Oxidation Behavior of WC-TiC-TaC Binderless Cemented Carbide under Low Partial Pressure of Oxygen

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Abstract

WC-TiC-TaC binderless cemented carbide was oxidized under low partial pressure of oxygen (50ppm) at 873K for 1 to 20 h. Surface roughness was measured using atomic force microscope, and effect of TiC amount on oxidation behavior of the carbide was investigated. WC phase was oxidized more easily than WC-TiC-TaC solid solution phase. With an increase in TiC amount, WC-TiC-TaC phase increased and the oxidation resistance of the carbide increased.

Keywords : cemented carbide, oxidation, low pressure of oxygen, TiC content, atomic force microscope

1. Introduction

WC-TiC-TaC binderless cemented carbide has been developed to overcome a weakness in oxidation resistance of metallic binder phase and is used as mold in processing of precision parts such as micron drills and dies[1)]. Mechanical properties of the carbide have been investigated, but oxidation behavior of the carbide is still unclear. So in this paper, oxidation behavior of WC-TiC-TaC binderless cemented carbide was investigated under low partial pressure of oxygen and surface-roughening mechanism was considered.

2. Experimental procedure

Commercially available WC (mean diameter 0.6 μm), TiC (0.9 μm), WC-TiC-TaC (5:3:2) solid solution powder (1.0 μm) and Cr_3C_2 (1.4 μm), and VC (1.7 μm) with a composition shown in Table 1 were mixed, ball-milled for 96 h in methanol and then dried. The obtained powders were compacted, followed by hot pressing at 1993K for 90 min in vacuum. The sintered samples were further HIPed at 1723K for 90 min in 180 MPa Ar. Then they were cut into block of 3×3×1 mm and mirror-polished with diamond slurry.

Oxidation test was carried out at 873K, for 1 h, 5 h, 10 h, and 20 h, under N_2 gas containing 50 ppm oxygen, which was controlled by zirconia oxygen pump, with a flow rate of 100 ml/min. Surface morphology of the samples before and after oxidation was observed using scanning electron microscope (SEM) and mean surface roughness (*R*a), maximum undulations (*R*max), surface area, and surface height histograms of the sample were measured using atomic force microscope (AFM). The sintered samples were pulverized and examined by XRD. Element analysis of the samples and oxides formed on the sample surface was carried out by using EDX-SEM.

Table 1. Composition of sample (mass%)

Sample names	WC	TiC	WC / TiC / TaC solid solution (5 : 3 : 2)	Cr_3C_2 + VC (1 : 1)
A0	89.6	0	10.0	0.4
A1	84.6	5.0	10.0	0.4
A2	76.6	13.0	10.0	0.4
A3	66.6	23.0	10.0	0.4
A4	47.6	42.0	10.0	0.4

3. Results and Discussion

SEM observation revealed that the A0 sample was consisted of a WC phase and a WC-TiC-TaC solid solution phase, namely β-phase, which plays a role as binder phase. After 1 h oxidation, granular- and whisker-shaped oxides were observed on the WC phase. After 20 h oxidation, whisker-shaped oxides disappeared and granular-shaped oxides enlarged on the surface. Oxidation of the sample occurred first at the WC phase, indicating that the WC phase is oxidized more easily than the β-phase. Element analysis

