JOURNAL OF MATERIALS SCIENCE **38** (2003) 3559–3565

Mechanistic investigation of the field-activated combustion synthesis (FACS) of tungsten carbide with or without nickel additive

GUOJIAN JIANG, HANRUI ZHUANG, WENLAN LI
Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China
E-mail: jiangguojian@mail.sic.ac.cn

The activation of self-propagating combustion reactions in the W-C system and its composite with Ni as additive was achieved by using an electric field. The reaction mechanisms of Field-Activated Combustion Synthesis (FACS) of tungsten carbide and its composite have been investigated by using sample-quenched method. Through turning off electric field during FACS process, a series of combustion products with different phase compositions have been obtained. Layer to layer X-ray and microscopic analyses of these combustion products across quenched combustion front suggested that the synthesis of WC is a process involving the solid diffusion of carbon into a carbide layer. W_2C is the intermediate phase between WC and reactants (W and C). Metal additive produces liquid phase and accelerates the diffusion between solid reactants (W and C), which facilitates the formation of W_2C and the transformation from W_2C to WC phase. Moreover, melted Ni reacts with W and W_2C to form mixed compounds of type $W_xC_yM_z$.

1. Introduction

As a promising and energy-efficient technique, Combustion Synthesis (CS) or Self-propagating High-temperature Synthesis (SHS) [1] has been developed and has been used to prepare a series of advanced materials. In a typical SHS process, compacts of powder mixtures are ignited at one end to initiate the self-sustaining reaction. The products are synthesized after the combustion wave has passed. However, for the case of some systems, such as tungsten-carbon, ignition is impossible without addition activation. Primarily this is due to the thermodynamic limitation, i.e. a low reaction enthalpy or the relatively low adiabatic combustion temperature, T_{ad}, typically adopted for determining the feasibility of self-propagating reactions. For example, for the two carbides of tungsten, T_{ad}s of WC and W_2C are 1127°C and 673°C, respectively, which are considerably lower than the empirically established minimum of 1527°C for SHS reactions. By the way, in order to improve toughness in this brittle carbide, metallic nickel is added to make hard cemented carbides for use in practical applications. With the addition of nickel, the adiabatic combustion temperature of this reactant system will change lower. The effect of the addition of nickel on the adiabatic temperature of this system is shown in Fig. 1. Details of calculations of adiabatic temperature have been discussed in some references [2]. For systems which are relatively less exothermic, the common approach has been the preheating of the reactants, which accomplishes the goal of raising T_{ad}, but which can suffer from the formation of extraneous phases, such as pre-combustion phases through diffusion.

Recently, a new method, referred to in the literature as Field-Activated Combustion Synthesis (FACS) [3], based on the use of an electric field to activate self-propagating reactions in their relatively low heat of formation or less-exothermic systems, was developed. Experimental results and modeling studies have lead to the conclusion that the effect of the field is to provide Joule heating at a rate of σE^2 with σ being the conductivity and E the field (in reality per unit thickness of the sample) [4–6]. Depending on the electric conductivity of reactants and products, ignition results in the initiation and propagation of a combustion wave in reactant systems which heretofore could not be synthesized by SHS (without preheating), including SiC, SiC-AIN, TaC, B_4C-TiB_2, $MoSi_2$-SiC, Ti_3Al, and others [7–14]. Although SHS and FACS processes have many special characteristics, such as very high temperatures, high waves propagation velocities and low-energy requirments, etc., which make these techniques advantageous for industrial applications, it is very difficult to achieve commercial manufacture straightforward on a large scale without knowing the fundamental knowledge of the combustion reaction. In order to solve this problem, a detailed research on combustion

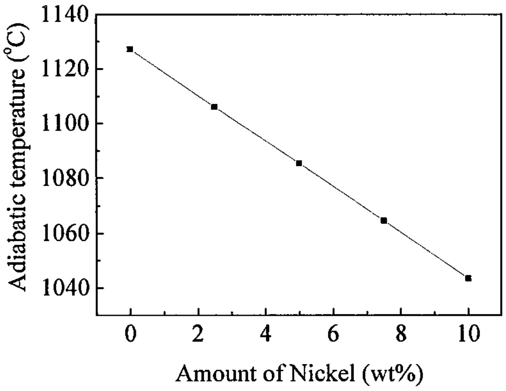

Figure 1 Variation of the adiabatic combustion temperature with the amount (wt%) of Ni for the formation of composites of WC-x wt%Ni.

synthesis reaction and structure formation mechanism is necessary.

