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Liquid phase sintering of functionally graded WC–Co composites

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Abstract

A new approach for manufacturing functionally graded WC–Co composites via liquid phase sintering is presented. These functionally graded WC–Co composites possess a continuous gradient in cobalt content within their microstructure. The new approach involves creating a carbon gradient in the green state prior to liquid phase sintering. During liquid phase sintering continuous cobalt gradient develops while carbon content homogenizes.
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1. Introduction

Cemented tungsten carbide, WC–Co, is one of the most widely used industrial tool materials owing to its superior combination of high modulus, high hardness, wear resistance, and moderate fracture toughness. However, the wear resistance and fracture toughness of WC–Co composites are inversely related to each other [1,2]. Wear resistance is often improved at the expense of the fracture toughness, or vice versa. Functionally graded WC–Co composites offer a solution to the trade-off by varying cobalt content from the surfaces to the interior of a sintered piece. The surface, with relatively low cobalt content, would have high wear resistance, while the interior, with relatively high cobalt content, would have high toughness. The functionally graded structure with a continuous cobalt gradient, therefore, offers advantages in terms of the combinations of fracture toughness and wear resistance in comparison to the conventional homogeneous WC–Co materials [3–5].

Cemented tungsten carbide is typically sintered via liquid phase sintering process in vacuum [6]. However, when WC–Co with an initial cobalt gradient is subject to liquid phase sintering, the flow of liquid phase can easily occur and any gradient of cobalt content is easily eliminated [7–9]. A solution to this problem is to employ pressure assisted sintering techniques such as hot isostatic pressing and spark plasma sintering to consolidate the graded WC–Co compact at solid state [10]. These alternative processes have limited industrial applications because (1) the high pressure processes are usually costly and (2) the mechanical properties of materials produced by pressure assisted process at solid state are often different from those produced by liquid phase sintering. Liquid phase sintering is the only viable option for manufacturing conventional as well as functionally graded WC–Co materials. The challenge then is to develop a method that maintains or creates cobalt gradation during liquid phase sintering.

There are two existing industrial technologies producing functionally graded cemented tungsten carbides. One is for use in cutting tools, which are made of cemented tungsten carbides with cobalt enriched surfaces [5], and the second is the so called dual properties carbide [4]. Different methods have been used to produce

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cemented tungsten carbides with cobalt enriched surfaces, most of which rely on the addition of nitrides and the establishment of a nitrogen partial pressure atmosphere during liquid phase sintering of cemented carbides [5,11,12]. It was also observed that cemented carbide with cobalt enriched surface can be formed without nitrogen [11], although at a lesser extent. Dual properties carbides are produced using a process developed by Fisher, Hartzell and Akerman which is based on carbon diffusion during a separate post sintering heat treatment. The process involves the liquid phase sintering of WC–Co with sub-stoichiometric carbon content followed by carburization at high temperatures [4], which yields a cemented carbide body with distinct microstructural zones each with different binder content.

In this study, the influence of carbon content on the formation of cobalt gradient is investigated and a new method is described for producing WC–Co with continuous cobalt gradient via liquid phase sintering process. This new method involves altering the carbon balance between the graded WC–Co layers in the green state relative to their respective stoichiometric carbon contents. The cobalt gradation develops when carbon homogenizes during sintering. A qualitative model is developed to explain the experimental findings in terms of the diffusion and distribution of carbon and the phase reactions during liquid phase sintering.

2. Experimental

The basic experimental approach of this study is to fabricate bi-layer samples with each layer having different initial carbon and/or cobalt compositions. Powders of each layer were prepared separately and pressed together into a single bi-layer specimen. The green bi-layer specimens were then dewaxed and liquid phase sintered in a vacuum furnace at 1400 °C for 60 min. The sintered bi-layer samples were ground and polished to 1 μm finish for microstructural examination. The cobalt distribution profile in WC–Co bi-layer was measured using the energy dispersive spectroscopy (EDS) on the scanning electron microscope.

To create an initial carbon gradient in the green part, pure tungsten metal powder or carbon powder were added to either reduce the carbon content to below the stoichiometric value or increase the carbon content above the stoichiometric value in the WC–Co alloy. The powder mixtures were ball milled using a rolling mill for 16 h in heptane. After milling, the powders were dried in a rotary evaporator under vacuum. The dried WC–Co powders having different compositions were cold pressed at 200 MPa in a cylindrical die into bi-layer WC–Co disks (19.4 mm dia × 4 mm thick) according to the sample matrix shown in Table 1.

