The influence of high temperature oxidation on the Vickers hardness of a cemented carbide, tungsten carbide (WC) added with cobalt (Co), was investigated in order to determine its suitability for improvement of hardness. The Vickers hardness of WC-Co was improved by high temperature oxidation treatment. The oxidation thickness of the sample from 973 to 1273 K depended on oxidation temperature and time. The oxidation thickness increased with increasing oxidation temperature and time, especially, significant oxidation of samples occurred at 1073 K.

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1. Introduction

The process of production cemented carbide materials does not provide necessary dimensional precision, given geometrical forms and quality of working surface in most cases. Therefore, additional technological methods of surface dimensional treatment are used. The abrasive treatment by means of diamond instrument got the widest using cases. Therefore, additional technological methods of surface dimensional treatment are used. The necessary form can be obtained by means of chemical engineering method. The object of investigation was a cemented carbide insert, made from tungsten carbide ceramics treatment testifies about enable of diamond disk prior to oxidation studies.

The microstructure of the surface of the sample was observed by means of scanning electron microscope (SEM). The metallographical analysis consists of determination of phase quantity on the testing surface. The measurement of Vickers hardness at room temperature was repeated five times for each sample, under conditions, load: 9.8 N and load time: 30 s. The specimens were cleaned off with oxide after heat treatment, cut in half and polished for measurement of inner layer hardness and estimation of oxidation thickness.

2. Experimental procedures

The samples of WC–Co sintered bodies made by Ukrainian Institute of Hard Alloys (VK8, GOST 880–75) were used as a starting materials (catalogued values: purity = 99%, WC grain size = about 2 μm, composition = 92 mass% WC–8 mass% Co). The sintered bodies were cut into φ12 × 15 mm in size and the surfaces were polished with a diamond disk prior to oxidation studies.

Isothermal oxidation in air was carried out in an electric furnace maintained at the desired temperature (± 1 K). The sample to be evaluated was weighed carefully and placed in an α-alumina boat. This highly pure α-alumina boat containing several samples was directly introduced in the hot zone of the furnace at a predetermined operating temperature onto a low-density stabilized zirconia setter. After a prescribed period, the sample, together with its boat, was removed from furnace, allowed to cool and reweighed carefully. Mass data were obtained with an accuracy of ±0.1 mg using an electric balance. The treatment route of specimen from as-received to specimen with grinded and polished surfaces showed in Fig. 1. The starting material (Fig. 1 (a)) oxidised over certain period, covering by oxidation layer (Fig. 1 (b)). After removing the oxidation layer, specimen was cleaned and graded for testing inner and outer surface (Fig. 1 (c)).

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3. Results and discussion

In general, the evaluation of oxidation of nonoxide ceramics as a carbide, nitride and boride at high temperature is carried out by investigating the weight gain accompanying the following reactions:

SiC + 3/2O₂ → SiO₂ + CO
Si₃N₄ + 3O₂ → 3SiO₂ + 2N₂
SiB₃ + 4O₂ → SiO₂ + 2B₂O₃

The oxidation of the WC–Co is carried out according to the following reactions:

4. Conclusion

The sintered bodies of WC–Co obtained in this study were evaluated for oxidation in air at 973, 1073 and 1273 K. The oxidation layer thickness increased with increasing oxidation temperature and time, especially, significant oxidation of samples occurred at 1073 K.
The oxidation films on the surface of the samples are raised as a result of the reaction Eqs. (4) and (5). The oxidation mechanism of the oxidation process consists of two stages: a) oxygen diffuses through porous medium and b) chemical reaction on surface of the sample.

The oxidation rates of WC and Co were determined and results were used for determination of quantitative dependence of oxidation time. The thickness of oxidation layer was calculated using linear measurement of oxidized sample. All dependencies of oxidation time are linear for reaction Eq. (6). It means that oxidation process is occurring in kinetic area.

The oxidation thickness of WC and Co of the WC-Co sintered body are shown in Figs. 2 and 3, respectively. The oxidation thickness of WC and Co of the sample from 973 to 1273 K depend on oxidation temperature and time. Significant oxidation of samples started at 1073 K, the oxidation thickness increased with increasing oxidation temperature and time. The oxidation rate of WC is about 38 times higher than oxidation rate of Co.

The result shows that the oxidation layer of cobalt will create on surface of cemented carbide samples as a result of high temperature oxidation. Metallographical analysis permitted to determine quantity both phases of oxidized sample in dependence on the oxidation temperature and distance from surface. Figures 4 and 5 show the contents of Co(W, C) and WC at inside and surface in WC-Co sintered bodies.
after oxidized at temperatures range of 973 to 1273 K for 30 min, respectively. It was determined that quantity of bind phase (Co) increased whereas quantity of WC decreasing on surface. The content of cobalt on surface increases as a result of unequal oxidation rate. It leads to increasing of the plastic component in the surface layer. This effect can be used for cemented carbide inserts of drill and bit instrument applications. It is commonly known fact that inserts are placed into the rolling cutter bores with trip. These high stresses lead to micro cracks of roller cone. The large quantity of soft constituent of cemented carbide Co, provides cohesion between insert and bore of roller cone along the full flank surface.

The influence of high temperature oxidation on all volume of WC-Co specimen also is showed in Fig. 1. The samples were divided in half with the purpose of determining phase redistribution inside. It was observed unequal phase redistribution in all volume of the sample. It means that phase quantity changes along all volume of the sample. The carbide phase content of surface layer is bigger than inner layer.

It is clear that phase redistribution occurs as a result of high temperature oxidation and leads to changes of mechanical properties. The Vickers hardness measuring of inner layers confirmed this expectation. The dependence of Vickers hardness on oxidation time within range of 1 mm from surface is shown in Fig. 6. The Vickers hardness has peak value near surface and decreasing toward to the center of the sample.

The surface peak of Vickers hardness increases because of heating treats that area more than other within the specimen. The other reason of hardness increasing is appearance of intermetallic compound of W and Co on the border of binding Co phase and WC particles. That is also lead to mechanical properties improvement, because the fracture crack of WC-Co ceramic material occur on the border of Co phase and WC. The intermetallic compound was identified as Co7W6.

The lowest Vickers hardness has sample of oxidized at 973 K, and the highest Vickers hardness has sample of oxidized at 1173 K. The oxidation temperature of the sample increased up to 1273 K decreasing Vickers hardness. The Vickers hardness of the as-received sample is also shown in Fig. 7. The Vickers hardness of the as-received sample is equal in all capacity.

The changes of Vickers hardness at 1073 K and 1173 K in different oxidation time are shown in Figs. 8 and 9, respectively. It is recognized to the fact that increasing of oxidation time leads to increasing Vickers hardness of surface as well as under surface layer and decreasing Vickers hardness of inner layer.

Figure 9 shows the Vickers hardness of the sample oxidized at 1173 K for 600 s. The surface layer of the oxidized sample has the initial hardness. However, Vickers hardness of inner layer is lower than surface layer. It was thus considered, based on the above results, that the Vickers hardness of WC-Co was improved by high temperature oxidation treatment. It is possible to adjust Vickers hardness in different spaces of cemented carbide samples by means of chang-
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