



Formation of Co-capping during sintering of straight WC–10 wt% Co

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ABSTRACT

Co-capping is a term that refers to a thin layer of Co occasionally observed on the surface of sintered WC–Co parts. It is usually considered undesirable and needs to be removed. The mechanism of its formation has been a myth in the industry and not fully understood to date. In this study, the effects of several factors, including cooling rate, atmosphere and carbon content in specimens, on the formation of Co-capping during sintering of straight WC–Co materials were experimentally examined. The mechanism of Co-capping formation was discussed based on the principles of liquid-phase migration.

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1. Introduction

During sintering of cemented tungsten carbide materials including both straight WC–Co and those with cubic carbide additions, a thin layer of binder phase, Co, is sometimes formed on surfaces of sintered parts. This thin Co layer, often termed as Co-capping, is typically from submicron to a couple microns thick. Co-capping may be beneficial for subsequent brazing, but it is usually considered undesirable and removed by mechanical grinding following sintering [1]. Co-capping may occur in various grades of cemented carbides in a seemingly random and inconsistent way. For sintering a material of the same composition, Co-capping may occur in one sintering run, but not the other. Even during the same sintering run of the same material, Co-capping may occur on some of the parts, while not on the other parts.

Although the Co-capping phenomenon is of considerable industrial practical importance, there have been few published studies in the literature that deal with this issue directly. In the few studies that can be found in the literature, Co-capping is linked to the phenomenon of cobalt enrichment near the surface region after sintering, the mechanism of which did receive considerable attention from the research community [1,2]. Taniguchi and their coworkers [2] found that Co enrichment occurred in the surface region of 20–500 μm thickness during the heat-treatment in a decarburizing atmosphere. The treatment temperature was around 1300 °C so that solid Co and liquid Co coexisted with WC during the decarburizing treatment. They attributed the observed Co enrichment in the surface region to the differences in the temperatures of solidi-

fication between the surface and the interior. The liquid Co in the surface region started to solidify when the liquid Co in the interior region remained in liquid state, resulting from the higher solidification temperature in the surface region where there was a lower carbon content due to the decarburizing treatment. The solidification-induced shrinking of Co phase in the surface region caused the flow of liquid Co from the interior region towards the surface region where it was decarburized and solidified. This procedure was repeated, resulting in the Co enrichment in the surface region. It should be pointed out that the authors did not discuss Co-capping directly; rather, Co enrichment was the main subject.

Janisch and coworkers [1] thought that the above-mentioned mechanism could not be applicable to the formation of Co-capping. It was suggested that the liquid Co near the region where the liquid Co starts to solidify should experience compression, thus squeezing the liquid Co away rather than drawing it towards the solidification front. Further, the solidification of liquid Co in the surface region would block the paths towards the surface and prevent the formation of Co-capping. Based on experiments using WC–Co with cubic carbonitride additions, (Ti, Ta, Nb) (C, N), a different mechanism was proposed which stipulates that the liquid Co in the interior region solidifies first before the liquid Co in the surface region does, and the solidification in the interior region exerts a compression on the surface region which is soaked with liquid Co, thus squeezing the liquid Co out to the surface. Although this theory is different from that by Taniguchi and their coworkers [2], both of the above studies showed that Co-capping and Co enrichment occurred in the temperature range where solid and liquid Co coexisted and both considered that the flow of liquid Co depended on the shrinking induced by the solidification of liquid Co.

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In this study, a different mechanism for the formation of cobalt capping is studied. A systematic experimental study was conducted to examine the effects of cooling rate, atmosphere and carbon content of straight WC–Co on the formation of Co-capping at 1300 °C in straight WC–Co alloys. The underlying mechanism of the Co-capping phenomenon is explained based on the principles of liquid Co migration driven by the difference in volume fractions of liquid cobalt between the surface region and the interior region.

2. Experimental

2.1. Raw material and composition

Straight WC–Co materials were used in this study without any addition of cubic carbides, nitride or carbonitrides. The simplicity of the composition of the material system made it possible to analyze the mechanism of Co-capping formation using the phase diagrams that are well established.

Specimens with two different carbon contents were prepared in this study. Symbols $10\text{Co}_{(\text{C}+)}$ and 10Co are used here to designate specimens with super-stoichiometric carbon (5.66 wt%) content and stoichiometric carbon content (5.51 wt%), respectively. Commercially available WC–Co mixed powders with 10 wt% Co were used as the starting raw material for 10Co , while graphite powders were added to the WC–Co mixed powders to increase the total carbon content to above the stoichiometric value for $10\text{Co}_{(\text{C}+)}$.

