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4.2 A Study on Temperature Effect of Ta + N Implanted Hard Alloy

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Key words　Hard alloy　Ta + N ion implantation　Temperature effect

The ion implantation is an efficacious surface modification technology and notable effect has been produced in the surface hardness, wearability and corrosion resistance of materials. However, the major limitation for wide use in industry was that the modification layer was too shallow to be fit to industrial application. Although the modification layer can be improved by increasing the implantation energy, a lot of X-ray must be induced so as to be harmful to health. Elevating implantation is a new method that can improve implantation layer, and the optimum surface modification layer can be obtained. It is reported that the elevated temperature of a single ion implantation has been succeeded, but there has been none of report on elevated temperature of dual ions implantation up to now yet.

In this paper, a study of N + Ta dual ion implantation in typical hard alloy is presented. It includes that the target temperature varied over a wide range by varying the frequency of high pulse power and the present results of investigation about the temperature effect on dual nitrogen plus tantalum concentration profile and the mechanical properties of hard alloy.

1 Experimental methods

The samples were type YT15 hard metal, composed of: WC-79%, TiC-15%, Co-6%. The samples were cleaned in an alcohol ultrasonic bath before treatment. PSII treatment was carried out in the PSII-IBED device at southwestern institute of physics. Determination of the target temperature was made using a thermocouple. The chamber was filled with nitrogen at a working pressure of 5.3×10^{-3} Pa. Tantalum ions were implanted into the surface consecutively with a cathodic arc plasma source, at the same time, nitrogen ions were implanted by PSII. The implantation conditions are shown in Table 1. The target was uncooled.

Table 1 Ion implantation conditions

Sample No.	A	C
Implanted ions	N + Ta	N + Ta
Ion energy/keV	50(N) + 40(Ta)	50(N) + 40(Ta)
Dose/10^{17} ions · cm^{-2}	8(N) + 8(Ta)	8(N) + 8(Ta)
Temperature/℃	100	400
Frequent/Hz	100(N) + 33(Ta)	400(N) + 100(Ta)

Auger electron spectroscopy (AES) with Ar^+ ion gun sputtering was used to determine the nitrogen and tantalum concentration depth profile. Scanning electron microscopy (SEM) was employed to observe the microstructural changes. X-ray diffraction (XRD) with Cu K_α radiation was used to determine the phases in the modified layer. A Vickers microhardness tester was employed to determine the hardness change. Measurements were performed at various loads in the range of 25 ~ 300 gf.

2 Result and discussion

2.1 Nitrogen and tantalum concentration depth profile

Nitrogen and tantalum concentration profiles are shown in Fig. 1 (a) and (b) for the samples implanted at 100 ℃ and 400 ℃. By comparison, it had a very different shape. It is very evident that the specimens at 100 ℃ [(Fig. 1(a)] hard a typical Gauss distribution, the maximum nitrogen atomic concentration measured was about 32% after a sputtering time of 5 min, the nitrogen concentration is disappeared after a sputtering time of 30 min. However, to tantalum concentration profile, the maximum atomic concentration measured is only 11% after a sputtering time of about 2 min, the area under the tantalum profile is smaller in the sample at 100 ℃, indicating that the nitrogen plus tantalum modification layer at 100 ℃ is very shallow.

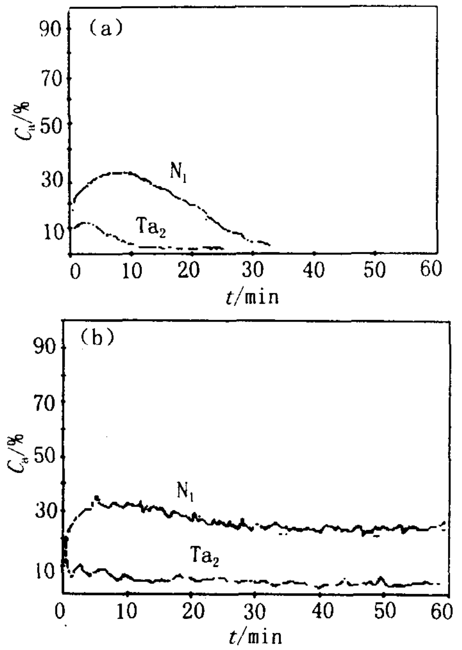

Fig. 1 Nitrogen and tantalum profile of specimen implanted at 100 ℃ (a), 400 ℃ (b), respectively

The distribution curve of the high temperature implantation had a very different shape, the nitrogen and tantalum concentration profile across the diffusion zone for the sample are presented in Fig. 2. A peak of about 34% in nitrogen atomic concentration is observed at the sputtering time of 8 min, which represents the penetration depth of the energetic nitrogen ions. At greater depths a plateau at about 28% can be observed, it can not drop off after a sputtering time of 60 min (approximately 1.5 μm). The profile of tantalum shows that a maximum peak near the surface was about 18% , followed by a long tail. The maximum penetration of injected atomic species has increased.

