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Combustion synthesis of tungsten carbides under electric field II. Field-activated pressure-assisted combustion synthesis

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Abstract

The field-activated pressure-assisted combustion synthesis (FAPACS) process, which combines the simultaneous synthesis and densification of materials, was utilized to produce tungsten carbides material from tungsten and carbon powders with different mole ratio between them, i.e. W + 1.0C, W + 1.1C, W + 1.2C, W + 1.3C and W + 1.4C. The percentages of the total shrinkage occurring before and during the synthesis reaction were measured. The effects of the temperature, the reactants composition, different carbon sources on the products composition, densities and microhardness were investigated. The end-product relative densities ranged from 81.1 to 89.9%. Vickers microhardness measurements (at 1 kg force) on the dense samples gave values ranging from 731 to 423 kg mm^{-2}.

Keywords: C. Hardness; D. Carbides

1. Introduction

Cemented carbides have grown in stature to find extensive use in a variety of applications that demand wear resistance and high temperature capability. Many methods have been used to synthesize these materials. In the first part of the paper, field-activated combustion synthesis of tungsten carbides have been investigated. Owing to low reaction rate between solid tungsten and carbon, it is difficult to attain single-phase tungsten carbide, WC. Thus, it needs long-time application of an electric field on the sample and more carbon added in the reactants. However, unexpected phenomena take place. More application time causes the sample to change shape or even crash. The influence of the applied electric field on the propagation wave velocity for the synthesis of WC from the elements, shown in Fig. 2 in the first part of the work, gives us some revelation to solve the sample-distortion problem. At very high current, no ignition source is required and the phenomena are referred to as simultaneous or volume combustion with the implication that the reaction takes place over the entire sample with no wave propagation. Therefore, the Field-Activated Pressure-Assisted Combustion Synthesis (FAPACS) process [1–6], which is based on the idea of the simultaneous (volume) combustion synthesis of FACS and material densification, was chosen to synthesize single carbide because it can ensure that no sample-crash phenomena take place and the combustion reaction has enough time to complete.

In addition, as we know, most of the processing techniques used to synthesize cemented carbides, by a combination of multi-step process, such as the synthesis of product powder, powder grinding and consolidation, lead to the formation of relatively dense material. However, this high-temperature treatment to densify materials can lead to significant grain coarsening (Ostwald ripening), which results in a loss of the fine grain structure and the associated benefits of enhanced mechanical properties. It is essential to minimize grain growth through careful control of consolidation parameters, particularly temperature and time. An alternative route to enhance densification and avoid excessive grain growth is the so-called fast firing method. FAPACS is also one kind of such methods. Through utilizing field activation and pressure,

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FAPACS method has been successfully employed to simultaneously synthesize and densify materials in one step. The method has been demonstrated to be an efficient field-activated sintering technique that can successfully consolidate ceramic, metallic and even intermetallic powders to near theoretical density [1–6] and recently been modified to prepare dense nanomaterials [7–11]. The imposition of a field during synthesis reactions has been shown to have a marked influence on the dynamics of the reaction (e.g. reaction rate and reaction mechanism), and on the nature of the product (e.g. the phase composition in composites and the elemental distribution in solid solutions), which is attributed to a variety of phenomena, including Joule heating, enhanced mass transport by electromigration, and the creation of a plasma with its concomitant influence on reactivity [8].

Furthermore, tungsten carbide exists in different phases and most important are WC and W_2C [12]. Although the W_2C phase is unstable below 1300 °C [13], normally a mixture of both WC and W_2C was found in most of tungsten carbide powders. Thus, it is essential to do the detailed research on the synthesis of single carbides from elemental reactants.

In the second part of our work we report on the fabrication of dense WC by the FAPACS method, present the results of the effects of various processing parameters on FAPACS of tungsten carbides and examine the influence of processing parameters, such as temperature, the ratio of C/W in reactants' mixtures and different carbon sources on product composition, densities and microhardness of bulk tungsten carbide samples. No previous results on the study of FAPACS of tungsten carbides have been reported.