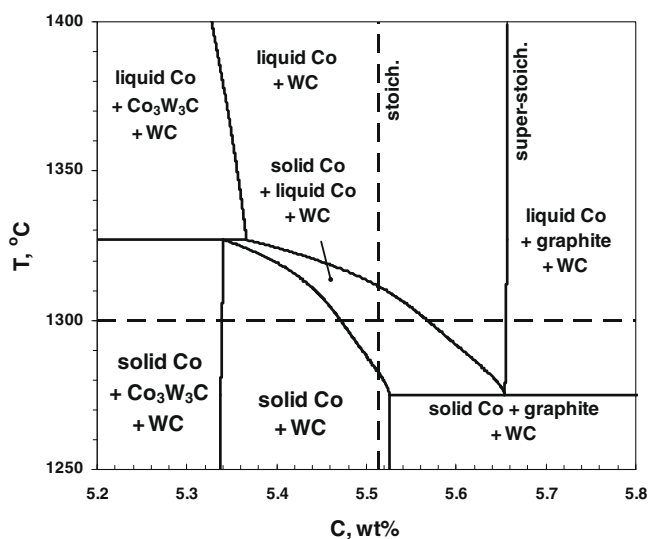


Fig. 1. The vertical section of the ternary phase diagram of W–Co–C at constant 10 wt% Co [3].

2.2. Compaction and sintering

Powder mixtures were ball milled in heptane for 4 h in an attritor mill. After milling, the powders were dried in a Rotovap at 80 °C and then pressed under 200 MPa into green compacts with dimension of $2 \times 0.6 \times 0.7 \text{ cm}^3$.

The samples were liquid-phase sintered in vacuum at 1400 °C for 1 h. No Co-capping was observed on any of the sintered specimens. Those specimens were then heat treated in atmospheres designed to generate Co-capping under various atmospheric conditions at 1300 °C.

2.3. Heat-treatment

The fully sintered specimens were heat treated in a tube furnace. The atmosphere in the reaction tube was either decarburizing or neutral, controlled by adjusting the ratios of methane (CH_4) to hydrogen (H_2) in the gas mixture using digital mass flow meters. The treatment was conducted at 1300 °C, except for Run 6 at 1315 °C. The temperature of 1300 °C was selected such that the treatment would take place in the phase region in which WC, liquid Co and solid Co coexist, as illustrated in the vertical section of the ternary phase diagram [3] of W–Co–C system with 10 wt% Co (Fig. 1).

In the initial tests, these specimens were directly heated to 1300 °C and held at that temperature for 1 h and then cooled either rapidly or slowly in the decarburizing atmosphere. No Co-capping was observed in these specimens. The absence of Co-capping can be understood based on the surface-decarburization of the specimens during heating up, which increases the liquid forming temperature of the surface region to above the selected holding temperature, resulting in no or very low fractions of liquid Co in the surface region, thus blocking any liquid Co migration.

A different heat-treatment procedure was then designed to induce Co-capping. Specimens were heated to 1400 °C at 20 °C/min and held at this temperature for 2 min, in order to ensure that there is liquid-phase on and near the surface. The specimens were then cooled down to selected holding temperatures (1315 °C for Run 6, 1300 °C for other runs) at 10 °C/min and held at that temperature for 60 min. Thereafter, the samples were cooled down to room temperature with selected cooling rates, 5 °C/min above 1200 °C for slow cooling or 50 °C/min above 1200 °C for rapid cooling. Below 1200 °C, the cooling rates were not controlled. However, the actual cooling rates at the temperature below 1200 °C were 18–25 °C/min until 800 °C, 6–9 °C/min until 500 °C, then 3–4 °C/min until room temperature. After heat-treatment, the cross-sections of the treated specimens were polished and examined using optical microscopy and scanning electronic microscopy techniques.

Table 1
The heat-treatment conditions and observed Co-capping.

