The Korean Journal of Ceramice, **5**[3] 230-234 (1999)

Effect of Mo_2C Content on the Microstructure and Properties of Ti(CN)-Mo_2C Ceramics

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(Received April 29, 1999)

Ti(CN) – 0~3 mole% Mo_2C ceramics were prepared by pressureless sintering. Mo_2C dissolved in Ti(CN) more easily in a nitrogen environment than in the other environment because nitrogen forced Mo to form a solid solution, (Ti,Mo)(C,N). A"core-rim" structure developed within the grains. The boundary between the "core" and the rim was delineated by thermal etching in the sample with more than 2 mole% Mo_2C. The rim thickness and the grain size decreased as the Mo_2C content increased. The hardness and the flexural strength showed maxima of 18.2 GPa and 1.23 GPa, respectively when the Mo_2C content was 2 mole%. The post-sintering heat treatments improved the properties.

Key words : Ti(CN), Mo_2C, Solid Solution, Environment, Sintering, Microstructure, Properties

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I. Introduction

Ti(CN) has been widely used in the cermet industry. It is a major ingredient of the cermet cutting tool material. Mo_2C has been one of the most widely used compounds along with Ti(CN) for manufacture of the cermet. Mo_2C surrounds Ti(CN) grains and makes a solid solution which prevents coalescence of the Ti(CN) grains and suppresses the grain growth. Addition of Mo to the TiC-Ni cermet was reported to improve the wetting of TiC toward Ni by forming (Ti, Mo)C "shell" around TiC "core" grains.[1] A similar core-shell structure is formed in Ti(CN)-Mo cermets. According to Suzuki and Matsubara,[2] the thickness of"shell"solid solution decreased as the Mo content increased in the Ti(CN)-Mo-Ni cermet. They also noticed that metallic Mo phase appeared in the $TiC_{0.5}N_{0.5}$-Mo-Ni cermet with more than 10 vol.% Mo. They also reported that the shell thickness and grain size of the Ti(CN)- Mo_2C ceramic became smaller as the Mo_2C content and the nitrogen gas pressure increased.[3] The flexural strength and hardness of the Ti(CN)-Mo_2C ceramics were lower than 950 MPa and 17.65 GPa, respectively.

Rudy examined the stability of pseudo-binary solid solutions based on thermodynamic consideration.[4] According to him, the two solid solutions in the Ti(CN)-Mo_2C systems, the core and rim, were formed by spinodal decomposition. He also mentioned that the grains of the core-rim structure exhibited more stable growth behavior than those consisting of one solid solution, the core or rim. Wally et al. claimed that the two solid solutions, or the core-rim structure, were thermodynamically stable in Ti(CN) based cermets.[5] According to them, the miscibility gap within the carbonitride phase (Ti, Mo)(C, N)$_{1-x}$ shrank as the nitrogen activity in the sintering environment increased.

In this study, Ti(CN)-Mo_2C powder mixtures were heated in a nitrogen environment and an argon environment. Variation of Mo_2C content in the sintered sample was examined in a qualitative way by using the relative intensity of Mo_2C peak obtained from the XRD patterns. Effect of Mo_2C addition on the microstructure and properties of Ti(CN)- Mo_2C ceramics was studied.

II. Experimental Procedure

$TiC_{0.5}N_{0.5}$ powder (0.75–0.85 μm, Kennametal Inc., Port Coquitlam, Canada) and Mo_2C powder (1–2 μm, Kennametal Co., Ltd) were ball milled for 48 h by using a stainless steel jar, acetone and WC-Co balls of 5 mm in diameter. Mo_2C content was 0, 1, 2, 3, 5, 10 and 20 mole%. After drying, the mixed powder was pressed under 10 MPa by a lever press. Cylindrical compacts of two sizes were prepared; 10 mm in diameter X 10 mm in height and 36 mm in diameter X 5 mm height. The small compacts, 10 mm in diameter X 10 mm in height, were placed in a graphite crucible and heated in a furnace with a graphite heating element for 1 h. The large ones, 36 mm in diameter X 5 mm height, were cold isostatically pressed under 250 MPa, and, then, were placed in a graphite crucible prior to heating in the furnace for 1 h. The small samples with 3, 5, 10, and 20 mole% Mo_2C were heated to a temperature between 1673 K and 2073 K, and the large ones with 0, 1, 2, 3 mole% Mo_2C at 1973 K. The small samples were heated in either a flowing nitrogen atmosphere or a flowing argon atmosphere, and the large ones were heated in a flowing nitrogen atmosphere.

