

Characteristics and Sintering Behavior of (Hf-Ta-Ti-Zr-Nb)C High-Entropy Carbides Fabricated by High-Energy Ball Milling and Spark Plasma Sintering

J. Song¹, L.V. Duong², Ph.V. Trinh², N.N. Linh², D.D. Phuong²,
J. Seok^{1, 3}, S.-Y. Kim^{1, 3}, J. Han¹, H. Kim^{*1}

¹Korea Institute of Industrial Technology, 156, Gaetbeol-ro, Yeonsu-gu, Incheon, Republic of Korea

²Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Str., Cau Giay Distr., Hanoi, Viet Nam

³Department of Materials Science and Engineering, INHA UNIVERSITY, 100 Inha-ro, Michuhol-gu, Incheon 22212, Republic of Korea

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Abstract

The present study aimed to analyze the sintering behavior and mechanical properties of (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide powder fabricated using an ultra-high-energy ball mill. The fabricated powder was sintered by means of spark plasma sintering (SPS) at a constant pressure of 50 MPa and for ten minutes with varying sintering temperature between 1700, 1800, and 1900 °C. Changes in the microstructure and mechanical properties of the powder and sintered carbides were examined. The high-entropy carbide powder obtained after 60 minutes of ball milling was found to be an assembly of uniformly distributed particles with a size of hundreds of nanometers. It was also found that the degree of X-ray line broadening increased with increasing milling time. When the milling time was relatively long, that is 60 minutes, the elements that initially existed in the form of multi-carbides tended to merge as part of a single FCC phase. In addition, an increase in the temperature of the spark plasma sintering process was found to help to improve the sintering density and hardness. This result confirmed that the temperature change was one of the most important process parameters that determined the degree of densification of sintered high-entropy carbides.

Keywords: High-entropy carbide, ultra-high-energy ball milling, spark plasma sintering

I. Introduction

With the recent rapid advancement of high-tech industries, including the aerospace and polar marine sectors, there has been a rising demand for the development of high-performance materials capable of providing excellent properties even in harsh conditions, such as extreme temperatures, high-pressure, and highly corrosive environments. Conventional materials, such as metals, alloys, and ceramics are generally fabricated by adding small amounts of various alloying elements to a single major element or a combination of two major elements. Even though the addition of alloying elements does improve material properties, if the amount of the addition exceeds a certain limit, then a second phase may be generated, degrading the physical and chemical characteristics of the material. For that reason, in alloying design, the addition of large amounts of alloying elements and the use of multiple elements with similar ratios have been almost entirely avoided up until recently. In reality, however, it is difficult to achieve the desired properties of extreme-environment materials required by high-tech industries based

on conventional materials only. In order to overcome this limitation, research has been conducted on the development of high-entropy materials¹⁻⁴. High-entropy materials are obtained by combining multicomponent elements with similar crystalline structures with almost the same ratio rather than by adding small amounts of alloying elements to one or two major elements, as conventionally applied. As a result, high mixing entropy is achieved, and the material exists in the form of a single solid solution without forming any intermetallic compounds. These high-entropy materials are subjected to internal stress arising from severe lattice distortion due to the unique crystalline structure of each component. Furthermore, dislocation motion is difficult, and slip behavior is suppressed due to the limited number of slip systems available. Consequently, unlike existing commercial alloys, these materials exhibit unique characteristics, such as excellent corrosion resistance, high-temperature strength, and high specific strength⁵⁻⁸. Until recently, the focus of research has been placed on the development of high-entropy alloys based on metals to meet the demand of the industrial sector. The scope of research has now been broadened to include high-entropy materials based on various non-metal-

* Corresponding author: hyoseop1231@kitech.re.kr

lic compounds, including nitrides, carbides, and oxides. Notably, carbides of transition metals, which fall into the category of Group IV and V of the periodic table, are similar to each other in terms of atomic radius and crystalline structure while fulfilling the condition of δ (atomic size parameter) $\leq 6.6\%$ required by the Hume-Rothery rules^{8,9}. Thus, these carbides are suitable for forming single-phase high-entropy carbides. Meanwhile, there has been an urgent demand for improvement in the mechanical properties of WC, one of the most widely used conventional superhard materials, in terms of hardness, strength, and toughness. However, as it stands now, it is difficult to expect further improvement due to the current technological limitations. Therefore, it is critical to perform research that helps to develop high-entropy materials based on carbides. Previous studies have been focused on the fabrication and chemical synthesis of single-phase carbide powder along with relevant theoretical calculations and computer-based numerical simulations. However, there is still more scope for further research work on high-entropy carbides¹⁰.

J. Potschke¹¹ tested the applicability of high-entropy carbides as a replacement for superhard materials, including WC, and compared various sintering processes. High-entropy carbides are expected to be mainly used in the cutting tool industry, which requires a very large operating temperature range. Furthermore, given their component elements, these materials will be difficult to form and sinter. Thus, it is necessary to perform research on the optimization of sintering conditions, encompassing even the powder fabrication process. The sintering process of high-entropy carbides is critical because this process contributes to improving their ultimate mechanical properties, such as density and microstructure. The spark plasma sintering (SPS) process has been steadily attracting attention as a promising fast sintering process capable of increasing the temperature up to over 2 000 °C within a short time while effectively controlling the growth of crystalline grains. With these advantages, the SPS process has been applied to various ceramic materials and it is also considered to be suitable for the sintering of high-entropy carbides with no additives used. Not only that, the particle size, size distribution, shape, and aggregation of powder materials used in the sintering process affect not only the driving force but also the reaction kinetics of the process. In light of this, the powder fabrication process is also as important to the properties of the high-entropy carbide. In the present work, (Hf-Ta-Ti-Zr-Nb)C high-entropy carbides, which have excellent properties but are difficult to form and sinter, were studied and analyzed as a candidate for superhard materials. Furthermore, the effect of the temperature, pressure, and duration of the SPS process on

their microstructure and mechanical properties was measured and analyzed.