Run #	Composition	Hold temperature (°C)	Atmosphere	Cooling	Co-capping and its morphology
1	$10\text{Co}_{(\text{C}+)}$	1300	Decarburizing	Slow	Yes Continuous
2	$10\text{Co}_{(\text{C}+)}$	1300	Decarburizing	Rapid	Yes Continuous
3	$10\text{Co}_{(\text{C}+)}$	1300	Neutral	Slow	No
4	$10\text{Co}_{(\text{C}+)}$	1300	Neutral	Rapid	No
5	10Co	1300	Decarburizing	Slow	Yes Non-continuous
6	10Co	1315	Decarburizing	Slow	Yes Continuous

Note: (a) Atmosphere: $P_{\text{CH}_4}/P_{\text{H}_2}^2 = 1/2000 \text{ atm}^{-1}$ for decarburizing one; $P_{\text{CH}_4}/P_{\text{H}_2}^2 = 1/1000 \text{ atm}^{-1}$ for neutral one. (b) Cooling: 5 °C/min above 1200 °C for slow one; about 50 °C/min above 1200 °C for rapid one.

After heat-treatment, the Vickers hardness values as measured in the center of the specimens using a 10 kg load were 1334 and 1343 kg/mm² for 10Co_(C+) and 10Co_(O) materials, respectively. The WC grain size measured in the center of the specimen was approximately 1.3 μ m (intercept length) for both materials.

Table 1 summarizes the heat-treatment conditions conducted in this study. The presence or absence of Co-capping in different specimens is also listed.

3. Results and discussion

3.1. Effects of cooling rate

First, the effects of cooling rate were examined by comparing test Runs 1 and 2 as shown in Table 1. The carbon content, atmosphere, and temperature were kept to be the same for the tests Run 1 and Run 2. However, the cooling rate used in Run 1 was lower (5 °C/min above 1200 °C) than that in Run 2 (about 50 °C/min above 1200 °C). It was observed that Co-capping formed in both cases. Figs. 2 and 3 are the microscopic images of the specimen

in Run 1 before and after the heat-treatment, clearly demonstrating the presence of Co-capping. In these micrographs, WC appears in gray surrounded by Co matrix in slightly darker contrast. Free-carbon phase was also visible as small black spots.

Before the heat-treatment, the microstructure of the specimen of Run 1 was uniform. There was free-carbon distributed throughout the microstructure because the total carbon content of the specimen was substantially above the stoichiometric value (as shown in Figs. 2a and 3a). After the treatment, a thin continuous layer of Co phase, i.e., Co-capping layer, formed on the outermost surface (Fig. 2b). Note that the carbon phase in the inner part was unaffected, while the carbon phase disappeared in the peripheral surface region (Fig. 3b), indicating a decarburization of the surface region during the heat-treatment in the decarburizing atmosphere.

The microstructure of the specimen of Run 2 (Fig. 4) is similar to that of Run 1 with Co-capping, indicating that the cooling rate change from 5 °C/min to 50 °C/min had little influence on the formation of Co-capping. In conventional liquid-phase sintering of WC-Co, the products are usually cooled from sintering tempera-

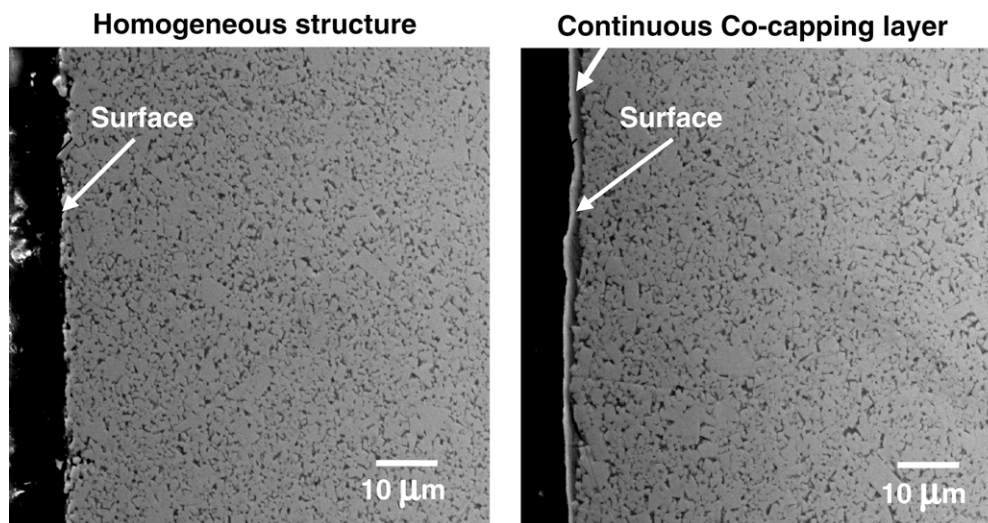


Fig. 2. Cross-sectional SEM micrographs of the super-stoichiometric specimen (from Run 1) (a) before treatment and (b) after decarburizing treatment followed by slow cooling.