The small samples were ground by using an agate mortar and pestle, and analyzed by X-ray diffraction method. They were gold-coated for electrical conductivity and examined under the scanning electron microscope (SEM) equipped with energy disperse spectroscopy (EDS). XRD was performed under a 35 KV–25 mA condition. The scan speed was 4 degree/min. From the patterns, the intensities of Ti(CN) peak and Mo_2C peak were obtained, and the relative intensity ratio was recalculated as follows. From the patterns of the starting powder, the intensities of (200) peak of Ti(CN) and (101) peak of Mo_2C were obtained. The (101) peak intensity of Mo_2C/((200) peak intensity of Ti(CN)+(101) peak intensity of Mo_2C) ratio was set equal to 10. The ratio obtained from the heat treated sample was divided by that of the starting powder and was multiplied by 10. This relative intensity ratio gives only a qualitative description on how the Mo_2C content varied according to the heat treatment. But the information is still valuable. Carbon content and nitrogen content of the ground powders were analyzed by using a carbon analyzer (WR112, Leco Corp., St. Joseph, MI, USA) and a nitrogen analyzer (TC436, Leco Corp.). The large samples were sintered to a full density and their densities were obtained by Archimedes method. They were subjected to the property measurements including the hardness, the three point flexural strength and the fracture toughness. Vickers hardness was obtained by using 9.8 N load. The average three point flexural strength was obtained from 9 measurements. The dimensions of the bend bars were 3 mm × 4 mm × >20 mm. The span was 20 mm and the crosshead speed was 0.5 mm/min. Lengths of the cracks generated by Vickers indentation under 196 N load were measured, and the fracture toughness was obtained according to Evans and Charles equation.[6)] Some of the large samples were thermally etched by heating at 1723 K for 1 h in a flowing argon atmosphere and, then, were examined by SEM equipped with EDS after gold-coating. The grain size was measured by the linear intercept method. About 80 grains were measured for the average grain size.

III. Results and Discussion

1. Samples heated at temperature between 1673 K and 1973 K

Fig. 1 shows variation of the relative intensity ratio of Mo_2C peak obtained from the XRD pattern of Ti(CN)-10 mole% Mo_2C sample. Even though the Mo_2C content can not be quantified, it is readily recognized that it decreased as the temperature increased. Also, the Mo_2C peak intensity decreased faster in the nitrogen environment than in the argon environment. The Mo_2C peak intensity of the sample after the heat treatment at 1873 K in a nitrogen environment was too weak to detect while the sample heated in an argon environment exhibited a strong Mo_2C peak. Nitrogen environment forced Mo to form a solid solution with Ti(CN) because of low affinity of Mo with N. According to Wally *et al.*,[5)] occupation of more non-metal sub-lattice in the solid solution reduces the miscibility gap in the Ti(CN)-Mo_2C system. So, Mo_2C dissolved in Ti(CN) more readily in the nitrogen atmosphere than in the argon atmosphere. Fig. 2 shows variation of the N/C ratio according to the heat treatment temperature. The ratio was higher in the nitrogen atmosphere than in the argon atmosphere. One of the reasons for the higher ratio in the nitrogen atmosphere is the fact that Ti(CN) absorbs nitrogen during the heat treatment as reported by Kieffer *et al.*[7)] Another reason for the higher ratio in the nitrogen atmosphere is more nitrogen occupying the non-metal sub-lattice in the (Ti,Mo)(C,N) solid solutions. When the sample was heated in the nitrogen environment, the carbon content decreased noticeably and the nitrogen content increased. But (N+C) content was increased by the heat treatment in the nitrogen environment while it was decreased in the argon environment. It means that more non-metal sub-lattice of the solid solution was occupied by

