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High temperature capillarity in hardmetal surface layers

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ABSTRACT

A reason for the presence or absence of thin Co layers on a surface of WC–Co hardmetal articles after sintering has been a riddle for a long time. Such shiny Co layers are sometimes present on the surface of sintered WC–Co articles and their formation is referred to as “Co capping” in literature. Here we propose a detailed mechanism explaining the presence or absence of such thin cobalt layers on hardmetal articles after sintering. The proposed mechanism is based on considering wetting phenomena of WC by liquid Co in hardmetal surface layers and capillarity pressures acting on the liquid Co in narrow channels between WC grains in the surface layers. The mechanism explains all the phenomena of the Co layer formation during sintering of various hardmetal grades followed by either fast or slow cooling.

1. Introduction

A reason for the presence or absence of thin Co layers on a surface of WC–Co hardmetal articles after sintering has been a riddle for a long time. Such shiny Co layers are sometimes present on the surface of sintered WC–Co articles and their formation is referred to as “Co capping” in literature. Fig. 1a illustrates the abovementioned showing carbide articles of different grades and geometries sintered in various furnaces. Some of these articles have a shiny surface indicating the presence of the Co layers, but some of them are dull indicating only little Co on the surface.

Different mechanisms of Co capping were suggested in Refs. [1–3]; these mechanisms, however, cannot explain all the phenomena related to Co capping. The authors of Ref. [1] believe that if the interior, and not the surface, is first to solidify then liquid cobalt shrinks and thereby squeezes the remaining liquid cobalt outwards towards the surface. Jun Guo et al. [2] explain the phenomenon of Co capping using the principle of liquid cobalt migration driven by the difference in volume fractions of liquid cobalt between the surface and interior regions. In contrast to Refs. [1,2], the authors of Ref. [3] believe that the major phenomena leading to Co capping are related to the transport of liquid cobalt towards the surface and high surface tension of liquid cobalt.

Patents [4–7] disclose technologies, by which a cobalt enriched hardmetal surface can be produced. These technologies are generally based on slow cooling of carbide articles after sintering down to temperatures below the melting point of WC–Co. However, mechanisms explaining the formation of Co layers on hardmetal articles as a result of slow cooling are not understood.

Here we propose a detailed mechanism explaining the presence or absence of cobalt layers on hardmetal articles as a result of sintering followed by either fast or slow cooling.

2. Experimental details

Samples of various WC–Co grades with WC mean grain size varying from roughly 0.8 μm to about 5 μm and Co contents varying from 5 to 10 wt% were sintered in laboratory and industrial Sinter-HIP furnaces. The hardmetal surface was examined on a high-resolution scanning electron microscope (Philips XL-30S). Co contents on hardmetal samples and cross-sections after sintering were measured by EDX. The samples were sintered at 1420 °C followed by either fast cooling at nearly 2 degrees per minute or slow cooling at rates below 0.5 degrees per minute.

3. Results and discussion

To establish the reason why the Co capping phenomenon sometimes occurs on the hardmetal surface and sometimes does not, the wettability of WC grains in the hardmetal near-surface layer was examined by use of ultra-coarse WC–Co samples. Fig. 1b and c shows the surface of this carbide grade and the cross-section

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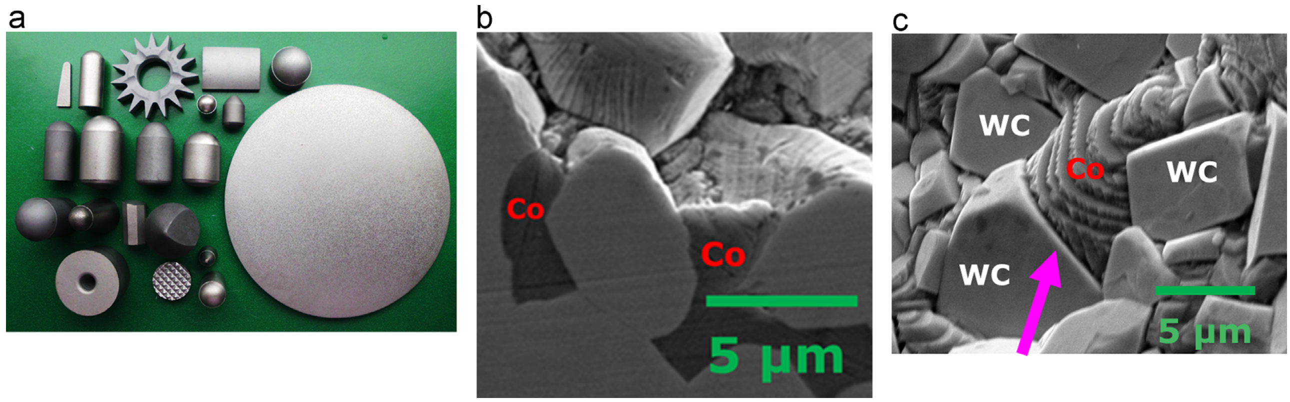

Fig. 1. (a) Typical appearance of articles of various WC–Co grades after sintering.in industrial Sinter-HIP furnaces; (b) – cross-section of the near-surface layer of ultra-coarse WC–Co hardmetal after sintering indicating convex Co menisci among WC grains, and (c) –surface morphology of ultra-coarse WC–Co hardmetal after sintering (the arrow shows a gap between the Co binder and WC grain indicting incomplete wetting of WC by the binder of the sample surface).

of the carbide near-surface region after conventional sintering. It can be seen that the Co menisci have a shape of between concave and convex ones providing evidence that the wettability of WC by liquid Co on the surface is incomplete. This is presumably related to the fact that the surface of WC grains after conventional sintering is contaminated by various impurities [8].