II. Experimental Procedure

Five commercial carbides, including HfC(99.5 %, <10 μm), TaC(99.5 %, 1 μm), TiC(99.5 %, 2–3 μm), ZrC(99.5 %, <10 μm), and NbC(99 %, <3 μm), were utilized as starting materials in the present study, and their chemical composition is presented in Table 1. In order to determine the optimal powder fabrication conditions suitable for the sintering process, the carbide powders with different particle sizes and shape were hand-mixed or milled in a high-energy ball mill. The effect of the milling time on the refinement and homogeneity of the mixtures was observed. The cylindrical cemented carbide jar used in the ball mill had a diameter of 74 mm and a length of 60 mm. The equipment was designed to cool down the external surface of the jar using cooling water due to the high frictional heat on the outer surfaces of rails and jars. The cover of the jar was equipped with an O-ring to keep the internal pressure constant by preventing atmospheric gases from leaking. Cemented carbide balls with a diameter of 5.0 mm were used in an atmospheric environment, and the weight ratio of balls to powder was set to 10:1. During the refinement process, the ball-milling rotation speed was fixed at 600 rpm, while the ball-milling time was varied from 0 (hand mixing only) to 15 and 60 minutes. The specifications of the powder fabrication process are summarized in Table 2. In addition, circulation cooling was performed using cooling water to prevent powder particles from adhering to each other due to the frictional heat generated from the high rotation speed of the ball mill while facilitating fragmentation over the entire course of the refinement process. Four grams of the obtained (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide powder were put into a graphite mold with an inner diameter of 10 mm and an outer diameter of 30 mm and then subjected to the SPS process to obtain a bulk sample. Before the sintering process, a thin layer of boron nitride spray was applied as a release agent to provide lubrication between the inner surface of the graphite mold and the powder particles. Thermal imaging cameras were also equipped to accurately measure the sintering temperature. During the SPS process, the sintering pressure was fixed at 50 MPa, and the sintering temperature was set to 1 700, 1 800, and 1 900 °C. Subsequently, changes in the microstructure, phase, and mechanical properties of the sintered carbides obtained with the SPS process were observed using an X-ray diffractometer (XRD, BRUKER AXS, D8ADVANCE) and a field emission scanning electron microscope (FE-SEM, HITACHI). Their mechanical properties were further

Table 1: The nominal composition of (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide.

%	HfC	TiC	TaC	ZrC	NbC	Composition
at. %	1	1	1	1	1	(Hf-Ta-Ti-Zr-Nb)C
wt. %	29.2	9.2	29.6	15.9	16.1	

characterized based on measurement of the Archimedes density (Alfa Mirage, SD-120L) and Vickers hardness (Wilson VH3300). Indentation and crack dimensions were measured, and the corresponding fracture toughness was calculated and analyzed. Based on the results, the applicability of these materials as a candidate for superhard tool materials was verified.

III. Results and Discussion

Fig. 1 presents FE-SEM images of the (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide powder samples obtained with varying duration of ball milling. Fig. 1(a) shows an image of the initial mixture of raw powders. The size and shape of the powder particles remained the same compared to the initial state. Several irregularly shaped coarse particles of approximately 10 μm were observed. EDS mapping was performed to determine the homogeneity of the five types of carbides in the obtained powder. The results showed that HfC, ZrC, and TiC powders remained unmixed and separate from the mixture. When the milling time was set to 15 minutes, as shown in Fig. 1(b), the size of coarse-grained, irregular-shaped particles decreased to 5–7 μm , while the portion of finer particles increased. The irregular-shaped particles that were observed in the initial mixture of powders were found to have more smooth edges compared to the initial state. Fig. 1(e) shows that even though some TiC and ZrC powders still remained unmixed, the degree of homogeneity of the mixture was gradually improved due to the increased milling time. As shown in Fig. 1(c), when the milling time was 60 minutes, some of the coarse-grained particles were refined to the size of hundreds of nanometers, and only a few fine particles were found to have remained as aggregates.

Fig. 1(f) reveals that the five types of hard carbides used in the present study were homogeneously mixed due to the long milling time. This was attributed to the characteristics of the high-energy ball milling process. In general, ball milling is designed to provide powder materials with sufficient energy for them to be fine-ground. When processing hard carbide powder into fine powder by means of ball milling, it is essential to consider the relationship between the target particle size and the amount of energy required to achieve the target. The amount of energy required to achieve fine powder with the desired particle size in the ball milling process can be expressed using the Charles equation as follows ^{12,13}.

$$E = g \left(\frac{1}{D_F} - \frac{1}{D_I} \right) \quad (1)$$

Table 2: Experiment conditions for (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide powders.

Milling Condition		
Jar media/Capacity	Cemented carbide/	100cc
Ball media/Size	Cemented carbide/	5 Φ
Ball to Powder Ratio (BPR)		10:1
	Ball (200 g):Powder (20 g)	
RPM		600
Time (min)		As mixed, 15, 60
Atmosphere		Air
Cooling		Water
		(Jar external water cooling)