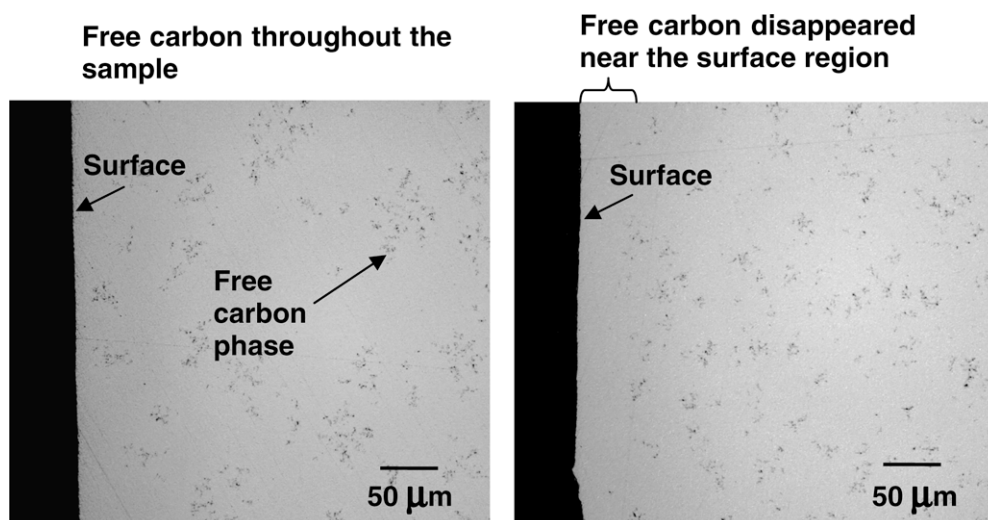


Fig. 3. Cross-sectional optical micrographs of the super-stoichiometric specimen (from Run 1) (a) before treatment and (b) after decarburizing treatment followed by slow cooling.

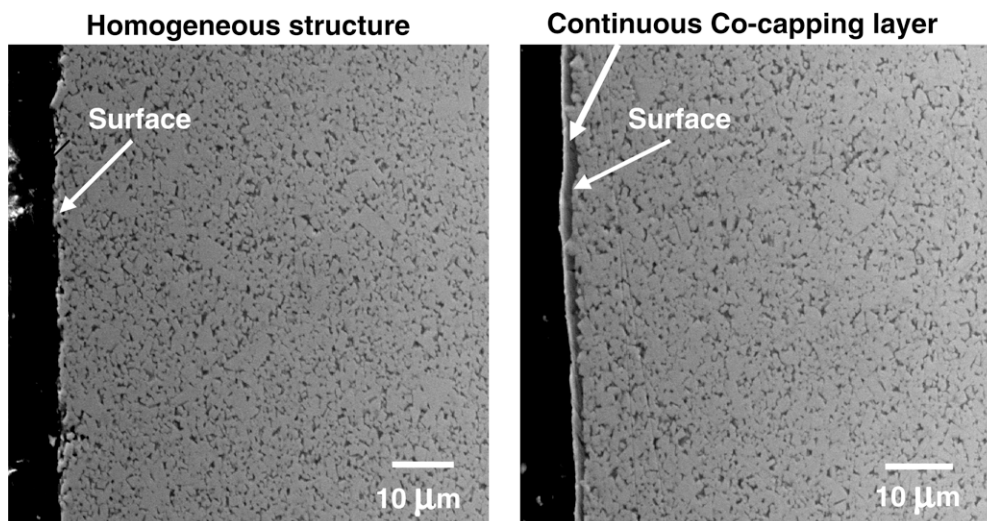


Fig. 4. Cross-sectional SEM micrographs of the super-stoichiometric specimen (from Run 2) (a) before treatment and (b) after decarburizing treatment followed by rapid cooling.

tures without an isothermal hold at 1300 °C, thus the formation of Co-capping is expected to be affected by the cooling rate.

