

Mechanical properties of nanostructured (W,Ti)C and (W,Ti)C-FeAl₃ rapidly sintered by the high-frequency induction-heating

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In the case of cemented (W,Ti)C, Ni or Co is added as a binder for the formation of composite structures. However, the high cost and the low hardness of Ni or Co, and the low corrosion resistance of the (W,Ti)C-Ni and (W,Ti)C-Co cermets have generated interest in recent years for alternative binder phases. In this study, FeAl₃ was used as a novel binder and sintered by the high frequency induction heated sintering (HFIHS) method. The method was found to enable not only the rapid densification but also the inhibition of grain growth preserving the nano-scale microstructure. The average grain sizes of the sintered (W,Ti)C and (W,Ti)C-FeAl₃ were lower than 100 nm. Highly dense (W,Ti)C and (W,Ti)C-FeAl₃ with a relative density of up to 99% was obtained within three min by HFIHS under a pressure of 80 MPa. The addition of FeAl₃ to (W,Ti)C enhanced the toughness at the expense of the slight decrease in hardness due to crack deflection and nanostructured phase.

Key words: Nanomaterials, Sintering, Hardness, Fracture Toughness, Hard Materials.

Introduction

(W,Ti)C has a high melting point and high hardness. In this regard, the transition metal carbide is primarily used as cutting tools and abrasive materials as a single phase or composite structures. In the case of cemented (W,Ti)C, Co or Ni is added as a binder for the formation of composite structures. However, the binder phase has inferior chemical characteristics compared to the carbide phase. Most notably, corrosion and oxidation occur preferentially in the binder phase [1]. Hence, the high cost and the low hardness of Ni or Co and the low corrosion resistance of the (W,Ti)C-Ni or (W,Ti)C-Co cermet have generated interest in recent years to find alternative binder phases [2, 3]. It has been reported that aluminides show a higher oxidation resistance, a higher hardness and a cheaper materials compared to Ni or Co [4].

The improvement of mechanical properties and stability of cemented carbides could be achieved through microstructural changes such as grain size refinement [5, 6]. Recently, nanocrystalline powders have been produced by high-energy milling [7-9]. 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 [10-12]. The grain size in sintered materials becomes much

larger than that in pre-sintered powders due to rapid grain growth during a conventional sintering process. Therefore, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. 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 min) [13-15].

We present here the results of the sintering of (W,Ti)C and (W,Ti)C-FeAl₃ 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)C and (W,Ti)C-FeAl₃ hard materials in very short sintering times (< 3 min). The effect of novel FeAl₃ binder on the sintering behavior and mechanical properties of (W,Ti)C-FeAl₃ composites was examined.

Experimental Procedures

(W,Ti)C powders with a grain size of < 1 μm and 99% purity was supplied by H.C. Starck. FeAl₃ (< 45 μm, 99.5% pure, Sejong Co.) was used as binder material. Powders of three compositions corresponding to (W,Ti)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10vol.%FeAl₃ were prepared by weighing and milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm for 10 hrs. WC-6 wt.%Co 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

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Suryanarayana and Grant Norton's formula [16].

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

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. [17–19]. The HFIHS apparatus includes a 50 kHz, 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. An 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 $600\text{ }^{\circ}\text{C min}^{-1}$ 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 sintered compact after polishing and etching 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) (maker; Hitachi), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) and field-emission scanning electron microscopy (FE-SEM) (maker; Rigaku). Vickers hardness was measured by performing indentations at a load of 10 kg_f with a dwell time of 15 s.