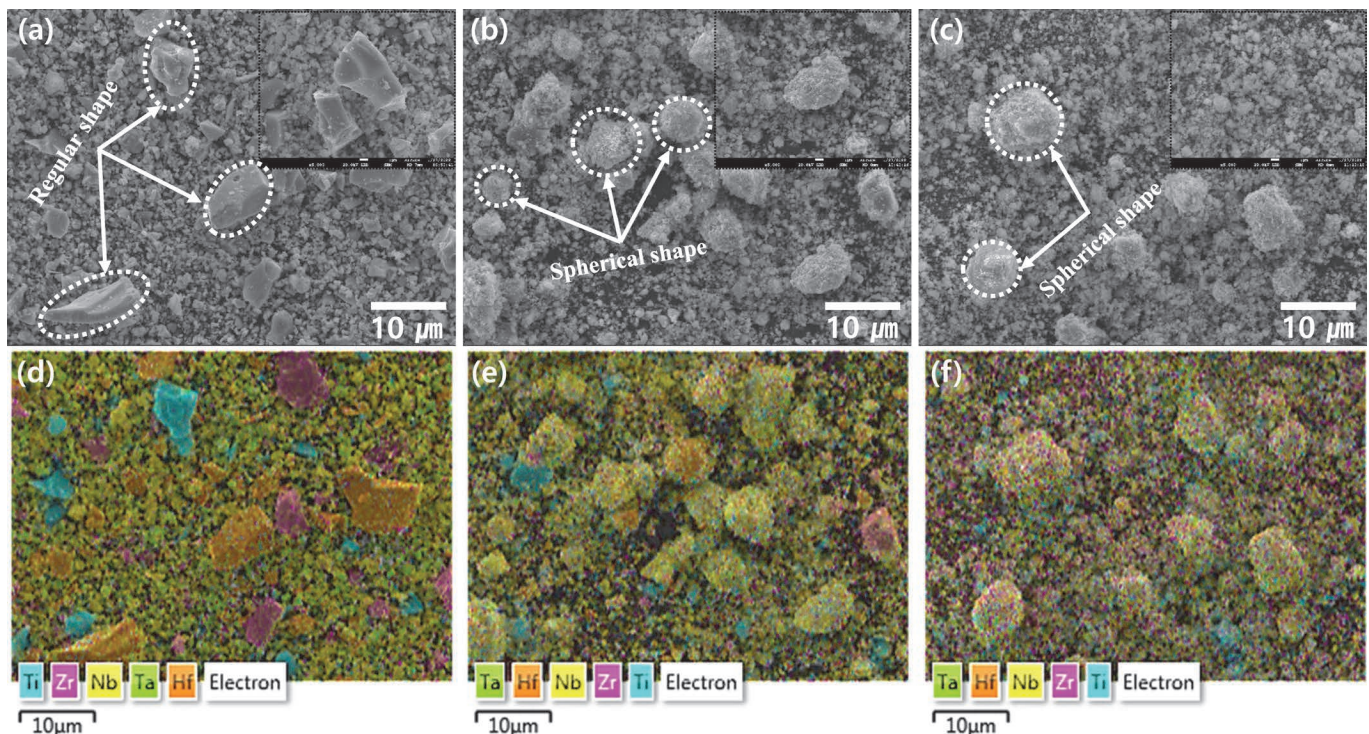


Fig. 1: FE-SEM morphology and EDS mapping results of (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide milled powder as a function of milling time (a,d) as-mixed, (b,e) 15 min, and (c,f) 60 min.

Here, D_I refers to the initial particle size, E is the energy exerted, and D_F is the final particle size, and g is a constant related to the material used. The structure of the ball mill, ball milling conditions, and the exponent “ a ” are normally set to a value between 1 and 2. According to Eq. (1), the energy required for powder refinement is dependent on the difference between the initial and final particle size. This energy is most closely related to the rotation speed of the ball mill along with various parameters involved in the ball milling process. N refers to the number of rotations per unit time, in other words, the rotation speed of the ball mill. N can be expressed with the equation below ¹⁴.

$$t = C \frac{d^2}{N^{1/2}} \quad (2)$$

Here, d is the ball diameter of the ball mill, and C is an empirical constant that may vary depending on the type of process. As can be seen in Eq. (2), the time required to reach the final particle size is determined based on the rotation speed. For example, refining coarse-grained silicon powder to the desired level would require dozens of hours of conventional low-energy ball milling. The high-energy ball mill used in the present study allowed high rotation speed and was thus capable of delivering a large amount of energy in an instant. Accordingly, this high-energy ball mill was able to effectively refine difficult-to-grind materials such as coarse-grained powder or carbides within a relatively short period of time compared to conventional general-purpose ball mills when all the other conditions were assumed to be the same. This result was consistent with a study by Song *et al.* ¹⁵, concerning the refinement behavior of high-entropy carbide powder. Fig. 2 presents X-ray diffraction patterns of the (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide powder samples fabricated with various ball milling times. As the milling time increased from 0 (hand mixing) to 15 to 60 minutes, the X-ray peak broadening increased due to the supplied milling energy resulting in particle refinement. Therefore, it is expected that a phase in which five elements are combined is advantageous for forming a single FCC phase rather than the existing individual carbides peak.

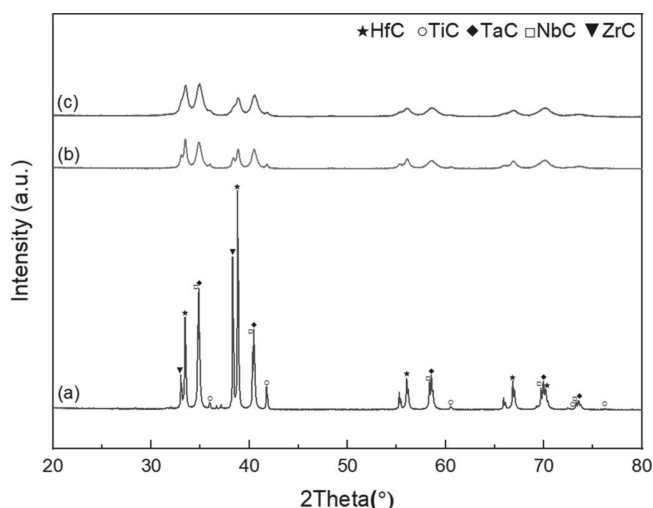


Fig. 2: XRD patterns of (Hf-Ta-Ti-Zr-Nb)C milled powders as a function of milling time (a) as-mixed (b) 15 min and (c) 60 min.