3.2. Effects of atmosphere

The effects of atmosphere on Co-capping were studied by comparing the results of heat-treatments in decarburizing (Runs 1 and 2) and neutral atmosphere (Runs 3 and 4). The carbon activity in the neutral atmosphere with carbon potential ($P_{\text{CH}_4}/P_{\text{H}_2}^2$) of $1/1000 \text{ atm}^{-1}$ was approximately equal to that in the specimen at the holding temperature, such that neither carburizing nor decarburizing would occur during heat-treatment in the neutral atmosphere.

After the treatment in the neutral atmosphere, followed by either slow cooling (Run 3) or rapid cooling (Run 4), Co-capping was not observed, as shown in Fig. 5 for Run 3 and Fig. 6 for Run 4. The examination of the microstructures of Runs 3 and 4 showed that the free-carbon phase throughout the material was unaffected, indicating that neither carburizing nor decarburizing occurred during the heat-treatment in the selected neutral atmosphere. By considering this result with that of Runs 1 and 2,

which was performed under decarburizing atmosphere, it can be inferred that without surface-decarburization, Co-capping would not form. In other words, the decarburizing atmosphere and the resultant surface-decarburization are critical for the formation of Co-capping.

3.3. Effect of carbon content in specimen

In the test Run 5, the specimen with stoichiometric carbon (designated as 10Co) was treated under the same conditions as for the super-stoichiometric specimen ($10\text{Co}_{(\text{C}+)}$) in Run 1. The microstructure of the 10Co specimen before and after treatment is shown in Fig. 7. Before the treatment, the structure was uniform and there was no free-carbon. After the treatment, Co-capping was observed in various sections on the surface. However, the Co-capping did not form a continuous layer as observed in the $10\text{Co}_{(\text{C}+)}$ specimen. Except for this non-continuous Co-capping layer, the microstructure showed little change from its initial state.

In the test Run 6, the heat-treatment temperature was increased to 1315 °C, while the other experimental conditions were

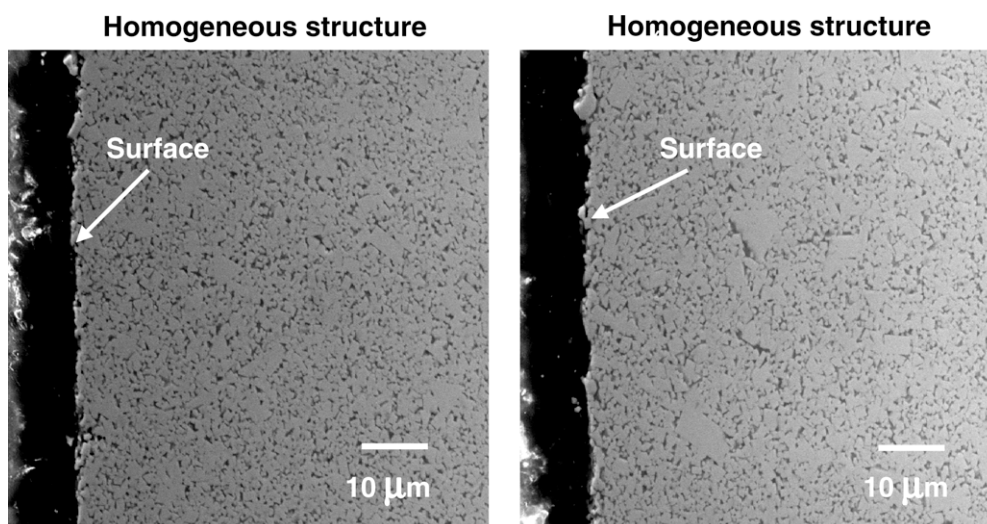


Fig. 5. Cross-sectional SEM micrographs of the super-stoichiometric specimen (from Run 3) (a) before treatment and (b) after treatment in neutral atmosphere followed by slow cooling.

