

Enhanced mechanical properties of nanostructured (W, Ti)CN-TiAl₃ composites rapidly sintered by the high frequency induction heating

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In the case of metal carbonnitride, Ni or Co is added as a binder for the formation of composite structures. However, the high cost of Ni or Co and the low corrosion resistance of the metal carbonnitride cermets have generated interest in recent years for alternative binder phases. In this study, TiAl₃ was used as a novel binder and consolidated by the high frequency induction heated sintering (HFIHS) method. Highly dense (W, Ti)CN-TiAl₃ with a relative density of up to 98% was obtained within 2 min by HFIHS under a pressure of 80 MPa. The method was found to enable not only the rapid densification but also the inhibition of grain growth preserving the nano-scale microstructure. The addition of TiAl₃ to (W, Ti)CN simultaneously improved the fracture toughness and hardness of (W, Ti)CN-TiAl₃ composite.

Keywords: Nanomaterials, Sintering, Hardness, Fracture Toughness, Composite.

Introduction

Metal carbonnitride is one of the promising ceramic materials, because it exhibits unusual combinations of physical and chemical properties such as high hardness, high melting point and excellent resistance to oxidation [1, 2]. Industrial applications of the compound are in cutting tools and hard coatings. It is used extensively in cutting tool and abrasive materials in composite with a binder metal, such as Ni or Co. The binder phase has inferior chemical characteristics compared to the carbide or nitride phase. Most notably, corrosion and oxidation occur preferentially in the binder phase [3]. Hence, the high cost of Ni or Co and the low corrosion resistance of the metal carbonnitride cermet have generated interest in recent years to find alternative binder phases [4, 5]. It has been reported that aluminides show a higher oxidation resistance, a higher hardness and a cheaper materials compared to Ni or Co [6].

The improvement of mechanical properties and stability of cemented carbides could be achieved through microstructural changes such as grain size refinement [7, 8]. Nanocrystalline materials have received much attention as advanced engineering materials with improved physical and mechanical properties [9, 10]. Since they possess a high strength and hardness as well as excellent ductility and toughness, they have garnered more attention recently

[11, 12]. Recently, nanocrystalline powders have been produced by high-energy milling [13, 14]. The sintering temperature of high-energy mechanically milled powder is lower than that of unmilled powder due to the increased reactivity, internal and surface energies, and surface area of the milled powder, which contribute to its so-called mechanical activation [15-17]. However, the use of conventional methods to consolidate nanopowders often leads to grain growth due to the extended time for sintering. Generally, the grain growth could be minimized by sintering at lower temperatures and for shorter times. In this regard, the high frequency induction heated sintering (HFIHS) technique has been shown to be effective in the sintering of nanostructured materials in a very short time (typically within 1 minute) [18-21].

We present here the results of the sintering of (W, Ti)CN and (W, Ti)CN-TiAl₃ composites by a high frequency induction heated sintering with simultaneous application of induced current and high-pressure. The goal of this study was to produce dense and nanocrystalline (W, Ti)CN and (W, Ti)CN-TiAl₃ hard materials in very short sintering times (< 2 min). The effect of novel TiAl₃ binder on the mechanical properties, sintering behavior and relative density of (W, Ti)CN-TiAl₃ composites was also examined.

Experimental Procedures

The (W, Ti)CN powder used in this research was supplied by Treibacher Industry AG (Germany). The average particle size was about 1.4 μm and the purity

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was 99%. TiAl_3 (<45 μm , 99% pure, Sejong Co.) was used as binder material. Powders of three compositions corresponding to (W, Ti)CN, (W, Ti)CN-5 vol.% TiAl_3 , and (W, Ti)CN-10 vol.% TiAl_3 were prepared by weighing and milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm for 10 h. WC balls (9 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. The weight ratio of balls-to-powder was 30 : 1. The grain size of the powders was calculated from the full width at half-maximum (FWHM) of the diffraction peak by Suryanarayana and Grant Norton's formula [22].

$$B_r(B_{\text{crystalline}} + B_{\text{strain}}) \cos\theta = k \lambda / L + \eta \sin\theta \quad (1)$$

where B_r is the full width at half-maximum (FWHM) of the diffraction peak after instrumental correction; $B_{\text{crystalline}}$ and B_{strain} are FWHM caused by small grain size and internal stress, respectively; k is constant (with a value of 0.9); λ is wavelength of the X-ray radiation; L and η are grain size and internal strain, respectively; and θ is the Bragg angle. The parameters B and B_r follow Cauchy's form with the relationship: $B = B_r + B_s$, where B and B_s are the FWHM of the broadened Bragg peaks and the standard sample's Bragg peaks, respectively.

