



Letter

The selective oxidation behaviour of WC–Co cemented carbides during the early oxidation stage



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ABSTRACT

The oxidation experimental of WC–Co cemented carbides was carried out at 500 °C in air. Selective oxidation phenomenon of Co phase in WC–Co cemented carbides was observed and proved by EPMA and AFM. At first, the O content in Co phase increases quickly, and then tends to be stable after oxidation of 20 min. In sharp contrast, no change of O content in WC phase was observed. Moreover, it was found that the oxide scales thickness of Co phase increased parabolically with oxidation time. And thermodynamic and kinetic analysis of oxidation was done.

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1. Introduction

Cemented carbides belong to a class of hard, wear-resistant, refractory materials in which hard carbide particles (WC, TiC, TaC, NbC, etc.) are bonded with a soft and ductile metal binder (Co, Ni, Fe, etc.). It is known to all that they are used in a wide range of applications, such as metal cutting, mining, construction, rock drilling, metal forming, structural components and wear parts. However, they are often exposed to various corrosive environments, such as acid, alkali, salt, elevated temperature, which will result in the degradation of mechanical property of cemented carbides products, such as hardness, strength and wear resistance, and finally will result in the decreasing of their service lifetime. For instance, the oxidation of WC–Co cemented carbides cutting tools at elevated temperature is one of the key factors in determining the lifetime of cemented carbides products. As a matter of fact, their service lifetime is greatly determined by their oxidation. The reasons are as follows: first of all, oxide films with porous and cracks will form during the oxidation. These oxide films are very easy to flake off, and will definitely decrease wear resistance [1–10]. Additionally, it has been proved that the strength of the cemented carbides is weakened because of surface oxidation [4–6,11–13]. Thus, the investigation of oxidation of cemented

carbides is significant to the design and applications of these materials.

As for the oxidation of cemented carbides, many results have been reported [1–3,7–10,13–17]. Kinetic analysis, the macro-, and micro-structure and the phase constitute of oxide scales are the most important aspects of the investigation of oxidation. Attaining the curves of mass gain or the thickness of the oxide scales vs. oxidation time by isothermal method and calculating the apparent activation energy (E_a) by isothermal or non-isothermal method are the major task of kinetic analysis. Barbatti et al. [7] have reported that the linear law or parabolic law of mass gain vs. oxidation time was influenced by temperature. E_a was influenced by many factors, such as consist of cemented carbides and oxidation temperature [2,3,8,9]. The reported values of E_a for WC–Co cemented carbides with the same chemical constituents are very different. For instance, the E_a of WC–15Co (in wt%) was reported to be 190 kJ/mol by Aristizabal et al. [9] and 234.1 kJ/mol by Voitovich et al. [15], respectively. The great difference of E_a may be caused by instruments and/or experimental methods.

From the previous literature, we know that the oxide scales formed on a WC–Co substrate mainly consist of WO_3 and $CoWO_4$, and a small amount of Co_2O_3 and Co_3O_4 [1–3,7–10,13]. The WO_3 phase has rather low resistance to oxidation because it contains numerous pores and cracks which may become a channel for the diffusion of O_2 and CO_2 . Comparatively, the $CoWO_4$ phase is denser than WO_3 , and has better resistance to the oxidation. The

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previous researches have indicated that the oxidation resistance of cemented carbides was improved by the increase of Co content and the addition of cubic carbides, such as TiC and/or (Ta, Nb)C [1–3,7,9,14]. However, the oxidation resistance was decreased when Co binder was partly substituted by Ni binder because of the decrease of complex oxide (Co, Ni)WO₄ content [15].

However, the above researches were mainly about the later oxidation stage of cemented carbides that the oxide scales had already covered the surface of the samples. The phenomena related to the early oxidation stage, such as selective oxidation and oxidation location (intra-grain, grain boundary or phase boundary), are not reported in any paper. And actually selective oxidation is a common phenomenon in alloys, such as iron-based alloy [18–20], cobalt-based alloy [21,22], steel [23–25], and so on. As a composite material, WC–Co cemented carbides consist of at least two phases, and have the potential for selective oxidation. Additionally, the results of thermodynamic calculation of the oxidation of WC and Co indicate that the oxidation of WC is easier than the oxidation of Co. However, in our exploratory experiment the contrary phenomena were found, and the preliminary results showed that Co was firstly oxidised and WC did not.

Therefore, based on the results of exploratory experiments, a detailed study of the selective oxidation of WC–Co cemented carbides during the early oxidation stage was carried out in this paper. Three approaches were used to prove that the oxidation of Co phase is prior to the oxidation of WC phase. The first approach is to reveal the changes of the oxygen distribution at the same location of a sample with the increasing oxidation time by element map analysis of electron probe X-ray micro-analyzer (EPMA). The second one is to measure the content change of W, C, Co and O, which is particularly important, of WC phase and Co phase with the increasing oxidation time by quantitative analysis of EPMA. And the third approach is to measure the thickness of oxide scales with the increasing oxidation time by atomic force microscope (AFM).