Results and Discussion

Milling time and rotation speed are the main factors in high-energy ball milling process. For a fair comparison, the experimental parameters in this study were chosen to be as consistent as possible with our previous studies [20, 21]. SEM images of (W,Ti)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10 vol.%FeAl₃ powders milled for 10 hrs are shown in Fig. 1. The milled powders were very fine and have an irregular shape and a some agglomeration. Sintering temperature and pressure are the important factors during high-frequency induction heated sintering process. It is reported that the relative density increased with the increase in heating temperature and pressure [22]. Nanostructured materials could be obtained with high heating rate because grain growth can be inhibited due to the relatively short term exposure of the nanopowders to the high temperature. In view of this, the heating rate and

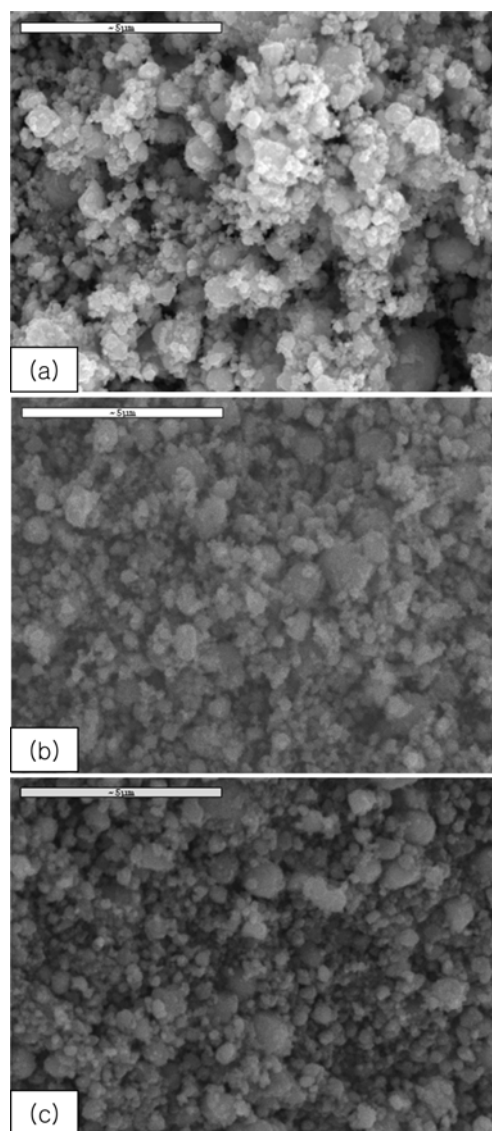


Fig. 1. SEM images of powders milled for 10 hrs; (a) (W,Ti)C, (b) (W,Ti)C-5 vol.%FeAl₃, and (c) (W,Ti)C-10 vol.%FeAl₃.

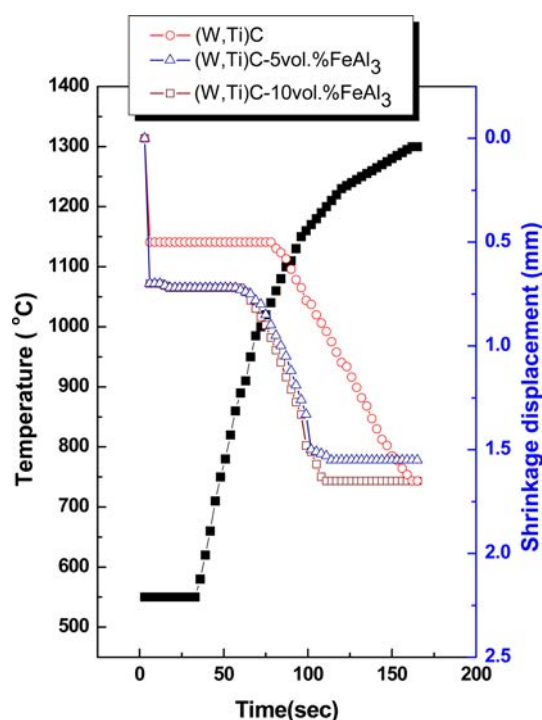


Fig. 2. Variations of temperature and shrinkage displacement with heating time during the sintering of (W,Ti)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10 vol.%FeAl₃ hard materials by HFIHS.