It is well known that experimental mechanistic investigations on SHS and FACS are difficult and most are proposed usually through the analysis of indirect experimental results. However, if the indirect experiments are precise, they provide important information about reaction mechanism. There are many research approaches to perform mechanistic investigation at the experimental level, such as investigation of the effect of processing variables, the synchrotron radiation technique, the particle-foil technique, the combustion front quenching technique, etc. Among them, the latter one is often preferred because it is easily realized only through the rapid extinction of the reaction front during its propagation and the experimental results provide relatively accurate and necessary information for mechanism research. For those less-exothermic systems which are synthesized through the FACS technique, the method could be more easily accomplished by the removal of the field during wave propagation. By analyzing product microstructure and composition at different areas relative to the location of the frozen reaction wave, it is possible to obtain the information of intermediate species and phase transformation taking place during the combustion.

This method is applied in this work to investigate the reaction mechanism of FACS of WC with or without nickel additive from elemental powders. No previous results on the mechanism investigation of FACS of WC and WC-Ni composites have been reported.

2. Experimental procedures

Equiatomic mixtures of tungsten and activated carbon were used to investigate the reaction mechanism of FACS of WC. Tungsten powder with a reported purity of 99.99% and an average particle size of 0.6 μm (Korea Tungsten Co.), was dry-mixed in an alumina ball mill with 99.9% pure activated carbon powder (an average particle size of 20 μm, supplied by Kojondo Chemical Co.). In some experiments, 99.8% pure nickel powder (supplied by Aldrich Chemical Co.) with an average particle size of 30 μm was added to the reactants' mixtures to study the reaction mechanism of FACS of WC-Ni composite. Tetragonally shaped pellets with dimensions of 10 mm × 10 mm × 15 mm were cold-pressed under compaction pressure in a two-plunger steel die. The pellets were then placed between two spring-loaded graphite electrodes across which a voltage was applied. A tungsten heating coil, placed near the edge of the sample, was used to initiate the combustion and was turned off immediately after the reaction was initiated. A schematic representation of this set-up is shown in Fig. 2. The field-activated combustion synthesis experiments were carried out inside a stainless steel pressure chamber under one atmosphere of argon gas. The combustion process evolution was recorded from video camera equipped with a time-code generator. In all experiments the voltage was abruptly reduced to zero after the wave had propagated halfway through the sample, which caused the wave to stop and the combustion process to extinguish immediately. More details concerning the field-activated combustion experiments can be found in the literature [4, 5].

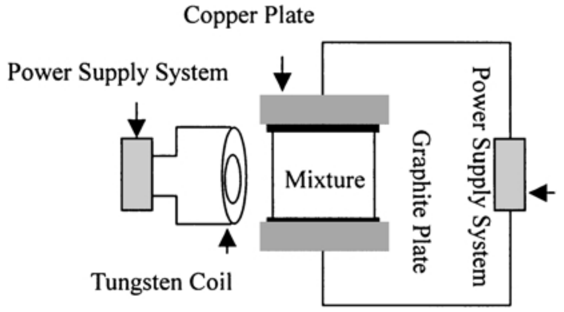

Figure 2 Schematic representation of field-activated combustion synthesis, FACS.

Structure, microstructural and compositional analyses of the products were made through X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

3. Results and discussion

To understand the mechanism of conversion from the elemental starting powders to the final material, experiments were carried out in which the applied voltage (corresponding to $E = 12.5\ \text{V cm}^{-1}$) was interrupted after the wave had halfway advanced through the sample. Because the solid-phase reaction between tungsten and carbon is relatively slow, two opposite ends of quenched sample were chosen as zone 1 (reactant zone) and zone 5 (product zone). When the raw material mixtures only contained tungsten and carbon without any nickel additive, the reactant and combustion product are in solid state and thus the SEM back-scattered observations become increasingly difficult to evaluate due to the low contrast among the various product phases. For this reason, we also made XRD investigations on sections cut parallel to the quenched reaction front. Three relatively distinct zones where the designations zone 2, zone 3, zone 4 represent, respectively, the regions ahead of the wave, the region inside the wave and the region behind the wave, can be clearly identified through a layer to layer X-ray diffraction analysis at various