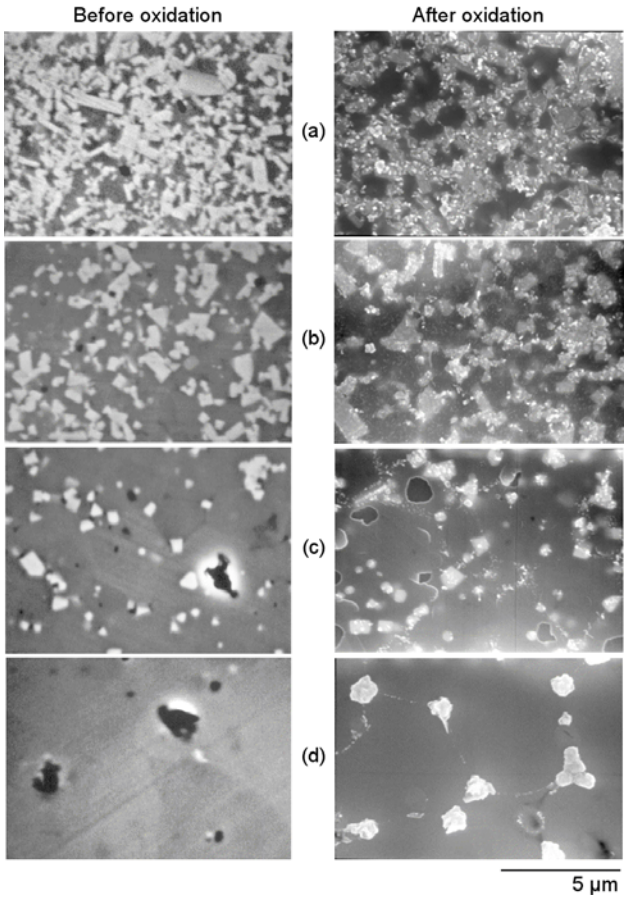

Fig. 1. SEM microstructure of the samples (a) A1, (b) A2, (c) A3 and (d) A4 before and after 5 h oxidation.

of the granular- and whisker-shaped oxides revealed that compositions of the both shaped oxides were almost the same, where main composition was W. Therefore, it can be considered that these oxides were WO_3 formed by oxidation of WC, but it is not clear why the shape of the oxide formed was different depending on oxidation time.

Figure 1 shows surface morphology of the A1, A2, A3 and A4 samples before oxidation and after 5 h oxidation. β-phase (dark part) amount increases and WC phase (light gray part) decreases with an increase of TiC content. The A4 sample consists of only β-phase, while the other samples consist of both WC phase and β-phase. In the A1, A2 and A3 samples, oxides were formed on the WC phase, while no oxide was formed on the β-phase. In the case of the A4 sample, oxides were formed only at three-point junction of grain boundary.

AFM analysis results are shown in Table 2. Comparing with the A0 sample, the A1, A2, A3 and A4 samples possess lower values of Ra and Rmax up to 10 h oxidation, while they possess comparable values at 20 h oxidation. The A1, A2, A3 and A4 samples also show lower surface area against the A0 sample and the A4 sample shows the lowest surface area. As shown in Fig. 1(d), oxidation occurred at the three-point junction of grain boundary of the A4 sample, and

Table 2. Values of mean surface roughness, maximum unevenness and surface area of the samples.

Sample names	Oxidation time [h]	*R*a [nm]	*R*max [nm]	Surface Area [nm^2]
A0	1	26.3	365	1.26 E8
	2	153	1480	5.38 E8
	5	54.8	938	2.60 E8
	10	58.6	831	2.06 E8
A1	1	8.76	98.8	1.06 E8
	2	14.1	275	1.23 E8
	5	50.3	527	1.87 E8
	10	60.3	662	1.45 E8
A2	1	7.99	203	1.06 E8
	2	19.0	348	1.25 E8
	5	37.9	509	1.37 E8
	10	24.9	512	1.25 E8
A3	1	11.9	341	1.06 E8
	2	10.6	573	1.10 E8
	5	24.8	325	1.15 E8
	10	50.0	506	1.11 E8
A4	1	20.9	545	1.06 E8
	2	9.30	259	1.02 E8
	5	33.7	505	1.04 E8
	10	67.4	738	1.03 E8

no oxide was formed on the β-phase. This could explain the lowest surface area against slightly larger *R*a and *R*max.
Point analysis of element for the oxides formed at three-point junctions of grain boundary of the A4 sample revealed that there is a very small amount of Fe. The Fe contamination was considered to be from stainless steel ball during ball milling.

4. Conclusions

The oxidation behavior of WC-TiC-TaC binderless cemented carbide was investigated in terms of surface roughness, and its mechanism was considered. The results obtained are as follows: 1) Oxidation occurred first at WC phase, showing that WC phase is oxidized more easily than β-phase. 2) There are granular- and whisker-shaped oxides on surface, but their compositions were not different, and it is not clear why shapes are different depending on oxidation time. 3) In the sample mostly consisted of β-phase, oxidation occurs preferentially at three-point junction of grain boundary.

5. References

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