Table 1
Compositions of bi-layer specimens with variations in cobalt and carbon contents

Sample	Layers	Compositions
1	Top layer	WC–6%Co with stoichiometric carbon content
	Bottom layer	WC–16%Co with stoichiometric carbon content
2	Top layer	WC–6%Co with excess carbon content
	Bottom layer	WC–16%Co with deficient carbon content
3	Top layer	WC–6%Co with deficient carbon content
	Bottom layer	WC–16%Co with excess carbon content
4	Top layer	WC–10%Co with excess carbon content
	Bottom layer	WC–10%Co with deficient carbon content

3. Results

3.1. The effects of initial carbon gradient on cobalt gradient

To demonstrate the effects of initial carbon gradient on the formation of cobalt gradation during liquid phase sintering, two bi-layer samples were compared. Both bi-layer samples consisted of one layer with 6% cobalt and the other layer with 16% cobalt at green state. For one of the two samples, there was no initial carbon gradient. For the other, initial carbon content of the 6% Co layer had 6.1% C which is significantly higher than stoichiometric value of 5.80% (excess carbon). Carbon content of the 16% Co layer was 4.9% which is significantly lower than stoichiometric value of 5.2% C (carbon deficient). At liquid phase sintering temperatures, equilibrium phase compositions of the carbon deficient layer consist of WC, liquid cobalt phase, and the η phase which is a complex carbide compound of W and Co. Typical formula of η phase is W_3Co_3C. In the layer with excess carbon, however, there would be a graphite phase (free-carbon) in equilibrium with the WC and liquid cobalt phase. The carbon content of the bi-layer sample as a whole was designed such that the overall carbon content of the sample is stoichiometric which ensures that after sintering there will be neither η phase nor free-carbon in the microstructure because carbon will diffuse and homogenize during liquid phase sintering.

Fig. 1 shows a micrograph of sintered bi-layer WC–Co composite with initial gradients of both carbon and cobalt content. Fig. 1(a) and (b) show the microstructures of each layer sintered separately. The WC–6%Co layer with excess carbon shows free-carbon and the WC–16%Co layer with deficient carbon shows η phase in their microstructures. Fig. 1(c) shows the microstructure of the bi-layer specimen after liquid phase sintering. It shows no free-carbon nor η phase in the microstructure. It demonstrates that the excess
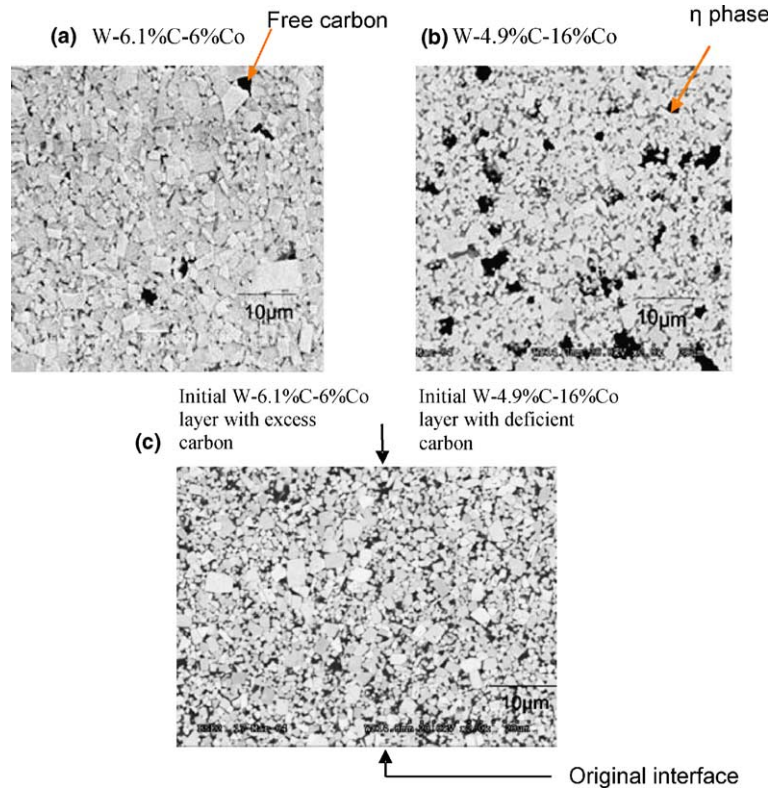
Fig. 1. SEM micrographs of (a) WC–Co with excess carbon, (b) WC–Co deficient in carbon and (c) WC–Co bi-layer with identical particle size but different initial carbon and cobalt content in the layers, sintered at 1400 °C for 1 h.

carbon has reacted with the η phase. The carbon content has completely homogenized across the bi-layers and the final part has stoichiometric carbon content. The cobalt content, however, was not homogenized across the two layers.