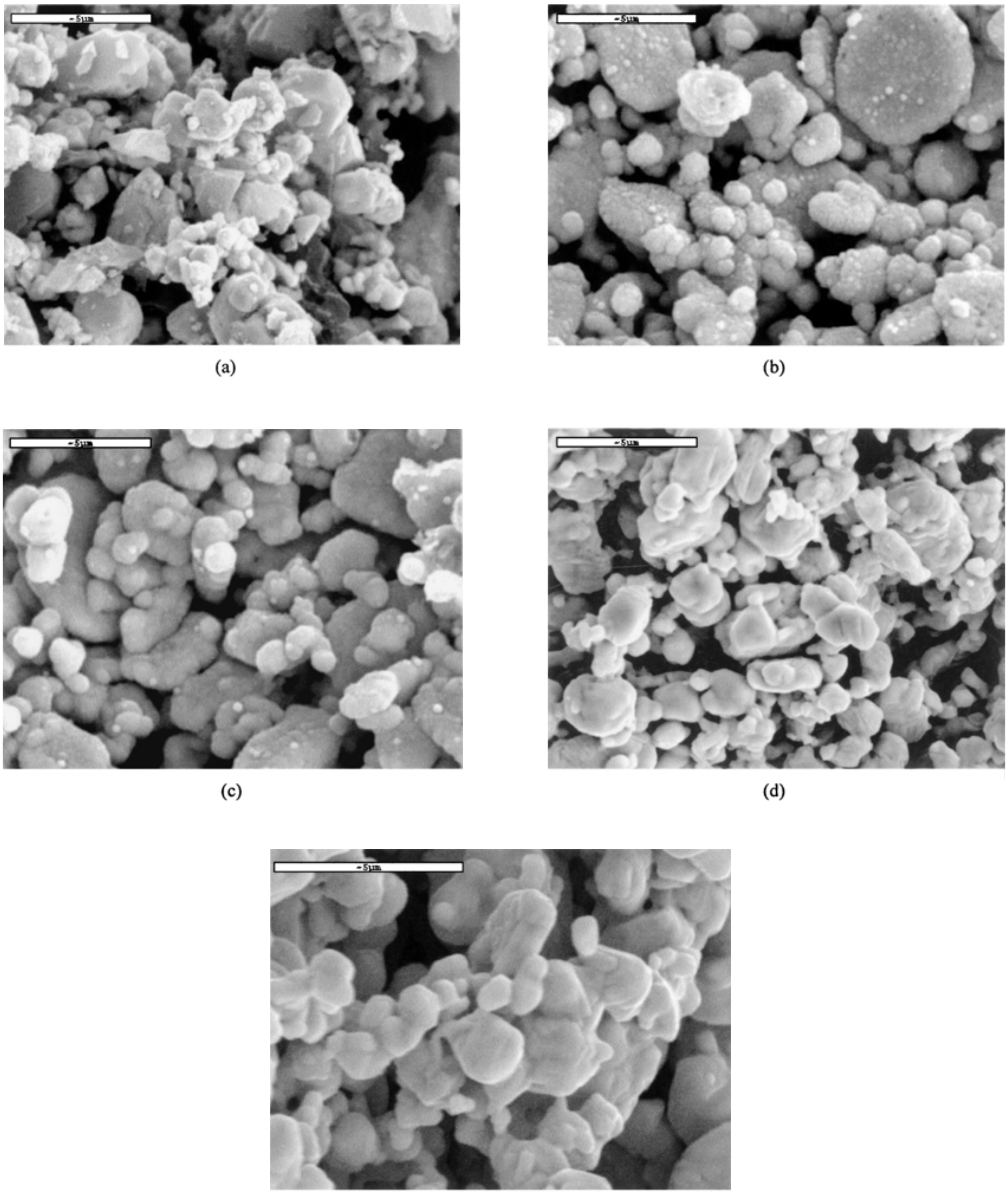
(a) (b) (c) (d) (e)

Figure 3 SEM micrograph of the quenched sample for the FACS of WC: (a) Zone 1, (b) Zone 2, (c) Zone 3, (d) Zone 4, and (e) Zone 5.

