*Radiation Effects and Defects in Solids*, 1996, Vol. 138, pp. 57–62
Reprints available directly from the publisher
Photocopying permitted by license only

# HARDENING OF WC–Co ALLOYS BY ION IMPLANTATION

M. I. GUSEVA,[1] M. V. ATAMANOV,[1] G. V. GORDEEVA,[1] V. E. NEUMOIN,[1]
B. N. CHOI,[2] W. KIM[2] and J. G. HAN[3]

*[1]RRC 'Kurchatov Institute', Institute of Nuclear Fusion, Kurchatov Square, 123182 Moscow, Russia; [2]Nuclear Fusion Research Department, Korea Atomic Energy Research Institute, P.O. Box 7, Daeduc-Dan J, I., Taejan 306–353, Korea; [3]Department of Metallurgical Engineering, Sung Kyun Kwan University, 300 Chan Chun-Dong, Suwon 440–746, Korea*

*(Received October 8, 1994; in final form May 8, 1995)*

The hardening effect on the surface layers of WC–Co alloys after $Ar^+$- and $N^+$-ion implantation with the fluence in the range $1 \div 8.7 \times 10^{17}$ cm$^{-2}$ has been investigated at room temperature and under heating with an ion beam. The depth of the Auger distribution profiles and the microhardness of implanted samples were measured. The radiation-stimulated diffusion of nitrogen atoms and the microhardness enhancement were observed. The contribution of the polymorphic Co-phase transformation and the production of Co–N compounds is discussed.

*Key words*: implantation, radiation-stimulated diffusion, WC–Co, hardening, phase transformation, microhardness.

## 1 INTRODUCTION

Implantation of $N_2^+$-ions is successfully used for the wear resistance enhancement of various tools made of the tungsten carbide cemented by cobalt.[1,2] However, at present there is no common view on the mechanism of wear resistance enhancement for this composite. Usually, the reason for the wear of baked WC with cobalt binding is regarded to be a process of its local removal.

Mezi[3] has detected martensite transformation in cobalt by transmission electron microscopy of WC–Co implanted with $N^+$-ions which indicates the emergence of stress in a crystalline lattice. This allowed one to make the conclusion about the possible strengthening of WC–Co under hard nitrogen dissolution. In nitrogen implanted WC–Co, the nitrogen can segregate towards interfaces between carbide grains and the cobalt binding, thus enhancing the chemical bonds on this surface and strengthening the composite.

In this paper our studies on the influence of radiation defects and temperature on the WC–Co hardening in the process of $N^+$-ions implantation are described.

## 2 EXPERIMENTAL TECHNIQUE

The experiments on $N_2{}^+$- and $Ar^+$-ion implantation were done in the KAERI- high current ion accelerator (without mass-analyzer). To measure the beam parameters and its components, mass analyzer, a mobile Faraday cup were used for beams analysis of 1 cm$^2$ in size. The ion mass spectrum was registered with the XY-recorded connected to the Faraday trap. Calorimetric current measurements, allowing one to take into account the contribution of the high energy atoms produced in the process of charge-exchange, were also realized. Thus the fluence calculations summarize all the presence of molecular, atomic and two-charged ions, as well as that of charge-exchange high energy-atoms,