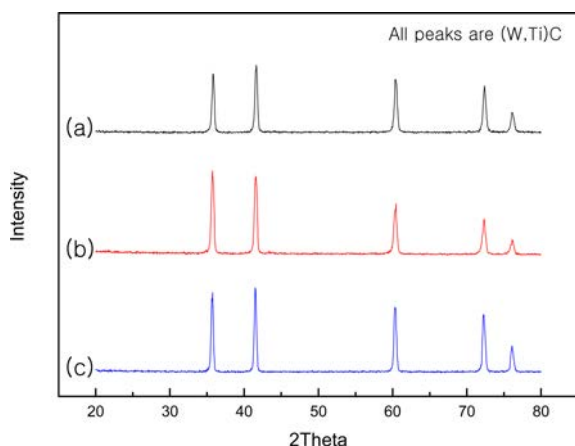


Fig. 3. XRD patterns of (a) (W,Ti)C, (b) (W,Ti)C-5 vol.%FeAl₃, and (c) (W,Ti)C-10 vol.%FeAl₃ hard materials produced by HFIHS.

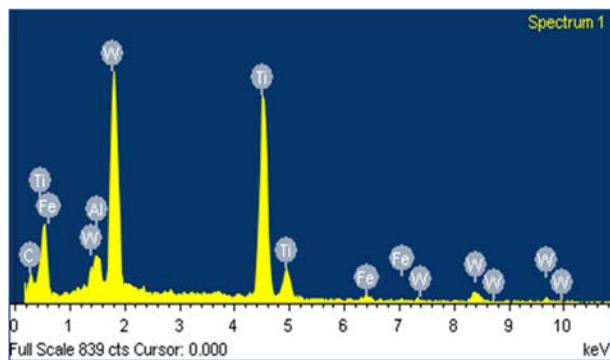


Fig. 4. EDS of (W,Ti)C-10 vol.%FeAl₃ sintered from powders milled for 10 hrs.

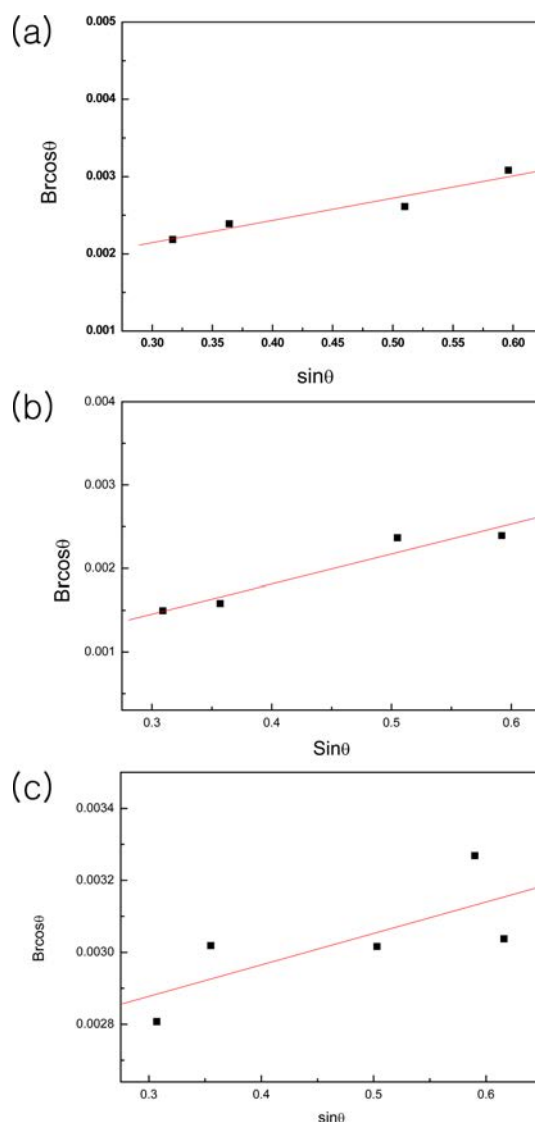


Fig. 5. Plot of B_r ($B_{\text{crystalline}} + B_{\text{strain}}$) $\cos\theta$ versus $\sin\theta$ for (W,Ti)C in (a) (W,Ti)C, (b) (W,Ti)C-5 vol.%FeAl₃, and (c) (W,Ti)C-10 vol.%FeAl₃ hard materials sintered from milled powders.

pressure used in this study was 600 °C/min and 80 MPa, respectively.

