O U R N A L O F

Ceramic Processing Research

Pressureless sintering of TaC-nanoGr-SiC composites

A. Motaharinasab^{a,*}, N. Ehsani^{a,*} and B. Shahbahrami^b

^aFaculty of Materials and Manufacturing Technology, MU University of Technology, Tehran, Iran ^bDepartment of Material Science Engineering, Saveh Branch, Islamic Azad University, Saveh, Iran

Tantalum carbide (TaC) matrix composites were produced by the pressureless sintering at temperatures of 2200 °C and 2300 °C. Various combinations of TaC, nano-Gr (nano-graphite) and SiC were used. The amount of nano-Gr was constant at 10 vol%, and the SiC content was 0-20 vol% variable. The amount of SiC had a significant influence on the sinterability and mechanical properties of the TaC. The SiC particles locate on the grain boundaries and inhibit grain growth through the sinter process. The relative density was decreased for both temperatures as a result an increasing of amount SiC. It was decreased from 94.2% to 82.5% at 2200 °C, and from 96.1% to 85.7% at 2300 °C, when the amount of SiC was increased from 0 to 20 vol%. By increasing the amount of SiC to 10 vol%, the hardness was enhanced and reached to 1610 HV and 1760 HV at sintering temperatures of 2200 °C and 2300 °C, respectively. However, above 10 vol%, sinterability and as a result the hardness was reduced.

Key words: Tantalum carbide, Silicon carbide, Pressureless sintering, Composite.

Introduction

Refractory metal carbides are promising ceramic materials, because these compounds exhibit unusual combinations of physical and chemical properties such as high hardness, high melting point, good electrical and thermal conductivities, and a high resistance to thermal shock and wear [1-3]. Among the metal carbides, tantalum carbide (melting point > 3500 °C) has attracted much attention for high-temperature and wear-resistant applications [1-3]. Compared to its potential, the applications of TaC are rather limited, mainly because of the difficulties that exist in obtaining fully-dense bodies. Monolithic TaC is difficult to densify even by hot pressing at high temperature because of its highly covalent bonding, low selfdiffusion coefficient and rapid grain growth at high temperatures [4-8].

Scholz [4] found that the presence of small amounts of Fe strongly affected the sintering of certain refractory materials due to the formation of a liquid phase. Roeder and Klerk [5] pointed out that Mn and Ni had the same effect in reducing the onset sintering temperature of TaC. While the onset densification temperature was decreased with the metal additions, the presence of the liquid phase resulted in exaggerated grain growth, which led to porosity entrapment within the large grains in the final stage of densification. Full densification of the samples was prevented by this phenomenon. Further, the presence of metallic phases at the grain boundaries limits the high-temperature applications of the ceramics [6]. Zhang et al. [6] obtained a relative density of 97% at 2300 °C for TaC with 0.78 wt% C addition, 94% at 2100 °C with 0.36 wt% B_4C addition and >96% at 2100 °C when 0.43 wt% B₄C +0.13 wt% C was added. Zhang et al. [7] also obtained a relative density of 98.6% at 2100 °C and 2200 °C for a composition consisting of 10 wt% TaB_2 - 90 wt% TaC. Due to the relatively high density of the TaC-10 wt% TaB₂, it's mechanical properties were equal or better than monolithic TaC. Fracture toughness was similar for both monolithic TaC and TaC-10 wt% TaB₂. Patterson et al. [8] used TiC, ZrC, HfC, VC and NbC as the additives to produce TaC matrix composites. These carbides had useful effects but did not reduce the grain size of the specimens under the applied processing conditions. The interstitial carbides are fully soluble in TaC. Therefore, they slightly increase the grain size of TaC, through the formation of solid solutions. Interstitial carbide additives increase both the strength and hardness of TaC. The amount of reported hardness is NbC (14 Gpa), HfC/ZrC (19 Gpa), VC (22 Gpa) and TiC (25 Gpa). All of these samples were produced by hot pressing under similar conditions, which is an effective technique to densify TaC. However, it can only produce ceramics with simple shapes. For the preparation of ceramics with complex shapes, pressure-less sintering is a costeffective method.

Liu *et al.* [9] investigated the pressureless sintering of TaC without the use of additives. They obtained a relative density of 97.5% by using fine powders with a narrow size distribution at a sintering temperature of

^{*}Corresponding author

Tel : +98-255-224-1511

Fax: +98-255-224-0111

 $E\text{-mail:} nase_ehsan@yahoo.com; azam_motahari@yahoo.com$

2300 °C. Silvestroni and Sciti [10] consolidated TaC by pressureless sintering with the addition of $MoSi_2$. They have reported that 10 vol% $MoSi_2$ is enough to achieve full density at 1950 °C.

In the previous studies, different sintering aids have been used for tantalum carbide, but SiC has not been yet used as a sintering aid for TaC. SiC has been used as a suitable sintering aid in numerous materials [11, 12]. In this study, the effect of the SiC on the pressureless sintering of TaC was investigated. Nano graphite, was also added to the samples because its thermal expansion behavior is similar to that of TaC. Also it has a low elastic modulus and a high thermal conductivity, which have useful effects on the thermal shock resistant of the samples [13]. The mechanical properties such as hardness were measured and correlated to the microstructural evolution and densification behavior.