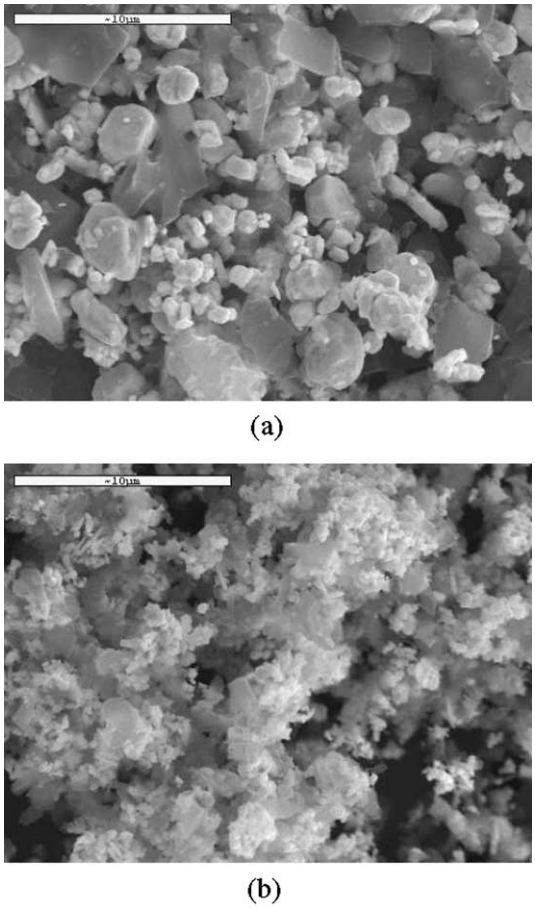

Fig. 1. SEM image of W + C mixtures for different carbon sources (a) activated carbon (b) carbon black.

2. Experimental procedures

Mixtures of tungsten and carbon with several different mole ratios of W/C, 1:1, 1:1.1, 1:1.2, 1:1.3 and 1:1.4, were used to synthesize tungsten carbides. Two kinds of carbon powders (both with a reported purity of 99.9%, one activated carbon with an average particle size of 20 μm (Kojondo Chemical Co.) and another carbon black with an average particle size of 20 nm (Korea Carbon Black Co., Ltd) were chosen as carbon sources. Either of them was dry-mixed in an alumina ball mill with 99.9% pure tungsten (an average particle size of 0.6 μm, Korea Tungsten Co.). Taking equiatomic mixtures as examples, SEM images of reactants mixtures for activated carbon and carbon black are shown in Fig. 1(a) and (b), respectively. Tungsten uniformly distributed in the reactants' mixtures, as seen from the analysis result of Electronic Probe Mass Analysis of tungsten in starting powders (Fig. 2). To form a sample, the appropriate quantity of mixed powder was weighed out and poured into a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) lined with graphite foil and then cold pressed at 4 MPa for 2 min. After packing, the samples were introduced into the FAPACS apparatus, which consists of a uniaxial 60 MPa press combined with a 27 V, 3000 A DC power supply, to simultaneously provide current and pressure to a conductive die sample. A schematic of the experimental setup is shown in Fig. 3. The system was evacuated (stage 1) and a uniaxial pressure of 60 MPa was applied (stage 2). A high DC current was then applied to the two punches on the die, Joule heating of the die and the sample, continued until the maximum operating temperature is reached, which is measured by a pyrometer focused on the surface of the graphite die. The applied pressure densified the sample at the same time and maintained until densification was attained, as indicated by a linear gauge measuring the sample shrinkage (stage 3). At the end of the process, the sample was cooled to room temperature at a fixed rate of 600 °C/min (stage 4). Typical parameters for the FAPACS process, which was carried out under a vacuum of 2×10^{-2} Torr, are presented in Table 1.

After the reactions, the samples were removed from the dies and lightly ground to remove the graphite foil.

