanning electron micrograph of a sample prepared at 1700 °C with soaking of 8 min. (A = $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$, B = Mo_2C, C = pore.)

impurity phases are present in considerable amounts, the hardness value is found to be different; the sample prepared at 1750 °C has a hardness of 18 GPa.

4. Conclusion

It is possible to prepare almost single-phase dense compacts of $Mo_{\leqslant 5}Si_3C_{\leqslant 1}$ by reactive hot pressing of elemental powders at 26 MPa and 1700 °C for 8–15 min. The materials so synthesized have Vickers hardness of 13–15 GPa.

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