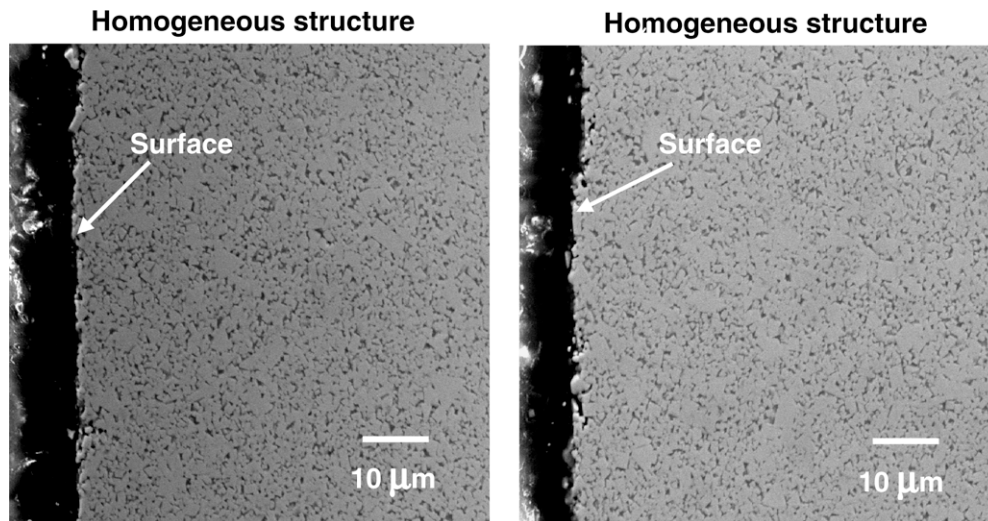


Fig. 6. Cross-sectional SEM micrographs of the super-stoichiometric specimen (from Run 4) (a) before treatment and (b) after treatment in neutral atmosphere followed by rapid cooling.

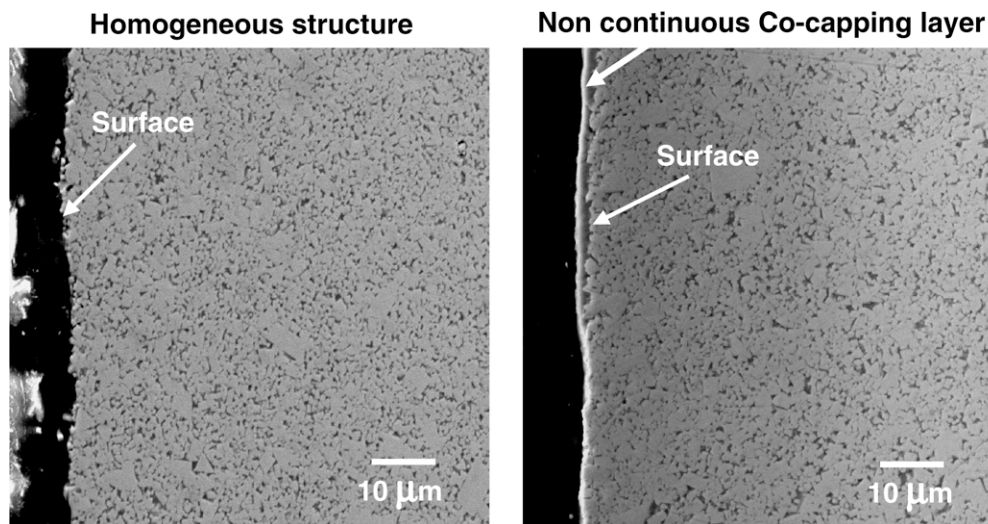


Fig. 7. Cross-sectional SEM micrographs of the super-stoichiometric specimen (from Run 5) (a) before treatment and (b) after decarburizing treatment 1300 °C followed by slow cooling.

maintained as in Run 5. It was found that a continuous Co-capping layer formed after the heat-treatment (Fig. 8).

4. Mechanism of Co-capping formation

Based on the above experimental results, a mechanism for the formation of Co-capping is proposed based on the migration of liquid cobalt phase. The driving force for the redistribution of liquid Co during sintering or heat-treatment at high temperatures is the reduction of interfacial energy. Based on reported studies on liquid migration [4–16], liquid Co redistribution or liquid Co migration is an interfacial-energy-driven flow dependent on three main factors – volume fraction of liquid Co, grain size of WC, and carbon content in liquid Co for straight WC–Co systems [16]. During liquid-phase sintering, liquid Co tends to migrate from a region with more liquid Co, coarser WC, and higher carbon content towards a region with less liquid Co, finer WC grain size, and lower carbon content in liquid Co [16].