Experimental

The starting powders were TaC (purity > 99.9 wt%, average particle size = 500 nm), graphite (purity >99.5 wt%, average particle size = 40 nm) and SiC (purity > 99 wt%, average particle size = 420 nm). Fig. 1 shows the morphology of the TaC powder by scanning electron microscopy (SEM).

Various amounts of silicon carbide powder (5, 10, 15 and 20 vol%) were added to TaC-nano graphite. The amount of nano-graphite was 10 vol% in all the samples. The powders were wet blended in hexane by a planetary ball mill (Fritsch company-model pulverisette 5), whose balls and container were made from ZrC. After mixing for 2 hours, the slurry was dried at 80 °C in an oven for 24 hours.

The powder mixtures were pressed into pellets using a 12 mm diameter die by a uniaxial press at a pressure of 100 MPa. They were also isostaticly pressed at a pressure of 400 MPa.

The sample pellets were then sintered for 1 h at 2200 °C and 2300 °C, using a heating rate of 5 °C minute⁻¹,



Fig. 1. Scanning electron micrograph (SEM) of the as-received tantalum carbide powder.

under a high-purity atmosphere (< 5 ppm of oxygen gas) in a graphite furnace. The relative_densities of the ceramics were measured by the Archimedes method based on ASTM B311. The phase analysis of the pellets was carried out on the solid samples by X-ray diffraction using CuK α radiation (Model 3003-IT-Seifert Company). The Vickers hardness was determined according to ASTM C1327. The microstructure of the samples was studied using SEM (Philips, model XL30), that was equipped with energy-dispersive X-ray spectroscopy (EDAX). For the microstructural evaluation, the surface of the specimens was polished by 1, 6 and 30 μ m diamond abrasive pastes and then etched for 90 s in 3:1 HNO₃ to HF solution.

Results and discussion

XRD analysis

An X-ray diffraction (XRD) pattern of a TaC-10 vol% nanoGr -20 vol% SiC composite sintered at 2300 °C for 1 h is shown in Fig. 2. It reveals that TaC and SiC are the only existing phases in the samples. The peaks are not shifted in the XRD pattern, therefore it can be suggested that contrary to other additives, SiC did not dissolve in TaC [8].



Fig. 2. X-ray diffraction pattern of a TaC-10 vol% nanoGr-20 vol% SiC composite sintered at 2300 °C for 1 h.



Fig. 3. The relative density as a function of SiC addition to TaCnanoGr compositions sintered at 2200 °C and 2300 °C, for 1 h.

Table1. The relative densities of the samples sintered at 2200 $^{\rm o}C$ and 2300 $^{\rm o}C$, for 1 h

Composition	Relative density (%) at 2200 °C	Relative density (%) at 2300 °C
TaC-10 vol% nanoGr	94.2	96.1
TaC-10 vol% nanoGr- 5 vol%SiC	93.6	95.8
TaC-10 vol% nanoGr- 10 vol%SiC	93.1	95.2
TaC-10 vol% nanoGr- 15 vol%SiC	86	89
TaC-10 vol% nanoGr- 20 vol%SiC	82.5	85.7

Densification

The effect the amount of SiC addition and sintering temperature on the relative density of the samples are illustrated in Fig. 3. As is shown, the density of all compositions was increased with an increase in the sintering temperature. It also can be seen that at 2200 °C the relative density of the pellets, were decreased from 94.2% to 82.5% when the amount of SiC was increased from 0 vol% to 20 vol%. A similar behavior was observed at 2300 °C. At this temperature, the relative density was decreased from 96.1% to 85.7% as the level of SiC was increased from 0 vol% to 20 vol% to 20 vol% (see table 1).

SiC particles locate on the grain boundaries and inhibit their movement. They also lead to the entrapping of the porosities between SiC and TaC grains. These phenomena prevent densification of the specimens [14].

Microstructure

The microstructures of the samples containing TaC-10 vol% nano-graphite without the SiC additive after

Fig. 4. Microstructures of the TaC-10 vol% nano Gr samples sintered at temperatures 2200 $^{\circ}$ C (a) and 2300 $^{\circ}$ C (b) for 1 h.

sintering at 2200 °C and 2300 °C are shown in Fig. 4. It shows that significant grain growth occurred during densification. The effect of the level of SiC addition on the microstructures of the samples after sintering at 2200 °C and 2300 °C are presented in Figs. 5&6. In these figures, the gray areas represent SiC, whereas the white areas are TaC, which were identified by the EDAX analysis in Fig. 7. It can be observed that the SiC grains have been located on the grain boundaries or triple junctions of the matrix (Figs. 5&6) [15]. Therefore, grain boundary mobility and the grain growth of the samples are inhibited by the SiC particles. This phenomenon reduces densification of the composite, as is shown in the Fig. 3. Figs. 5&6, also reveal that the grain sizes were slightly increased with an increase in the sintering temperature.