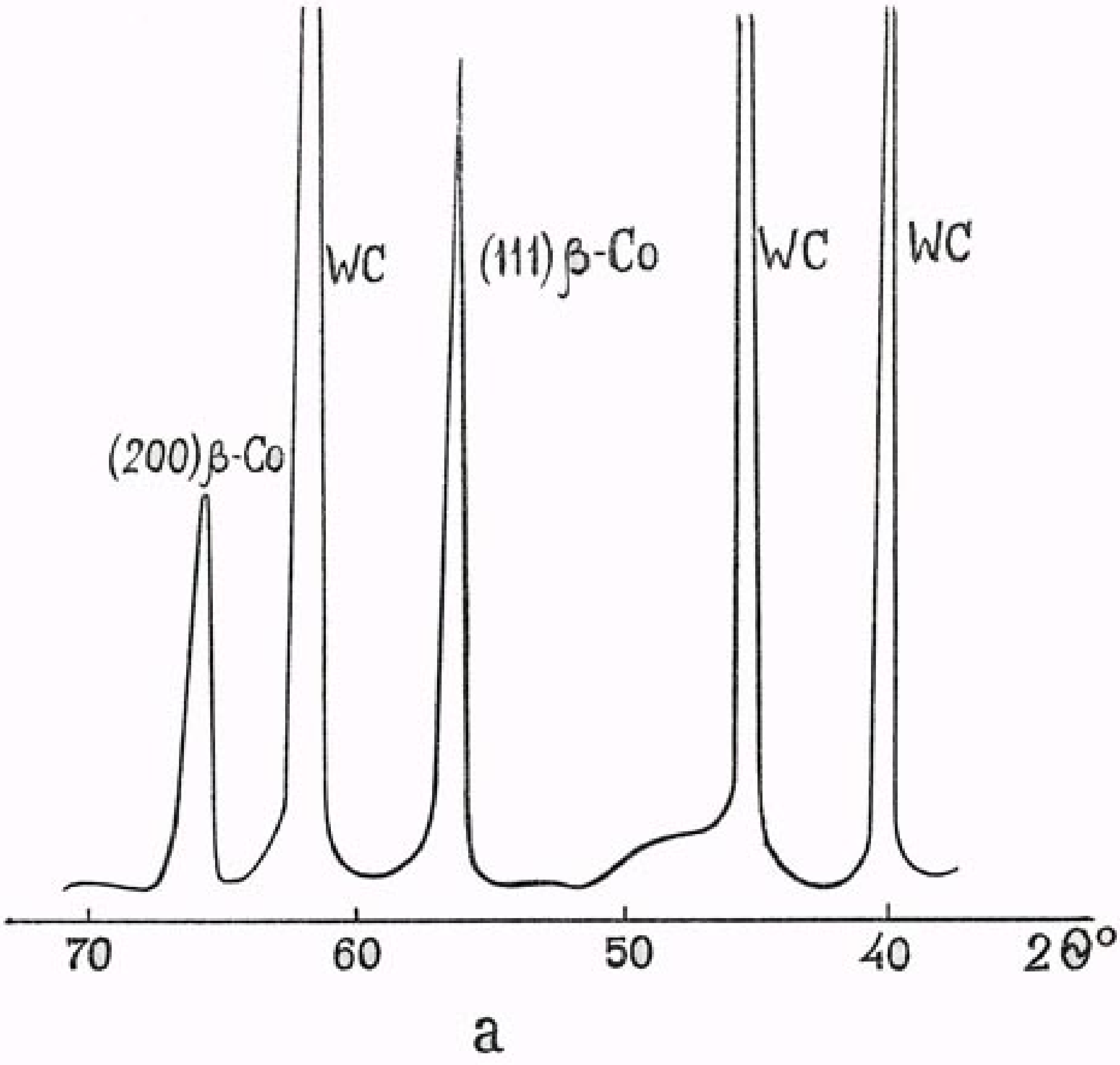

FIGURE 1 Diffractograms of Co-cemented tungsten carbide before (a)

without distinction. For the energy of 30 keV of the nitrogen ions and within the measured ion current and time the correction factor was equal to 1.73 in calculations of the fluence. The fluence values were varied from $1 \times 10^{17}$ cm$^{-2}$ to $8 \times 10^{17}$ cm$^{-2}$ (with corrector factor). The energy of $N_2^+$-ions was equal 30 and 120 keV. Two experimental runs were realized; one at room temperature with cooling targets and one with heated targets due to the released ion beam power in the process of implantation.

Tungsten carbide cemented with 16 at .% Co-atoms was used in the experiments. Measurements of microhardness by Vickers indenter at loadings of 25, 50, 75, 200 grams were carried before and after the ion implantation. The microhardness values were averaged from 10 measurements for each sample. The phase composition was investigated by the structural X-ray analysis. The elemental distribution in depth was studied by the Auger electron spectroscopy.