The variation of shrinkage and temperature with heating time during the sintering of (W,Ti)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10 vol.%FeAl₃ powders by HFIHS under 80 MPa pressure and induced current are shown in Fig. 2. The application of the induced current resulted in shrinkage due to consolidation. The temperature of shrinkage initiation was seen to reduce remarkably by the addition of FeAl₃. Obviously, it is related to the melting of FeAl₃ phase. Therefore, the main densification mechanism could be the rearrangement of carbide particles, enhancement of the diffusion, and viscous flow of the binder [23].

Fig. 3 shows the XRD patterns of (W,Ti)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10 vol.%FeAl₃ after sintering. In all cases, only (W,Ti)C peaks are detected. This agrees

to our previous result that only WC peak was observed after sintering WC-10 wt%Co, WC-10 wt%Ni and TiC-10 wt%Fe [24]. It is considered that the binder peaks were not detected because it melts during the liquid phase sintering. However, EDS and X-ray mapping of (W,Ti)C-10vol.% FeAl₃ composite reveals Fe and Al as shown in Fig. 4. This appears to suggest that major compositional change did not occur during sintering.

Plot of B_r ($B_{\text{crystalline}} + B_{\text{strain}}$) $\cos\theta$ versus $\sin\theta$ in Suryanarayana and Grant Norton's formula is shown in Fig. 5. The average grain sizes of the (W,Ti)C calculated from the XRD data are about 60, 62, and 53 nm for the samples with (W,Ti)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10 vol.%FeAl₃. FE-SEM images of the etched samples after being sintered up to about 1300 °C are shown

in Fig. 6. It is apparent that the (W,Ti)C 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)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10 vol.%FeAl₃ were approximately 99%.

The role of the current in sintering 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 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

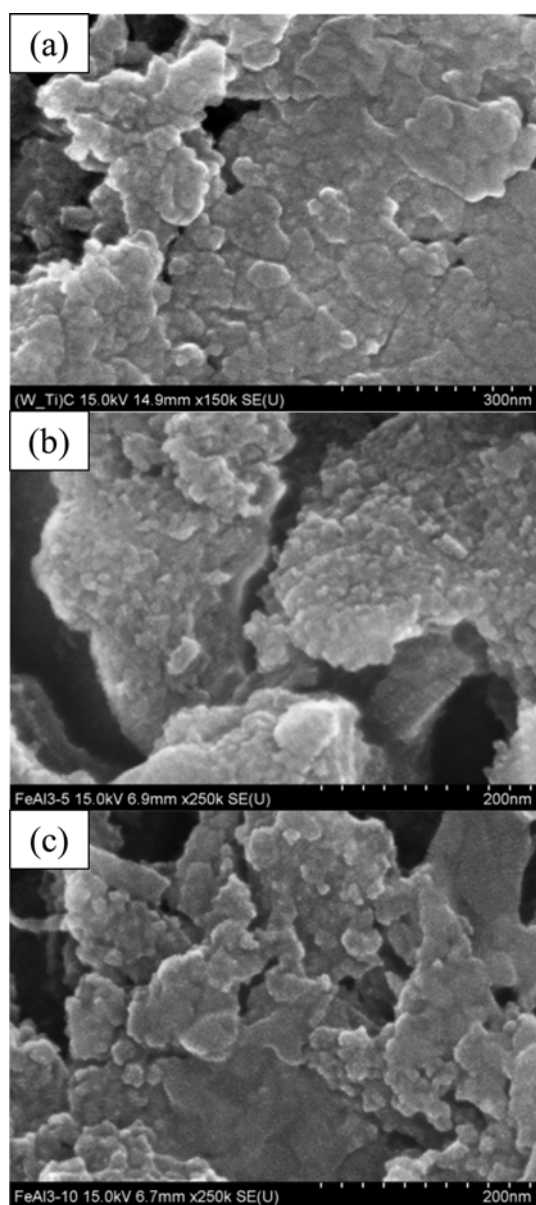


Fig. 6. FE-SEM images of (a) (W,Ti)C, (b) (W,Ti)C-5 vol.%FeAl₃, and (c) (W,Ti)C-10 vol.%FeAl₃ hard materials produced by HFIHS

