

Fabrication of MoSi₂-SiC Composites by a Spark Plasma Sintering Method

Kazuya Kurokawa¹⁾, Makoto Ube¹⁾, Hideaki Takahashi¹⁾, Heishichiro Takahashi²⁾

1) Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo 060-8628, Japan

2) Center for Advanced Research of Energy Technology, Hokkaido University, Japan

(Received 1998-10-29)

Abstract: Fully dense MoSi₂-SiC composites were fabricated from the mixed powder of the elemental constituents by a spark plasma sintering method. The sintering and densification of the Mo-Si-C mixed powder are accomplished through three processes. In particular, it proceeds rapidly by the formation of MoSi₂. The most suitable temperature for the fabrication of MoSi₂-SiC composites depends on the content of SiC and increases with the content of SiC increasing. As a result, fully dense MoSi₂-SiC composites can be prepared without difficulty by a spark plasma sintering method.

Key words: MoSi₂-SiC composite; spark plasma sintering; in-situ synthesis; sintering behavior

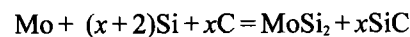
Molybdenum disilicide (MoSi₂) has high melting point (2 293 K), relatively low density (6.24 g/cm³), a brittle-to-ductile temperature at about 1 173 K [1] and outstanding oxidation resistance [2-4]. For this reason, the disilicide matrix composites are being considered as one of the most promising candidates for application in oxidizing environment at ultra-high temperature, such as engines and turbines towards 21st century. Although the improvement of mechanical properties such as low temperature ductility and high temperature strength are being achieved by addition of reinforcing materials such as ceramics and silicides, only the materials which little influence the outstanding oxidation resistance of MoSi₂ can be selected as the reinforcing materials for the MoSi₂-based composites. SiC, as well as MoSi₂, forms a protective SiO₂ layer to show outstanding oxidation resistance. Therefore, SiC may be the most promising additive as the reinforcing materials.

In the production of bulk MoSi₂, grain size control and low oxide content to improve mechanical properties and high densification are required. Powder metallurgy such as hot pressing and hot isostatic pressing has been usually utilized to product bulk MoSi₂. Self-propagating High-temperature Synthesis (SHS) process is also frequently utilized for the synthesis of MoSi₂ [5-7], because the negative enthalpy of formation of MoSi₂ by the reaction of Mo with Si is appreciably large. Recently, a Spark Plasma Sintering (SPS) method was newly developed. The method makes it possible to fabricate dense specimens briefly and to suppress grain growth.

In the present study, the in-situ synthesis of fully dense MoSi₂-SiC composites from the mixed powder consisting of elemental constituents of Mo, Si and C by SPS was carried out. The sintering behavior and the structures of synthesized compacts are described.

1 Experimental

The powders used in the present study are 99.90% pure Mo with the average grain size of about 2.5 μm, 99.90% pure Si with the average grain size of about 45 μm, and 99.95% pure carbon black with the average grain size of about 45 μm. Those powders were fully mixed with an agate mortar. The atomic ratio of each element was decided by assuming the following reaction



where, 0 (1Mo-2Si), 0.2 (1Mo-2.2Si-0.2C), 1.0 (1Mo-3Si-1C) and 2.0 (1Mo-4Si-2C) as the values of x were chosen. At the conclusion of the reaction, the volume fraction of SiC should be 0, 9.6%, 33.9%, and 50.6%, respectively.