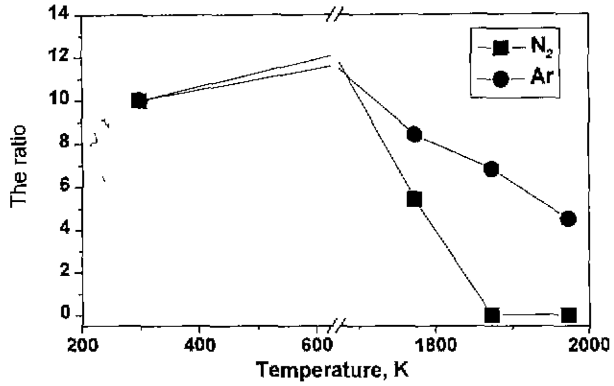

Fig. 1. Variation in the ratio of (101) peak intensity of Mo_2C with respect to the sum of (200) peak intensity of Ti(CN) and (101) peak intensity of Mo_2C according to the heat treatment temperature; the peak intensities were obtained from the XRD patterns.

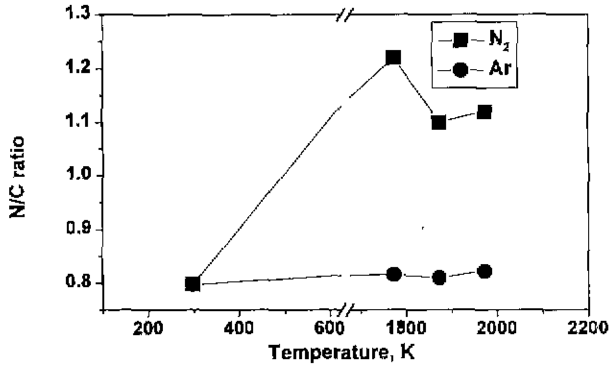

Fig. 2. Variation of the C/N ratio of the samples after the heat treatment in nitrogen atmosphere and argon atmosphere; data obtained from the carbon and nitrogen analyses.

the heat treatment in the nitrogen environment than in the argon environment. As the temperature increased from 1673 K, the N/C ratio of the samples heated in the nitrogen environment decreased as shown in Fig. 2. Nitrogen content in the carbonitride decreased at high temperatures due to thermodynamic instability, as reported by Kieffer *et al.*[8] In other words, Ti(CN) loses nitrogen as the temperature increased under a given nitrogen pressure. That explains why the N/C ratio was decreased as the temperature increased. It is interesting to note the variation of the N/C ratio of the samples heated in argon atmosphere. The ratio remained almost constant in the temperature range as shown in Fig. 2 because carbon as well as nitrogen was lost at the temperature higher than 1873 K in the argon environment.

2. *Microstructure and properties of the sintered samples*

The large samples were sintered at 1973 K for 1 h in a flowing nitrogen environment. The sintered densities were 5.27, 5.39, 5.47 and 5.55 g/cc for the samples with 0, 1, 2 and 3 mole% Mo_2C, respectively. According to the rule of mixture of the ceramic ingredients, i.e. $TiC_{0.5}N_{0.5}$ and Mo_2C, theoretical densities of the samples are 5.19, 5.20, 5.33 and 5.40 g/cc, respectively. So, the sintered densities were higher than the theoretical. The possible reasons for such high densities were explained in the previous report.[8] They are summarized as follows. The metallic impurities ground during ball milling facilitated sintering of the samples, and their presence increased the densities above the theoretical. The samples with 3 mole% Mo_2C were subjected to further heat treatment in the pressurized argon environments by using a gas pressure sintering furnace (1873 K for 0.5 h under 7 MPa argon pressure) and a HIP (1773 K for 1 h under 150 MPa agron pressure). After the post-sintering heat treatments, the density was slightly increased to 5.58 g/cc.