These XRD results suggested that the use of powder mixtures obtained with 60 minutes of ball milling would decrease the sintering temperature and time required. Based on this interpretation, the specifications of the SPS process for (Hf-Ta-Ti-Zr-Nb)C high-entropy carbides were determined, as shown in Table 3. In general, the key parameters involved in the SPS process include the size of powder particles, homogeneity of powder mixtures, and particle shape related to the fluidity ¹⁶. For high-temperature materials, such as high-entropy carbides, it has been reported that the smaller the initial particle size, the lower the sintering temperatures required ¹⁷. In fact, in most previous studies on high-entropy carbides, sintering was performed at high temperatures above 2 000 °C. In the present study, however, the sintering temperature was set to be relatively low, ranging from 1 700 to 1 900 °C, to examine their sintering behavior and further determine the relationship between the powder milling process and the required sintering conditions. Fig. 3 presents X-ray diffraction patterns of the (Hf-Ta-Ti-Zr-Nb)C carbides sintered at different temperatures. In general, the diffraction peaks of ceramic materials become sharper with increasing sintering temperature due to grain coarsening ¹⁸. A distinct characteristic of high-entropy carbides is that geometric distortion is induced in the cation lattice by randomly positioned five metal ions with different radii, which causes the anions to be displaced from their ideal sites in an attempt to accommodate the distortion ^{19,20}. The lattice deformation behavior of high-entropy carbides can also be understood based on the explanation above. As the sintering temperature increases, it can lead to larger lattice constant expansion. Indeed, the lattice constant tended to slightly increase to 2.58 Å, 2.59 Å, and 2.61 Å as the sintering temperature increased to 1 700, 1 800, and 1 900 °C, respectively. In the XRD graph of the carbide sintered at 1 700 °C, as shown in Fig. 3.(a), a peak corresponding to a single-phase FCC structure was observed, on the other hand, peaks attributed to individual carbides, including HfC and ZrC, as well as those corresponding to HfO₂ and ZrO₂ oxides, appeared as well. This observation indicates that the oxygen introduced during the milling process performed in an atmospheric environment caused the high-entropy carbide powder to be recrystallized into two phases, an FCC solid solution phase and an oxide phase. This is considered to be the reason that HfO₂, ZrO₂, and ZrHfO_x oxide phases were detected in the (Hf-Ta-Ti-Zr-Nb)C composition ²¹. The shape of the ball-milled carbide powder is also related to the particle size of the initial powder. The HfC and ZrC particle sizes were about 7–10 μm, coarser than that of the other carbides. Accordingly, despite being subjected to constant impact from balls, these carbide particles underwent slower refinement than the others. Therefore, even when the sintering temperature was set to 1 700 °C, peaks corresponding to some of these particles were detected. When the sintering temperature was 1 800 °C, as shown in Fig. 4(b), the scattering intensity of the peaks corresponding to ZrC and HfC were reduced. At the sintering temperature of 1 900 °C, as shown in Fig. 4(c), it was found that peaks corresponding to part of HfO₂ and ZrO₂ oxides remained, the (Hf-Ta-Ti-Zr-Nb)C

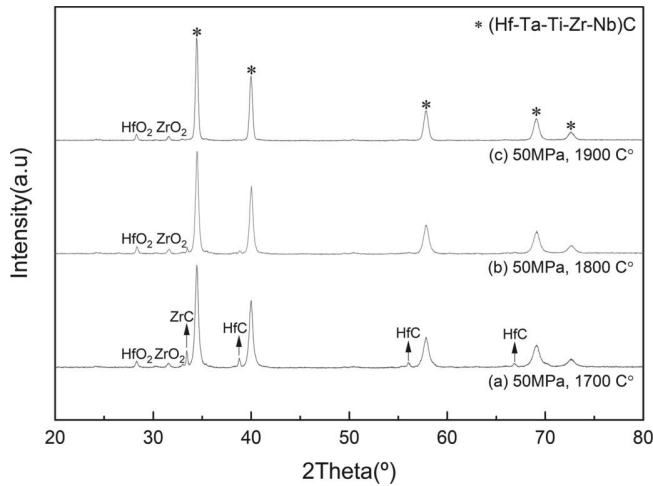


Fig. 3: XRD patterns of (Hf-Ta-Ti-Zr-Nb)C sintered bulk as a function of sintering conditions (a) 50 MPa, 1700 °C, (b) 50 MPa, 1800 °C, and (c) 50 MPa, 1900 °C.

carbide powder mostly exists in the form of a single FCC phase. These XRD results confirmed that the sintering of the (Hf-Ta-Ti-Zr-Nb)C high-entropy carbides was dependent on the sintering temperature. The effect of the degree of refinement and mixing was also significant. As mentioned above, the high-entropy carbide powder tended to transition into a single-phase FCC structure as the sintering temperature increased. The EDS mapping was also conducted on the cross-section of the sintered high-entropy carbides to determine the effect of the sintering temperature on their microstructure, as shown in Fig. 4. Fig. 4(a) presents the cross-sectional microstructure of the carbides sintered at 1700 °C. HfC and ZrC particles were found in the form of aggregates, and a number of micro-sized pores were observed. When the sintering temperature increased to 1800 °C, as shown in Fig. 4(b), some TaC particles were observed, and a portion of the coarse-grained carbides such as HfC and ZrC, observed in the 1700 °C microstructure, was found to have decreased. When the sintering temperature was 1900 °C, as shown in Fig. 5(c), some HfC, ZrC, and TaC particles remained, but the coarse carbide particles decreased in size due to the high sintering temperature. This indicates that densification had occurred. As such, the sintering behavior of high-entropy carbide powder is closely related to the powder fabrication step preceding the sintering process. This can be accounted for by using the strain-stress relationship below ²².