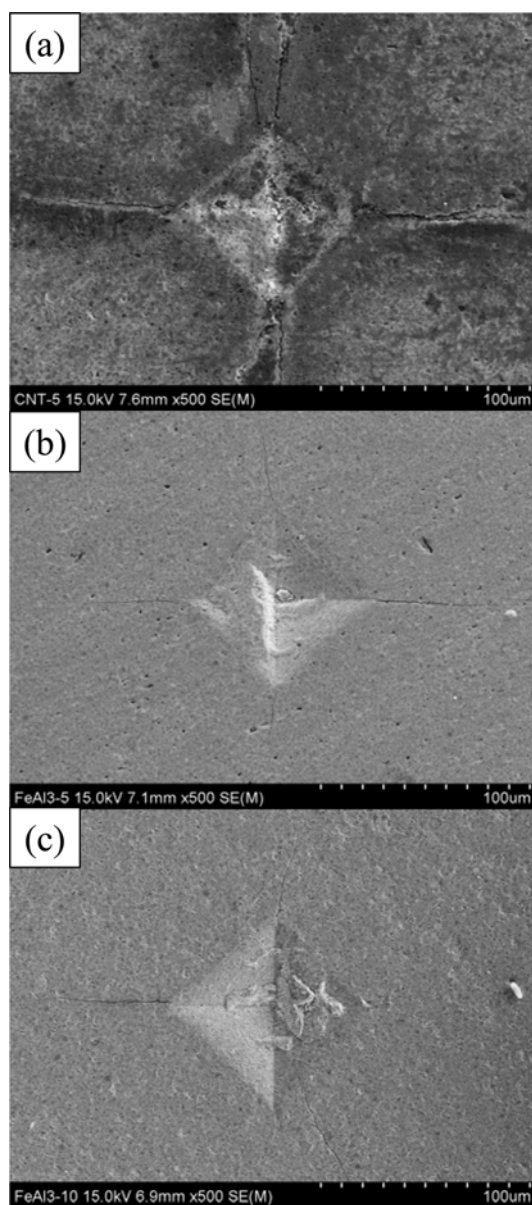


Fig. 7. Vickers hardness indentation in (a) (W,Ti)C, (b) (W,Ti)C-5 vol.%FeAl₃, and (c) (W,Ti)C-10 vol.%FeAl₃ hard materials produced by HFIHS.

mass transport [25-28].

Vickers hardness measurements were performed on polished sections of the (W,Ti)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10 vol.%FeAl₃ samples using a 10 kg_f load and 15 s dwell time. Indentations with 10 kg_f 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]:

$$K_{IC} = 0.023(c/a)^{-3/2} \cdot H_v \cdot a^{1/2} \quad (2)$$

where c is the trace length of the crack measured from 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)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10 vol.%FeAl₃ samples were 2820 kg/mm², 7 MPa·m^{1/2}, and 2540 kg/mm², 11.5 MPa·m^{1/2} and 2340 kg/mm², 12.5 MPa·m^{1/2}, respectively. These values represent the average of five measurements. Vickers hardness indentations in the (W,Ti)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10 vol.%FeAl₃ samples are shown in Fig. 7. They show typically one to three additional cracks propagating radially from the indentation. After the (W,Ti)C powders with about 100 nm size were cold-pressed at 125 MPa, they were sintered 1510 °C without the addition of a binder phase using conventional sintering method [30]. The compact were densified to a full density with a grain size of 1-2 μm. And the hardness and fracture toughness were reported as 18.9 GPa and 7.2 MPa·m^{1/2}. In this study, (W,Ti)C with a lower grain size (about 60 nm) was sintered to a full density at a lower temperature. And the hardness of (W,Ti)C in this study is higher than that in the other study [30] without decrease of fracture toughness due to grain refinement. In one of the reported studies [31], WC-10Co and WC-10Ni were consolidated at 1250 °C by high-frequency induction heated sintering. Comparing this investigation of (W,Ti)C-5FeAl₃, and (W,Ti)C-10FeAl₃ with a study of WC-10Co and WC-10Ni [31], there is a little difference in fracture toughness but hardness in this study is very higher than that in the other study [31]. Also, the addition of FeAl₃ to (W,Ti)C significantly improves the fracture toughness of cemented (W,Ti)C without greatly decreasing the hardness.