The milled powders were placed in a graphite die (outside diameter, 35 mm; inside diameter, 10 mm; height, 40 mm) and then introduced into the high frequency induction heated sintering (HFIHS) system made by Eltek Co. in the Republic of Korea. A schematic diagram of this system is shown in Ref. [18-21]. The HFIHS apparatus includes a 15 kW power supply and a uniaxial press with a maximum load of 50 kN. The system was first evacuated and a uniaxial pressure of 80 MPa was applied. A induced current was then activated and maintained until the densification rate became negligible, as indicated by the observed shrinkage of the sample. Sample shrinkage was measured in real time by a linear gauge measuring the vertical displacement. Temperature was measured by a pyrometer focused on the surface of the graphite die. A temperature gradient from the surface to the center of the sample is dependent on the heating rate, the electrical and thermal conductivities of the compact, and its relative density. The heating rates were approximately $1400^\circ\text{K minute}^{-1}$ during the process. At the end of the process, the current was turned off and the sample was allowed to cool to room temperature. The entire process of densification using the HFIHS technique consists of four major control stages: chamber evacuation, pressure application, power application, and cooling off. The process was carried out under a vacuum of 5.33 Pa.

The relative densities of the sintered samples were measured by the Archimedes method. Microstructural information was obtained from the product samples,

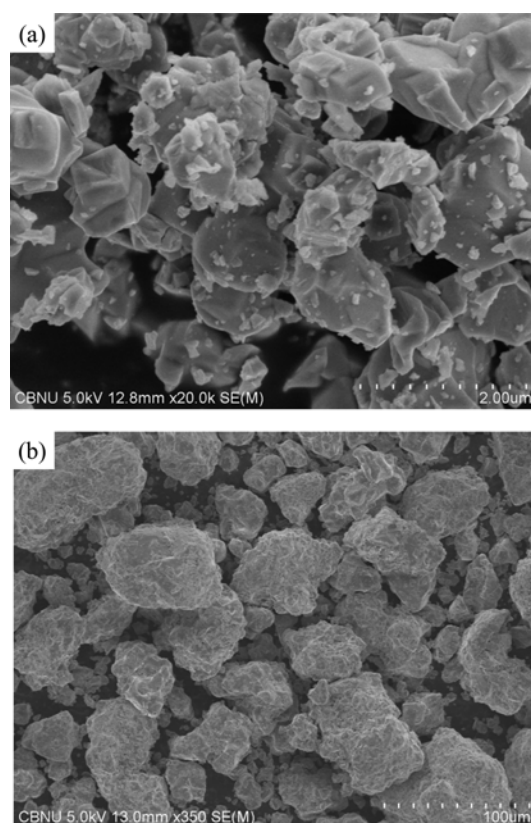


Fig. 1. FE-SEM images of raw materials: (a) (W, Ti)CN powder, and (b) TiAl_3 powder.

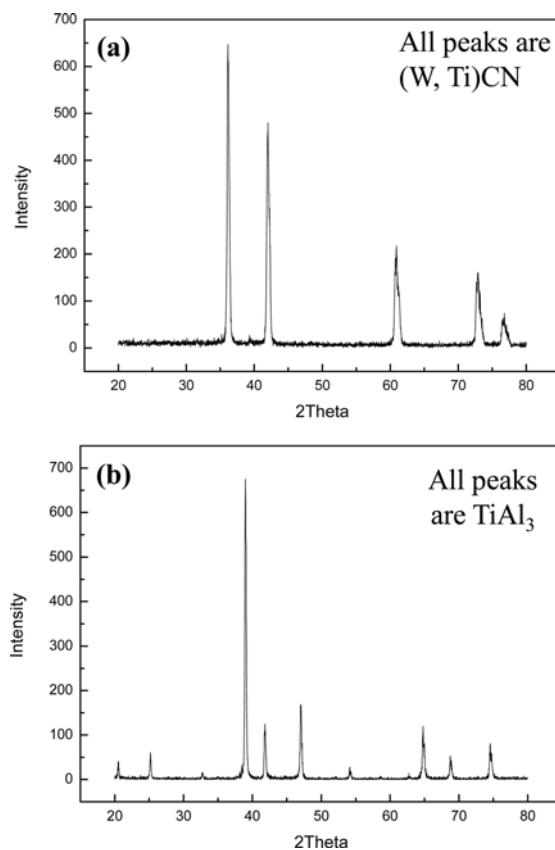


Fig. 2. XRD patterns of raw materials: (a) (W, Ti)CN powder, and (b) TiAl_3 powder.

which had been polished and etched, using Murakami's reagent (10 g potassium ferricyanide, 10 g sodium hydroxide, and 100 ml water), for 1-2 minutes at room temperature. Compositional and microstructural analyses of the samples were carried out through X-ray diffraction (XRD), and field-emission scanning electron microscopy (FE-SEM). Vickers hardness was measured by performing indentations at a load of 10 kg_f with a dwell time of 15 s.