locations (i.e. parallel to wave propagation) of the quenched sample. A series of SEM micrograph and corresponding X-ray diffraction analysis results on these zones are shown in Figs 3 and 4, respectively. Zone 1 (Fig. 3a) represents the elemental reactants: the relatively larger and darker carbon particles are surrounded by the small and bright tungsten particles. In Zone 2 (Fig. 3b), the region ahead of the wave, the passage of the combustion front is indicated by the sudden appearance of product layers around the carbon grains. The morphology of the product layers suggests that an interaction between solid tungsten and carbon has taken place. However, carbon grains are still clearly discernible. Tungsten and carbon along with minor amounts of the reaction products, W_2C and WC, are present in this zone. The latter two compounds are the major phases in Zone 3 (Fig. 3c) but tungsten and carbon are still present. Zone 4 (Fig. 3d), the region behind the combustion front, contained only traces of tungsten and carbon. Finally, only W_2C and WC are observed in Zone 5 (Fig. 3e). Although the phase composition in Zone 3 and Zone 4 is essentially the same, the position of WC diffraction peak in XRD diagram in zone 3 shifts to lower angle than that in the zone 4. Taking the second diffraction peak of WC from the left of XRD diagram as an example, the position of WC diffraction peak in zone 3 is 35.55° and 35.6° in zone 4 while 35.9° in zone 5. The phenomena confirm that with the propagation of combustion wave, the carbonization degree of combustion wave-passed zone increased. The phenomena are similar to those observed when synthesizing TaC material [15]. This is possible because

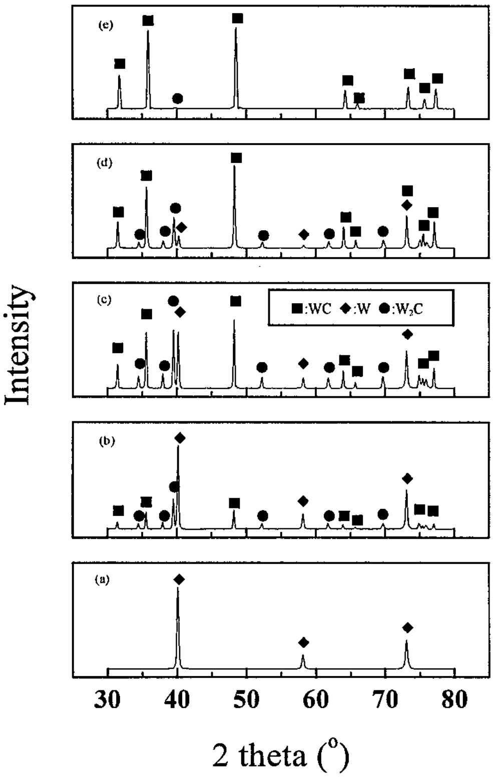

Figure 4 XRD patterns of the corresponding zones of the quenched sample for the FACS of WC.

tungsten carbide exists in a relatively wide range of composition, as it may be seen from the W-C phase diagram [16]. When moving from the reactants region to the final product, more diffusion of carbon into WC crystal lattice and thus the crystal cell changes smaller and the distance between crystal faces becomes smaller. According to Bragger's equation, 2-theta angle changes bigger and the position of diffraction peaks in XRD diagram somewhat shifted right, indicating a change in the lattice parameter corresponding to the specific elemental ratio. Furthermore, it should be remembered that in these experiments W_2C phase is always observed in the combustion products. As cited in the reference [17], the equiatomic ratio of C/W resulted in an incomplete reaction between W and C and more carbon was required to obtain WC single phase. XRD analysis of the present work from these systems showed the presence of W_2C along with WC, which confirms the above opinion.

Under the similar synthesis condition ($E = 10$ V cm^{-1}), amount of nickel was added to the tungsten and carbon mixtures to investigate the function of metal in FACS of WC-Ni composite. The same approach described above to analyze the quenched samples was adopted for the system considered in this work, i.e. WC-10wt%Ni. A series of low magnification SEM micrographs of these regions across the quenched front for the quenched sample (WC-10wt%Ni) and corresponding XRD analysis results on these zones are shown in Figs 5 and 6, respectively. Five visually distinguished zones can be also clearly identified at various locations (i.e. parallel to wave propagation) of the quenched sample. Zone 1 only contains the reactants (Fig. 5a) and no indication of any interaction between the two elements can be observed. In Zone 2 (Fig. 5b), which corresponds to the region ahead of the reaction front, tungsten and carbon together with minor amounts of the reaction products, W_2C and WC, are present. The carbide compounds, WC and W_2C, are the major phases in Zone 3 (Fig. 5c) but tungsten and carbon are still observed. The morphology change also proves that the reaction between tungsten and carbon has initiated. Moreover, Ni grains are not clearly discernible, indicating that massive melting of Ni has taken place. Moving further towards the product region, the microstructure and phase composition gradually change. In zone 4 (Fig. 5d), tungsten can not be detected in the combustion product and massive melting of nickel is discerned from the micrograph. Finally, only W_2C, WC and Ni_2W_4C are observed in Zone 5 (Fig. 5e). In the product region, some W_2C diffraction peaks have disappeared as compared with the phase composition in Zone 4. Even though the addition of metallic Ni to the reactants mixtures causes the adiabatic temperature of the system lower about 80°C than that of W/C system, the similar combustion products was obtained under the lower electric field. This is due to the addition metallic Ni melts, which is helpful to the diffusion between solid reactants to form carbides. Moreover, trace W_2C phase can also be detected in the combustion products. This aspect further confirms that the stoichimetric WC is obtained only when carbon completely disappears as a consequence of a gradual diffusion of C into the W_2C phase. Furthermore, Ni_2W_4C phase exists in the combustion product, which is from the reaction among W_2C, metallic W and Ni to form mixed compounds of type $W_xC_yM_z$ [18, 19] (Ni_2W_4C in this system).

