Effect of C/Ti Atomic Ratio of TiCx Raw Powder on the Properties of Ti-Mo-W-TiC Sintered Hard Alloy

Kenji Nakahara[1,a], and Shigeya Sakaguchi[1,b]

[1] Nippon Tungsten Co., Ltd., 3173-2, Oaza-Sonobe, Kiyama-Cho, Miyaki-Gun, SAGA, 841-0203, Japan
[a]nakahara@nittan.co.jp, [b]skgchi@nittan.co.jp

Abstract

We have studied the effect of C/Ti atomic ratio of TiCx (x=0.5, 0.75 and 1.0) raw powder on the properties of the Ti-Mo-W-TiC sintered hard alloy. The decrease of C/Ti atomic ratio accelerated the densification in the sintering process. The hardness was remarkably improved up to 1350HV with decreasing the C/Ti atomic ratio because of increase of TiCx phase volume content and its fine dispersion. From the results of electro-chemical tests in acid and 3% NaCl solutions, it was obvious that every alloy had excellent corrosion resistance, which meant about 200 times better than that of WC-Co cemented carbide.

Keywords : Ti-Mo-W-TiC sintered hard alloy, C/Ti atomic ratio of TiCx raw powder, wear and corrosion-resistance

1. Introduction

Recently the market needs of pump components that require corrosion resistance such as mechanical seals and ceramic shaft sleeve materials have been increasing. The Ti-based sintered hard alloys having excellent corrosion-resistance have hitherto been developed[1-4], and applied especially for bearing sleeves for sea-water pumps. However, they could not satisfy the needs from market enough because the wear resistance and tribological property were less than that of conventional sintered hard alloy. In the present work, the effect of C/Ti atomic ratio in TiC raw powder on the sintering, physical and corrosion properties were investigated.

2. Experimental Procedure

A commercial Ti powder (less than #325 mesh), Mo powder (mean particle diameter of 4μm), W powder (1μm) and TiCx powders (X=0.5, 0.75 and 1.0) (1μm) were mixed to the specified composition: W1, W2 and W3 alloys (as shown in TABLE 1.) at a constant atomic ratio of Ti/W/Mo/C by using a fluidizing mixer in argon gas for 3.6 ks, and pressed into shape (5×10×30mm) at a pressure of 0.2 GPa. They were obtained by vacuum pre-sintering at 973K and vacuum sintering at 973 to 1873K for 3.6ks. For the obtained alloys, the sintering behavior and physical properties were measured to investigate the effect of C/Ti atomic ratio in TiCx raw powder through SEM observation of alloy structure, X-ray diffraction analysis and so on. The corrosion behavior of the alloys was studied by electro-chemical measurement such as potentio-dynamic polarization curves (Counter electrode: Pt, Potential range: −1 to +1.5V vs. Ag/AgCl, Scanning rate: 1mV/sec) in an acid (3%NaCl+0.1N-H_2SO_4) solution and neutral (3%NaCl) solution at 297K.

Table 1. The raw powder content of samples of Ti-Mo-W-TiC alloys. (mass%)

	$TiC_{0.5}$	$TiC_{0.75}$	$TiC_{1.0}$	Ti	Mo	W
W1	0	0	40.30	34.46	2.96	22.28
W2	0	51.04	0	23.72	2.96	22.28
W3	72.52	0	0	2.24	2.96	22.28

3. Results and Discussion

The hardness and relative density of each alloy as a function of sintering temperature are shown in Fig.1. W2 and W3 alloys showed higher hardness than W1 alloy in the whole range of sintering temperature, and W3 alloy reached maximum hardness of 88.7HRA at 1573K. Considering from the results of relative density, the progress of densification was W3, W2 and W1 alloy in descending order at the same sintering temperature. The SEM image photograph of microstructure for each alloy at sintering temperature of 1573K showed that every alloy had gray white area and dark area, which were β-Ti and TiCx phase respectively. Analyzing these photographs, it can be seen that alloy phase content of TiCx is W3, W2 and W1 alloy in descending order. From the above, it is supposed that the reasons, which hardness of W2 and W3 alloys is higher than that of W1 alloy in the range of lower temperature, are the acceleration of densification, increase of alloy phase content of TiCx and its fine dispertion due to increase of C/Ti atomic ratio in TiCx raw powder.

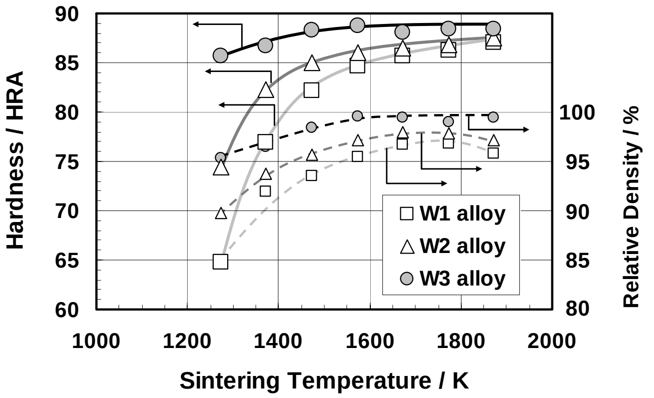

Fig. 1. The hardness and relative density of Ti-Mo-W-TiCx hard alloys as a function of sintering temperature.