$$\dot{\epsilon} = A \left(\frac{DGb}{kT} \right) \left(\frac{\sigma}{G} \right)^n \quad (3)$$

Here, D is the diffusion coefficient, k is the Boltzmann constant, and n is the stress index (n corresponds to $1/m$ when m is the strain rate sensitivity exponent). G is the dynamic shear modulus, b is the Burgers vector, A is the microstructure function (representing the effect of the grain size, sub-grain size, and dislocation density), and T is the absolute temperature. The particle size (A) of the high-entropy ball-milled carbide powder and the diffusion coefficient D , which is affected by the sintering temperature, tend to increase with increasing sintering temperature. Thus, according to the relationship above, this also leads to an increase in the ultimate strain ($\dot{\epsilon}$), indicating that the densification of its microstructure has been accelerated. The superhard tool industry requires carbides with sufficient hardness and fracture toughness because these properties are closely related to the cutting and machining performance of tools. Achieving high density in the sintering process is then essential to meet the requirements. Fig. 5 presents the relative density of the high-entropy carbides sintered at different temperatures. The results showed that the relative density increased from 96.1 % to 97.8 % as the sintering temperature increased. The microstructural homogeneity of the high-entropy carbide mixture, known to be related to its density, was achieved by the interdiffusion of the individual carbides, one of the most important factors that contribute to the formation of high-entropy phases. Furthermore, the application of the high temperature and pressure conditions not only increased the density of the multicomponent carbides but also enhanced the atomic diffusion ^{23–28}. Atomic interdiffusion is generally driven by the concentration gradient, one of the major driving forces of the mass transfer mechanism. Thus, the interdiffusion of atoms is slower when their distribution is more uniform. Accordingly, it was expected that a further increase in the sintering temperature would not improve the densification of the sintered high-entropy carbides. Furthermore, in the case of carbides with high melting points, it is difficult to achieve the maximum density in the sintering process. For binderless carbides, the density of 96–98 % is considered to be high ²⁹. It was also expected that a further increase in the density could be achieved by applying higher uniaxial pressure and increasing the sintering time. Fig. 6 shows the hardness measurements of the sintered high-entropy carbides measured at a load of 30 kgf using a Vickers hardness tester. The results showed that as the sintering temperature increased, the hardness of the sintered carbides increased from 1730 to 1810 HV. This was attributed to the fact that defects were more likely to occur during the cooling stage due to the enhanced thermal

Table 3: Spark plasma sintering conditions for 60-min-milled (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide.

Sample	Pressure (MPa)	Temperature (°C)	Heating rate (K/min)	Holding time (min)	Vacuum (Pa)
A	50	1700	100	10	10 ⁻³
B	50	1800	100	10	10 ⁻³
C	50	1900	100	10	10 ⁻³