## 3 EXPERIMENTAL RESULTS AND DISCUSSION

The structure of unimplanted WC–Co alloys is characterized by the presence of mainly two phases: tungsten monocarbide α-WC and β-Co (Figure 1a). The X-ray structural

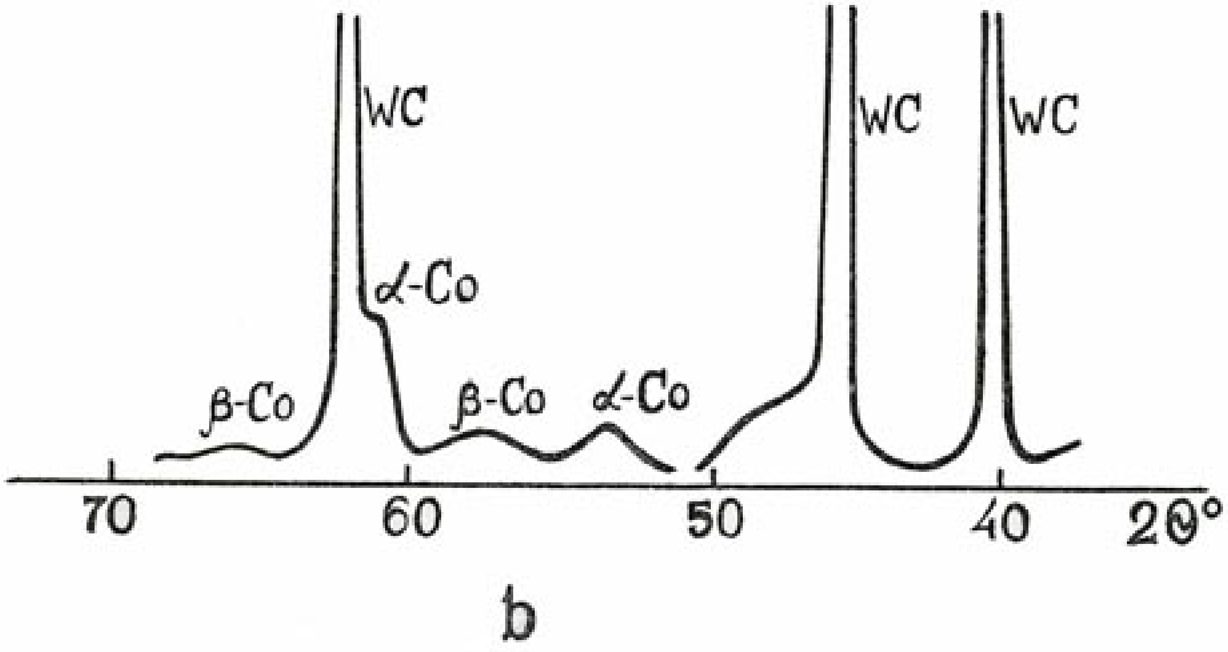

FIGURE 1 after (b) irradiation by $Ar^+$-ions.

analysis data have shown that $Ar^+$ and $N_2^+$-ions implantation of the cemented tungsten carbide results in an essential change within the cobalt phase composition. The implantation leads to a cobalt transition from the metastable $\beta$-modification with a face-centered-cubic structure into the stable hexagonal $\alpha$-modification. The polymorphic transformation $\beta \rightarrow \alpha$, is of the martensite nature, and it is accompanied by the emergence of inner stresses as an effect of phase cold working. The $\beta \rightarrow \alpha$ transition is totally completed under irradiation. One should note that only heating up to 500°C, which is higher than the temperature of polymorphic transformation in cobalt, 450°C, results in a partial transition of cobalt from a cubical modification into a hexagonal one. Such a process shows up in X-ray patterns as a reduction of the intensities of diffracrion peaks of the $\beta$-phase (111) and (200). At the same time these peaks disappear almost completely in diffractograms of implanted WC–Co alloy (Figure 1b).