Fig. 3 shows SEM micrographs of the samples after thermal etching. The grain size decreased from 4.74 μm to 2.89 μm when 1 mole% Mo_2C was added to Ti(CN). When the Mo_2C content was increased from 1 mole% to 2 mole%, the grain appeared to be divided into the "core" and "rim" grains. EDS on the two grains, the "core" and "rim" grains, in Fig. 3(c) revealed that the "core" grain was rich in Ti and did not contain Mo. Mo content in the "rim" grain was higher than the average Mo content of the sample. So, a single grain of the "core-rim" structure where the "core" is rich in Ti and the "rim" rich in Mo appeared to be divided into the two grains during thermal etching. When the Mo_2C content was increased to 3 mole%, the "core" grains and rim grains became smaller and some of them were completely separated from each other. Fig. 3 explicitly confirms the results on the grain size variation with Mo_2C content in the Ti(CN)- Mo_2C

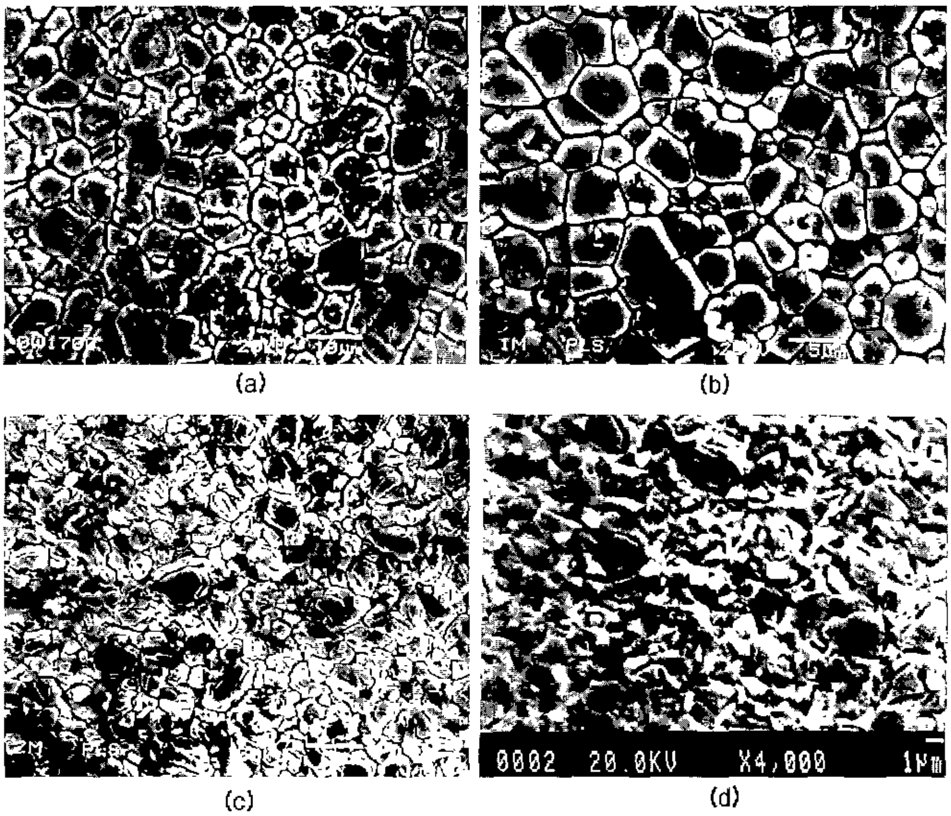

Fig. 3. SEM micrographs of the sintered samples after thermal etching; (a) Ti(CN), (b) Ti(CN)-1 mole % Mo_2C, (c) TiCN)-2 mole% Mo_2C and (d) Ti(CN)-3 mole% Mo_2C.