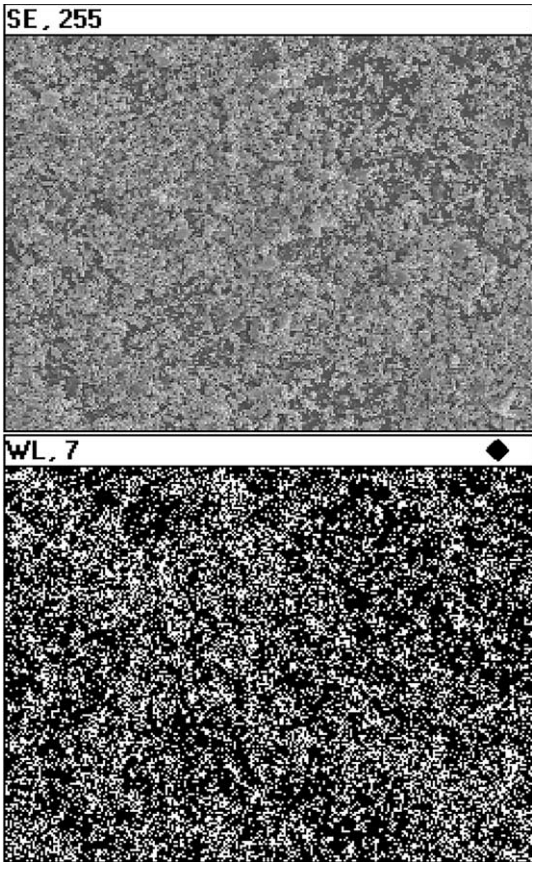

Fig. 2. Electronic probe mass analysis of tungsten for reactants mixtures.

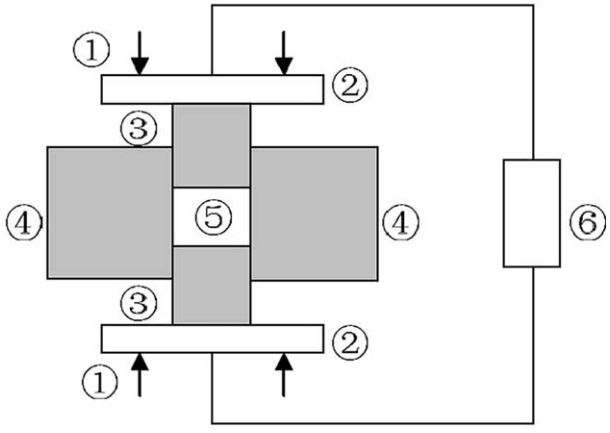

Fig. 3. Schematic diagram of field-activated and pressure-assisted combustion synthesis and densification ①: pressure application ②: graphite block ③: graphite punch ④: graphite die ⑤: reactants ⑥: power supply.

Samples were polished on SiC paper and further diamond for microscopic examination. The density of the combustion products was measured by the Archimedes method. Compositional and microstructural analyses of the products were made through X-ray diffraction (XRD), scanning electron microscopy (SEM) and electronic probe, respectively. Vickers microhardness measurements (under a 1 and 10 kg load with a dwell time of 15 s) were made on the synthesized samples.

Table 1
Processing parameters for field-activated and pressure-assisted combustion synthesis of WC

Parameter	Applied value
Vacuum level	2×10^{-2} Torr
Applied pressure	60 MPa
Resistance heating	
Voltage	18 V
Current	3000 A
Duration	3 min
Heating rate	1200 °C/min
Maximum temperature	1250 °C
Cooling rate	600 °C/min

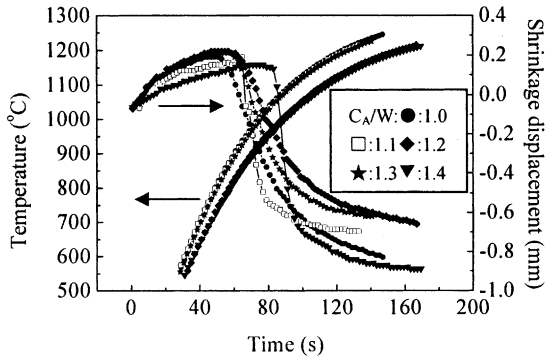

Fig. 4. Variation of shrinkage displacement and temperature with heating time during synthesis (pre-established temperature: 1200 °C): (a) $W+1.0C_A$ (b) $W+1.1C_A$ (c) $W+1.2C_A$ (d) $W+1.3C_A$ and (e) $W+1.4C_A$.

3. Results and discussion

The variations of shrinkage displacement and temperature of the die surface with heating time during the processing of these reactants' mixtures with the starting compositions of $W+1.1C_A$, $W+1.2C_A$, $W+1.3C_A$ and $W+1.4C_A$ are shown in Fig. 4. In this and the other following figures and their captions, the patterns labeled A and B represent activated carbon and carbon black, respectively. The shrinkage displacement increased gradually with temperature up to about 850 °C and then abruptly at about this temperature. When a stoichiometric $W+1.0C_A$ mixture was heated under 60 MPa pressure to 850 °C, no reaction took place and no significant displacement was observed. X-ray diffraction result, shown in Fig. 5, exhibits only peaks pertaining to the reactants, which confirmed that a reaction between W and C did not take place under these conditions. However, when the temperature was raised to 1200 °C, the starting powders reacted to form two kinds of carbides,