In all above quenched samples, W_2C coexists with WC phase in the quenched samples. As we know, with the decrease of electric field, combustion temperature decreases. In order to confirm whether W_2C is intermediate phase or not, an experiment was conducted in which the applied voltage (2V, $E = 2$ V cm^{-1}) was turned off during the combustion. X-ray diffraction pattern of the region near reactants' mixtures in the quenched front is shown in Fig. 7. The fact that the region only contains W_2C together with W and C demonstrates that W_2C is intermediate phase.

Owing to low reaction rate between tungsten and carbon, it is difficult to synthesize single carbide even with dispersion of nickel, as mentioned above. Thus, it needs long-time application of electric field on the sample. However, other 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, shown in Fig. 8 for the synthesis of WC from the elements, gives us some revelation to solve the sample distortion phenomena. The figure shows three regions, relative to the strength of the applied field. At low fields, ≤ 1 V cm^{-1}, no SHS reaction takes place, but above this threshold value the rate of self-sustaining reactions increases

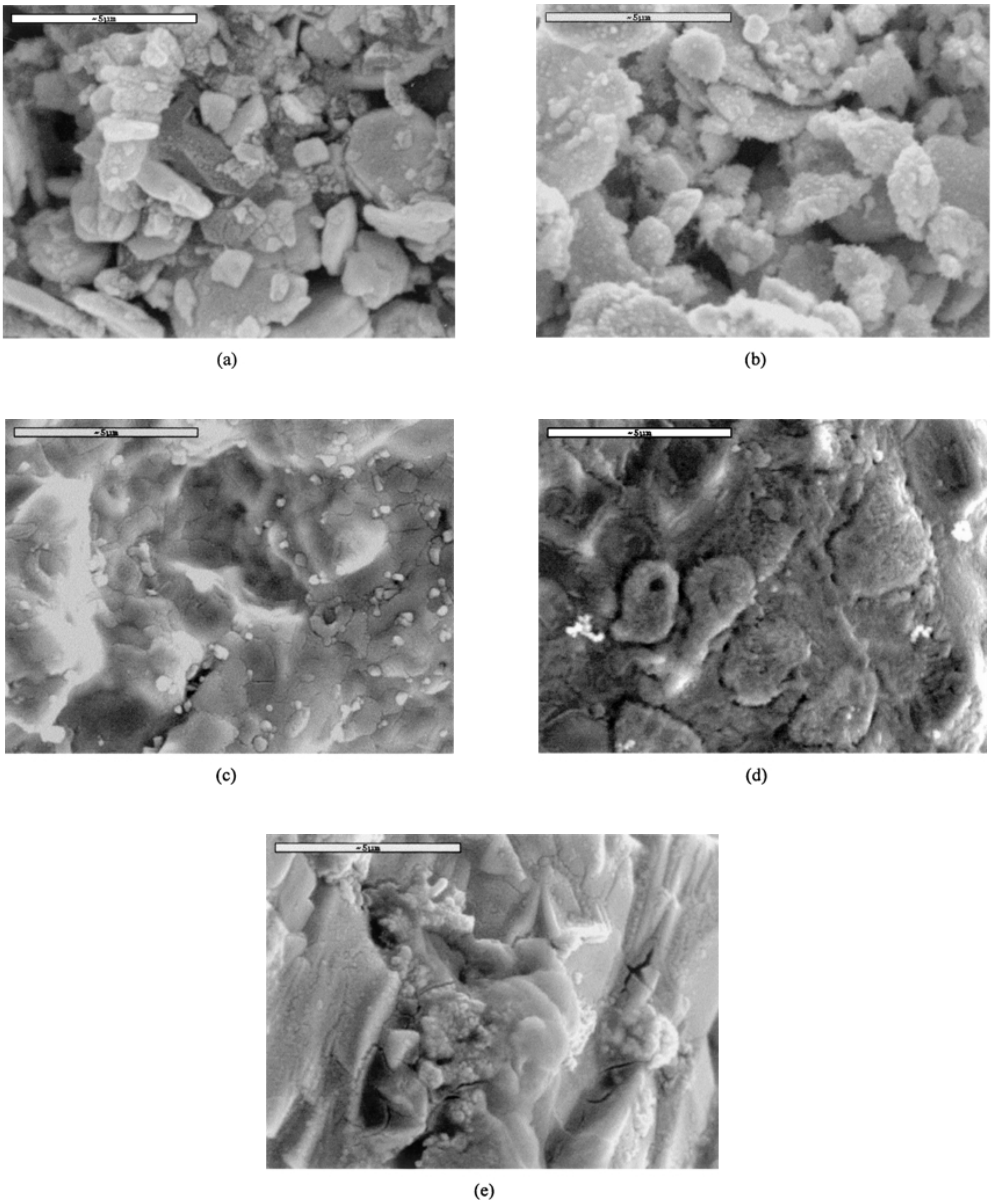

Figure 5 SEM micrograph of the quenched sample for the FACS of WC-10wt%Ni composite: (a) Zone 1, (b) Zone 2, (c) Zone 3, (d) Zone 4, and (e) Zone 5.