ceramics reported by Suzuki and Matsubara[3]; the grain size and the rim thickness decrease as the Mo_2C content increases. Also, it implies that the boundary energy between the two solid solutions, the core and rim, within a single grain is high enough to be delineated by thermal etching. In other words, it is in as high energy state as the grain boundary. The boundary became more easily etched as the sample contained more Mo_2C. This suggests that Mo_2C concentration in the rim increased and the boundary energy increased as the Mo_2C content increased. Then, it is probable that there is a strain along the boundary and it increased as the Mo_2C content increased. Fig. 4 shows the samples sintered at 2073 K for 1 h in an argon environment. It clearly shows grains of the "core-rim" structure. It is interesting to note that some grains have bright cores while the dark cores are more popular. The dark cores were rich in Ti, while the bright cores were rich in Mo. As Mo_2C content increased to 20 mole%, the grain size and the rim thickness decreased. Also, it is noticed that there were many bright regions in the micrograph. EDS on this bright area revealed that they are rich in Mo. The XRD pattern showed that the Mo_2C peaks remained strong after the heat treatment at 2073 K, as Fig. 1 shows. The microstructure was not changed noticeably during the post-sintering heat treatments.

Fig. 5 shows the mechanical properties of the samples. The hardness was increased by adding Mo_2C to Ti(CN); from 15.9 GPa for Ti(CN) sample to 18.2 GPa for Ti(CN)-2 mole% Mo_2C sample. For the samples with more than 2 mole% Mo_2C, the hardness decreased slightly. The three point flexural strength values also showed a maximum of 1.23 GPa when the sample contained 2 mole% Mo_2C. Even though the strength data showed a big scatter, the average values were higher than 1 GPa. So, Ti(CN)-Mo_2C ceramics with both high hardness and high strength were fab-

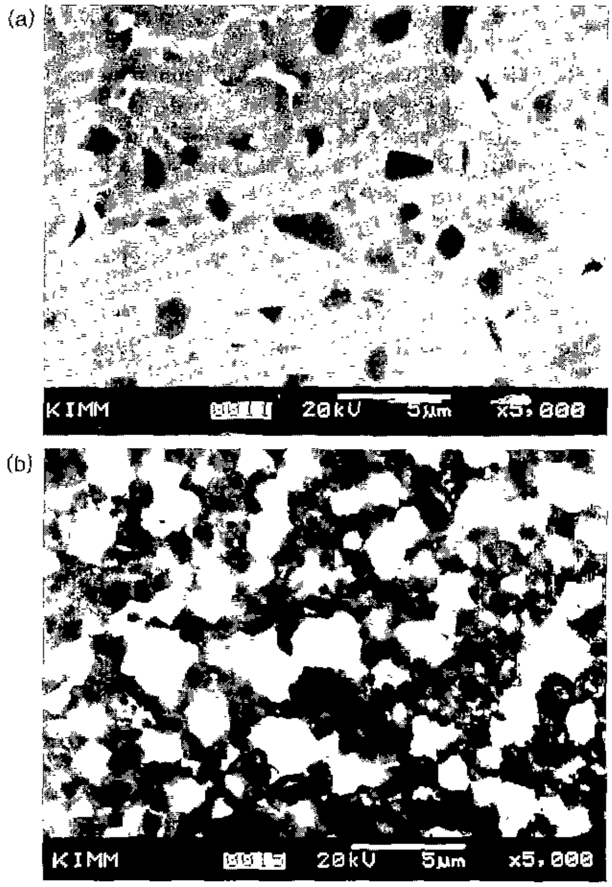

Fig. 4. As-polished surfaces of the samples sintered in an argon environment; (a) Ti(CN)-3 mole% Mo_2C and (b) Ti(CN)-20 mole% Mo_2C.

