

# Kinetics of cobalt gradient formation during the liquid phase sintering of functionally graded WC–Co

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## Abstract

Carbon is a critical factor that can be used to produce a gradient of cobalt content in WC–Co composites. The cobalt gradient formed during liquid phase sintering of WC–Co involves migration of the liquid phase, diffusion of carbon in the liquid phase and reaction of carbon with  $W_3Co_3C$  phase particles. The graded microstructure produced in this study exploiting the kinetic process of carbon diffusion and the phase reaction of carbon with  $\eta$  phase ( $Co_3W_3C$ ) is a non-equilibrium or metastable microstructure. Thus, the graded microstructure is a function of time at the sintering temperature as well as other factors. A study of the kinetics of the process is therefore necessary to fully understand the process, hence control the microstructure. This paper studies the effect of carbon gradient and holding time at the sintering temperature on the overall kinetics of the process.

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**Keywords:** Functionally graded materials; WC–Co (Cemented tungsten carbide); Liquid phase sintering; Liquid phase migration

## 1. Introduction

Functionally graded WC–Co composites offer a solution to the trade-off between wear resistance and fracture toughness in WC–Co composites by varying the cobalt content from the surface to the interior of a sintered piece [1–3]. The surface, with relatively low cobalt content, would have high wear resistance, while the interior, with relatively high cobalt content, would have a high toughness.

Although various methods can be used to make functionally graded WC–Co composites, liquid phase sintering remains the only economically viable manufacturing method. However, when two or more WC–Co layers with the same WC particle size but different cobalt contents are sintered together in an effort to produce a functionally graded WC–Co part, the cobalt content evens out across the layers resulting in a sintered part with uniform cobalt

content [4,5]. This type of liquid migration in a two-phase system such as the WC–Co system can be attributed to the driving force for the system to decrease its total interfacial energy. Lisovsky [6–8] proposed that the existence of migration pressure gradient within the WC–Co composite is responsible for the migration of the liquid phase within the system. The homogenization can be avoided; that is the cobalt gradient can be retained, however, under specific conditions. There are two examples in the industry.

Cemented tungsten carbide with a cobalt-enriched surface layer is one example of the technology that creates the cobalt gradient within the cemented tungsten carbide part during sintering [9]. The graded structure in this case is attributed to an outward diffusion of nitrogen out of the part and an inward diffusion of titanium away from the surface [10,11]. This results in the surface zone being depleted of cubic carbides and enriched in cobalt. The enrichment of cobalt at the surface of the cemented carbide body is a by-product of the diffusion processes involving nitrogen and titanium within system during sintering. Although the mechanism of the migration of cobalt to

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the surface of the sintered cemented carbide body is not fully understood, it is known that carbon content also affects the formation of the cobalt-enriched surface layer [12,13].

Another example of cemented tungsten carbide with a graded structure is the dual phase (DP) carbide [14]. The graded structure of the so-called DP carbide is produced during a separate heat treatment process after liquid phase sintering. During the heat treatment process, pre-sintered parts that are carbon deficient are exposed to a carbon rich atmosphere. The diffusion of carbon into the carbon deficient parts results in a cobalt gradient within the sintered parts. Although the DP carbide technology is currently used in the industry, there are no published studies on the theoretical principles governing the formation of the graded structure in DP carbide. In both of these examples, carbon is a pivotal factor that influences the formation of the cobalt gradient in cemented tungsten carbides during sintering.

A recent study by Fang and Eso [15] systematically examined the effect of all factors including carbon content, grain size, cobalt content and sintering time on the development of cobalt gradient during liquid phase sintering in a bi-layer WC–Co sample. The study explained the formation of a cobalt gradient during liquid phase sintering based on three underlying processes: (1) The flow of the liquid phase due to a capillary force gradient from areas with relatively larger mean free path (MFP) to areas with relatively smaller MFP. The variation in the MFP is due to the variation in the grain size and the cobalt content; (2) The variation of the volume fraction of the liquid phase as a function of carbon content based on the requirements for thermodynamic equilibrium; and (3) The variation of the volume fraction of the liquid phase due to phase reaction between carbon and  $\eta$  phase ( $\text{Co}_3\text{W}_3\text{C}$ )  $\cdot$   $\text{Co}_3\text{W}_3\text{C}$  ( $\eta$ ) phase is a complex phase formed in WC–Co alloy during sintering due to a significant carbon deficiency. Based on carbon diffusion and phase reaction processes, carbon was identified as a key factor affecting the cobalt gradient within a sintered WC–Co sample.