approximately linearly with field strength as the applied field was increased in the interval between fields of 1 and 15 V cm^{-1}. When the field is about 15 V cm^{-1} or higher, no ignition source is required, in other words, the reaction is initiated by the Joule heating of the field itself. The phenomena of Fig. 9 are referred to as simultaneous or volume combustion with the implication that the reaction is taking place over the entire sample with no wave propagation. Therefore, the Field-Activated, and Pressure-Assisted Combustion Synthesis (FAPACS) process, which is based on the thought of the simultaneous (volume) combustion synthesis of FACS and materials densification, was chosen to synthensize single carbide because it can ensure that no sample-crash phenomena take place and the combustion reaction has enough time to complete. As an example, the variations of shrinkage displacement and temperature of the die surface with heating time during FAPACS of $W + C + 10$wt%Ni was shown in Fig. 9. The XRD diagram of FAPACS of WC-10wt%Ni is shown in Fig. 10. The detailed work will be discussed in other place further.

On the basis of these above experimental results, FACS of WC, WC-Ni composite and the research results of FAPACS of WC-Ni composite from $W + C + Ni$, it is possible to postulate the sequence of transformation during FACS of WC with or without metal additive, as summarized in Table I.

Since both adiabatic temperatures of W_2C and WC are less than their corresponding melting points

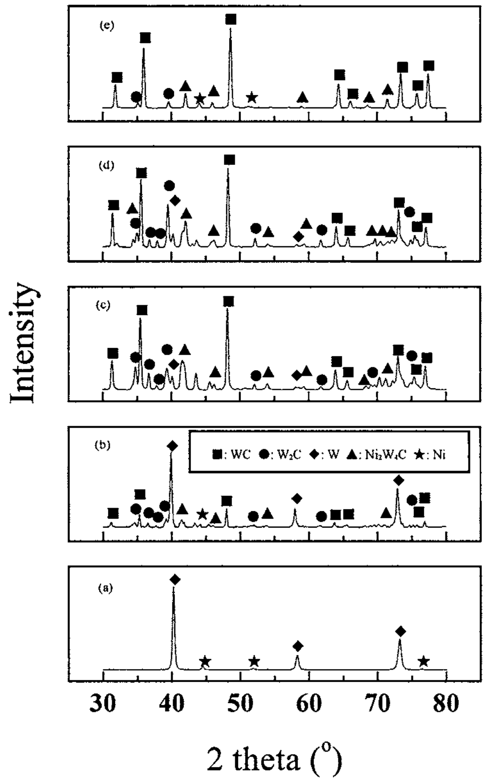

Figure 6 XRD patterns of the corresponding zones of the quenched sample for the FACS of WC-10wt%Ni composite.

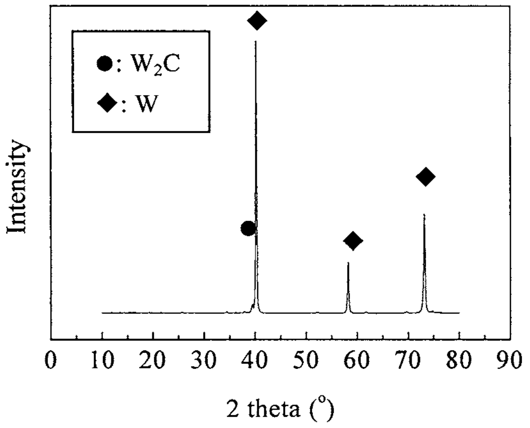

Figure 7 X-ray diffraction patterns of W-C products synthesized at the electric field of 2 V cm^{-1}.