The distribution of cobalt of both samples with or without initial carbon gradient was measured using EDS as shown in Fig. 2. It shows clearly that there is no cobalt gradient after sintering in the bi-layer sample that did not have initial carbon gradient. The cobalt content of this sample is approximately 12% uniformly

distributed across the sample after sintering. However, the bi-layer WC–Co sample with an initial carbon gradient shows a continuous gradient in cobalt after sintering at 1400 °C. The cobalt content at the surface with lower content is higher than its original value of 6%. The cobalt content at the surface with higher cobalt is lower than its original value of 16%.

It appears from the above results that cobalt migrates in the direction of carbon diffusion. In order to further verify the phenomena, a sample similar to the one used in Figs. 1 and 2 was made with reversed initial carbon
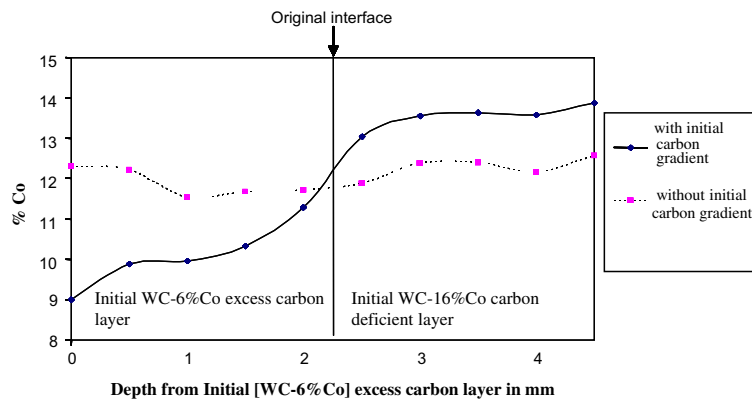

Fig. 2. Comparative plot of the cobalt distribution of WC–Co with identical initial grain sizes but different initial carbon and cobalt contents (solid line) and WC–Co with identical initial grain sizes and stoichiometric carbon contents but different initial cobalt contents (dotted line), sintered at 1400 °C for 1 h.
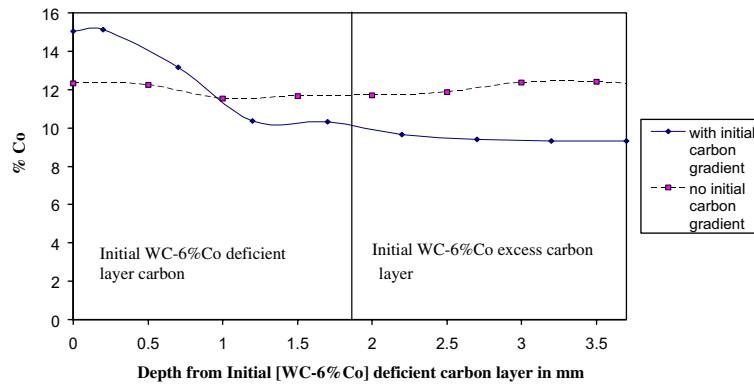
Fig. 3. Comparative plot of the cobalt distribution of WC–Co with identical initial grain sizes but different initial reversed carbon and cobalt contents (solid line) and WC–Co with identical initial grain sizes and stoichiometric carbon contents but different initial cobalt contents (dotted line), sintered at 1400 °C for 1 h.

gradient. In this case the low Co layer (6%) is carbon deficient and the high Co layer (16%) has excess carbon prior to sintering. Fig. 3 is the EDS analysis results of these samples. It shows that the cobalt gradient after sintering is also reversed when the initial carbon gradient before sintering is reversed. This result reaffirms the observation that cobalt seems to migrate in the direction of carbon diffusion during liquid phase sintering.