In the reported studies, the graded microstructure produced in WC–Co alloys due to carbon diffusion and phase reaction with  $\eta$  phase ( $\text{Co}_3\text{W}_3\text{C}$ ) is a non-equilibrium or metastable microstructure. If the process is allowed enough time to attain equilibrium, the gradient in both carbon and cobalt will be eliminated and a homogenous composite will be produced. A comprehensive study of the kinetics of the process is therefore necessary to fully understand and control the process and achieve the desired graded microstructure. Presently, there is no published work on the kinetics of cobalt gradient formation due to carbon diffusion and phase reaction processes in WC–Co alloys. Also, the extent of cobalt gradient that can be achieved for a given carbon content and the effect of variation in carbon content on the microstructural stabilities of the sintered WC–Co part are issues of practical interest. A significant increase or decrease in carbon content of WC–Co alloy with respect

to the stoichiometric carbon content will result in the formation of free carbon phase and  $\eta$  phase ( $\text{Co}_3\text{W}_3\text{C}$ ). These phases are undesirable in the sintered WC–Co part because of their detrimental effects on mechanical properties [16]. Thus, the ultimate goal is to be able to achieve a cobalt gradient within a WC–Co alloy and avoid the presence of free carbon and  $\eta$  phase ( $\text{Co}_3\text{W}_3\text{C}$ ) in the final sintered WC–Co part.

The present research investigated the kinetics of the process of cobalt gradient formation during liquid phase sintering of WC–Co alloys. The effect of carbon gradient and holding time at the sintering temperature on the overall kinetics of the process is studied. Experimental results and discussions on the processes that influence the kinetics of cobalt gradient formation are presented.

## 2. Experimental

WC–10% Co powders with 5  $\mu\text{m}$  particle size were used as the starting raw material for this study. The composition of the WC–10% Co powders was modified by adding graphite and tungsten powders. Graphite powders were added to increase the total carbon content above the stoichiometric value while tungsten powders were added to reduce the total carbon content below the stoichiometric value. The powder mixtures were milled in heptane in a Nalgene<sup>®</sup> bottle containing WC balls for fourteen hours on a rolling mill. The milled powders were dried in a Rotovap at 80 °C. Samples were compacted at 200 MPa into bi-layer cylinders and dewaxed at 300 °C. The composition of each bi-layer cylindrical sample is shown in Table 1.

Sintering experiments were carried out in a vacuum furnace using a heating rate of 10 °C/min. The samples were sintered at 1400 °C for holding times of 15 min, 60 min, 120 min, and 180 min and then furnace cooled. The sintered samples were polished and etched with Murakami's reagent for 10 s to examine  $\text{Co}_3\text{W}_3\text{C}$  ( $\eta$ ) phase and for 2 min to examine tungsten carbide and cobalt phases. The cobalt distribution in the WC–Co bi-layers was measured using the Energy Dispersive Spectroscopy (EDS) on the scanning electron microscope (SEM). Each data point on the cobalt distribution profile was generated by averaging EDS scans over an area of 0.2 mm by 12 mm.

Table 1  
Compositions of bi-layers WC–Co with different initial carbon gradients

Sample	Layers	Initial total % cobalt content	Initial total % carbon content	$\Delta\text{C}$
A	Layer 1	9.96	5.8	0.6
	Layer 2	9.45	5.2	
B	Layer 1	9.94	6.0	1.0
	Layer 2	9.09	5.0	
C	Layer 1	9.92	6.2	1.4
	Layer 2	8.72	4.8	
D	Layer 1	9.90	6.4	1.8
	Layer 2	8.36	4.6	

3. Results

In this section, experimental results are presented to show the effects of sintering time and initial carbon gradient on the kinetics of the process of forming the graded structure and the relationship between the transformed region (WC + Co) of the bi-layer and sintering time. Two terms extracted from the results are also presented: the degree of the transformation during the process as a function of time and the extent of cobalt gradient produced in the sintered WC–Co part as the result of the initial carbon gradient.