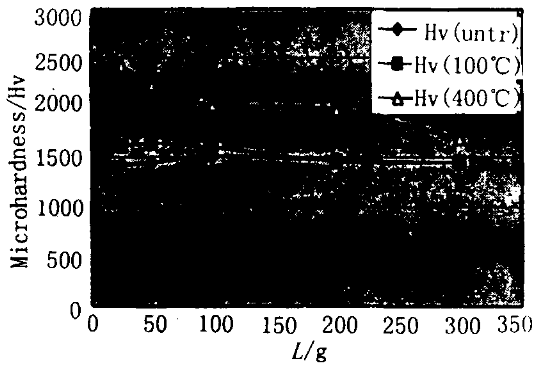

Fig. 2 Vickers microhardness of specimens

The effect of diffusion on the nitrogen and tantalum curve at high temperature is very significant. This can be seen by comparison of Fig. 1(a) and (b). It is apparent that the combination of thermal-radiation-enhanced diffusion and perhaps thermal gradient diffusion has resulted in further substantial penetration of nitrogen atom into the substrate interior.

2.2 Microhardness measurement

Fig. 2 shows results of the microhardness measurements as function of load. For high temperature implantation the surface hardness increased by 200% under a load of 25 gf. This hardness improvement is more significant than that observed at low temperature. This can be explained by (1) the more stable nitrides formed during high temperature implantation and (2) the thicker implanted layer in the high-temperature-implantation specimen. The hardness decreased as the load increased and the indentation penetrates more deeply into the specimens, the hardening effect of the implanted layer becomes less significant.

2.3 X-ray diffraction (XRD) analysis

The reason for the hardening effect was elucidated by phase analysis. Fig. 3 shows the results of X-ray diffraction patterns at an incidence of 5°. At a low processing temperature, it showed that compound WC, TiC and Co phase were detected due to weight percent about 79 WC, 15 TiC and 60 Co in YT15 hardmetal, respectively, similar to untreated hardmetal, no evidence of the formation of nitrides were found. At 400 ℃, the X-ray peaks indicate the formation of XRD of the Ta + N implant. The peak of TaN, WN and the WC became broad, this phase is the hardest one in this system.

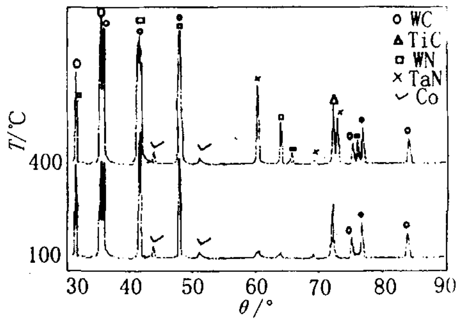

Fig. 3 The XRD of the Ta + N implant

This work shows that the effect of elevated temperature implantation is very significant, it controls the phase formation, and a considerable improvement in the surface property of hardmetal without any deterioration or even with an improvement in chemical stability can be achieved.

2.4 Structure changes

Scanning electron microscopy of unimplanted hardmetal indicated the presence of a fine distribution of precipitate with a strip and spherical morphology. These strip precipitates are WC crystal structure. These spherical precipitates are TiC-WC crystal structure. After Ta + N dual ion implantation the near-surface microstructure changed substantially and became more complicated. The microstructure shows the sample implanted at 100 ℃, the presence of dark spots is implanted N + Ta ions, but the wholly surface structure hasn't obviously changed. The microstructure shows the sample implanted with Ta + N dual ion at 400 ℃, the surface microstructure has been obviously changed, these strip precipitates has disappeared, the presence of many dark spots which could be either second phases (possibly nitrides) or defect clusters(e. g. dislocation loops) formed during irradiation. A possible explanation for the presence of such fringes may be the juxtaposition of the matrix and nitride phase with substantially different lattice parameters. Near-surface chemical analysis of the implanted sample using XRD showed the presence of TaN, WN phases formed from the reaction between dual implanted nitrogen and tantalum and hardmetal elements present in solid solution. These nitride phases would be expected to contribute significantly to the improvement of surface properties.

3 Conclusion

By means of elevated temperature N + Ta dual ion implantation, a hardened layer of substantial thickness can be achieved in relatively short time. The characteristics of this layer depend upon the compositon of implanted material and to a certain extent its microstructure. Dual N + Ta ion implantation of hardmetal at a temperature of 400 ℃ resulted in significantly deeper penertration of nitropen and tantalum as compared with specimens implanted at 100 ℃. In addition, stable in nitride precipitates were observed after high temperature implantation. This resulted in higher hardness.

The extent of dual TA + N diffusion observed during high temperature implantation was in excess of that expected by thermal mobility alone. It is proposed that the steep thermal gradient that existed during implantation played a significant role in enhancing nitrogen and diffusion.