2. Materials and experimental

WC–15Co (in wt%) cemented carbides were provided by Zhuzhou Cemented Carbide Group Company Limited. The most of WC grains of sample are 6–8 μm. The size of specimens is 5 mm × 5 mm × 10 mm. In order to obtain a smooth surface before oxidation, one of the 5 mm × 10 mm surface was ground and polished. All specimens were wet ground using 40 μm and 20 μm diamond discs. After that, they would be polished using 9 μm and 1 μm water-based diamond suspension.

Samples were oxidised in air at 500 °C between 5 and 150 min in a muffle (±2 °C). Fourteen samples were used in this paper. One of them was oxidised for different times. While the other thirteen samples were separately oxidised for 0, 5, 10, 15, ..., 55, 60 min.

The element mapping and quantitative composition analysis of samples were done by EPMA (JXA-8230) with tungsten filament. The EPMA was operated under the following settings: accelerating voltage is 15 kV; probe current, dwell time and step size are about 11.3 nA, 70 ms and 93.8 nm for element mapping, 10.1 nA, 50 ms and 50 nm for quantitative composition analysis. The thickness of oxide scales was measured by tapping mode AFM (multimode V) using silicon tip. Scan areas are 20 μm × 20 μm and 10 μm × 10 μm and 512 lines per image were scanned with 512 samples per line.

3. Results and discussion

Fig. 1(a) shows the backscatter electron (BSE) image of WC–15Co sample, in which the dark areas represent Co phase containing small amounts of dissolved W and C, and the grey areas

represent WC phase containing a very small amount of dissolved Co. Element map analyses by EPMA were executed in the region displayed in Fig. 1(a). In order to ensure the element map analyses by EPMA are at the similar same region, the sample was marked by Vickers indentation on the polished surface before oxidation. The average O contents of mapped regions vs. oxidation times are plotted in Fig. 1(b). It should be noted that the results of O mapping are qualitative rather than quantitative. Before oxidation, the average O content is 4%. High O content comes from chemical and physical adsorption of oxygen in air, and few oxide particles adhered to the polished surface. The average O content is 10%, 17%, 20%, 25% after oxidising for 5, 35, 90, 150 min, respectively. The curve of average O content vs. oxidation time roughly follows a parabola. From 0 to 5 min, the average O content increases rapidly; from 5 to 35 min, the growth rate becomes lower; after 35 min, the increasing of average O content becomes slow. Fig. 1(c)–(f) shows the O distributions after oxidising for 0, 5, 35, 150 min, respectively. From Fig. 1(c)–(f), it is found that O content in Co phase goes up with the increasing oxidation time. In contrast, O content in WC phase has scarcely changed with the increasing oxidation time.

From Fig. 1, it is seen that only Co phase was oxidised at 500 °C. In order to further confirm the above result, samples were oxidised at 500 °C from 0 to 60 min and then quantitatively analysed by EPMA to ascertain the elements content. For each time interval, 5 points of Co phase and 5 points of WC phase were measured respectively.

Fig. 2 shows the variation of the W, C, Co and O content in the Co phase and the WC phase with oxidation time. There is little change of C content in Co phase. And the W content in Co phase fluctuates around 9% without obvious change. However, Co and O content varies greatly with oxidation time. Within 20 min, Co content firstly goes down quickly with the increasing oxidation time; over 20 min, Co content goes down slowly and tends to be constant. The change of O content in Co phase is contrary to the change of Co content. Firstly, it increases quickly and then tends to be stable. It is certain that Co phase was oxidised at 500 °C. In Fig. 2(b), the W, C, Co and O content of WC phase all fluctuated around a constant value. O content is about zero. It is implied that WC phase was not oxidised at 500 °C. To sum up the above results, WC–Co cemented carbides have the selective oxidation characteristic at 500 °C.

The selective oxidation of Co phase in WC–Co cemented carbides resulted in the change of surface topography characterised by the thickening of the oxide scales of Co phase. AFM is a very powerful technique for providing high-resolution three-dimensional (3-D) surface topography on the submicron scale has been used as an alternative or supplementary tool to other techniques for studying the selective oxidation behaviour of some materials during the early oxidation stage [26]. In this research we also used AFM to measure the variation of surface topographies with oxidation time. Fig. 3(a) shows the thickness variation of oxide scales of Co phase with oxidation time at 500 °C. Each data is an average of 20 random measured values. Before oxidation, the height of WC phase is 31 ± 5 nm higher than Co phase. However, after 5 min, the oxide scales thickness of Co phase increased to 93 ± 6 nm. This suggested that the Co phase has been oxidised. And then, the oxide scales thickness of Co phase increased from 141 ± 9 nm to 215 ± 14 nm corresponding to oxidising for 15 min and 35 min. After 35 min, the increasing of the oxide scales thickness of Co phase is slow. AFM topographies for 0, 5, 15, 35, 60 min oxidation are shown in Fig. 3(b)–(f), respectively. The selective oxidation of Co phase is clearly seen from Fig. 3.

The oxide scales thickness of pure Co in previous literature are 775 nm (temperature 500 °C, time 20 min, P(O₂)/P⁰ = 0.1) [27], 440 nm (467 °C, 20 min, P(O₂)/P⁰ = 0.21) [28], 360 nm (505 °C, 19 min, P(O₂)/P⁰ = 1) [29] and 500 nm (500 °C, 15 min, P(O₂)/

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