3.1. Effects of holding time and initial carbon content on the kinetics of cobalt gradient formation

An important aspect for kinetic study is to determine the effect of time on the process under consideration. In this study, the effect of time is investigated by holding the WC–Co bi-layer samples (Table 1) at a fixed sintering temperature (1400 °C) for different times and tracking the microstructural changes in the sintered WC–Co samples. Fig. 1 shows the measured cobalt concentration profile of sintered bi-layer WC–Co samples A, B, C and D with initial compositions listed in Table 1. Each sample was held for 15 min, 60 min, 120 min and 180 min at 1400 °C. A cobalt gradient is observed in each of the sintered WC–Co bi-layer sample (Fig. 1). The cobalt gradient shifts towards the edge of the sample as the holding time at 1400 °C is increased. Furthermore, two moving fronts are formed within the

bi-layer WC–Co samples during sintering as illustrated in Fig. 2. The moving boundary ( $M_c$ ) in layer 1 separates WC + Co + free carbon region from WC + Co region while the moving boundary ( $M_\eta$ ) in layer 2 separates WC + Co region from WC + Co +  $Co_3W_3C$  region within the bi-layer WC–Co sample (Fig. 2). The dissolution of graphite particles occurs at the moving front  $M_c$  while the phase reaction between carbon and  $Co_3W_3C$  occurs at the moving front  $M_\eta$ . Consequently, during sintering the WC + Co region expands while the WC + Co + free carbon and the WC + Co +  $Co_3W_3C$  ( $\eta$ ) regions shrink in size with increase in holding time at 1400 °C.

Fig. 3 shows a plot of the square of the WC–Co region thickness ( $X$ ) as a function of sintering time.  $X$  is the thick-

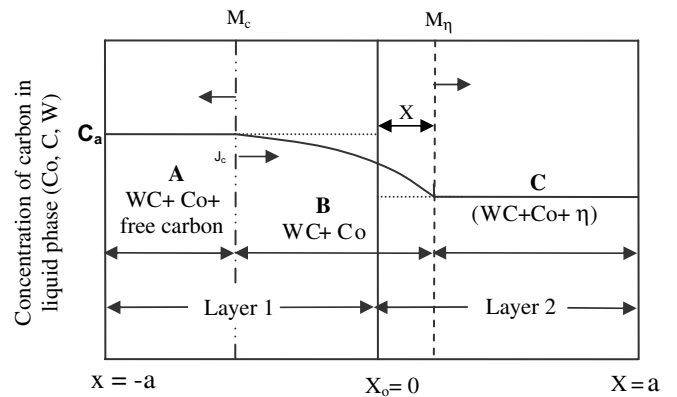


Fig. 2. A schematic illustration of the different regions formed during sintering within a WC–Co bi-layer with an initial carbon gradient.