For the in-situ synthesis of MoSi₂ and MoSi₂-SiC composites from the mixed powder consisting of elemental constituents of Mo, Si and C, the SPS equipment, Dr. Sinter SPS-1020 (Sumitomo Sekitan Co. Ltd., Japan), was used. The mixed powder of about 3×10^{-3} kg was packed in a graphite mold with two graphite punches, as shown in **figure 1**. The assembly was set in the SPS chamber evacuated to 5 Pa, and then a compressive stress of 39 MPa was applied to the mixed powder. The sintering temperature was heated up to

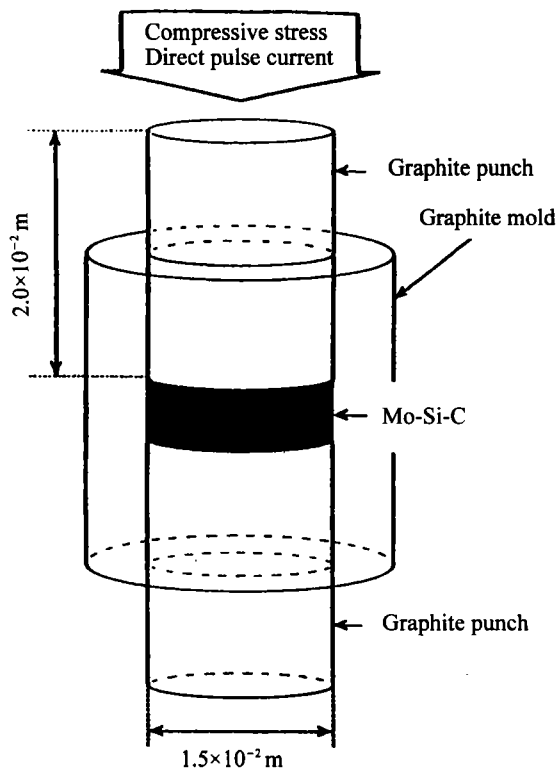


Figure 1 Assembly schematic for spark plasma sintering.

1 473, 1 673 or 1 873 K (SPS temperature expression) in a heating rate of 0.17 K/s by impressing direct pulsating current through the graphite punches. The temperature was measured in the surface of the graphite mold by a photoelectric pyrometer. The sintering behavior of the mixed powder was evaluated from measurement of z-axis displacement which expresses the change in thickness by shrinkage or expansion of the specimen. After holding for 600 s at the maximum temperature, the current was immediately turned off and then the compressive stress was relieved.

X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Electron Probe Micro-Analyzer (EPMA) were used to characterize the synthesized specimens. The densities of the specimens were measured by Archimedes method.

2 Results and Discussion

2.1 Sintering behavior

Shown in **figure 2**, the displacement (right vertical axis) indicates the change in thickness of a specimen. The displacements toward negative or positive directions mean expansion or shrinkage, respectively. In addition, the temperature for sintering is expressed in the following manner: SPS 1 773 K. This is because the measurement of temperature is done in a surface of a graphite mold and the measured temperature therefore is thought to be different from the true temperature of

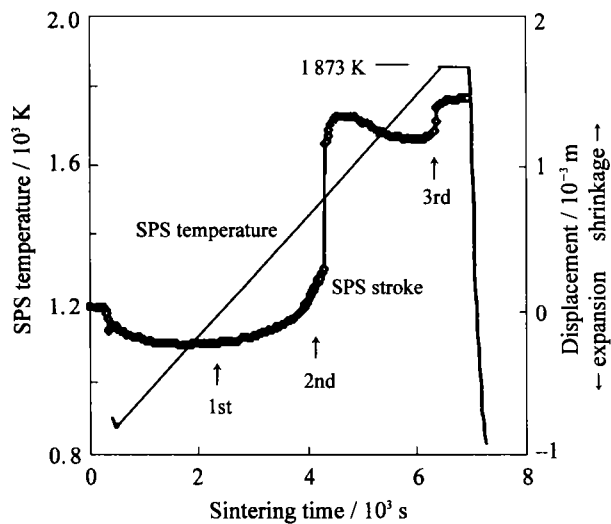


Figure 2 Sintering behavior of the 1Mo-3Si-1C mixtures.

the specimen. According to this figure, the densification of the mixed powder is accomplished through three processes. Namely, the first shrinkage starts at about SPS 1 200 K, the second at about SPS 1 470 K and the third at about SPS 1 850 K. In particular, the second shrinkage is tremendous. The sintering behavior of other mixtures was similar to that of the 1Mo-3Si-1C mixture, except that the third shrinkage was not observed in the 1Mo-2Si mixture.