In the case of Co enrichment and Co-capping during the heat-treatment in decarburizing atmosphere, it is reasonable to consider

that the observed outward liquid Co migration is driven by the decrease of liquid Co in the surface region induced by the surface-decarburization, of which the mechanism can be explained with the help of the schematics in Fig. 9. Initially, assuming that a WC–Co specimen is held at a temperature T (e.g. 1300 °C) between the liquidus and solidus temperatures, the volume fractions of liquid Co and solid Co (V_l and V_s) are uniform in the whole specimen. In other words, the distribution of liquid Co is balanced between the surface region and the interior region, as shown in Fig. 9a. With the progress of the surface-decarburization, the carbon content of liquid Co in the surface region decreases and the solidification temperature of liquid Co in this region are increased accordingly to above the present temperature T , as shown in Fig. 9b. Thus, the liquid-phase in the surface region is undercooled due to the surface-decarburization, which will consequently solidify. The solidification of the undercooled liquid Co in the surface region decreases the volume fraction of the liquid Co and increases the volume fraction of solid Co, resulting in less liquid Co in the surface region than that in the interior region, as shown in Fig. 9c. The imbalance of liquid Co distribution between the surface region and the interior

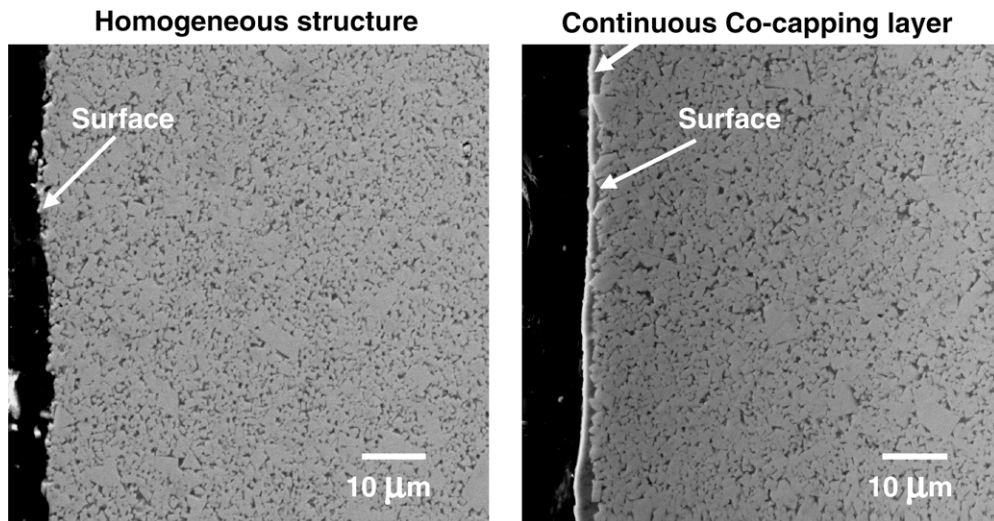


Fig. 8. Cross-sectional SEM micrographs of the super-stoichiometric specimen (from Run 6) (a) before treatment and (b) after decarburizing treatment at 1315 °C followed by slow cooling.