Measurements of distribution profiles after irradiation by $Ar^+$-ions indicate that the surface region is depleted from carbon-atoms. Carbon concentration near the surface is reduced to $\sim 30$ at.%. Such layer is formed due to carbon dominant sputtering. The modified layer of 1 $\mu$m thickness exceeds the projected range of 30 keV $Ar^+$-ions considerably ($R_p$ of 30 keV $Ar^+ \rightarrow$ WC not much differs from $R_p^w$ ($\sim 100$ Å)).[4]

The atoms ratio of W : O near the surface is approximately 1 : 3 ; in greater dephs the concentration of W-gradually rises and of oxigen decreases. In the layer of 1000 to 6000 Å the concentrations of oxigen and cobalt atoms coincide that allows one to spiculate about production of the Co–O–bond.

Measurements of surface microhardness (HV) after implantation of $Ar^+$-ions ($\Phi = 10^{17}$ cm$^{-2}$) and $N_2^+$-ions ($\Phi = 2 \times 10^{17}$ cm$^{-2}$), at an energy of 30 keV at room temperature show that the main contribution to the microhardness enhancement is introduced by structural disorder since the effect of HV-increasing practically the same for bombardment by heavy $Ar^+$ and by $N_2^+$-ions.

In Figure 2 the fluence dependence of WC–Co-microhardness, implanted by $N_2$-ions with the energy 120 keV at the loadings 25, 50, 75, g to the indenter, is shown. The temperature in the process of irradiation was 500°C. With increasing $N_2^+$-fluence an increase in microhardness is observed, up to a factor four at the fluence $5 \times 10^{17}$ cm$^{-2}$.

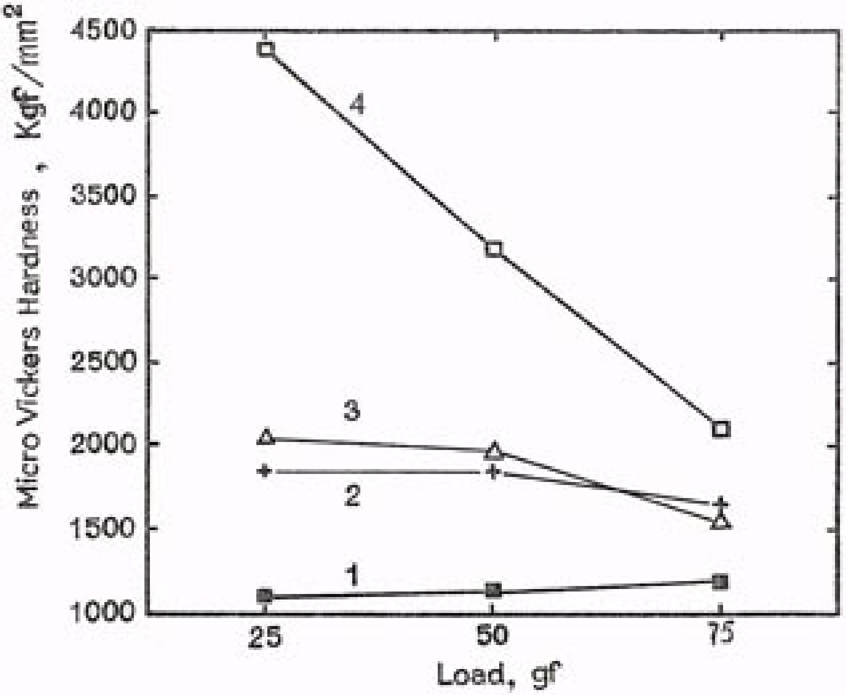

FIGURE 2 Fluence dependence of microhardness for WC–Co alloys implanted by 120 keV $N_2^+$-ions, at loads 25, 50 and 75 gf ($T_{impl.}$ = 500°C): unimplanted (1); $\Phi = 2 \times 10^{17}$ cm$^{-2}$ (2); $\Phi = 3 \times 10^{17}$ cm$^{-2}$ (3); $\Phi = 5 \times 10^{17}$ cm$^{-2}$ (4).