The sintering method in this study was proven to be very effective to consolidate monolithic (W,Ti)C and (W,Ti)C-FeAl₃ cermets. The use of FeAl₃ binder instead of Co or Ni is very effective especially to maintain the high hardness of monolithic (W,Ti)C at the expense of slight toughness reduction. The hardness of (W,Ti)C-FeAl₃ cermets is more than 40% higher than that when the binder was Co or Ni. Apparently, their high hardness values should be originated from their fine grain size and higher hardness of FeAl₃ than of

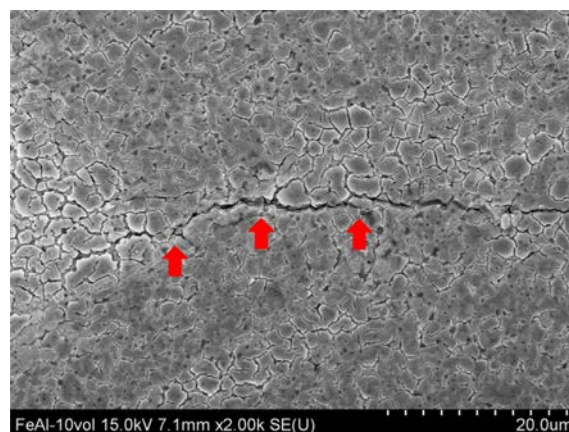


Fig. 8. Crack propagation in (W,Ti)C-10 vol.%FeAl₃ hard materials produced by HFIHS.

Ni or Co. The addition of FeAl₃ to (W,Ti)C improved the hardness of cemented (W,Ti)C without decreasing its fracture toughness. In this regard, it would be worthwhile to consider FeAl₃ as the possible replacement for Co or Ni especially for the applications requiring a high hardness such as water jet nozzle and spray dryer nozzle. Fig. 8 shows a crack propagated in a deflective manner (↑) in (W,Ti)C-10 vol.%FeAl₃ composite. The enhanced fracture toughness of (W,Ti)C-10 vol.%FeAl₃ composite is believed that (W,Ti)C and FeAl₃ in the composite may deter the propagation of cracks and (W,Ti)C and FeAl₃ have nanostructure phases.

Conclusions

Using high-frequency induction heated sintering (HFIHS), the rapid consolidation of the (W,Ti)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10 vol.%FeAl₃ was accomplished successfully. Nearly full-dense (W,Ti)C and (W,Ti)C-FeAl₃ composites could be obtained within 3 min. The densification temperature of (W,Ti)C was reduced remarkably by the addition of FeAl₃. The grain size of (W,Ti)C in (W,Ti)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10 vol.%FeAl₃ hard materials were about 60 nm, 62 nm and 53 nm, respectively. The Vickers hardness and the fracture toughness values of the (W,Ti)C, (W,Ti)C-5 vol.%FeAl₃, and (W,Ti)C-10 vol.%FeAl₃ samples were 2820 kg/mm², 7 MPa·m^{1/2}, and 2540 kg/mm², 11.5 MPa·m^{1/2} and 2340 kg/mm², 12.5 MPa·m^{1/2}, respectively. The addition of FeAl₃ to (W,Ti)C improved the hardness of cemented (W,Ti)C without a loss of its toughness. It would be worthwhile to consider FeAl₃ as the possible replacement for Co or Ni especially for the applications requiring a high hardness such as water jet nozzle and spray dryer nozzle.

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