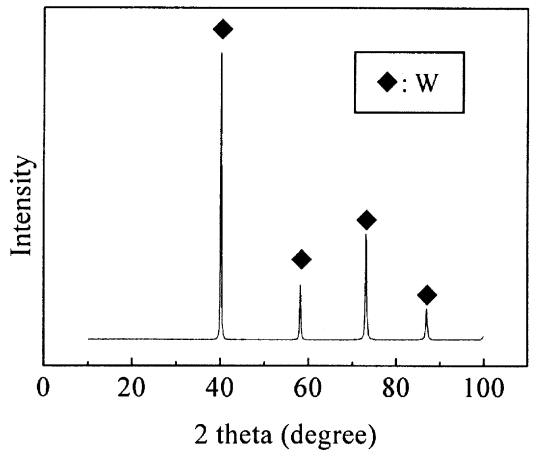

Fig. 5. XRD patterns of the W + C system heated to 850 °C.

WC and W_2C, which was determined from an XRD analysis (Fig. 6).

In addition, the displacement in Fig. 4 for the reactants of $W + 1.4C_A$ was initially gradual and then became sudden after 83 s while about 60 s for the reactants with other composition, $W + 1.0C_A$, $W + 1.1C_A$, $W + 1.2C_A$, $W + 1.3C_A$. Under the condition of more activated carbon in the mixtures, on one side, the combustion temperature is lower owing to relatively less reactants in the mixtures; on the other side, it is disadvantageous to densify the material because of big-particle size of activated carbon. The corresponding XRD results of the reacted products are shown in Fig. 5. No appreciable difference in phase composition was observed, regardless of the ratio between carbon and tungsten in the reactants. For all cases, under low combustion temperature (1200 °C), W_2C is present in the combustion products. Although there were small differences in the relative amounts of the phases for different reactants' compositions, two kinds of carbides exist in the combustion products together, as can be seen in Fig. 6.

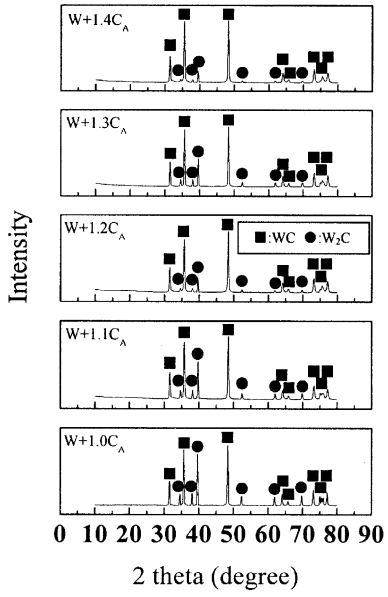

Fig. 6. X-ray powder patterns for the FAPACS reaction products heated to 1200 °C corresponding to the composition of reactants (a) $W + 1.0C_A$ (b) $W + 1.1C_A$ (c) $W + 1.2C_A$ (d) $W + 1.3C_A$ and (e) $W + 1.4C_A$.

In order to eliminate W_2C from the combustion products, the temperature was set up in advance again and increased from 1200 to about 1250 °C. For the reactant mixtures, $W + 1.1C_A$, $W + 1.2C_A$ and $W + 1.3C_A$, their variations of shrinkage displacement and temperature of the die surface with heating time during the process are shown in Fig. 7. For $W + 1.1C_A$ and $W + 1.2C_A$, the displacement was initially gradual and then became sudden after about 5s. As compared with the case of 1200 °C, higher current causes the earlier occurrence of the reaction. Unlike the above cases, the displacement for $W + 1.3C_A$ was gradual and sudden change is not evident which is due to more carbon in the mixture. Table 2 shows values of the density, sample volume, and volume change at different stages in the synthesis and densification of WC. These results show that 2.85% of the total volume shrinkage occurred prior to ignition and 97.15% occurred during the synthesis stage for $W + 1.1C_A$, 2.76% and 97.24% for $W + 1.2C_A$, 2.97% and 97.03% for $W + 1.3C_A$, respectively. The corresponding relative densities of the synthesized samples were determined as 84.2, 84.1 and 81.1% of theoretical, respectively. With the increase of ratio between tungsten and carbon in the reactants, the densities of synthesized products decrease. It is probably associated with the remained big-particle carbon in the synthesized products, which is disadvantageous to densify the samples. The corresponding XRD analysis results are shown in Fig. 8. In contrast to the above condition, i.e. 1200 °C, a clear variation in the product composition between $W + 1.3C_A$ and $W + 1.1C_A$, was observed. When the high combustion temperature (1250 °C) is enacted and