These results are not in agreement with the experimental data by Burnett and Page, according to which the softening of the implanted material WC-9%[5] occurs under

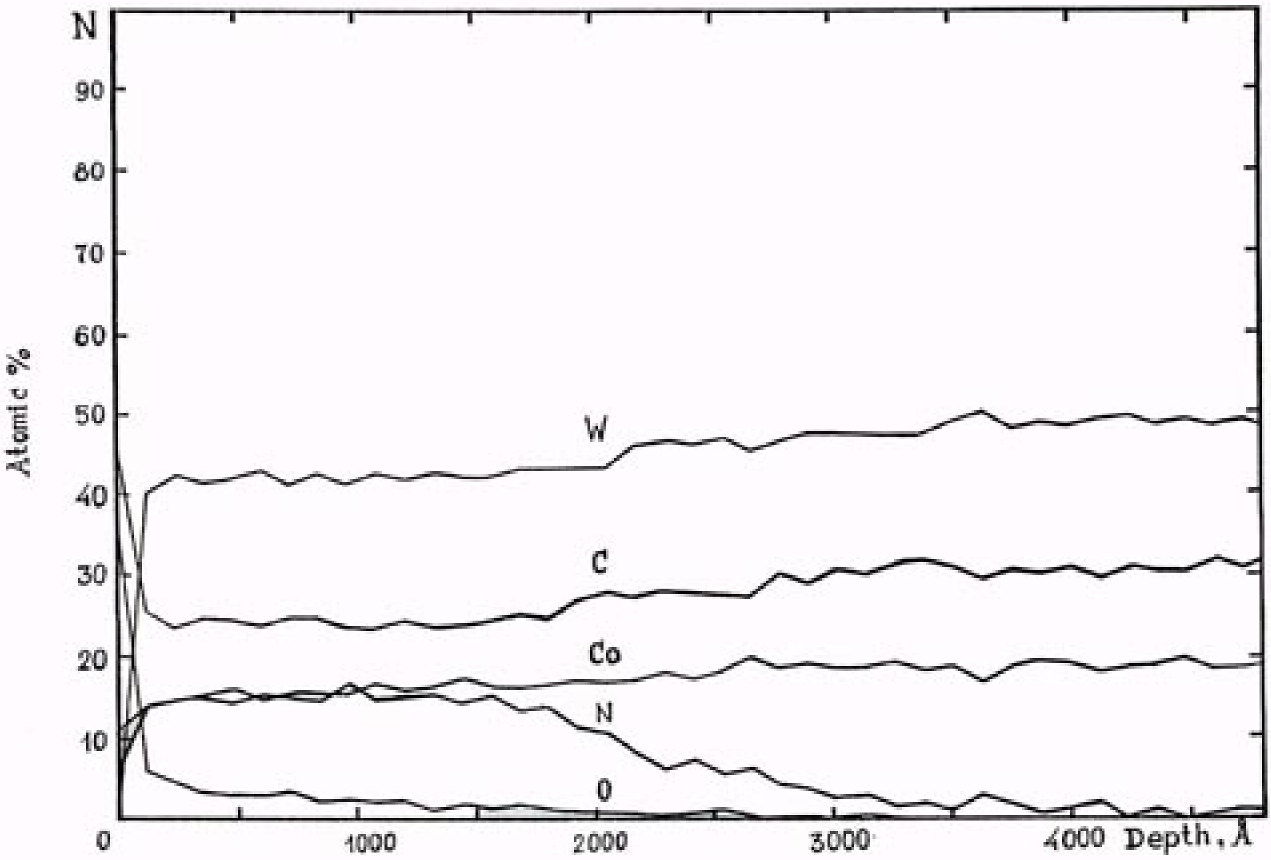

FIGURE 3 Auger depth profiles for WC–Co after irradiation by 120 keV $N_2^+$-ions at $\Phi = 5 \times 10^{17}$ cm$^{-2}$.