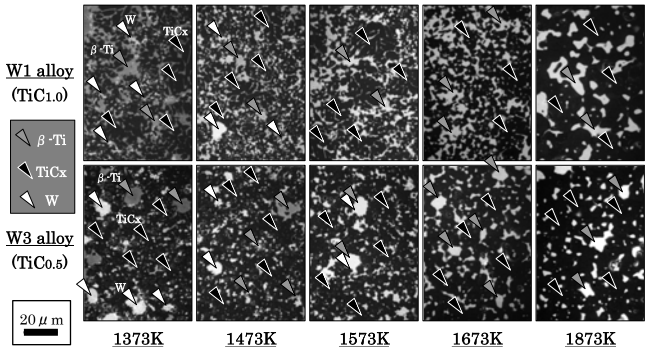

Fig. 2. SEM images of microstructure of W1 and W3 alloys sintered at the range of 1373 to 1873K.

Table 2 shows the C/Ti atomic ratio in TiCx phase estimated by calculating lattice parameter from peak positions of TiCx phase on the X-ray diffraction patterns of these alloys sintered at 1573K. The estimated C/Ti atomic ratio in TiCx phase decreased with decreasing C/Ti atomic ratio in TiCx raw powder, which correponds to the above supposition regarding the relationship between hardness and C/Ti atomic ratio of TiCx raw powder.

Table 2. Lattice parameter and C/Ti atomic ratio in TiCx phase of W1, W2 and W3 alloys sintered at 1573K.

	W1	W2	W3
Lattice parameter (nm)	4.317	4.314	4.307
Estimated C/Ti atomic ratio in TiCx phase[5)]	$TiC_{0.62}$	$TiC_{0.60}$	$TiC_{0.55}$
Change of C/Ti atomic ratio after sintering	−0.38 $TiC_{1.0 \rightarrow 0.62}$	−0.15 $TiC_{0.75 \rightarrow 0.6}$	+0.05 $TiC_{0.5 \rightarrow 0.55}$

The relationship between 3 points bending transverse rupture strength (TRS) and sintering temperature on each alloy indicated that the position of maximum TRS of W1, W2 and W3 alloy existed at sintering temperature of 1673, 1673 and 1573K respectively, and the maximum TRS value were W1, W2 and W3 alloy in ascending order. The sintering temperature for maximum TRS shifted on the lower temperature side because the sintering densification was accelerated by increasing C/Ti atomic ratio in TiCx raw powder as stated above.

Fig.2 shows SEM images of microstructure of W1 and W3 alloy sintered at the range of 1373 to 1873K. According to the SEM observation, it could be found that TRS decreased because of increase of pore up to the maximum TRS temperature, because of coarsening of β-Ti and TiCx phase over the temperature respectively. Also, it was confirmed that for W1 alloy coarse TiCx phase was first crystallized ($TiC_{1.0}$ + Ti→TiCx), that for W3 alloy the densification was accelerated through starting sintering densification among fine $TiC_{0.5}$ raw powders at lower temperature ($TiC_{0.5}$ + $TiC_{0.5}$→TiCx).

From the result of immersion test and potentio-dynamic polarization curves of W1, W2 and W3 alloys in an acid solution (3%NaCl + 0.1N-H_2SO_4) and neutral solution (3%NaCl), it was confirmed that every alloys had exceptionally excellent corrosion-resistance in both acid and neutral solution mainly because of suppression of anodic reactions, which meant about 200 times higher than conventional WC-15mass%Co cemented carbide.

3. Summary

The effects of lower C/Ti atomic ratio of TiCx raw powder on the propeties of Ti-Mo-W-TiC sintered hard alloys were: 1) Accelaration of densification in sintering process, 2) Increase of hardness due to increase of volume content of TiCx phase, 3) Drop of the sintering temperature showing maximum TRS. In addition there was no effect on the corrosion resistance in acid and neutral solutions, which meant the Ti-Mo-W-TiC sintered hard alloy with the lower C/Ti atomic ratio of TiCx raw powder could combine excellent corrosion resistance with higher hardness.

4. References

1. K. Tokumoto, T. Kitada, H. Shinoaki and S. Sakaguchi: J. Jpn.Soc. Powder and Powder Metallurgy, **40**, 66(1993).
2. K. Tokumoto, H. Shinoaki, T. Kitada and S. Sakaguchi: J. Jpn. Soc. Powder and Powder Metallurgy, **41**, 27(1994).
3. K. Tokumoto and S. Sakaguchi: J. Jpn. Soc. Powder and Powder Metallurgy, **44**, 301(1997).
4. K. Nakahara, S. Imasato, S. Sakaguchi and Y. Hayashi: J. Jpn. Soc. Powder and Powder Metallurgy, **49**,257(2002).
5. E. K. Storms: THE REFRACTORY CARBIDES, ACADEMIC PRESS INC, p8 (1967).