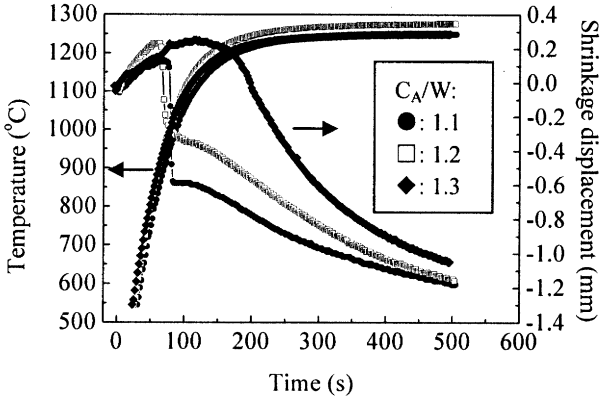

Fig. 7. Variation of shrinkage displacement and temperature with heating time during synthesis (preestablished temperature: 1250 °C): (a) $W + 1.1C_A$ (b) $W + 1.2C_A$ and (c) $W + 1.3C_A$.

Table 2
Density, volume and volume change during field-activated and pressure-assisted combustion synthesis of $W+(1+x)C$ $(0.1 \leqslant x \leqslant 0.3)$ (activated carbon)

C/W		Initial sample	Before ignition	Reactant (Theo.)	Product	
					Expt.	Theo.
1:1.1	Density (g cm^{-3})	9.454	9.192	13.526	12.378	15.236
	Sample volume (cm^3)	1.54	1.59	1.08	1.18	0.96
	Pore volume (cm^3)	0.46	0.51	0	0.22	0
	Volume change (%)	0	2.85	30.11	23.63	37.95
	Incremental volume (%)	0	2.85	27.26	6.48	14.32
1:1.2	Density (g cm^{-3})	9.494	9.239	13.194	12.011	14.804
	Sample volume (cm^3)	1.71	1.76	1.23	1.35	1.10
	Pore volume (cm^3)	0.48	0.53	0	0.25	0
	Volume change (%)	0	2.76	28.04	20.96	35.87
	Incremental volume (%)	0	2.76	25.28	7.09	14.91
1:1.3	Density (g cm^{-3})	8.924	8.666	12.881	11.037	14.401
	Sample volume (cm^3)	1.69	1.74	1.17	1.37	1.05
	Pore volume (cm^3)	0.52	0.57	0	0.32	0
	Volume change (%)	0	2.97	30.72	19.14	38.03
	Incremental volume (%)	0	2.97	27.74	11.57	18.89

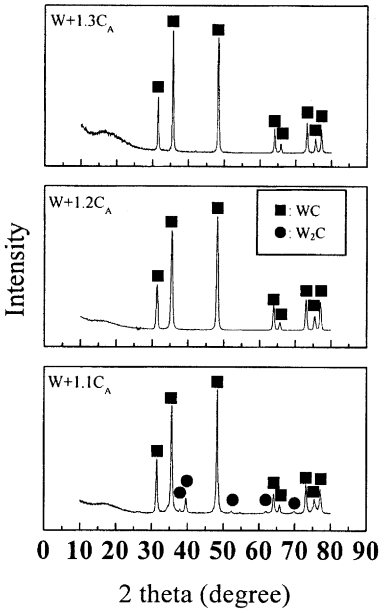

Fig. 8. X-ray powder patterns for the FAPACS reaction products heated to 1250 °C corresponding to the composition of reactants (a) $W+1.1C_A$ (b) $W+1.2C_A$ and (c) $W+1.3C_A$.

applied, the $W+1.3C_A$ and $W+1.2C_A$ mixtures reacted completely and the W_2C phase could not detected in the combustion products, while for $W+1.1C_A$ WC phase is the major component and much W_2C phase also exists in the combustion products.