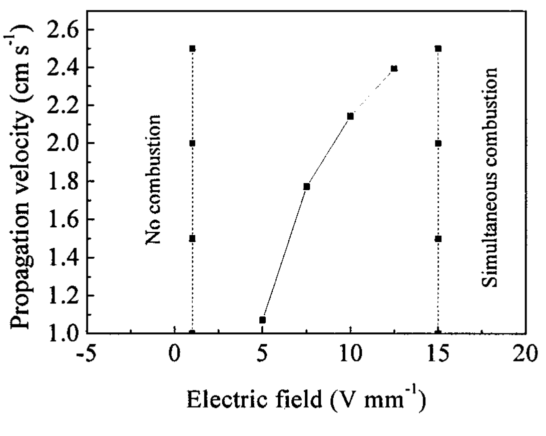

Figure 8 Dependence of wave velocity on field strength in the synthesis of WC.

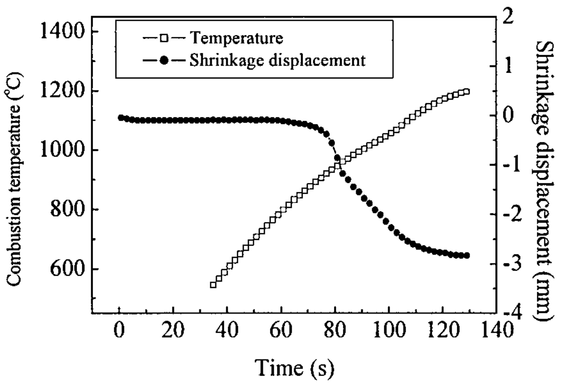

Figure 9 Variations of shrinkage displacement and temperature of the die surface with heating time during FAPACS of W + C + 10wt%Ni reactants.

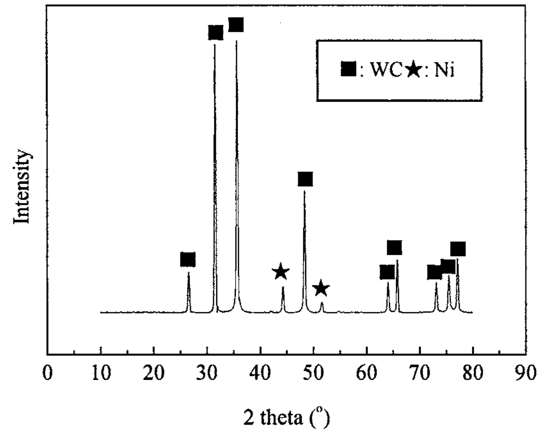

Figure 10 XRD patterns of the sample of the FAPACS of WC-10wt%Ni composite.

(2327–2577°C for WC and 2785°C for W_2C, respectively) as well as the melting points of W (3407°C) and C (3527°C), a solid-solid mechanism is the only likely process during the combustion synthesis of the carbide phase in the absence of any Ni. The experiment suggests that initial stage consists of the reaction between tungsten and carbon to form W_2C. This step is followed by the transformation from W_2C to WC. Since only small amount of W_2C is found in the quenched products, the latter step is assumed to take place relatively rapidly and therefore is not considered as rate controlling stage. The progress of the synthesis involves also the diffusion of carbon into WC lattice, which is the controlling step.

As for the system of W + C with the additive Ni, the relative content of Ni in the reactants is very small as compared with W and C, thus the reaction mechanism is similar to that for FACS of WC as shown in Table Ia. The main difference is that metal melts and reacts with W and C to form $W_xC_yM_z$, which decomposes to metal and WC with the diffusion of carbon finally. The function of melted Ni (the melting point of Ni is 1453°C) increases the interconnection between particles, redounds reactants diffusion and the transformation from W_2C to WC phase. Nickel diffuses in WC and spreads around WC grains to form WC-Ni composites.