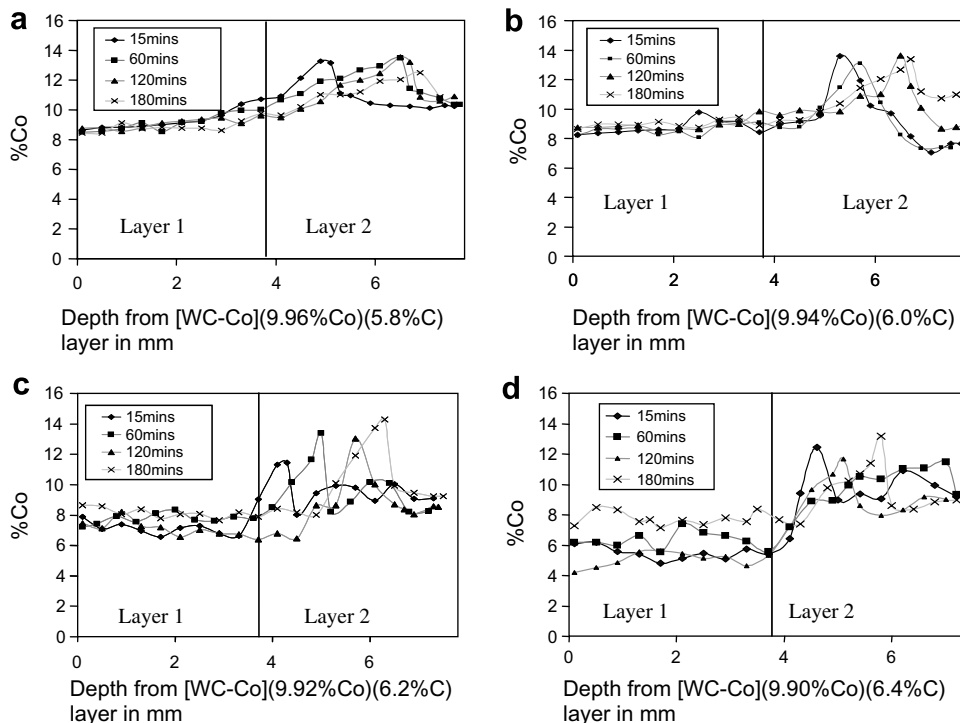


Fig. 1. Cobalt distribution profile of (a) Sample A, (b) Sample B, (c) Sample C, and (d) Sample D, with initial compositions given in Table 1. The samples were sintered for different holding times (15 min, 60 min, 120 min, and 180 min) at 1400 °C.

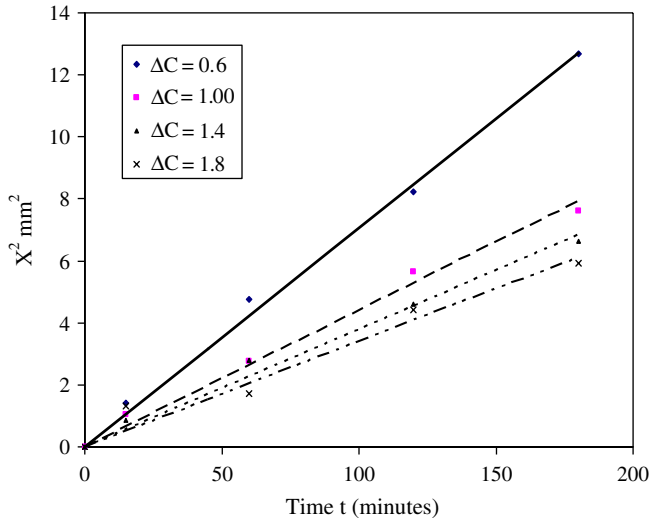


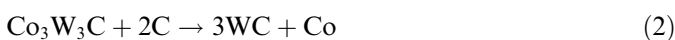
Fig. 3. Width of WC + Co product layer ( $X$ ) as a function of holding time ( $t$ ) at sintering temperature.

ness of the transformed region (WC + Co) in layer 2. A linear dependence is observed between the square of the thickness ( $X$ ) of the WC + Co region in layer 2 and sintering time ( $t$ ),  $X = Kt^{1/2}$ . This suggests that the  $[WC + Co + Co_3W_3C] \rightarrow [WC + Co]$  transformation process is controlled by the diffusion of carbon, where  $K$ , the slope of the line, is the rate constant determined by effects of other factors on the kinetics. Fig. 3 shows that the rate of the  $[WC + Co + Co_3W_3C] \rightarrow [WC + Co]$  transformation process decreases with the initial carbon gradient between WC–Co bi-layers which is counter-intuitive because the  $Co_3W_3C \rightarrow WC + Co$  transformation reaction depends on the supply of carbon to the reaction sites and the diffusion of carbon is one of the underlying processes that leads to cobalt gradient. This phenomenon will be further explained later in the discussion section.

The kinetics of the process can also be studied by using the approach that describes the kinetics of phase transformations. The kinetics of phase transformations is often given by the dependence of the fraction of phase transformed on time [17]. Using that approach, Fig. 4 shows the plot of the fraction of transformation ( $f$ ) of  $[WC + Co + Co_3W_3C] \rightarrow [WC + Co]$  as a function of sintering time. The degree of transformation ( $f$ ) is defined as

$$f = (X - X_0)/(X_1 - X_0) \quad 0 \leq f \leq 1 \quad (1)$$

where  $X$  (Fig. 2) is the measured thickness of the WC–Co region formed from the phase reaction of  $Co_3W_3C$  and carbon according to the reaction



and  $X_0$  and  $X_1$  correspond to the value of  $X$  at the start and end of the transformation.  $X_0 = 0$  for the samples used in this study. From the plot (Fig. 4), the rate of transformation of  $[WC + Co + Co_3W_3C] \rightarrow [WC + Co]$  reduces with the increase of holding time at the sintering temperature. The rate of transformation also reduces with the initial carbon

