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Long-Range Effect in Ion-Implanted Titanium Alloys

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Surface modification of titanium alloy (Ti6Al4V) by nitrogen ion implantation and ion beam-assisted deposition (C, N) was investigated. The depth distribution of implanted nitrogen atoms was analysed using the Rutherford backscattering technique. Nitrogen implantation reduces the coefficient of friction and wear. A better effect can be obtained when nitrogen implantation is combined with carbon deposition. Based on the changes in the coefficients of friction and wear as well as profilograms of wear tracks, the improvement of the tribological properties was found at a depth exceeding nearly 5 times the range of the implanted nitrogen ions. Identification of the long-range effect for Ti6Al4V alloy was performed on the basis of tribological analyses. This study is a continuation of research conducted for AISI 316L and H11 steel.

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1. Introduction

Ion implantation changes various physical, chemical and mechanical properties of the surface layer of metals. These changes are assumed to occur in a layer with a thickness equal to the range of implanted ions. They are induced by the implanted ions and radiation defects produced during implantation. Measurements of the microhardness of the surface layer show that the thickness of a layer with increased hardness is several-times greater than the range of implanted ions. This phenomenon is known as a long-range effect. So far, the effect has been detected only during microhardness measurements. Although it has been presented in several papers [1-3], its range is questionable due to the difficulty in determining the thickness of the layer with increased hardness by measurements performed with the use of a microhardness tester. A modified layer is penetrated by the indenter, which can be laterally supported by the layer; this leads to overestimation of the thickness of the layer. It is assumed that the depth of the hardness tester indenter cannot exceed 1/10 of the thickness of the measured layer [4]. It has to be mentioned that the authors of papers [2, 3]used a Vickers pyramid penetrating a depth of $1-5 \ \mu m$ at 15–20 g loads. The aim of the present study is to determine the thickness of a layer with improved tribological properties by measurements of the friction coefficient and wear of Ti6Al4V alloy. For the first time, the magnitude of the long-range effect was determined on the basis of tribological investigations for AISI 3126L [5] and H11 [6]. The authors of paper [3] explain its occurrence by movement of implantation-induced radiation defects along the depth of the sample and defects accompanying penetration of the hardness indenter into the sample material.

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In this paper, we aim at whether the long-range effect can also be observed in non-ferrous alloys.

2. Experimental details

Nitrogen implantation and nitrogen implantation combined with deposition of carbon atoms were performed using the method described in paper [7]. The implantation energy was 120 keV, and the fluence was in the range $10^{16} \div 10^{18}$ cm⁻². The depth profiles of the distribution were measured by the Rutherford backscattering (RBS) technique using a He beam with the energy 2.0283 MeV scattered at an angle of 170° [8]. The wear behaviour of the samples was evaluated by a pin/ballon-disc tribometer [9] at a sliding speed of 56.5 mm/s against WC — 6 wt% Co balls with a 0.5 mm diameter. The ball was pressed into the sample with a force of 0.49 N. The friction measurements were carried out under technically dry friction. Since the wear of the counter sample made of tungsten carbide (WC-Co) was low in comparison with the wear of the sample, the volume of sample wear was calculated on the basis of the ASTM G99-95a standard. The ball left traces on the sample, which were analysed using a Form Talysurf Intra Taylor-Hobson profilometer. The wear values were calculated from the cross-sectional areas of the profilograms, as explained earlier [10]. The wear behaviour was evaluated by calculating the wear coefficient k:

$$k = V/(P \times L) \ [\mu m^3/Nm], \tag{1}$$

where V is the lost volume, P is the indentation load, and L — the sliding length.

3. Results and discussion

Implanted nitrogen ions and recoiling carbon atoms lose their energy in successive collisions with sample atoms until stopping. This leads to formation of vacancies, interstitial atoms, dislocations and other types of lattice damage in the region around the ion track. It is generally assumed that the depth profile of radiation defects coincides with the distribution of vacancies but the so-called radiation enhanced diffusion may also occur. The depth profile of implanted nitrogen ions and vacancies appearing during implantation can be calculated using computer software, e.g. SRIM, SATVAL. The predicted distribution of nitrogen atoms and displacement vacancies calculated by means of the SRIM code [11] are presented in Fig. 1. This figure



Fig. 1. Predicted distribution of nitrogen ions implanted with energy of 120 keV at a fluence of 10^{18} N⁺/cm² and formed vacancies calculated using computer software SRIM [11]. The figure shows the distribution of nitrogen atoms measured with the RBS method as well.

shows also the depth distribution of nitrogen atoms measured by the RBS method. Computer simulations show that the maximum range of implanted ions should be $R_{\rm max} = 0.42 \ \mu$ m. The range measured by RBS is equal to $R_{\rm exp} = 0.45 \pm 0.01 \ \mu$ m. The measured range is slightly greater than the calculated range. This may be associated with two factors: diffusion of nitrogen atoms inside the sample and sputtering of the surface layer of the sample during implantation. Diffusion of atoms inside the sample is probably attributable to strong repulsion forces between the first and second nearest neighbours of nitrogen atoms [12].