Results and Discussion

Fig. 1 and b2 show FE-SEM images and X-ray diffraction patterns of (W, Ti)CN and TiAl₃ raw powders, respectively. The powders has irregular shape and In XRD patterns, only (W, Ti)CN peaks and TiAl₃ peaks are detected in Fig. 2(a) and Fig. 2(b), respectively. FE-SEM images of milled to (W, Ti)CN,

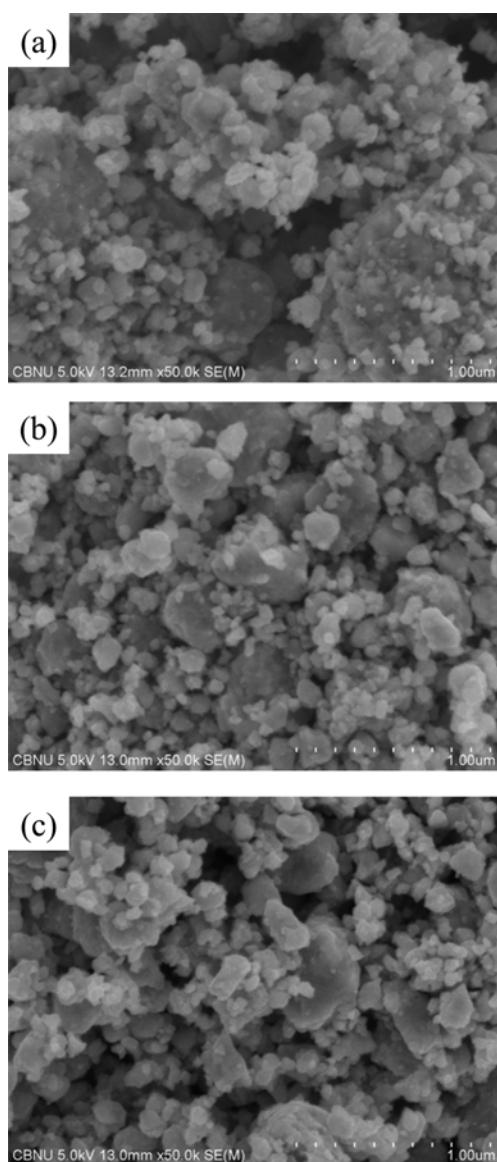


Fig. 3. FE-SEM images of powders milled for 10 h; (a) (W, Ti)CN, (b) (W, Ti)CN-5 vol.% TiAl₃, and (c) (W, Ti)CN-10 vol.% TiAl₃.

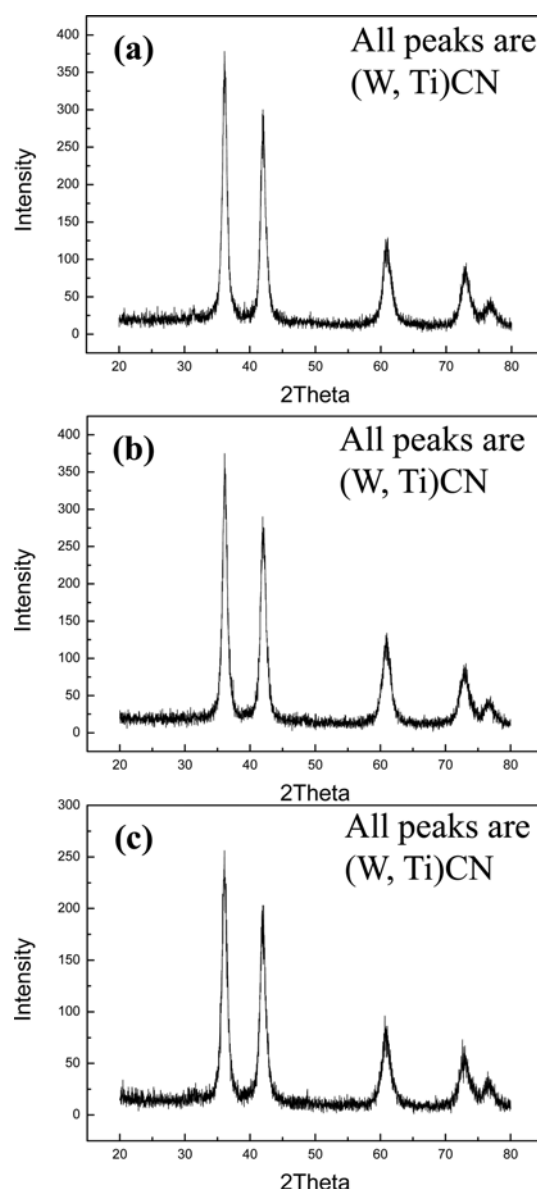


Fig. 4. XRD patterns of (a) (W, Ti)CN, (b) (W, Ti)CN-5 vol.% TiAl₃, and (c) (W, Ti)CN-10 vol.% TiAl₃ powders milled for 10 h.