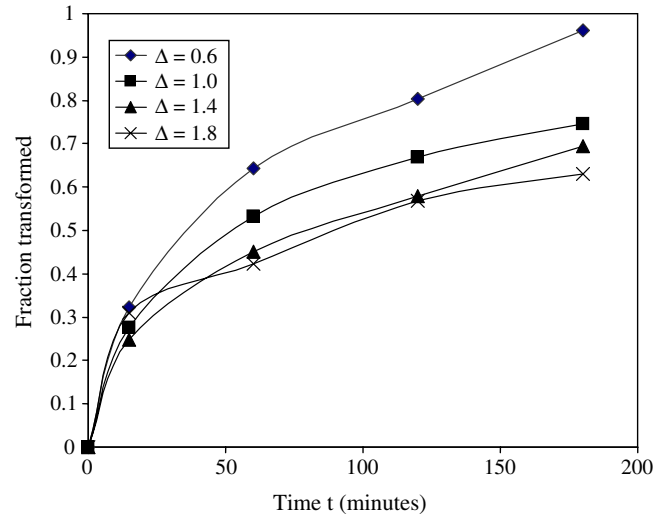


Fig. 4. The degree of transformation ( $f$ ) of (WC + Co +  $Co_3W_3C$ ) region into (WC + Co) within WC–Co bi-layers sample with an initial carbon gradient as a function of holding time at 1400 °C.

content gradient within the WC–Co bi-layers, which is consistent with the finding described in the previous paragraph.

### 3.2. Effect of initial carbon content and time on the final cobalt gradient

It is observed in Fig. 1 that the cobalt gradient formed with the WC–Co bi-layer samples is a function of the initial carbon gradient. A parameter that can be extracted from the plots in Fig. 1 is the extent of cobalt gradient. The extent of cobalt gradient is the degree of variation of the cobalt content within the sintered WC–Co. The extent of cobalt gradient as a function of the initial carbon gradient can be determined by plotting a measurable parameter  $\Delta G_{p-v}$  as a function of the initial carbon gradient.  $\Delta G_{p-v}$  is defined as the difference between the highest cobalt content (peak) and the lowest cobalt content (valley) for each composition of WC–Co bi-layers in Fig. 1. Fig. 5 shows the extent of cobalt gradient ( $\Delta G_{p-v}$ ) formed as a function of the initial carbon gradient within the WC–Co bi-layers. An increase in the initial carbon gradient produces an increase in the extent of cobalt gradient within the sintered WC–Co bi-layers (Fig. 5). The extent of cobalt gradient produced in the sintered WC–Co bi-layer varied from about 5% Co for an initial carbon gradient of 0.6%–9% Co for an initial carbon gradient of 1.8%.

There was no significant change in the extent of cobalt gradient as a function of time (Fig. 1). However, in all the compositions studied the location of the peaks of the cobalt gradient is shifted towards the edge of the bi-layer WC–Co sample with sintering time.

## 4. Discussion

The experimental results show that the kinetics of the process of cobalt gradient formation depends on several

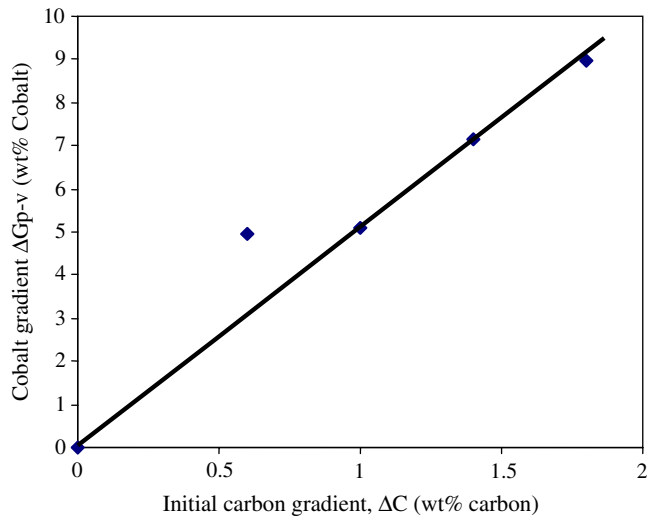


Fig. 5. The extent of cobalt gradient ( $\Delta G_{p-v}$ ) as a function of initial carbon gradient within WC–Co bi-layers sintered at 1400 °C.

different processes occurring during sintering including: carbon diffusion and phase reaction. In addition, the dissolution of graphite and the migration of the liquid phase are also involved. In the following sections, we discuss the roles of these processes and their contributions to the overall kinetics of cobalt gradient formation in WC–Co alloys during liquid phase sintering.