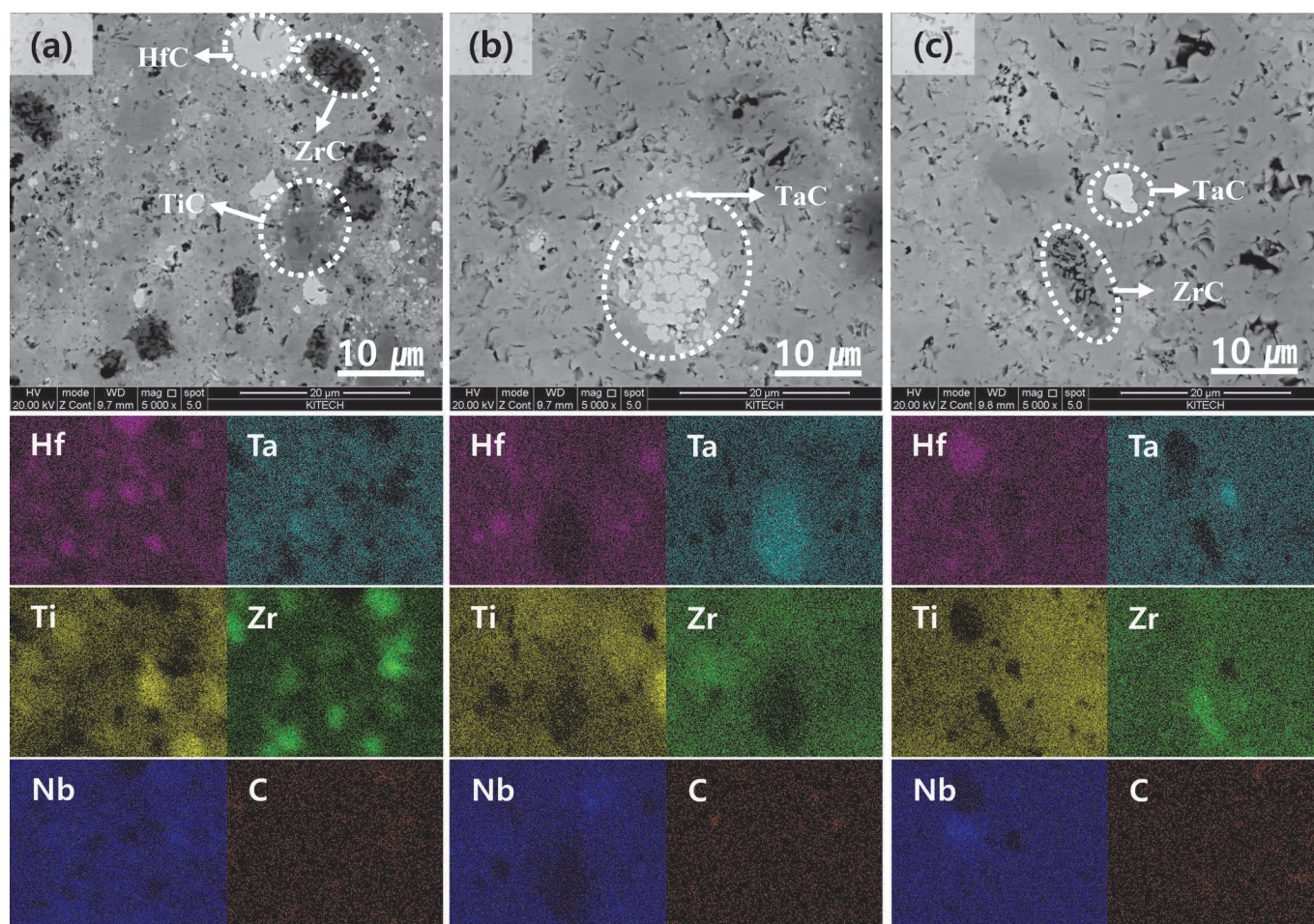


Fig. 4: Cross-sectional FE-SEM micrographs and EDS mapping results of (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide sintered bulk with various temperatures (a) 1700 °C, (b) 1800 °C, and (c) 1900 °C.

mobility of atoms³⁰. In addition, the increased diffusions of atoms contributed to enhancement of the high-entropy effect, thereby leading to an increase in the hardness. Overall, the Vickers hardness of the high-entropy carbides was found to increase with higher sintering temperature even though the density did not change significantly.

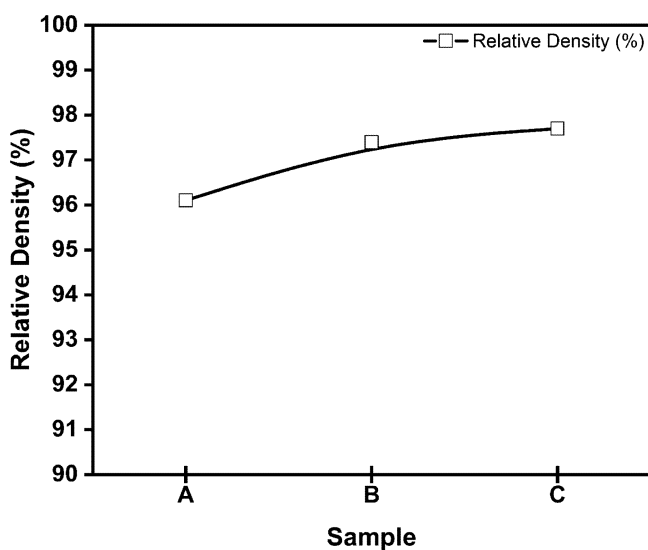


Fig. 5: Relative density of (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide sintered bulk as a function of sintering temperature (A) 1700 °C, (B) 1800 °C, and (C) 1900 °C.

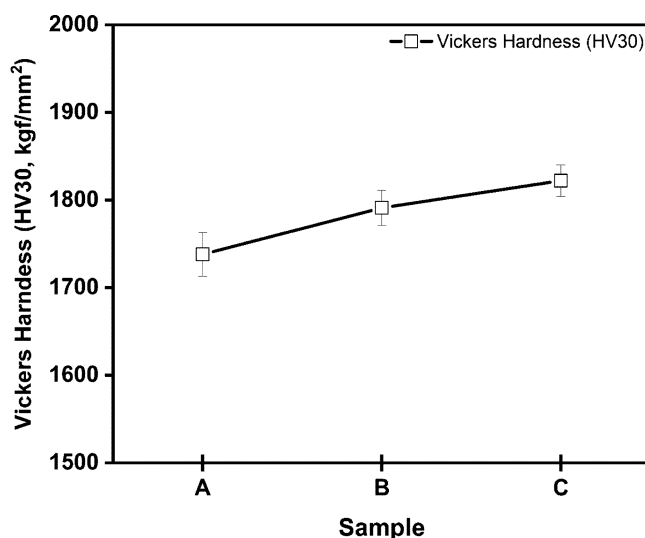


Fig. 6: Vickers hardness result of (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide sintered bulk as a function of sintering temperature (A) 1700 °C, (B) 1800 °C, and (C) 1900 °C.

The fracture toughness (K_{IC}), known to be related to the cracking of high-entropy carbide materials, is one of the most important parameters that determine the mechanical properties of superhard materials. Fig. 7 presents the fracture toughness measured from the carbide samples sin-

tered at different temperatures. The equation proposed by Palmqvist below was employed to calculate fracture toughness values, and the results are as follows.

$$W_G = \frac{P}{T} \quad (4)$$

Here, W_G is the Palmqvist fracture toughness, T is the total crack length from the crack tip to the edge of the indenter, and P is the applied test load (30 kgf). The crack length was measured to be about 200, 216, and 203 μm when the sintering temperature was 1 700, 1 800, and 1 900 $^{\circ}\text{C}$, respectively. This indicated that the sintering temperature did not significantly affect the crack length. Based on these results, the fracture toughness of the sintered samples was measured. As shown in Fig. 7, their fracture toughness was found to be in the range of 7.0–7.3 $\text{MPa} \cdot \text{m}^{1/2}$. The fracture toughness of the high-entropy carbides sintered with no additives added in the present study was found to be 10 % higher than that of binderless WC at 6.56 $\text{MPa} \cdot \text{m}^{1/2}$, reported by T. Kuo Ming²⁹. This confirms the applicability of high-entropy carbide materials as a replacement for conventional superhard alloys, including WC materials.