3.2. The effects of initial carbon gradient when there is no initial cobalt gradient

The results presented above demonstrate that the cobalt migration as the result of carbon diffusion and phase reactions counters the effects of cobalt migration due to the initial difference in cobalt content (initial

Δ%Co is 10% for the example in Fig. 2). Another sintering experiment was then designed to isolate the effects of an initial carbon gradient by using samples with no initial cobalt gradient between layers. A bi-layer sample was prepared with two layers having identical initial cobalt contents at 10%. The initial carbon content of one of the two layers is 5.0% which is significantly lower than the stoichiometric value of 5.5%. The initial carbon content of the other layer is 6% which is significantly higher than the stoichiometric value.

Fig. 4 shows the cobalt distribution of this sample after sintering. After sintering, the cobalt content varies gradually from about 8% in the layer that initial has excess carbon content to about 13% in the layer initially deficient in carbon. The micrographs in the figure show the different microstructural zones formed in the sample
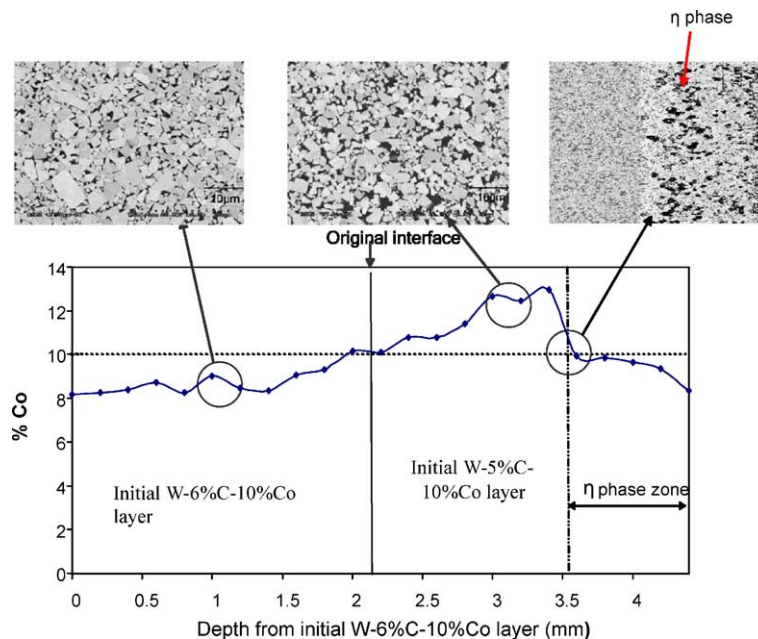

Fig. 4. Cobalt distribution in a WC–Co bi-layer specimen with identical initial cobalt content and grain sizes but different initial carbon content, sintered at 1400 °C for 1 h.

after sintering. A η phase zone can be observed towards the edge of the layer initially deficient in carbon. This shows that there is only partial homogenization of the carbon content across the structure. In this η phase zone, there is a sudden decrease in the cobalt content below the nominal value and just outside the η phase zone the highest cobalt peak of about 13% is observed. The result demonstrates that a cobalt gradient can be created in a sintered specimen even when there is initially no cobalt gradient, solely by manipulating carbon contents of the specimen in the green state.

4. Discussion

First of all, the formation of cobalt gradient during sintering in this study has similarities with the cutting tools with cobalt enriched surfaces [5,11–15] and the DP carbide [4] mentioned in the introductory section of this paper. Different mechanisms have been proposed to explain the cobalt enrichment phenomena in cemented carbides [13–15]. Each of these mechanisms requires the establishment of nitrogen gradients in the cemented carbides through addition of cubic nitrides or nitrification by nitrogen gas during sintering [5,11,12]. In the case of DP carbide, the formation of layered structures is the result of carbon diffusion from an atmosphere, during separate heat treatment, into the parts and the reaction of carbon with η phase within the parts. DP carbide does not rely on the presence of nitrogen. Similar to DP carbide, the formation of cobalt gradient within the microstructure of this study relies on the diffusion of carbon, although not from an atmosphere, rather from one position to another within the specimen. However, to date, there are no published works on the principles and mechanism of the formation of the graded structure in DP carbide.