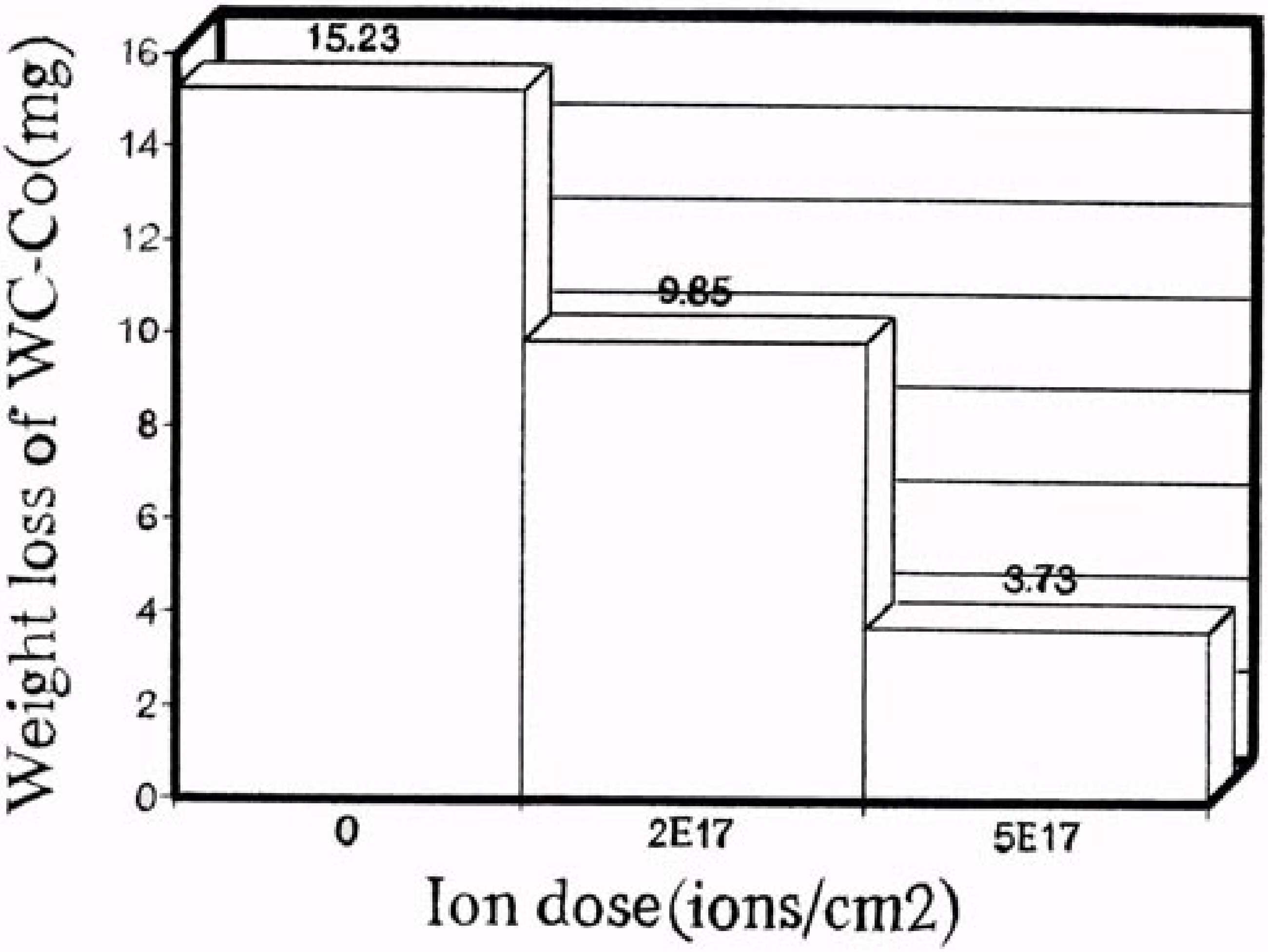

FIGURE 4 Variation of WC–Co weight loss with fluence.