(W, Ti)CN -5 vol.% TiAl₃, and (W, Ti)CN -10 vol.% TiAl₃ for 10h are shown in Fig. 3. The powders are very fine and have a round shape. Fig. 4 shows X-ray diffraction pattern of the (W, Ti)CN, (W, Ti)CN-5 vol.% TiAl₃, and (W, Ti)CN -10 vol.% TiAl₃ powders after milling for 10 h. The broadening of (W, Ti)CN peaks due to crystallite refinement and strain is evident after milling for 10 h. The milling process is known to introduce impurities from the ball and/or container. However, in this study, peaks other than (W, Ti)CN were not identified. The average grain sizes of the (W, Ti)CN in the (W, Ti)CN, (W, Ti)CN-5 vol.% TiAl₃, and (W, Ti)CN-10 vol.% TiAl₃ powders after milling for 10 h. calculated from the XRD data using Suryanarayana and Grant Norton's formula [22] were about , 49, 30 and 27 nm, respectively.

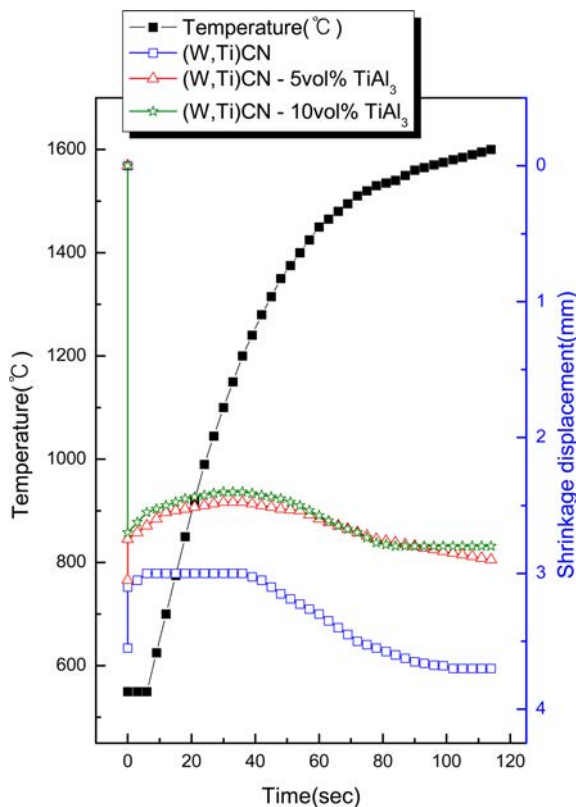


Fig. 5. Variations of temperature and shrinkage displacement with heating time during the sintering of (W, Ti)CN, (W, Ti)CN-5 vol.% TiAl_3 , and (W, Ti)CN-10 vol.% TiAl_3 hard materials by HFIHS.

The shrinkage displacement-time (temperature) curve provides an important information on the consolidation behavior. Fig. 5 shows the shrinkage record of (W, Ti)CN in the (W, Ti)CN, (W, Ti)CN-5 vol.% TiAl_3 , and (W, Ti)CN-10 vol.% TiAl_3 compacts under the applied pressure of 80 MPa. In all cases, as induced current was applied, thermal expansion shows up to in the range 1100 and 1200 °C according to TiAl_3 content. And then shrinkage displacement abruptly increased above the temperature. The application of the induced current resulted in shrinkage due to consolidation. The temperature of rapid shrinkage initiation was seen to reduce by the addition of TiAl_3 . It is considered that it is related to the melting of TiAl_3 phase due to large Joule heat at contact of powders. Therefore, the main densification mechanism could be the rearrangement of carbide particles, enhancement of the diffusion, and viscous flow of the binder [23].

Fig. 6 shows the XRD patterns of (W, Ti)CN, (W, Ti)CN-5 vol.% TiAl_3 , and (W, Ti)CN-10 vol.% TiAl_3 after sintering. In all cases, only (W, Ti)CN peaks are detected. Fig. 7 shows plot of B_r ($B_{\text{crystalline}} + B_{\text{strain}}$) $\cos\epsilon$ versus $\sin\epsilon$ in Suryanarayana and Grant Norton's formula [22] to calculate particle size. The average grain sizes of the (W, Ti)CN in (W, Ti)CN, (W, Ti)CN-5 vol.% TiAl_3 , and (W, Ti)CN-10 vol.% TiAl_3 calculated from the XRD data using Suryanarayana and Grant