Fig. 8 illustrates the effect of the amount of SiC additive and sintering temperature on the average TaC grain size. As is shown the average grain size was increased with an increase in the sintering temperature, which has previously been confirmed in Figs. 5&6. The amount of SiC additive is another important factor that affects the grain growth significantly. Grains of the



Fig. 5. Microstructures of TaC-10 vol% nanoGr-SiC composite pressurless sintered at 2200 °C for 1 h.



Fig. 6. Microstructures of TaC-10 vol% nanoGr-SiC composite pressure-less sintered at 2300 °C for 1 h.



Fig. 7. EDAX analysis of a TaC-10 vol% nanoGr-SiC composite for a sample containuis 20% SiC.



Fig. 8. Effect of SiC content on the average grain size of TaC for the samples sintered at 2200 $^{\circ}$ C and 2300 $^{\circ}$ C for 1 h.

samples without SiC additive grow considerably. The average grain size are $11.2 \,\mu\text{m}$ and $12.8 \,\mu\text{m}$ for the

samples sintered at 2200 °C and 2300 °C, respectively. The TaC grain size was decreased with an increase in the SiC volume percentage. At 2200 °C The grain size of the samples was decreased from 11.2 to 3.9 μ m with an increase in the amount of SiC from 0 vol% to 20 vol%, whereas, it was decreased from 12.8 to 5.1 μ m at 2300 °C.

Hardness

The density, microstructure and grain size variations may have a significant influence on the hardness of the specimens. The hardness of the specimens as a function of the SiC content is shown in Fig. 9. Experimental results show that the hardness was increased with an increase in the sintering temperature. Increasing the sintering temperature enhances the density, and reduces the amount of porosity. Therefore, the hardness was increased with an increase in the sintering temperature. The hardness of specimens also was improved by increasing the level of SiC up to 10 vol%, as is shown in Fig. 9, while the density was decreased (Fig. 3). It can be subjected that despite the densification



Fig. 9. The hardness as a function of SiC addition to TaC-nanoGr compositions sintered at 2200 $^{\circ}C$ and 2300 $^{\circ}C$ for 1 h.

reduction effect of SiC, and due to the higher hardness of SiC (28.2 GPa) than that of the TaC (16.7 GPa) [1] and according to the rule of mixture the hardness of the composites was increased with the amount of SiC. However, above 10 vol% of SiC, the hardness was reduced with an increasing amount of SiC. This is because of the considerable amount of porosity within these samples, which demolish the enhancement effect of the high hardness of SiC.

Conclusions

(1) Due to insolubility of SiC in TaC, a solid solution was not produced therefore TaC and SiC are the only phases existing in the samples.

(2) The relative density of the composites was decreased from 94.2% to 82.5% when the amount of SiC was increased from 0 vol% to 20 vol% at 2200 °C. It also was decreased from 96.1% to 85.7% at 2300 °C.

(3) Significant grain growth occurred during densification of SiC-free samples. The TaC grain size was considerably

decreased with an increase in the additive level of SiC. The average grain size was increased with the sintering temperature.

(4) The hardness was improved with an increase in the sintering temperature. It also was also increased by increasing the level of SiC up to 10 vol%. However, above 10 vol% of SiC, the hardness was reduced with the amount of SiC.

References

- 1. O.P. Hug, *Handbook of refractory carbides and nitrides*, Noyes Publications, 1996.
- 2. C.L. Yeh and E.W. Liu, Journal of Alloys and Compounds, 415, (2006), 66-72.
- 3. D. Hwan Kwon, S. Hyeon Hong and B. Kee Kim, Journal of Materials Chemistry and Physics, 93, (2005), 1-5.
- 4. S. Scholz, Proceedings of a Symposium held by the British Ceramic Research, Academic Press Inc., New York, (1963), 293-307.
- 5. E.Roeder and M. Klerk, Z. Metalkunde, 54, (1963), 462-70.
- X. Zhang and GE. Hilmas, W.G Fahrenholtz, Journal of the American Ceramic Society, 90, (2007), 393-401.
- 7. X.Z hang and GE. Hilmas, W.G Fahrenholtz, Journal of the American Ceramic Society, 91, (2008), 4129-4132.
- M.C.L. Patterson, M. Fulcher, GE. Hilams, W.G Fahrenholtz, S.E.L. Landwehr, AIAA, 41, (2005).
- 9. J.X. Liu, Y.M. Kan, GJ. Zhang, Journal of the American Ceramic Society, (2009), 1-4.
- L. Silvestroni, D. Sciti, Advances in materials science and engineering, 11, (2010), 835018.
- 11. Songhe Meng, Guoqian Liu, Yue Guo, Xianghong Xu and Fan Song, Materials Design, 30, (2009), 2108-2112.
- James W. Zimmermann, Greg E. Hilmas and William G. Fahrenholtz, Materials Chemistry and Physics, 112, (2008), 140-145.
- R.P. Radtke and L.M. Swope, Technical Report AFRPL-TR-68-143, (August 1968).
- H.Z. Wang, L. Gao, J.K. Guo, Ceramics International, 26, (2000), 391-396.
- 15. K. Nihara, Journal of Ceramic Society Japan, 9, (1991), 970-974.