The results presented above prove that cobalt migrates in the direction of carbon diffusion and this phenomenon can be utilized to sinter functionally graded WC–Co materials. The mechanisms of the formation of the cobalt gradient is, however, still unclear. A model based on the diffusion and distribution of carbon content and phase reactions during liquid phase sintering is discussed as follows. We propose that the formation of the cobalt gradient is the result of (1) carbon diffusion and the migration of liquid phase to attain equilibrium phase composition as a function of the carbon content distribution and (2) the phase reactions between carbon and the η phase particles.

4.1. The effect of carbon content on equilibrium volume fraction of liquid phase

The equilibrium phase compositions of WC–Co are the functions of total carbon content. Fig. 5 shows a ver-
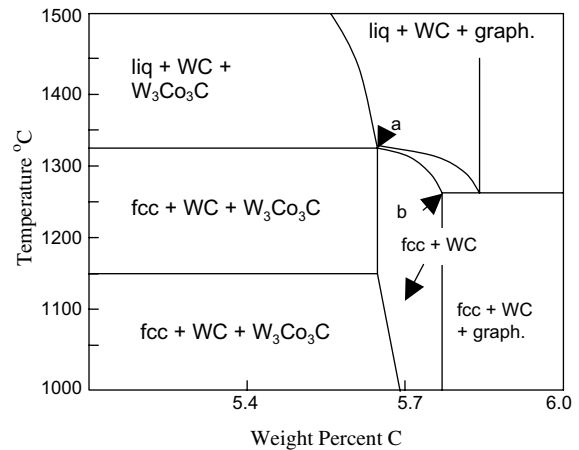
Fig. 5. Vertical section of the W–Co–C phase diagram calculated at 6 wt% Co. The points a and b define, respectively, minimum and maximum carbon contents of alloy which are in two-phase state of fcc (binder) + WC just after the equilibrium solidification.

tical section of a ternary phase diagram of W–Co–C at a constant 6%Co (by weight) with varying carbon content [16]. Since the stoichiometric carbon content of pure WC is 6.13% by weight, the stoichiometric carbon content of WC–6%Co is 5.76% by weight. Two phases, namely WC and a cobalt based solid solution (β), appear in the sintered microstructure if the carbon composition corresponds to this value. However, small deviations from the stoichiometric carbon content will result in the presence of either graphite, if the carbon content is above the stoichiometric value, or the complex carbide W_3Co_3C (η), if the carbon content falls significantly below the stoichiometric value.

Based on the phase diagram, it can also be shown that when carbon content deviates from the stoichiometric values, apart from the change in phases that are present, there is also a change in the relative volume fraction of each phase. Particularly, the volume fraction of liquid phase formed at the sintering temperature is a function of the total carbon content. In a study by
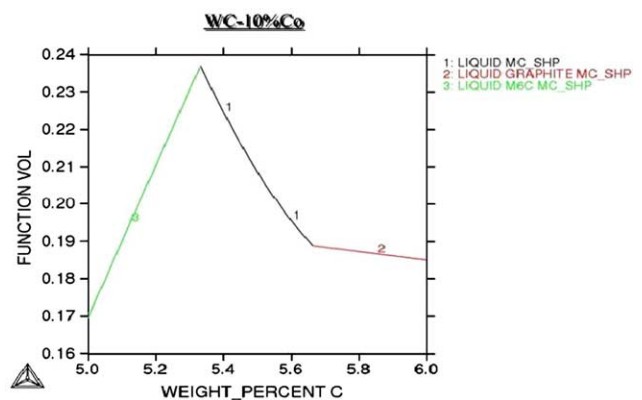
Fig. 6. Calculated volume fraction of liquid phase as a function of carbon content of WC–10%Co at 1400 °C.

Urhenius [17], using thermodynamic based calculations, a deviation from the stoichiometric carbon value to 5.5%C in WC–6%Co yields a significant reduction of 4% by volume of liquid at 1350 °C. Fig. 6 shows the volume fraction of liquid phase as a function of the carbon content for WC–10%Co [18]. The plots were generated using thermodynamic software-Thermo-Calc™. The thermodynamic database for cemented carbides is available in the literature [19].

Evidently, from these plots, any local inhomogeneity in carbon content within a WC–Co system will result in a corresponding difference in volume fraction of liquid, which could lead to cobalt migration.