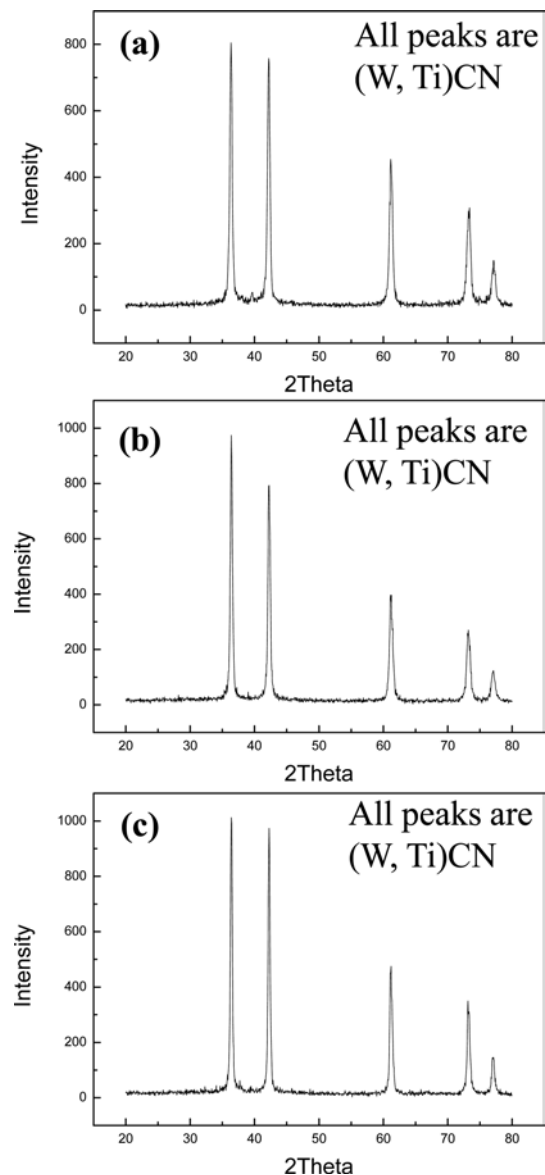


Fig. 6. XRD patterns of (a) (W, Ti)CN, (b) (W, Ti)CN-5 vol.% TiAl_3 , and (c) (W, Ti)CN-10 vol.% TiAl_3 hard materials produced by HFIHS.

Norton's formula are about 70, 37, and 28 nm. FE-SEM images of the samples being sintered up to about 1600 °C are shown in Fig. 8. It is apparent that the (W, Ti)CN grains consist of nanocrystallites suggesting the absence of grain growth during sintering. This retention of the fine grain structure can be attributed to the high heating rate and the relatively short exposure to the high temperature. Relative densities corresponding to (W, Ti)CN, (W, Ti)CN -5 vol.% TiAl_3 , and (W, Ti)CN -10 vol.% TiAl_3 were approximately 98, 96 and 97%, respectively.

The role of the current in sintering and/or synthesis has been the focus of several attempts to provide an explanation for the observed sintering enhancement and the improved characteristics of the products. The role played by the current has been variously interpreted. The

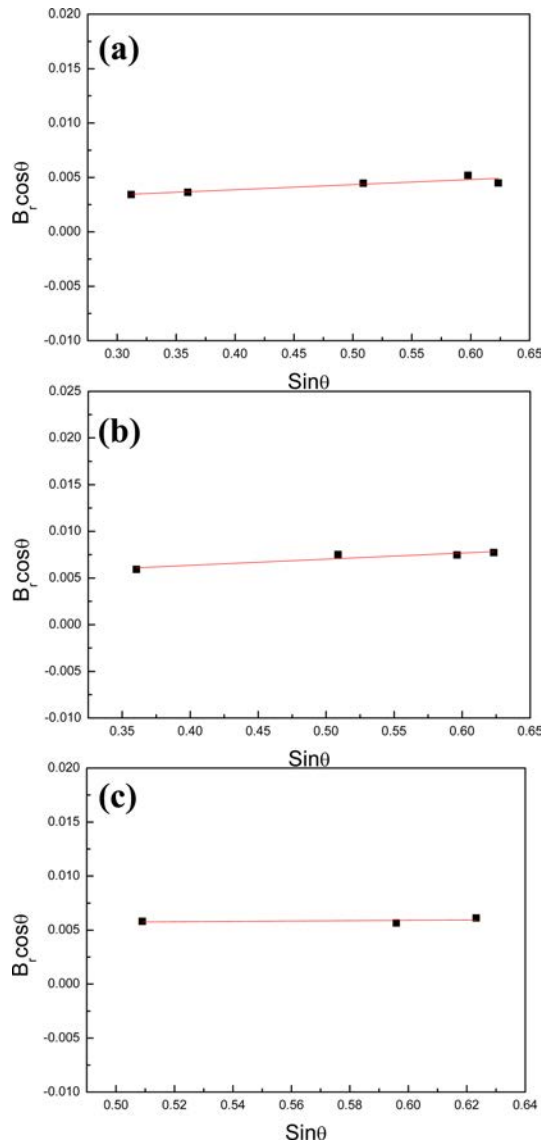


Fig. 7. Plot of $Br (B_{\text{crystalline}} + B_{\text{strain}}) \cos\theta$ versus $\sin\theta$ for (W, Ti)CN in (a) (W, Ti)CN, (b) (W, Ti)CN-5 vol.% TiAl₃, and (c) (W, Ti)CN-10 vol.% TiAl₃.

effect has been explained by fast heating due to Joule heating at contacts points, the presence of plasma in pores separating powder particles, and the intrinsic contribution of the current to mass transport [24-28].