Furthermore, different kinds of carbon sources also influenced the composition of synthesized products. For the reactant mixtures with carbon black as carbon source, $W+1.1C_B$, $W+1.2C_B$, and $W+1.3C_B$, their

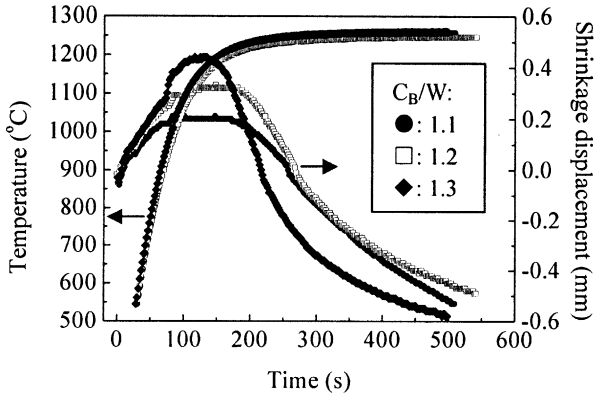

Fig. 9. Variation of shrinkage displacement and temperature with heating time during synthesis (preestablished temperature: 1250 °C): (a) $W+1.1C_B$ (b) $W+1.2C_B$ and (c) $W+1.3C_B$.

Table 3
Density, volume and volume change during field-activated and pressure-assisted combustion synthesis of $W+(1+x)C$ $(0.1 \leqslant x \leqslant 0.3)$ (carbon black)

C/W		Initial sample	Before ignition	Reactant (Theo.)	Product	
					Expt.	Theo.
1:1.1	Density (g cm^{-3})	12.025	11.549	13.526	13.521	15.236
	Sample volume (cm^3)	1.45	1.51	1.29	1.29	1.14
	Pore volume (cm^3)	0.16	0.22	0	0.14	0
	Volume change (%)	0	4.12	11.10	11.06	21.07
	Incremental volume (%)	0	4.12	6.98	0.04	10.01
1:1.2	Density (g cm^{-3})	11.706	11.128	13.194	13.132	14.804
	Sample volume (cm^3)	1.45	1.53	1.29	1.30	1.15
	Pore volume (cm^3)	0.16	0.24	0	0.16	0
	Volume change (%)	0	5.19	11.27	10.17	20.92
	Incremental volume (%)	0	5.19	6.08	1.10	10.75
1:1.3	Density (g cm^{-3})	10.887	10.317	12.881	12.845	14.401
	Sample volume (cm^3)	1.59	1.68	1.35	1.38	1.20
	Pore volume (cm^3)	0.25	0.33	0	0.18	0
	Volume change (%)	0	5.52	15.48	13.21	24.40
	Incremental volume (%)	0	5.52	9.95	2.26	11.18

variations of shrinkage displacement and temperature of the die surface with heating time during the process are shown in Fig. 9. Unlike the case of activated carbon, the displacement after the ignition is gradual in all cases. This is associated with smaller particle size of carbon for which it is easy to obtain raw sample with high density. What is more, there is more carbon in the combustion products owing to high reactivity of carbon black and less carbon is needed to obtain WC. Table 3 shows values of the density, sample volume, and volume change at different stages in the synthesis and densification of WC. The results show that 4.12% of the total volume shrinkage occurred prior to the ignition of the reaction, with the remaining 95.88% occurring during and subsequent to synthesis for $W+1.1C_B$, 5.19 and

94.81% for $W+1.2C_B$, 5.52 and 94.48% for $W+1.3C_B$, respectively. The corresponding relative density of the combustion products was determined as 89.9, 89.3 and 88.6% of theoretical, respectively. The trend of the product densities with the ratio between tungsten and carbon in the reactants is the same as that with activated carbon as carbon source. X-ray analysis results for the combustion products from the reactant mixtures, $W+1.1C_B$, $W+1.2C_B$, and $W+1.3C_B$, are shown in Fig. 10. With the increase of carbon amount in reactants, the final state of reaction increases. In all cases the carbide in the product was nearly a pure single phase. The composition of $W+1.3C_B$ and $W+1.2C_B$ resulted in the formation of WC and only for the $W+1.1C_B$ very trace W_2C exists in the combustion products.