The X-ray diffraction patterns for the mixture heated up to various temperature showed that any reaction product was not formed in the mixture heated up to SPS 1 273 K and the formation of MoSi_2 and small amount of SiC occurred by heating up to SPS 1 473 K. At higher temperature, the formation of composites consisting of MoSi_2 and SiC is accomplished completely.

From the above results, the sintering behavior of Mo-Si-C mixtures is concluded as follows:

(a) The first shrinkage. In this stage, any reaction product is not formed. Therefore, the shrinkage is due to the sintering of elemental constituents.

(b) The second shrinkage. In this stage, MoSi_2 and SiC are formed. The shrinkage is mainly due to the sintering and densification of MoSi_2 . Actually, it is well known that MoSi_2 has a ductile-to-brittle transition temperature at about 1 200 K [1].

(c) Third shrinkage. The shrinkage is due to the sintering of SiC. This is because the third shrinkage was not observed in the 1Mo-2Si mixture and the displacement increased with the content of SiC increasing.

2.2 Density and structure of composites

Figure 3 shows the effect of SPS temperature on the relative density for the theoretical values of sintered composites. In the 1Mo-2Si and 1Mo-2.2Si-0.2C mix-

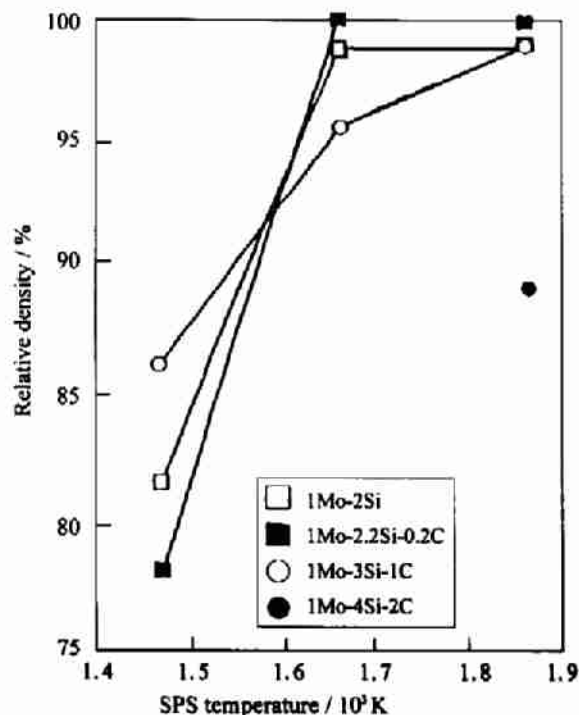


Figure 3 Dependence of relative density on SPS temperature.

tures, the densities of MoSi_2 and MoSi_2 -SiC composite attain the theoretical density by heating up to SPS 1 673 K. Higher sintering temperature with the content of SiC increasing is required to prepare fully dense composites. For example, heating up to SPS 1 873 K is required for the 1Mo-3Si-1C mixture, and the SPS temperature of 1 873 K for the 1Mo-4Si-2C mixture is insufficient to fabricate a dense composite. The reason is probably that SiC is hard to sinter even at SPS 1 873 K. However, heating up to higher temperature results in grain growth of MoSi_2 . Therefore, it is difficult to prepare fully dense composites with the content of SiC above 35% in volume fraction by the present sintering method.