Vickers hardness measurements were performed on polished sections of the (W, Ti)CN, (W, Ti)CN-5 vol.% TiAl₃, and (W, Ti)CN-10 vol.% TiAl₃ samples using a 10 kg load and 15 s dwell time. Indentations with 10 kgf load produced median cracks around the indentation from which fracture toughness can be calculated. The lengths of these cracks permit estimation of the fracture toughness of the materials by means of the expression [29]:

$$K_{IC} = 0.203(c/a)^{-3/2} \cdot H_v \cdot a^{1/2} \quad (2)$$

where c is the trace length of the crack measured from

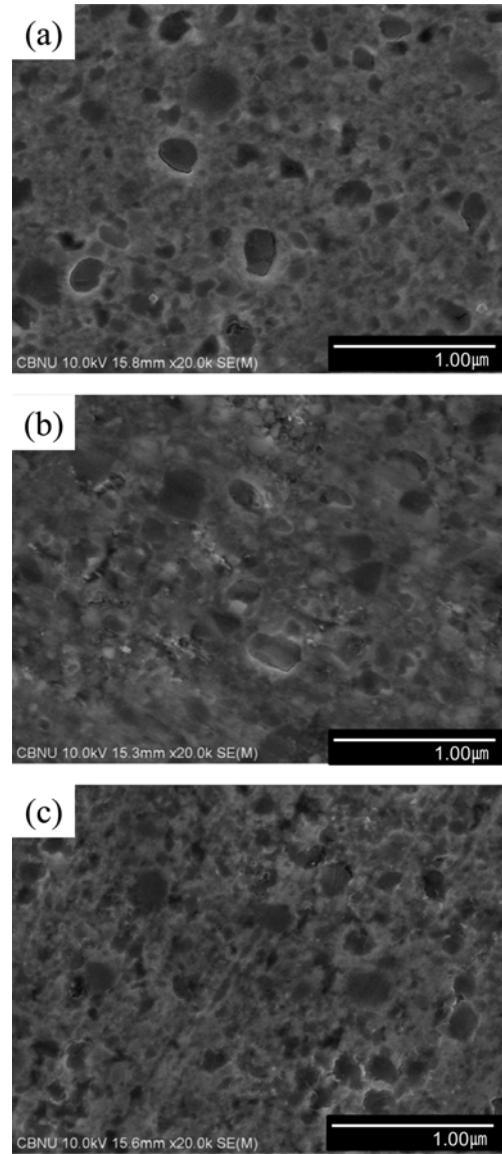


Fig. 8. FE-SEM images of (a) (W, Ti)CN, (b) (W, Ti)CN-5 vol.% TiAl₃, and (c) (W, Ti)CN-10 vol.% TiAl₃ hard materials produced by HFIHS.

the center of the indentation, a is one half of the average length of the two indent diagonals, and H_v is the hardness.

The Vickers hardness and the fracture toughness values of the (W, Ti)CN, (W, Ti)CN-5 vol.% TiAl₃, and (W, Ti)CN-10 vol.% TiAl₃ samples were 1072 kg/mm², 2 MPa · m^{1/2}, and 1170 kg/mm², 5 MPa · m^{1/2} and 2420 kg/mm², 5.7 MPa · m^{1/2}, respectively. These values represent the average of five measurements. The fracture toughness and hardness of (W, Ti)CN-5 vol.% TiAl₃, and (W, Ti)CN-10 vol.% TiAl₃ samples are higher than that of monolithic (W, Ti)CN. It is generally accepted that the grain refinement may increase the hardness according to the Hall-Patch type strengthening effect. This may be the case since the addition of TiAl₃ refined the grain size of (W, Ti)CN significantly in this study. The hardness of metal carbide greatly decreased by addition of Co or Ni