Compared with the synthesized products of the same composition for activated carbon and carbon black in the reactants, the shrinkage displacements for carbon black as carbon source prior to ignition for all cases are bigger. This is due to more gas adsorbed on the surface of carbon black and released during the reaction, which partly counteracts the compaction pressures. The relative densities of the combustion products are also bigger than those for activated carbon as carbon source. This is explained by the smaller particle size of carbon black [Fig. 1(b)] and the concomitant relatively higher reactivity and more diffusivity of carbon in tungsten particle than those of activated carbon, which is confirmed by X-ray analysis results of the synthesized products from the same reactant mixtures. Taking the reactant with the composition of $W+1.1C$ as an example, very trace W_2C is found in the combustion products for carbon black (Fig. 10) while there are much W_2C in the case of activated carbon (Fig. 8).

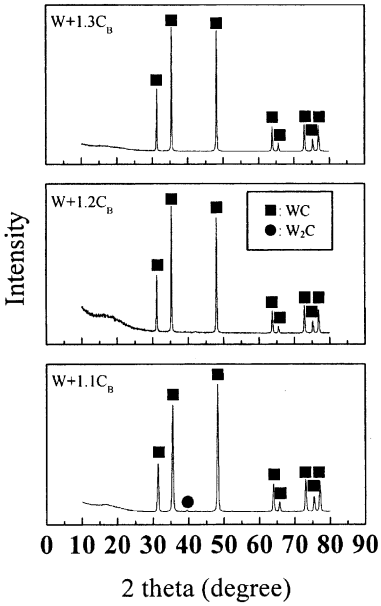

Fig. 10. X-ray powder patterns for the FAPACS reaction products heated to 1250 °C corresponding to the composition of reactants (a) $W+1.1C_B$ (b) $W+1.2C_B$ and (c) $W+1.3C_B$.

The experimental result that only WC together with carbon was found in the combustion products also proves WC is the final product of the reaction between tungsten and carbon, which confirms the reaction mechanism of tungsten carbide under the electric field, depicted in the first part of our work.

Finally, Vickers microhardness measurements were made on the polished products using a 1 kg load. The microhardness values of synthesized products with different compositions and carbon sources in the reactants are shown in Table 4. These values represent averages of measurements on at least 15 indentations. The microhardness for $W+1.1C$ is the highest as compared with that of $W+1.2C$ and $W+1.3C$ no matter which carbon sources are used. As we know, the microhardness of W_2C (3000 kg mm^{-2}) is higher than that of WC (2400 kg mm^{-2}), and the microhardness of carbon black or activated carbon is much lower than that of tungsten carbides. For the former case, the final state of the reaction between tungsten and carbon is relatively lower and there are much W_2C in the combustion product. As for the latter case, there is too much carbon in the reactants, leading to lower microhardness. Comparing the microhardness of products fabricated from different carbon sources with the same composition, the hardness is lower for all cases when carbon black is used as carbon source. This is probably associated with the amount of remained carbon in the products, which has just been discussed above. In fact, even though only WC can be obtained in very short time of FAPACS through adding more carbon in the reactants, however, there is also large amount of remained carbon in the combustion products. Compared with conventionally synthesized method by heating a mixture of metallic tungsten powder and carbon black in a graphite furnace under a flowing hydrogen atmosphere [14], the ratio between tungsten and carbon is far from 1:1.

In typical hardness indentations for fabricated products from the reactants of $W+1.3C_B$, shown in Fig. 11, cracks were observed at the micro-indentation corners of the sample. The brittleness of WC at room temperature is a serious drawback for this material. One approach to improve toughness in this brittle carbide is to make composites with a more ductile phase, for

Table 4
Vickers microhardness of FAPACS products of $W+(1+x)C$ ($(0.1 \leqslant x \leqslant 0.3)$)

Sample	$W+1.1C_A$	$W+1.2C_A$	$W+1.3C_A$	$W+1.1C_B$	$W+1.2C_B$	$W+1.3C_B$
Hardness (kg/mm^2)	731	575	498	672	459	423

Note: A, B represent activated carbon and carbon black, respectively.

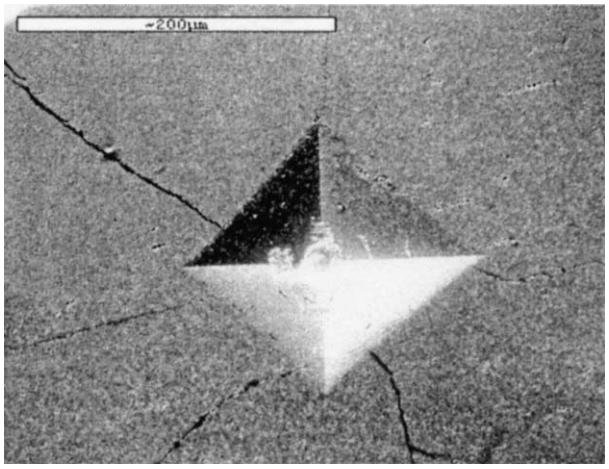

Fig. 11. Vickers microhardness indentations in $W+1.3C_B$ (10 kg load).

instance metallic cobalt or nickel. This is known as ductile phase toughening. The study of simultaneous synthesizing and densification of WC–Co and WC–Ni composites by using FAPACS method have been done and the results will be reported in other places.