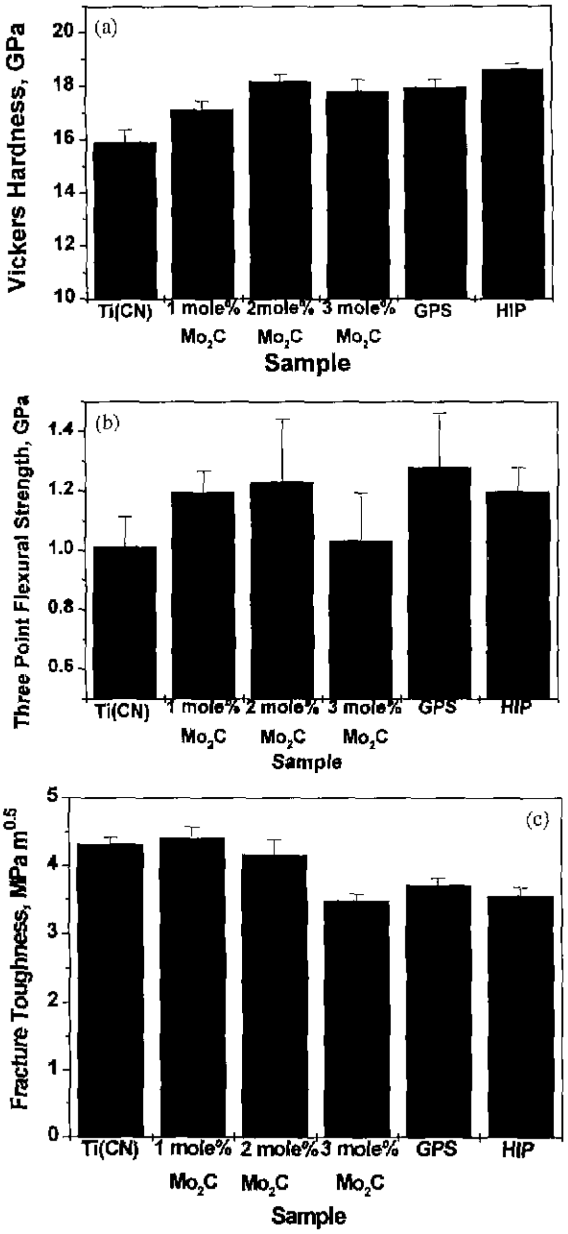

Fig. 5. Mechanical properties of the samples sintered in nitrogen environment; (a) microvickers hardness, (b) the three point flexural strength and (c) the fracture toughness.

ricated by pressureless sintering. By the post-sintering heat treatments, the density of the sample with 3 mole% Mo_2C was increased as previously indicated. The hardness was increased to 18.6 Gpa by HIP treatment and the flexural strength to 1.28 Gpa by the heat treatment in GPS. As the Mo_2C content increased, the fracture toughness decreased except the case where it increased from 0 to 1 mole%. Although the metallic film forms a continuous grain boundary in the sample as previously reported,[8] the fracture toughness of the sample was low. Ductility and the high fracture toughness of the metallic phase was not fully reflected in the samples. The fracture toughness of the ceramics decreased as the grain size decreased as reported by Becher.[9] So, the decrease of the fracture toughness according to the increase of the Mo_2C content as shown in Fig. 5(c) was in part due to the decrease of the grain size. Ti(CN) ceramics with more than 5 mole% Mo_2C were sintered in the nitrogen environment, but they were not proper for property measurement due to the cracks observed after grinding.

IV. Conclusion

During the heat treatment of Ti(CN)-Mo_2C ceramics, Mo_2C dissolved in Ti(CN) more easily in a nitrogen environment than in an argon environment because nitrogen forced Mo to dissolve in the solid solution. Ti(CN)-Mo_2C ceramics were sintered to a full density by sintering at 1973 K in a flowing nitrogen environment. The boundary between the core and the rim in the sample with more than 2 mole% Mo_2C was delineated by thermal etching, which implies that the boundary is in as high energy state as the grain boundary. The grain size and the rim thickness decreased as the Mo_2C content increased. Vickers hardness and the three point flexural strength showed maximum values of 18.2 GPa and 1.23 GPa, respectively. The post-sintering heat treatments improved the hardness and the flexural strength of the sample with 3 mole % Mo_2C.

Acknowledgment

This work has been supported by Korea Ministry of Science and Technology. The carbon and nitrogen analyses performed by Korloy Co., Cheongju, Chung-buk, were deeply appreciated.

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