TABLE I Transformation zones and their characteristics during FACS of WC with or without metal additive (M represents Ni)

Kinds	Zones	Chemical species	Nature of structure transformation	Result of the chemical interaction
a	Reactants	W, C	No transformation	No interaction
	Combustion (1)	W, C, W_2C	Reaction between W and C	Formation of W_2C
	Combustion (2)	W, C, W_2C, WC	Transformation of W_2C into WC	Formation of WC
	Final product	WC	Diffusion of carbon into WC lattice	No chemical interaction
b	Reactants	W, C, M	No transformation	No interaction
	Combustion (1)	W, C, W_2C,	Reaction between W and C	Formation of W_2C
		$W_xC_yM_z$	M melted	
			Decomposition of WC to W_2C or W	Formation of W_2C or W
			Reaction between W, M and W_2C	Formation of $W_xC_yM_z$
	Combustion (2)	W, C, W_2C, WC	Transformation of W_2C into WC	Formation of WC
		$W_xC_yM_z$	Reaction between $W_xC_yM_z$ and carbon	Formation of WC and M
	Final product	WC, M	Diffusion of carbon into WC lattice	No chemical interaction

4. Summary and conclusions

Experimental studies were carried out to investigate the reaction mechanism of field-activated combustion synthesis reactions between tungsten and carbon. The relatively complete levels of these combustion reactions across the combustion front are different, which was reflected in the phase composition and the position of diffraction peaks in XRD diagram. The position of resulting tungsten carbide diffraction peaks shifted somewhat right when moving from the reactants region to the final product. X-ray analysis on an ‘electrically quenched’ sample revealed the sequence of the field activated reaction between W and C. The reaction mechanism of tungsten carbide was proposed. The process begins with the reaction between W and C to form W_2C. This is followed by the formation of WC. The function of melted Ni facilitates the reaction of solid reactants and the transformation from W_2C to WC phase.

Acknowledgment

This work was supported by the National Nature Science Foundation of China (No. 50232020).

References

1. A. G. MERZHANOV and I. P. BOROVINSKAYA, *Doklady Akademii Nauk SSSR* **204** (1972) 366.
2. Z. A. MUNIR, *Amer. Ceram. Soc. Bull.* **67** (1988) 342.
3. *Idem*., *Mater. Sci. Eng.* A **287**(2) (2000) 125.
4. I. J. SHON and Z. A. MUNIR, *ibid.* **202**(1/2) (1995) 256.
5. I. J. SHON, D. H. RHO, H. C. KIM and Z. A. MUNIR, *J. Alloy. Compd.* **327**(1/2) (2001) 66.
6. A. FENG, O. A. GRAEVE and Z. A. MUNIR, *Comp. Mater. Sci.* **12**(2) (1998) 137.
7. R. ORRÙ, A. CINCOTTI, G. CAO and Z. A. MUNIR, *Chem. Eng. Sci.* **56**(2) (2001) 683.
8. F. MAGLIA, U. ANSELMI-TAMBURINI, C. MILANESE, N. BERTOLINO and Z. A. MUNIR, *J. Alloy. Compd.* **319**(1/2) (2001) 108.
9. K. S. YUN, J. H. LEE and C. W. WON, *Mater. Res. Bull.* **35**(10) (2000) 1709.
10. R. ORRU, G. CAO and Z. A. MUNIR, *Chem. Eng. Sci.* **54** (15/16) (1999) 3349.
11. *Idem*., *Metall. Mater. Trans.* A **30A**(4) (1999) 1101.
12. S. GEDEVANISHVILI and Z. A. MUNIR, *Mater. Sci. Eng.* A **242**(1/2) (1998) 1.
13. H. XUE and Z. A. MUNIR, *J. Eur. Ceram. Soc.* **17**(15/16) (1997) 1787.
14. S. GEDEVANISHVILI and Z. A. MUNIR, *Mater. Sci. Eng.* A **211**(1/2) (1996) 1.
15. H. XUE and Z. A. MUNIR, *Int. J. SHS* **5**(3) (1996) 229.
16. Founding Editor J. J. Zuckerman, Inorganic Reactions and Methods, Volume 12b, Formation of Bonds to C, Si, Ge, Sn, Pb (Part 4), Edited by A. P. Rlagen, p. 129.
17. The Tungsten-Carbon Phase Diagram, *Amer. Soc. Met., Binary Alloy Phase Diagram* **1** (1986) 600.
18. M. E. VINAYO, F. KASSABJI, J. GUYONNET and P. FAUCHAIS, *J. Vac. Sci. Technol.* **A3**(6) (1985) 2483.
19. V. RAMNATH and N. JARAYAMAN, *Mater. Sci. Technol.* **5** (1989) 382.

Received 10 December 2002
and accepted 10 June 2003