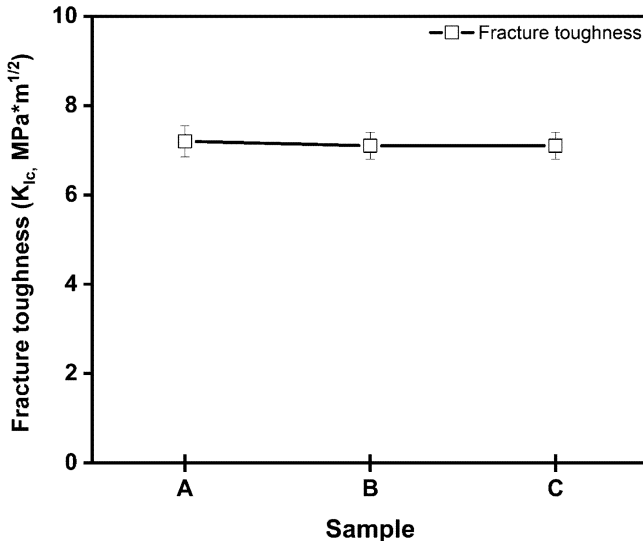


Fig. 7: Fracture toughness (K_{IC}) of (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide sintered bulk as a function of sintering temperature (A) 1 700 $^{\circ}\text{C}$, (B) 1 800 $^{\circ}\text{C}$, and (C) 1 900 $^{\circ}\text{C}$.

IV. Conclusions

In the present study, (Hf-Ti-Ta-Zr-Nb)C carbide powders were fabricated in the high-energy milling process with varying milling time. The fabricated carbide powders were subsequently subjected to the SPS process to obtain sintered high-entropy carbides with a single-phase FCC structure. Furthermore, the optimal conditions for the sintering of high-entropy carbides were determined accordingly. The major findings of the present study are as follows.

- As the milling time increased from 0 (hand mixing) to 60 minutes, the powder particles changed from irregularly angular to spherical shapes, their size continued to decrease through refinement, and the degree of homogeneity increased as well. As a result, ball-milled (Hf-Ta-Ti-Zr-Nb)C high-entropy carbide powder with a particle size of 10 μm was obtained.

- As the sintering temperature during the SPS process increased from 1 700, 1 800 to 1 900 $^{\circ}\text{C}$, peaks corresponding to a single-phase FCC structure started to appear. At a relatively low sintering temperature of 1 700 $^{\circ}\text{C}$, some coarse-grained particles of ZrC and HfC were observed. When the sintering temperature was 1 800 $^{\circ}\text{C}$ or higher, no peaks other than those corresponding to HfO₂, ZrO₂, and ZrHfO_x oxides were observed.
- The cross-sectional microstructure of the sintered high-entropy carbides indicated that when the sintering temperature was 1 700 $^{\circ}\text{C}$, HfC and ZrC particles in the form of aggregates, as well as a number of micro-sized pores, were observed. However, as the sintering temperature increased, the portion of aggregated coarse-grained particles decreased. Based on the strain-stress relationship, it was confirmed that the densification of the microstructure was accelerated during the sintering process.
- Even though the carbide powders ball-milled for 60 minutes were consolidated at the temperature of 1 700 $^{\circ}\text{C}$ in the SPS process, this result was achieved at a lower temperature than in previous studies, it was found that sintered high-entropy carbides with an almost single-phase FCC structure were successfully realized. Furthermore, these materials were found to meet the criteria for hardness and fracture toughness required for tool materials for machining high-hardness steel (1 700 — 2 000 HV). Their fracture toughness, in particular, was measured to be 7.0–7.3 $\text{MPa} \cdot \text{m}^{1/2}$, about 10 percent higher than that of WC, which has long been considered to be irreplaceable in the cutting tool industry.

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References

- Zhang, Y., Zuo, T.T., Tang, Z., Gao, M.C., Dahmen, K.A., Liaw, P.K., Lu, Z.P.: Microstructures and Properties of High-Entropy Alloys, *Prog. Mater. Sci.*, **61**, 1–93, (2014).
- Yeh, J.-W.: Alloy Design Strategies and Future Trends in High-Entropy Alloys, *JOM*, **65**, 1759–1771, (2013).
- Yeh, J.-W., Chen, S.-K., Lin, S.-J., Gan, J.-Y., Chin, T.-S., Shun, T.-T., Tsau, C.-H., Chang, S.-Y.: Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes, *Adv. Eng. Mater.*, **6**, 299–303, (2004).
- Chuang, M.-H., Tsai, M.-H., Wang, W.-R., Lin, S.-J., Yeh, J.-W.: Microstructure and Wear Behavior of Al_x-Co_{1.5}CrFeNi_{1.5}Ti_y High-Entropy Alloys, *Acta Mater.*, **59**, 6308–6317, (2011).
- Ye, Y.F., Wang, Q., Lu, J., Liu, C. T., Yang, Y.: High-Entropy Alloy: Challenges and Prospects, *Mater. Today*, **19**, 349–362, (2016).
- Zhang, Y., Zhou, Y.J., Lin, J.P., Chen, G.L., Liaw, P.K.: Solid-Solution Phase Formation Rules for Multi-Component Alloys, *Adv. Eng. Mater.*, **10**, 534–538, (2008).
- Wei, X.-F., Qin, Y., Liu, J.-X., Li, F., Liang, Y.-C., Zhang, G.-J.: Gradient Microstructure Development and Grain Growth Inhibition in High-Entropy Carbide Ceramics Prepared by