4.2. The mechanisms of the formation of cobalt gradient due to carbon gradient

The formation of the cobalt gradient during liquid phase sintering when there is an initial carbon gradient is directly related to the diffusion and distribution of the carbon content. Due to the difference in the chemical potential of carbon in the two layers, carbon will diffuse from the layer where it is in excess to the layer where it is deficient. The diffusing carbon will react with η phase at the interface between the layers with and without η phase which yields WC and liquid Co:

$$2C + W_3Co_3C \Rightarrow 3WC + 3Co(L)$$
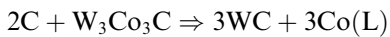
The carbon diffusion and the phase reaction will result in a carbon content distribution as illustrated in Fig. 7. At the far side of the carbon rich layer, the carbon content is at the initial high value of C_1. At the η phase side, the carbon content maintains the initial low value of C_2 until the entire layer is reacted. Between the interface and the far side of the carbon rich layer,

there is a continuous carbon distribution. As the result of this continuous carbon distribution, there will be a corresponding distribution of the volume fraction of the liquid phase at the sintering temperature as dictated by the equilibrium phase compositions as shown in Fig. 6, which suggest there will be locally a higher volume fraction of liquid at the reaction front compared with the surrounding area.

The distribution of the volume fraction of the liquid phase is also schematically shown in Fig. 7 at times t_1 and t_2. V_o is the volume fraction of the liquid phase at the sintering temperature if the sample had stoichiometric carbon content in both layers. In order to reach the equilibrium distribution of the volume fraction of the liquid phase, there must be a migration of liquid cobalt from surrounding areas, most likely from the carbon rich side because initially it has a higher volume fraction of liquid than the η phase side. The reaction of carbon with the η phase will also release the cobalt that was tied-up in the η phase.

Between times t_1 and t_2, the reaction front has advanced a distance "x" within the sample. It also implies that between the times t_1 and t_2, η-phase in the area within length "x" in the sample has reacted with carbon and produced WC–Co. As the carbon diffuses and the liquid phase migrates, both toward the η phase region, the reaction front moves in the same direction and the cobalt distribution exhibits a similar shape during the process. The overall shape of the distribution should be the sum of the effects of carbon diffusion, reactions with η phase, and the effects of cobalt migration due to possible initial cobalt gradient regardless of the carbon content. Further work is ongoing to study the kinetics of this process and model the formation of cobalt gradient quantitatively.
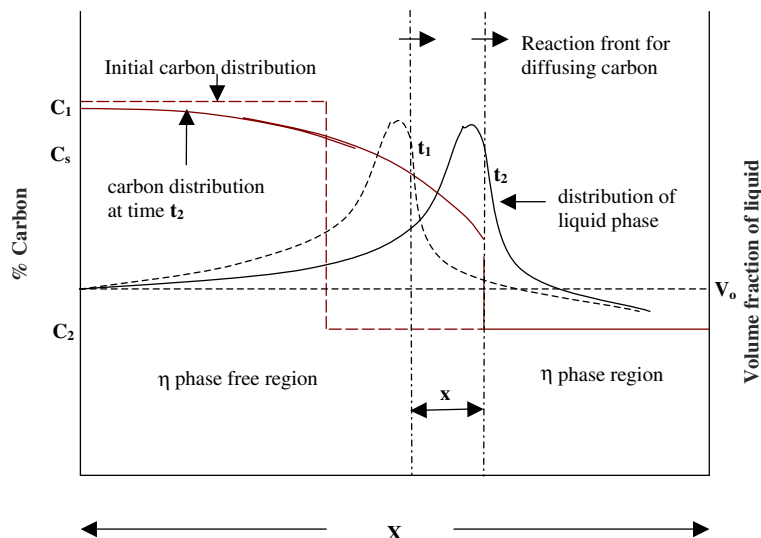

Fig. 7. Schematic diagram showing the time dependence of cobalt gradient formation during liquid phase sintering of graded WC–Co.

5. Summary

From this study, it has been shown that cobalt migration during liquid phase sintering can be controlled by manipulating initial carbon gradient prior to sintering. Liquid phase cobalt migrates in the direction of carbon diffusion during liquid phase sintering, which will lead to a continuous cobalt gradient in the final sintered microstructure while maintaining stoichiometric carbon content of sintered products. The cobalt gradient formation process can be explained in terms of the diffusion and distribution of carbon content and phase reactions in W–Co–C system during sintering. It can be concluded from this study that functionally graded WC–Co with continuous cobalt gradient can be produced by liquid phase sintering.

Acknowledgments

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