The structures of MoSi_2 -SiC composites fabricated by heating the 1Mo-3Si-1C and the 1Mo-2.2Si-0.2C mixtures up to SPS 1 873 K are shown in figure 4. In the photographs, the dark and light colored phases are SiC and MoSi_2 , respectively. The structure of the MoSi_2 -33.9%SiC composite (1Mo-3Si-1C) shows that SiC is dispersed uniformly. On the other hand, in the MoSi_2 -9.6%SiC composite (1Mo-2.2Si-0.2C), the dispersion of SiC is relatively nonuniform. This is probably caused by the grain growth of MoSi_2 . The grains of MoSi_2 are liable to grow with a decrease in the content of SiC and an increase in sintering temperature. Therefore, the sintering temperature should be as low as possible. The most suitable temperature for the fabrication of MoSi_2 -SiC composites by a spark plasma sintering method was concluded to be 1 673 K for the 1Mo-2Si and the 1Mo-2.2Si-0.2C mixtures and 1 873 K for the 1Mo-3Si-1C mixture.

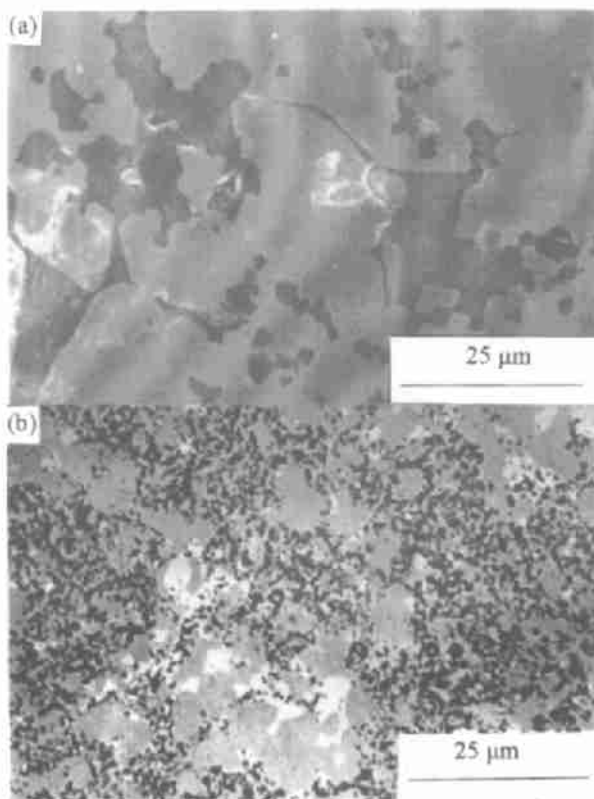


Figure 4 Structures of Mo-Si-C mixtures heated up to 1 873 K in SPS. (a) 1Mo-2.2Si-0.2C and (b) 1Mo-3Si-1C.

3 Conclusions

(1) The reaction products in the Mo-Si-C systems are only MoSi_2 and SiC. Thus, MoSi_2 -SiC composites having different content of SiC can be fabricated in situ from the elemental constituents of Mo, Si and C.

(2) The sintering and densification of the Mo-Si-C mixed powder is accomplished through three processes. In particular, it proceeds rapidly by the formation of MoSi_2 .

(3) The most suitable temperature for the fabrication of the MoSi_2 -SiC composites depends on the content of SiC and increases with the content of SiC increasing.

(4) Fully dense MoSi_2 -SiC composites can be fabricated without difficulty by a spark plasma sintering method.

References

- [1] Y. Umakoshi, T. Hirano, T. Sakagami, T. Yamane: *Scripta Metall.*, 23(1989). p.87.
- [2] E. Fitzer: [in:] *Proc. of the Second Plansee Seminar*. Springer Verlag, Wien, 1955. p.56.
- [3] K. Kurokawa: *Materia. Japan Inst. Met.*, 32(1993). p.668.
- [4] K. Kurokawa, H. Matsuoka, T. Nagai: *Trans. Mat. Res. Soc. Jpn.*, 14A(1994). p.255.
- [5] S. Zhang, Z. A. Munir: *J. Mater. Sci.*, 26(1991). p.3685.
- [6] S. C. Deevi: *J. Mater. Sci.*, 26(1991). p.3343.
- [7] S. C. Deevi: *Mater. Sci. Eng.*, A149(1992). p.241.