bombardment by 100 keV $N^+$-ions at fluence greater than 3 × $10^{17}$ $cm^{-2}$. However, as noted above, in the experiments by Burnett and Page the temperature was not registered in the process of implantation, and Dearnaley assumed[5] that it was below than 200°C. At the same time, our results are in accordance with the data of Kolitsch and Richer[6] who observed an increase in the microhardness of cemented tungsten carbide when rising the fluence of $N_2^+$-ions up to $10^{18}$ $cm^{-2}$. Thus, the difference in the experimental microhardness results is attributed to different temperatures in the process of nitrogen ion implantation.

The WC–Co heating by the released power of the ion beam stimulates radiation enhanced diffusion of the implanted impurity. There for, in order to obtain the hardening effect in a thick layer one needs to implant at high doses. This is also confirmed by the results of the Auger analysis on the depth profiles in surface layers of WC–Co–samples, irradiated by nitrogen ions at 500°C at two fluences, 2 × $10^{17}$ $cm^{-2}$ and 5 × $10^{17}$ $cm^{-2}$ (Figure 3). The N-atoms profile show a plateau up to 1900 Å followed by an extended 'tail'. In this case, the depth of nitrogen ion penetration exceeds their projected range considerably. Such depth profiles are due to radiation-stimulated diffusion. For this fluence concentration of nitrogen within the layer, of ~1500 Å thickness, coincides with the Co-concentration and is about ~16 at.%. At low fluence the nitrogen quantity near the surface is twice smaller.

The wear tests of the $N_2^+$-implanted samples have shown that a maximal wear resistance is observed at the fluence of 5 × $10^{17}$ $cm^{-2}$ (Figure 4). These results are correlated with the microhardness measurements data. The surface microhardness and wear resistance are increased up to a factor four under the same irradiation conditions.

## 4 CONCLUSIONS

1. Under bombardment of WC–Co alloys by $Ar^+$ and $N_2^+$-ions the dominant sputtering of carbon atoms and radiation-stimulated diffusion of N-atoms take place. The modified layer thickness exceeds the projected ions range in WC considerably. The N-atoms depth distribution looks like a plateau followed by an extended 'tail'.
2. The irradiation by $Ar^+$ and $N_2^+$-ions leads to polymorphic Co-phase martensite transformation $\beta \rightarrow \alpha$.
3. The $Ar^+$ and $N_2^+$-ion implantation results in surface hardening of WC–Co alloys. Maximal microhardness and wear resistance values are observed for fluence $5 \times 10^{17}$ $cm^{-2}$ by 120 keV $N_2^+$-ion implantation.
4. The important contribution to the hardening mechanism is introduced by cobalt phase transition, structural disorder and probable Co–N compounds production.

## REFERENCES

1. G. Dearnaley and N. E. W. Hartley, *Thin Solid Films*, **54**, 215, (1978).
2. G. Dearnaley, Science of Hard Materials (ed. R. Vis Wawadham, D. J. Rowcliffe, J. Gurland), Pl. Press Corf (1983).
3. J. K. Hirvonen and S. R. Cleiton, Surface Modification and Alloying by laser, Ion and Electron Beams (ed. Y. M. Poate, G. Foti, D. C. Jacobson), Pl. Press, N.Y., London, (1983).
4. M. A. Kumahov, V. A. Muraviev, E. G. Averjanov, V. A. Simonov, L. P. Havken. Projected range and straggling of 1240 target-ion combinations. VINITI, Moscow, (1975).
5. G. Dearnaley, F. Minter and P. K. Rol, *et al., Nucl. Instr. and Meth. in Phys. Res.*, **B7/8**, 188 (1985).
6. A. Kolitsch and E. Richter, *Crystal Research and Technology*, **K5**, 18 (1983).