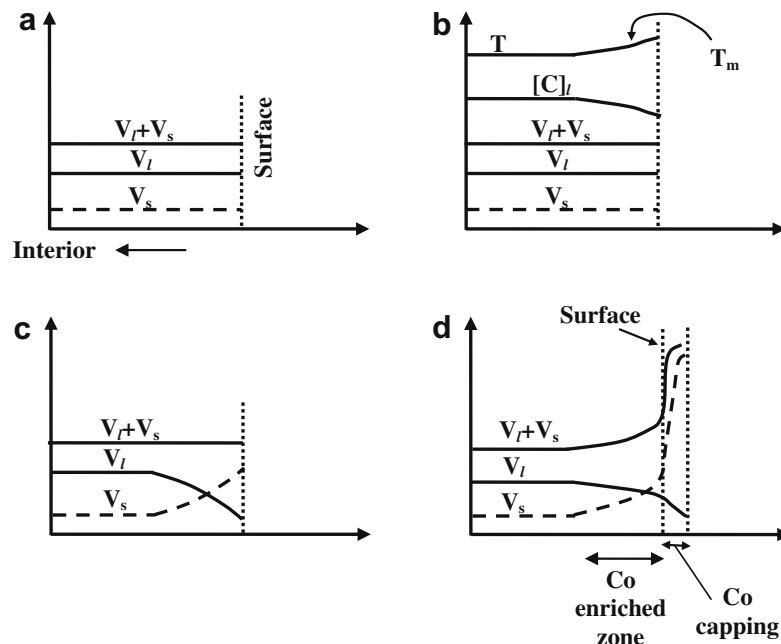


Fig. 9. Schematic plots showing the formation of Co enriched zone and Co-capping due to the migration of liquid Co during heat-treatment in decarburizing atmosphere. (a) Profiles of liquid Co volume fraction, V_l , and solid Co volume fraction, V_s , before decarburization. (b) Profiles of solidification temperature, T_m , and carbon content, $[C]_l$, after decarburization. (c) Profile of liquid Co volume fraction, showing the broken balance of liquid Co distribution. (d) Profiles of volume fractions of liquid Co and solid Co, showing the formation of Co enriched zone and/or Co-capping due to outward migration of liquid Co.

region drives the liquid Co to migrate from the interior towards the surface until the balance of liquid Co between the two regions is re-established. Further, the Co migrated from the interior region will be also decarburized in the near surface region and solidifies, the balance of liquid Co will be broken again and more liquid Co will migrate from interior towards the surface. Thus, with the progress of the surface-decarburization, a Co enriched zone and/or Co-capping can be formed, as shown in Fig. 9d.

The observed effects of various factors on the formation of Co-capping in this study can be reasonably explained using the above proposed mechanism. As described in Section 3.1, it was found that the cooling rate did not affect the morphology of Co-capping. This is understandable because the Co-capping in this study was

formed while being held at a fixed temperature. As described in Section 3.2, no Co-capping was formed in neutral atmosphere. This is also understandable because Co would not migrate towards the surface when there was no surface-decarburization.

Further, in contrast to that a continuous Co-capping was formed on the specimen with super-stoichiometric carbon content, a non-continuous Co-capping was formed on the stoichiometric specimen at the same holding temperature, while a continuous Co-capping was formed on the stoichiometric specimen at a higher holding temperature. This phenomenon can be explained by the different amounts of liquid Co in the specimens of the two compositions. As shown in the phase diagram of WC–Co (Fig. 1), at the same holding temperature of 1300 °C, the amount of liquid Co is

higher in the specimen with super-stoichiometric carbon composition than that in the stoichiometric specimen. In fact, at 1300 °C, all Co in the super-stoichiometric specimen is in liquid state, while around 50% of Co in the stoichiometric specimen is in solid state, based on the phase diagram. Less liquid Co in the stoichiometric specimen is considered to slow the kinetic rates of surface-decarburization and liquid migration thus resulting in less and non-continuous Co-capping. At the temperature of 1315 °C, however, all Co in the stoichiometric specimen is in liquid state. Thus, the kinetic rates of surface-decarburization and liquid migration are sufficiently fast for the formation of a continuous Co-capping layer.

Based on the proposed mechanism, there are two critical factors for the Co enrichment and/or Co-capping to form in straight WC–Co materials. One is that the atmosphere needs to be decarburizing; and the other is that the temperature needs to be in the 3-phase region, i.e., 1275–1325 °C according to the phase diagram of WC–Co system. Since the conventional liquid-phase sintering of WC–Co is usually conducted in vacuum, the carbon activity of the residual gas in the furnace chamber is expected to be very sensitive to many difficult-to-control parameters such as moisture level, raw materials, crucibles, and adsorbed air in the chamber. The carbon activity of the residual gas is also expected to vary from one location to another in the furnace chamber on different surfaces of a single product. Thus, it is understandable that the formation of Co-capping may vary from parts to parts and from one furnace run to another. Therefore, it is extremely difficult to predict whether Co-capping will form on a specific WC–Co product in a specific sintering run under conventional vacuum sintering conditions. In order to prevent Co-capping from forming, non-decarburizing atmosphere should be employed at least during the cooling from sintering temperatures. The pressure in the furnace chamber should not be too low as during the conventional vacuum liquid-phase-sintering process to control the carbon activity. Cautions must also be taken, however, to prevent excess carburization of the sintered products.

5. Summary

Co-capping can form on the surface of WC–Co specimens as a result of decarburizing heat-treatment within a temperatures range in which WC, solid Co, and liquid Co coexist. A mechanism

for the formation of Co-capping has been proposed based on the principles of liquid-phase migration. The observed outward migration of liquid Co is attributed to the imbalance of liquid Co distribution due to the decrease of the volume fraction liquid Co in the decarburized surface region, which induces the liquid Co to migrate from the liquid-rich interior towards the liquid-poor surface region.

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