- Reactive Spark Plasma Sintering, *J. Eur. Ceram. Soc.*, **40**, 935–941, (2020).
- 8 Feng, L., Fahrenholtz, W.G., Hilmas, G.E., Zhou, Y.: Synthesis of Single-Phase High-Entropy Carbide Powders, *Scr. Mater.*, **162**, 90–93, (2019).
- 9 Zhou, J., Zhang, J., Zhang, F., Niu, B., Lei, L., Wang, W.: High-Entropy Carbide: A Novel Class of Multicomponent Ceramics, *Ceram. Int.*, **44**, 22014–22018, (2018).
- 10 Yang, Y., Wang, W., Gan, G.-Y., Shi, X.-F., Tang, B.-Y.: Structural, Mechanical and Electronic Properties of (TaNbHf-TiZr)C High Entropy Carbide under Pressure: Ab Initio Investigation, *Physica B.*, **550**, 163–170, (2018).
- 11 Pötschke, J., Dahal, M., Herrmann, M., Vornberger, A., Matthey, B., Michaelis, A.: Preparation of High-Entropy Carbides by Different Sintering Techniques, *J. Mater. Sci.*, **56**, 11237–11247, (2021).
- 12 Charles, R.J.: Energy-Size Reduction Relationships in Comminution, *Trans. AIME.*, **9**, 80–88, (1957).
- 13 Gao, M., Forssberg, E.: Prediction of Product Size Distributions for a Stirred Ball Mill, *Powder Technol.*, **84**, 101–106, (1995).
- 14 German, R.M.: Powder Metallurgy and Particulate Materials Processing: The Processes, Materials, Products, Properties and Applications. Metal Powder Industries Federation, 2005.
- 15 Song, J., Han, J., Kim, S.-Y., Seok, J., Kim, H.: Preparation and Refinement Behavior of (Hf-Ti-Ta-Zr-Nb)C High-Entropy Carbide Powders by Ultra High Energy Ball Milling Process, *J. Powder Mater.*, **29**, 34–40, (2022).
- 16 Buravleva, A.A., Fedorets, A.N., Vornovskikh, A.A., Ognev, A.V., Nepomnyushchaya, V.A., Sakhnevich, V.N., Lembikov, A.O., Kornakova, Z.E., Kapustina, O.V., Tarabanova, A.E., Reva, V.P., Buravlev, I.Y.: Spark Plasma Sintering of WC-Based 10 wt% Co Hard Alloy: A Study of Sintering Kinetics and Solid-Phase Processes, *Mater.*, **15**, (2022).
- 17 Rumman, M.R., Xie, Z., Hong, S.-J., Ghomashchi, R.: Effect of Spark Plasma Sintering Pressure on Mechanical Properties of WC-7.5 wt% Nano Co, *Mater. Des.*, **68**, 221–227, (2015).
- 18 Oses, C., Toher, C., Curtarolo, S.: High-Entropy Ceramics, *Nat. Rev. Mater.*, **5**, 295–309, (2020).
- 19 Navrotsky, A., Kleppa, O.J.: The Thermodynamics of Cation Distributions in Simple Spinel, *J. Inorg. Nucl. Chem.*, **29**, 2701–2714, (1967).
- 20 Navrotsky, A., Kleppa, O.J.: Thermodynamics of Formation of Simple Spinel, *J. Inorg. Nucl. Chem.*, **30**, 479–498, (1968).
- 21 Moskovskikh, D.O., Vorotilo, S., Sedegov, A.S., Kuskov, K.V., Bardasova, K.V., Kiryukhantsev-Korneev, P.V., Zhukovsky, M., Mukasyan, A.S.: High-Entropy (HfTaTiNbZr)C and (Hf-TaTiNbMo)C Carbides Fabricated through Reactive High-Energy Ball Milling and Spark Plasma Sintering, *Ceram. Int.*, **46**, 19008–19014, (2020).
- 22 Li, W., Olevsky, E.A., McKittrick, J., Maximenko, A.L., German, R.M.: Densification Mechanisms of Spark Plasma Sintering: Multi-Step Pressure Dilatometry, *J. Mater. Sci.*, **47**, 7036–7046, (2012).
- 23 Liu, D., Zhang, A., Jia, J., Meng, J., Su, B.: Phase Evolution and Properties of (VNbTaMoW)C High Entropy Carbide Prepared by Reaction Synthesis, *J. Eur. Ceram. Soc.*, **40**, 2746–2751, (2020).
- 24 Taneja, K., Kumar, M., Mahajan, S.B.: Reaction Mechanism for Pressureless Sintering Silicon Carbide Boron Carbide Composite, *Mater. Today: Proceedings.*, **39**, 1921–1924, (2021).
- 25 Aygüzer Y.Z., DeLucca, V.A., Haber, R.A.: Effect of Boron Carbide Additive and Sintering Temperature - Dwelling Time on Silicon Carbide Properties, *Ceram. Int.*, **47**, 7177–7182, (2021).
- 26 Wei, X.-F., Qin, Y., Liu, J.-X., Li, F., Liang, Y.-C., Zhang, G.-J.: Gradient Microstructure Development and Grain Growth Inhibition in High-Entropy Carbide Ceramics Prepared by Reactive Spark Plasma Sintering, *J. Eur. Ceram. Soc.*, **40**, 935–941, (2020).
- 27 Zhang, Z., Fu, S., Aversano, F., Bortolotti, M., Zhang, H., Hu, C., Grasso, S.: Arc Melting: A Novel Method to Prepare Homogeneous Solid Solutions of Transition Metal Carbides (Zr, Ta, Hf), *Ceram. Int.*, **45**, 9316–9319, (2019).
- 28 Ghaffari, S.A., Faghihi-Sani, M.A., Golestani-Fard, F., Nojabayy, M.: Diffusion and Solid Solution Formation between the Binary Carbides of TaC, HfC and ZrC, *Int. J. Refract. Met. Hard Mater.*, **41**, 180–184, (2013).
- 29 Tsai, K.-M., Hsieh, C.-Y., Lu, H.-H.: Sintering of Binderless Tungsten Carbide, *Ceram. Int.*, **36**, 689–692, (2010).
- 30 Sun, K., Yang, Z., Mu, R., Niu, S., Wang, Y., Wang, D.: Densification and Joining of a (HfTaZrNbTi)C High-Entropy Ceramic by Hot Pressing, *J. Eur. Ceram. Soc.*, **41**, 3196–3206, (2021).