4. Summary and conclusions

The one-step synthesis and densification of tungsten carbides was achieved through the use of the field-activated pressure-assisted method from the reactants with different ratio between tungsten and carbon. Below 850 °C (on the surface of graphite die), the reaction between tungsten and carbon cannot take place. For little richer amount of carbon in the reactants, shrinkage displacement during the processing of W + C increased gradually with heating temperature up to the ignition temperature and then abruptly increased. However, gradual shrinkage displacement after the ignition can be observed for some systems. The sudden shrinkage is not evident during the processing and consolidation of W + C for much richer amount of activated carbon and carbon black. With the increase of carbon in the reactants, the relative density of synthesized products decreases. Vickers microhardness measurements were made on all hyper-stoichiometric samples. With different composition and carbon sources, microhardness are different.

Acknowledgements

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References

[1] Z.A. Munir, I.J. Shon, K. Yamazaki, Simultaneous synthesis and densification by field-activated combustion, US Patent 5 794 113, 11 August 1998.
[2] I.J. Shon, Z.A. Munir, K. Yamazaki, K. Shoda, Simultaneous synthesis and densification of $MoSi_2$ by field activated combustion, J. Am. Ceram. Soc. 79 (1996) 1875–1880.
[3] I.J. Shon, Z.A. Munir, Synthesis of $MoSi_2$–xNb and $MoSi_2$–$y ZrO_2$ composites by the field-activated combustion method, Mater. Sci. Eng. A 202 (1–2) (1995) 256–261.
[4] I.J. Shon, H.C. Kim, D.H. Rho, Z.A. Munir, Simultaneous synthesis and densification of Ti_5Si_3 and Ti_5Si_3–20 vol.% ZrO_2 composites by field-activated and pressure-assisted combustion, Mater. Sci. Eng. A 269 (1-2) (1999) 129–135.
[5] I.J. Shon, D.H. Rho, H.C. Kim, Z.A. Munir, Dense WSi_2 and WSi_2-20 vol.% ZrO_2 composite synthesized by pressure-assisted field-activated combustion, J. Alloy. Compd. 322 (1-2) (2001) 120–126.
[6] A. Feng, T. Orling, Z.A. Munir, Field-activated pressure-assisted combustion synthesis of polycrystalline Ti_3SiC_2, J. Mater. Res. 14 (1999) 925–939.
[7] Z.A. Munir, F. Charlot, F. Bernard, E. Gaffet, One-step synthesis and consolidation of nanophase materials, US Patent Application Serial No. 09/374.049, 13 August 1999.
[8] Z.A. Munir, Synthesis and densification of nanomaterials by mechanical and field activation, J. Mater. Synth. Processing 8 (3/4) (2000) 189–196.
[9] R. Orrù, J. Woolman, G. Gao, Z.A. Munir, Synthesis of dense nanometric $MoSi_2$ through mechanical and field activation, J. Mater. Res. 16 (5) (2001) 1439–1448.
[10] Jae Won Lee, Zuhair A. Munir, Synthesis of dense TiB_2-TiN nanocrystalline composites through mechanical and field activation, J. Am. Ceram. Soc. 84 (6) (2001) 1209–1216.
[11] Frédéric Bernard, Frédéric Charlot, Eric Gaffet, Zuhair A. Munir, One-step synthesis and consolidation of nanophase iron aluminide, J. Am. Ceram. Soc. 84 (5) (2001) 910–914.
[12] A. Cottrell, Chemical Bonding in Transition Metal Carbides, The Institute of Materials, London, 1995.
[13] F.A. Schrunk, Constitution of Binary Alloys, Genium, New York, 1991.
[14] K.J. Brookes, World Directory and Handbook of Hardmetals and Hard Materials, International Carbide Data, Hertfordshire UK, 1992.