Fig. 2 shows the surface of the sintered articles made from various hardmetal grades having different WC grain size and containing different amounts of Co after sintering followed by fast cooling. The articles of the ultrafine grade containing 15 wt% Co in the bulk are found to comprise over 80% Co on the surface forming either continuous or discontinuous Co films (Fig. 2a). When the Co content in the bulk of the ultrafine grades is decreased down to 10 wt%, there is less Co on the surface after sintering (typically 60±20 wt%). The surface of the ultrafine grades with less that 10% usually comprises very little Co after sintering (well below 8%), which can be seen in Fig. 2c.

Fig. 2d and e shows the surface of the sintered articles made from carbide grades with 10% Co and different WC grains sizes varying from nearly 1.9 µm for the medium-coarse grade to about 4.8 µm for the ultra-coarse grade. It can be seen that the surface of the both grades contain little Co or almost no Co (usually well below 15%), which is noticeably lower than the Co content on the surface of the ultrafine grade with the same Co content (10 wt% Co) in the bulk shown in Fig. 2b.

To explain the phenomena of the absence or presence of Co on the surface of carbide articles after their conventional sintering followed by fast cooling capillarity phenomena in the carbide near-surface layer should be considered. According to Ref. [9] a liquid in a pore or capillary of a composite body is acted upon by the capillary pressure on the one hand and the migration pressure or suction pressure on the other hand. Therefore, the liquid Co in thin channels or capillaries among WC grains in the carbide near-surface layer is subjected to both the capillary and suction pressure during sintering. The suction pressure tends to return the liquid Co into the composition body, whereas the capillary pressure acts on the liquid Co in such a way that it moves in the channels towards the surface. The capillary pressure is dependent mainly on the capillary diameter and the wettability of the capillary material by the liquid. The suction pressure depends mainly on the liquid content in the composite body.

The presence of contaminations on the surface of WC grains makes their wettability by liquid Co incomplete, however, the impurities are expected not to incorporate into the carbide article deeply below the surface. In case of the ultrafine grades the channels between the adjacent WC grains are narrow, therefore, the capillary pressures acting on the liquid Co towards the surface are high. On the other hand the liquid Co in the channels is subjected to the suction pressures depending on the Co content in the cemented carbide body. The capillarity pressure for the relatively high-Co fine-grain grades (10% Co and more) is presumably higher that the suction pressure. Therefore, the liquid Co moves towards the surface and is extruded onto the WC surface overcoming the repulsion related to the poor wettability. As a result the surface of WC-10%Co and WC-15% ultrafine-grade contains much Co (Fig. 2a and b). This can also lead to the partial dissolution of impurities on the surface of WC grains in the liquid Co extruded onto the WC surface.

When the Co content in the bulk of ultrafine grades is decreased, the suction pressure starts overcoming the capillary pressure thus preventing the Co migration towards the surface and the Co film formation. Therefore, no Co films usually form on the surface of ultrafine grades with 8% Co and below 8% Co and the Co content on the surface of such grades is very low. On the other hand, when the WC mean grain size and consequently the average diameter of the channels among WC grains are increased, the capillary pressures become much weaker and the liquid Co cannot be extruded onto the WC grains. Therefore little or almost no Co is present on the surface of medium-coarse and ultra-coarse hardmetal grades shown in Fig. 2d and e.

The phenomena mentioned above occur when the cooling rate of carbide articles after sintering is relatively high. In this case, if the carbide surface does not contain much Co on the final stage of liquid-phase sintering, the liquid Co in the carbide near-surface layer completely solidifies first as a result of cooling making impossible any Co migration from the article inner part towards the surface.

When cemented carbide articles are slowly cooled down from the region of the Co–W–C phase diagram shown in Fig. 3a, where the binder is completely liquid, to the region where both liquid and solid Co co-exist, the liquid binder starts solidifying in both the near-surface region and core almost simultaneously. As a result, nuclei of solid Co start precipitating from the liquid binder when the temperature reaches the point 1 indicated in Fig. 3a. After the original nucleation period, the nuclei of solid Co grow together forming a thin layer of solid Co on the surface of channels between WC grains in the carbide near-surface layer. As a result, the channel diameter decreases and the capillary pressure in the channels noticeably increases leading to extruding the liquid Co towards the surface. In this case, the capillary repulsion related to