#### 4.1. Carbon diffusion and phase reactions

The total carbon content of a WC–Co composite is altered by the additions of tungsten and graphite powders prior to sintering. The addition of a significant amount of graphite powders results in the precipitation of free graphite in the WC–Co microstructure while the addition of a significant amount of tungsten powders reduces the carbon content of the WC–Co alloy resulting in the formation of eta phase. Eta ( $\eta$ ) phase is a ternary compound of tungsten, cobalt and carbon that can exist in two forms, either  $\text{Co}_3\text{W}_3\text{C}$  ( $\text{M}_6\text{C}$ ) or  $\text{Co}_6\text{W}_6\text{C}$  ( $\text{M}_{12}\text{C}$ ). Although both forms of  $\eta$  phase are indistinguishable physically, a study by Sarin [18] has shown that  $\text{Co}_3\text{W}_3\text{C}$  formation occurs at 1425 °C while  $\text{Co}_6\text{W}_6\text{C}$  formation occurs at 1000 °C. The formation and microstructure of  $\eta$  phase depends on the carbon level and temperature [19]. At extreme deficiency level of carbon, studies have shown that the  $\text{Co}_3\text{W}_3\text{C}$  phase formed at the sintering temperature shows fine irregular shape while at minor carbon deficiency levels the  $\text{Co}_3\text{W}_3\text{C}$  phase formed during cooling shows a dendritic morphology [20]. In this study, the  $\eta$  phase formed in the samples is  $\text{Co}_3\text{W}_3\text{C}$ . Due to the extreme carbon deficiency levels of the samples used in this study,  $\text{Co}_3\text{W}_3\text{C}$  is formed in the bi-layer samples at the sintering temperature and the unreacted  $\text{Co}_3\text{W}_3\text{C}$  is retained after cooling from the sintering temperature. The final morphology and distribution of  $\text{Co}_3\text{W}_3\text{C}$  phase morphology range from finely dispersed

particles at lower carbon deficiency to larger areas of massive  $\text{Co}_3\text{W}_3\text{C}$  phase at higher carbon deficiency (Fig. 6).

During liquid phase sintering of bi-layer WC–Co with an initial gradient in carbon, a gradient of carbon is produced in the liquid phase between the two adjacent WC–Co layers. Due to the gradient in the chemical potential of carbon in the liquid phase, carbon will diffuse and react with the  $\text{Co}_3\text{W}_3\text{C}$  particles present within the carbon deficient WC–Co layer according to Eq. (2) nucleating WC particles and releasing the cobalt that is tied-up within the  $\text{Co}_3\text{W}_3\text{C}$  particles. At the position within the WC–Co bi layer sample where this reaction front is located, there is a sharp rise in the cobalt content as observed in Fig. 1. As the initial carbon gradient is increased between the two adjacent WC–Co layers, the volume fraction of  $\text{Co}_3\text{W}_3\text{C}$  phase formed within the carbon deficient layer increases. Consequently, the amount of cobalt released due to the reaction between  $\text{Co}_3\text{W}_3\text{C}$  and carbon increases as well as the extent of the cobalt gradient within the sintered WC–Co (Fig. 5).

It is known that carbon diffusion alone can cause the redistribution of the liquid phase during sintering [21,22]. The redistribution of liquid phase during sintering due to carbon diffusion is attributed to the need to achieve thermodynamic equilibrium volume fraction of liquid, which is a function of the carbon content, in the WC–Co composite [22]. Thus, the overall cobalt gradient formed is determined by both the carbon concentration profile in the liquid phase and the cobalt released from the phase reaction between carbon and  $\text{Co}_3\text{W}_3\text{C}$  particles.