For comparison, the predicted distribution of carbon atoms implanted using the method of recoiling implantation after nitrogen irradiation is shown in Fig. 2. The calculations were performed with the use of modified software SATVAL [13, 14]. The KrC interaction potential [15] was used to describe the collisions between projectiles and target atoms as well as between recoiling target atoms themselves. The Oen–Robinson method [16] was chosen in the case of electronic energy loss calculation. The carbon atom thickness is assumed to be 50 mono-atomic layers. As can be seen, the range of atoms implanted with the recoiling implantation method does not exceed 0.16 μ m and is lower than the range of implanted nitrogen ions. Then the recoil implantation of C atoms may not have a significant impact on the magnitude of the long-range effect in comparison with their radiation enhanced diffusion inside the sample.



Fig. 2. Results of the Satval code computer simulation of depth distribution of carbon after recoiling implantation for different fluences of 120 keV nitrogen ions irradiation.



Fig. 3. Changes in the friction coefficient observed with the increase in the number of cycles in a tribological test of unimplanted and implanted Ti6Al4V samples.

The results of measurements of the friction coefficient are presented in Fig. 3. The friction coefficient for the Ti6Al4V sample is about 0.78. After nitrogen implantation, it decreases to $0.25 \div 0.28$ and persists at this level until the layer modified by the implantation process is worn. An increase in the friction coefficient for a sample implanted at a fluence of $2 \times 10^{17} \text{ N}^+/\text{cm}^2$ is detected after ≈ 1600 cycles. With increasing fluences of implanted nitrogen ions, the friction coefficient increases following an increasingly higher number of cycles. The profilograms of wear tracks on the surface of the examined samples are shown in Fig. 4. By measuring the track depth when the friction coefficient of an implanted sample increases, it is possible to determine the thickness of the layer modified by the implantation process. The track depth is about 2.1 μ m. This implies that the thickness of a layer with a decreased friction coefficient is 4.7-fold larger than the measured range of implanted ions, which equals $R_{\rm exp} = 0.45 \pm 0.01 \ \mu {\rm m}$ (Fig. 1).



Fig. 4. Profilograms of wear tracks on unimplanted Ti6Al4V sample (a) and after implantation with a fluence of 2×10^{17} (b) and 10^{18} N⁺/cm² (c) after a 2000-cycle test.



Fig. 5. Wear of the sample occurring during 10 000 cycles of the measurement test.

The sample wear during 10,000 cycles is presented in Fig. 5. The wear of the sample increases after wearing the implantation-modified layer. This is clearly visible for samples implanted with fluences of 5×10^{17} N/cm² and 10^{18} N/cm². The changes in sample wear are confirmed by the results of friction coefficient measurements (Fig. 3).



Fig. 6. Friction coefficient of the Ti(N, C) layer formed on the surface of Ti6Al4V alloy during the recoiling implantation.

Changes in the friction coefficient observed during the tribological test of a sample with a layer of carbon deposited after nitrogen implantation are presented in Fig. 6. The deposited carbon layer after implantation decreases the friction coefficient to about 0.2, which then increases and reaches a value characteristic of an unimplanted sample only after wear of the implantationmodified surface layer. The increase in the implanted fluence is accompanied by an increase in wear resistance (thickness of a layer with a decreased friction coefficient). Wear of the surface layer characterised by enhanced tribological properties is evident after approximately 2000, 6500, and 9800 cycles in the case of samples with deposited carbon and implanted with a fluence of 2×10^{17} , 5×10^{17} and $10^{18}~\mathrm{N^+/cm^2}.$ The depth of the track was $\approx 2.1, 2.5, \text{ and } 2.8 \ \mu\text{m}$. This implies that the thickness of a layer with a decreased friction and wear coefficient is about 5-fold larger than the measured range of implanted ions. It is assumed that the long-range effect is caused by the movement of radiation defects (radiation-enhanced diffusion) and defects produced during the tribological test.

The increase of the friction coefficient observed during the first 4000 cycles of the sample implanted with the highest fluence up to a value of 0.3 is caused by sample sputtering during the implantation process.

4. Conclusions

Nitrogen implantation and nitrogen implantation combined with carbon deposition decrease the friction coefficient and wear of Ti-6Al-4V alloy in a layer with a thickness of about 2.5 μ m. This implies an implantation-induced modification of the mechanical properties of a layer with a thickness exceeding \approx 5-times the range of implanted ions. Wear resistance of a layer with a decreased friction coefficient and higher wear resistance increases with the increase in the fluence of implanted ions and, hence, the number of radiation defects produced. It is assumed that the long-range effect is caused by the movement of radiation defects (radiation-enhanced diffusion) and defects produced during the tribological test.

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