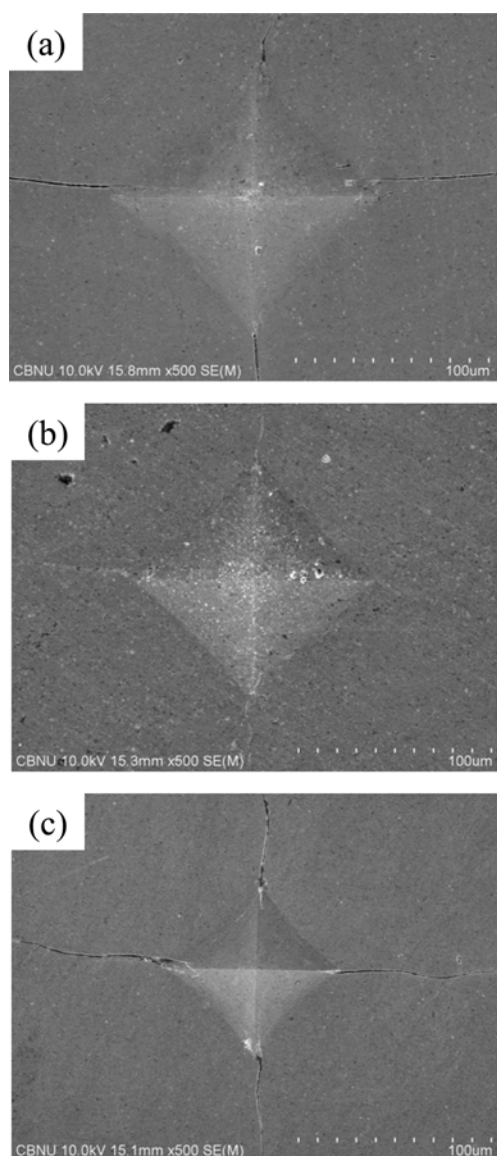


Fig. 9. Vickers hardness indentation of (a) (W, Ti)CN, (b) (W, Ti)CN-5 vol.% TiAl_3 , and (c) (W, Ti)CN-10 vol.% TiAl_3 hard materials produced by HFIHS.

[30]. The use of TiAl_3 binder instead of Co or Ni is very effective especially to maintain the high hardness of monolithic (W, Ti)CN without the expense of toughness reduction. In this regard, it would be worthwhile to consider TiAl_3 as the possible replacement for Co or Ni especially for the applications requiring a high hardness.

Vickers hardness indentations in the (W, Ti)CN-5 vol.% TiAl_3 , and (W, Ti)CN-10 vol.% TiAl_3 samples show typically one to three additional cracks propagating radially from the indentation in Fig. 9. Fig. 10 shows a crack propagated in a defective manner ($\uparrow$) in (W, Ti)CN-10 vol.% TiAl_3 composite. The enhanced fracture toughness of (W, Ti)CN-10 vol.% TiAl_3 composite is believed that (W, Ti)CN and TiAl_3 in the composite may deter the propagation of cracks and (W, Ti)CN and TiAl_3 have nanostructure phases.

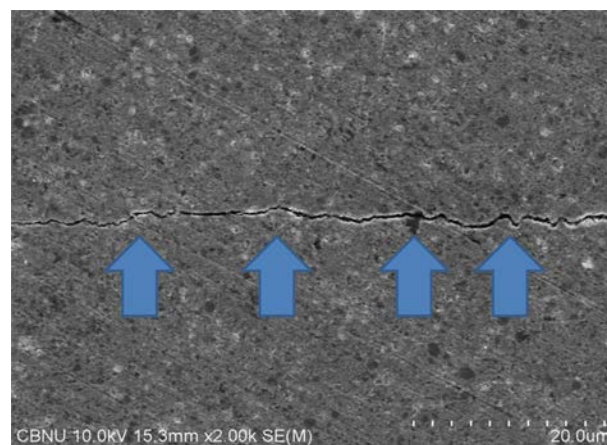


Fig. 10. Crack propagation in (W, Ti)CN-10 vol.% TiAl_3 hard materials produced by HFIHS.

Conclusions

Using high frequency induction heated sintering (HFIHS), the rapid consolidation of the (W, Ti)CN, (W, Ti)CN-5 vol.% TiAl_3 , and (W, Ti)CN-10 vol.% TiAl_3 was accomplished successfully. Nearly full-dense (W, Ti)CN- TiAl_3 composites could be obtained within 2 min. The starting temperature of rapid densification of (W, Ti)CN were reduced remarkably by the addition of TiAl_3 . The average grain sizes of the (W, Ti)CN in (W, Ti)CN, (W, Ti)CN-5 vol.% TiAl_3 , and (W, Ti)CN-10 vol.% TiAl_3 calculated from the XRD data using Suryanarayana and Grant Norton's formula are about 70, 37, and 28 nm. The Vickers hardness and the fracture toughness values of the (W, Ti)CN, (W, Ti)CN-5 vol.% TiAl_3 , and (W, Ti)CN-10 vol.% TiAl_3 samples were 1072 kg/mm^2 , 2 $\text{MPa} \cdot \text{m}^{1/2}$, and 1170 kg/mm^2 , 5 $\text{MPa} \cdot \text{m}^{1/2}$ and 2420 kg/mm^2 , 5.7 $\text{MPa} \cdot \text{m}^{1/2}$, respectively. The addition of TiAl_3 to (W, Ti)CN simultaneously improved the fracture toughness and hardness of (W, Ti)CN- TiAl_3 composite. This study demonstrates that the TiAl_3 can be an effective reinforcing agent for improved mechanical properties of (W, Ti)CN composites.