#### 4.2. Graphite dissolution and $\text{Co}_3\text{W}_3\text{C}$ transformation reaction fronts

An observable feature of the process is the formation of two moving fronts within the WC–Co bi-layers during sintering (Fig. 2). The moving front shown in layer 1 of the diagram in Fig. 2 represents the reaction front where the dissolution of graphite particles occurs within the WC–Co layer. Studies have shown that dissolution processes in WC–Co system are diffusion-controlled processes [23,24]. Based on this assumption, the velocity of the moving front in Layer 1 is controlled by the diffusion of carbon away from the graphite particles surfaces into the bulk of the liquid phase during sintering. The amount of carbon dissolved in the liquid phase is determined by the solubility limit for carbon by the liquid phase. The amount of carbon dissolved in the liquid phase does not increase beyond the solubility limit by adding more graphite to the WC–Co layer (layer 1 in Fig. 2) because the liquid phase is already saturated with carbon at the sintering temperature. Thus, an increase in the volume fraction of graphite in the layer reduces the velocity of the graphite dissolution front. As the sintering time is increased, the graphite dissolution front recedes from within the sample towards the surface of the sample due to the dissolution of the graphite particles in the liquid phase.



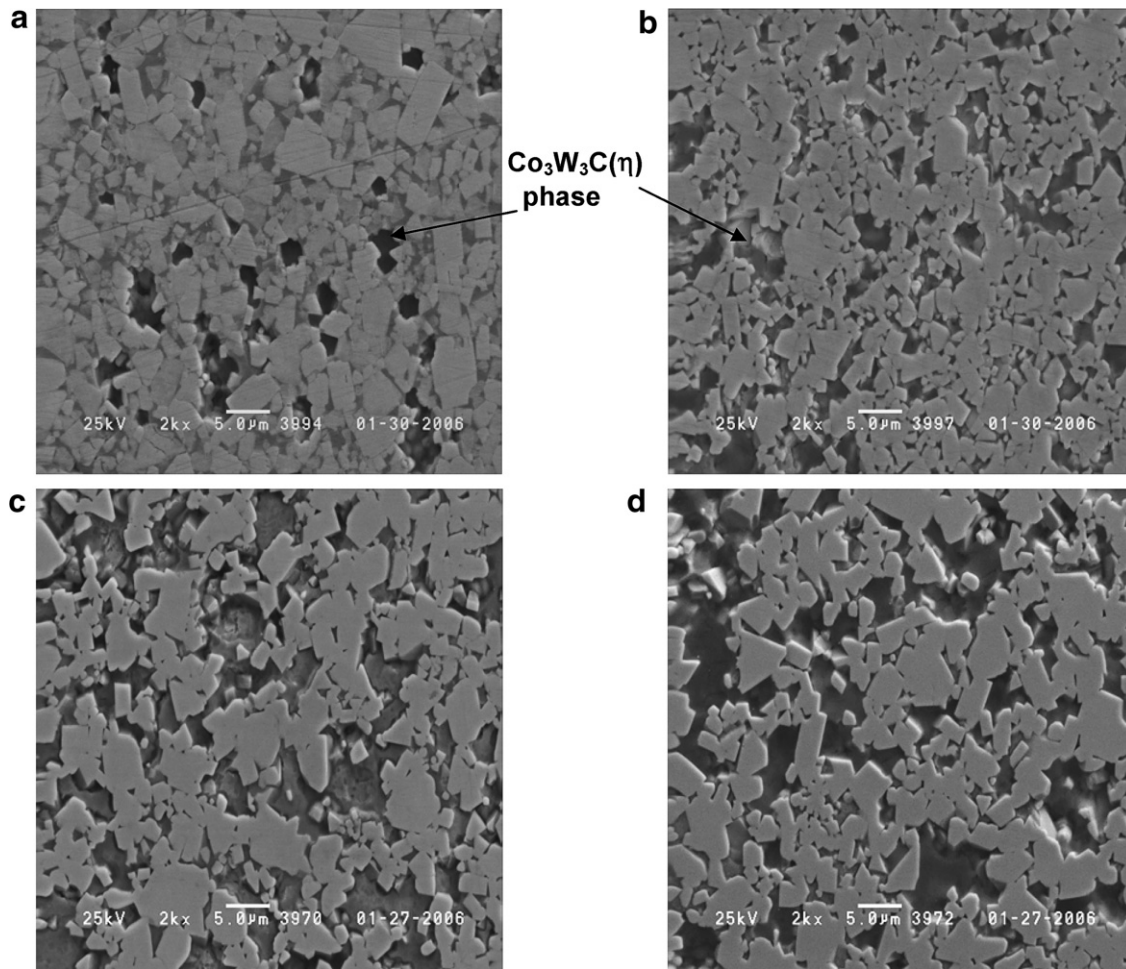


Fig. 6. Microstructure of the carbon deficient layer of the WC–Co bi-layers (Table 1) showing the progressive increase in volume fraction and size of  $\eta$  phase ( $\text{Co}_3\text{W}_3\text{C}$ ) particles as a function of total carbon content: (a) 5.2%C, (b) 5.0%C, (c) 4.8%C, (d) 4.6%C.

At the second moving front in layer 2 (Fig. 2), the transformation of  $\text{Co}_3\text{W}_3\text{C}$  to  $\text{WC} + \text{Co}$  occurs according to Eq. (2). The transformation of  $\text{Co}_3\text{W}_3\text{C}$  requires the supply of carbon through the liquid phase to the surface of  $\text{Co}_3\text{W}_3\text{C}$  particles. Carbon is supplied from the receding graphite dissolution front to the reaction front between carbon and  $\text{Co}_3\text{W}_3\text{C}$  in the adjacent layer (layer 2 in Fig. 2). Since the diffusion of carbon and reaction with  $\text{Co}_3\text{W}_3\text{C}$  within the bi-layer sample is coupled, the effects of chemical reaction and the fact that carbon must diffuse over large distances to the surface of  $\text{Co}_3\text{W}_3\text{C}$  particles tends to slow down the kinetics of the overall process [25]. Therefore, as the sintering time is increased,  $[\text{WC} + \text{Co} + \text{Co}_3\text{W}_3\text{C}] + [\text{C}] \rightarrow [\text{WC} + \text{Co}]$  transformation reaction reduces (Fig. 4). Furthermore, a progressive reduction in the carbon content of the adjacent WC–Co layer yields an increase in the volume fraction and particle size of  $\text{Co}_3\text{W}_3\text{C}$  phase formed within the sample (Fig. 6) which requires longer times to transform from  $\text{Co}_3\text{W}_3\text{C}$  to  $\text{WC} + \text{Co}$ . The effect of the volume fraction of  $\text{Co}_3\text{W}_3\text{C}$  phase is manifested in the progressive decrease in the slope of the plot  $X^2$  versus  $t$  with the initial carbon gradient.

Thus, an increase in the initial carbon gradient between the WC–Co bi-layer reduces the kinetics of transformation of  $\text{Co}_3\text{W}_3\text{C}$  phase to  $\text{WC} + \text{Co}$ .

#### 4.3. The role of migration pressure

As mentioned in the introduction, a cobalt gradient within a WC–Co alloy with uniform particle size tends to even out due to migration pressure during sintering. Studies have shown that the migration pressure is a function of volume fraction of liquid and WC particle size and the migration of liquid within the WC–Co system due to migration pressure is fast [6,26]. Liquid migration pressure decreases with liquid volume fraction and solid particle size. When there is no carbon diffusion or phase reaction but there is a difference in cobalt content within a WC–Co alloy with uniform WC particle size, the cobalt content tend to homogenize across the composite due to migration pressure. The liquid phase will migrate from the region with lower migration pressure (higher volume fraction of liquid and/or coarser particle size) to the region with high migration pressure (lower volume fraction of liquid and/or

finer particle size) until liquid migration pressure becomes uniform everywhere in the system. When there is carbon diffusion and phase reaction, and the WC particle size is uniform, the migration pressure has a counteractive effect on the level of cobalt gradient formed within the sintered WC–Co sample through homogenization of the cobalt content. However, if the WC particle size is different between the WC–Co bi-layers, the migration pressure will have either a counteractive effect or a favorable effect on the cobalt gradient formed through the migration of cobalt towards the finer WC particle size region of the WC–Co sample. Overall, the kinetics of the process and the final cobalt gradient in the sintered WC–Co alloy is a function of the complex interactions among different processes including the carbon diffusion, the phase reaction between carbon and  $\text{Co}_3\text{W}_3\text{C}$  phase, and migration pressure.

## 5. Summary

This research has demonstrated that by controlling the composition of WC–Co bi-layers and holding time at the sintering temperature, a cobalt gradient can be located at different positions within the sample. An increase in the initial carbon gradient between the WC–Co layers tends to produce a wider range of cobalt gradient within the sintered samples. However, when the carbon gradient is increased, the kinetic rate of the overall process is reduced. The cobalt gradient formed in WC–Co composites during sintering is a complex process involving the carbon diffusion, the phase reaction, and the flow of liquid phase due to migration pressure gradient.

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