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References

1. B Gomez, A Jimenez, E Gordo, *Int. Journal of Refractory Metals & Hard Materials* 27 (2009) 360-336.
2. D Mari, S Bologini, T Viatte, *Int. Journal of Refractory*

- Metals & Hard Materials 19 (2001) 257-65.
3. S Imasato, K Tokumoto, T Kitada, S Sakaguchi, Int J of Refract Met and Hard Mater 13 (1995) 305-12.
 4. G Gille, J Bredthauer, B Gries, B Mende, Int J of Refract Met and Hard Mater 18 [2-3] (2000) 87-102.
 5. P Goeuriot, F Thevenot, Ceramics International 13 [2] (1987) 99-103.
 6. Z.G. Zhang, F. Gesmundo, P.Y. Hou, Y. Niu, Corrosion Science 48 (2006) 741-765.
 7. H Gleiter, Progress in Materials Science 33 [4] (1989) 223-315.
 8. GE Fougere, JR Weertman, RW Siegel, S Kim, Scripta Metallurgica et Materialia 26 [2] (1992) 1879-1883.
 9. M. Sherif El-Eskandarany, J. Alloys & Compounds 305 (2000) 225-38.
 10. L Fu, LH Cao, YS Fan, Scripta Materialia 44 (2001) 1061-1068.
 11. K Niihara, A Nikahira, Advanced structural Inorganic Composite, Elsevier Scientific Publishing Co., Trieste, Italy, 1990.
 12. S Berger S, R Porat R, R Rosen, Progress in Materials, Progress in Materials 42 (1997) 311-320.
 13. G.W. Lee, I.J. Shon, Korean J. Met. Mater. 51, (2013) 95-100.
 14. I.J. Shon, G.W. Lee, J.M. Doh, J.K. Yoon, Electronic Materials Letters, 9 (2013) 219-225.
 15. F. Charlot, E. Gaffet, B. Zeghmati, F. Bernard, J. C. Liepce, Mater. Sci. Eng. A262 (1999) 279-278.
 16. W. Kim, C.Y. Suh, K.M. Roh, S.W. Cho, K.I Na, I.J. Shon, Journal of Alloys and Compounds 568 (2013) 73-77.
 17. M.K. Beyer, H. Clausen-Schaumann, Chem. Rev. 105 (2005) 2921-2948.
 18. In-Jin Shon, Ik-Hyun Oh, Jung-Han Ryu, Jun-Ho Jang, Hee-Jun Youn and Hyun-Kuk Park, Journal of Ceramic Processing Research. Vol. 14, No. 5 (2013) 641-647.
 19. I.J. Shon, Korean J. Met. Mater. 52 (2013) 573-580.
 20. Seung-Mi Kwak, Hyun-Kuk Park, and In-Jin Shon, Korean J. Met. Mater. 51 (2013) 341-348.
 21. Na-Ra Park, Kwon-Il Na, Hanjung Kwon, Jae-Won Lim, and In-Jin Shon, Korean J. Met. Mater. 51 (2013) 753-759.
 22. Suryanarayana C. and Grant Norton M., *X-ray Diffraction A Practical Approach*, Plenum Press, New York, 1998.
 23. GS Upadhyaya, Materials & Design 22 [6] (2001) 483-489.
 24. Z. Shen, M. Johnsson, Z. Zhao and M. Nygren, J. Am. Ceram. Soc. 85 (2002) 1921-1927.
 25. J. E. Garay, U. Anselmi-Tamburini, Z. A. Munir, S. C. Glade and P. Asoka- Kumar, Appl. Phys. Lett. 85 (2004) 573-575.
 26. J. R. Friedman, J. E. Garay. U. Anselmi-Tamburini and Z. A. Munir, Intermetallics. 12 (2004) 589-597.
 27. J. E. Garay, J. E. Garay. U. Anselmi-Tamburini and Z. A. Munir, Acta Mater., 51 (2003) 4487-4495.
 28. Rishi Raj, Marco Cologna, and John S. C. Francis, J. Am. Ceram. Soc., 94 [7] (2011) 1941-1965.
 29. K. Niihara, R. Morena, and D. P. H. Hasselman, J. Mater. Sci. Lett. 1 (1982) 12-16.
 30. In-Jin Shon, In-Kyoon Jeong, In-Yong Ko, Jung-Mann doh, Kee-Do Woo, Ceramics International 35 (2009) 339-344.