

Tribological properties of the Stellite 6 cobalt alloy implanted with manganese ions

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Abstract. The rapid development of automotive technology requires that designers should use modern materials. Materials used to construct the most heavily loaded components such as the components of internal combustion engines are often subjected to various treatments to enhance their mechanical properties. One of the well-known methods for modification of material in terms of tribological properties is ion implantation. The samples were implanted using manganese ions. The distribution of implanted ions and vacancies at various depths was calculated by the SRIM program. The implantation process was run with the energy $E = 175$ keV, and the dose of implanted ions was set to $D=5 \cdot 10^{16}$ Mn⁺/cm² and $D=1 \cdot 10^{17}$ Mn⁺/cm². Next, the samples were subjected to tribological tests on a pin-on-disc stand using the Nano Tribometer (NTR2) manufactured by Anton Paar. As a counter sample, we used a ball with a diameter 0.5 mm made of WC (tungsten carbide). A load of 0.5 N was applied to the ball. As a result, we determined variations in the friction coefficient for individual samples under dry friction conditions. Next, scanning electron microscopy (SEM) analysis was conducted using a Phenom ProX microscope. The wear trace was measured using the Taylor Hobson Form Talysurf 50mm Intra profile measurement gauge. The measurements provided profilograms facilitating determination of the mean wear and the depth of the wear trace. The implantation of manganese leads to a change in the friction coefficient and tribological wear of the Stellite 6 cobalt alloy.

Introduction

Nowadays, combustion engines have to meet many requirements associated with their efficiency and environmental impact. This prompts constructors to attempt to reduce energy consumption in vehicles by reducing their mass. Achievement of increased engine power per kilogram of its mass would not be possible without development of engine construction materials.

The most important aspect for engine efficiency is the effective supply of fresh air to the cylinder and removal of exhaust gas therefrom. Engine valves are responsible for these activities. They work in extremely difficult conditions and are subjected to both thermal and mechanical loads [1]. Given the frequency of valve operation and the necessity of maintenance of combustion chamber tightness, valves must be constructed from a material that will be resistant to high temperature, aggressive environment, and mechanical wear and will be characterised by a low thermal expansion coefficient [2]. The relatively



low hardness of valves and valve faces made of austenitic steel is improved by hardfacing [3] with stellite, which is the main material used in the process [4].

Stellite refers to alloys of cobalt with chromium, tungsten, carbon, and other elements. They are characterised by a multiphase structure. The alloys are resistant to abrasion and the impact of organic acids; they are also creep- and heat-resistant materials [3]. Stellites are widely used in aviation, space, and automotive technologies as well as biomedical engineering as implant materials [5]. They are used for production of the highest quality tools and parts of combustion engines as well as other elements working in extreme thermal conditions. Additionally, they can be applied not only as a base material or welding rod, but also as powder for production of surface layers [6].

The stellite welding technology has been known since the end of the 20th century. Since that time, the loads in combustion engines have increased substantially and search for more robust solutions has become indispensable. There are various methods for enhancement of stellite strength. Ion implantation is one of the methods for increasing the mechanical strength of materials. Doping the material structure with ions of any element leads to alterations in its mechanical and chemical properties. The authors have already carried out investigations to determine the effect of nitrogen ion implantation on the mechanical properties of the Stellite 6 alloy. The research demonstrated a decline in the friction coefficient and tribological wear [7] as well as increased microhardness. Investigations conducted in the atmosphere of motor fuels showed no deterioration in the resistance of the implanted material [9].

Manganese implantation induces changes in the structure of engineering materials [10,11]. It may also contribute to improvement of the tribological properties of the Stellite 6 cobalt alloy. The present paper shows the results of our analyses of manganese-implanted Stellite 6 samples.

2. Characteristics of the material and research methodology

Stellite was chosen for analysis due its multiple applications as a material for construction of valves and valve faces. A commercial variety Stellite 6 was chosen. The alloy comprises 27-32 % Cr, 4-6% W, and 0.9-1.4% C. The samples for the analyses were taken from a ϕ 25 mm-diameter rod. Sample surfaces intended for the analysis were polished in order to achieve a roughness value of $R_a < 0.02$.

The samples were subjected to the ion implantation process. The distribution of the implanted ions and vacancies at equal sample depths was calculated with the use of SRIM programs [12]. Manganese was the implanted element. The implantation was carried out evenly over the entire surface of the sample at energy 175 keV. The dose of the implanted ions varied between the samples; the values of the fluences of the implanted manganese ions are presented in Table 1.

Table 1. Fluences of the implanted ions for individual samples

Sample	Implanted element	Fluences of implanted ions (ions/cm ²)
12	Mn ⁺	$5 \cdot 10^{16}$
8	Mn ⁺	$1 \cdot 10^{17}$
NN	unimplanted	

After the ion implantation, the samples were subjected to a tribological test. The measurements of the friction and wear coefficients were carried out in conditions of technically dry friction on an Antonpaar Nano-Tribometer NTR2 (CFM Instrument). A tungsten carbide ball with a diameter of $\phi = 0.5$ mm and 500 mN contact force was used as a counter-sample.

Next, the wear trace was measured using the Taylor Hobson Form Talysurf 50mm Intra profile measurement gauge. The measurements provided profilograms facilitating determination of the mean wear of the wear trace. The wear values were calculated from the cross-sectional areas of the

profilograms, as explained earlier [13]. In order to assess the surface of the wear track, microphotographs were taken with the SEM-EDS method using a Phenom ProX microscope.

3. Results and discussion

For preliminary determination of ion implantation, a numerical simulation was performed. Typically, numerical simulations correspond well with experimental results. Figure 1 presents the calculated (predicted) distribution of manganese ions implanted at energy $E = 175$ keV and a fluence of $D=1 \times 10^{17}$ Mn^+/cm^2 into Stellite 6 and vacancies generated thereby. It is evident that the calculated range of the implanted manganese ions that does not exceed $0.15 \mu\text{m}$ and the maximum concentration of vacancies are noted at a depth of ~ 0.06 to $0.08 \mu\text{m}$.

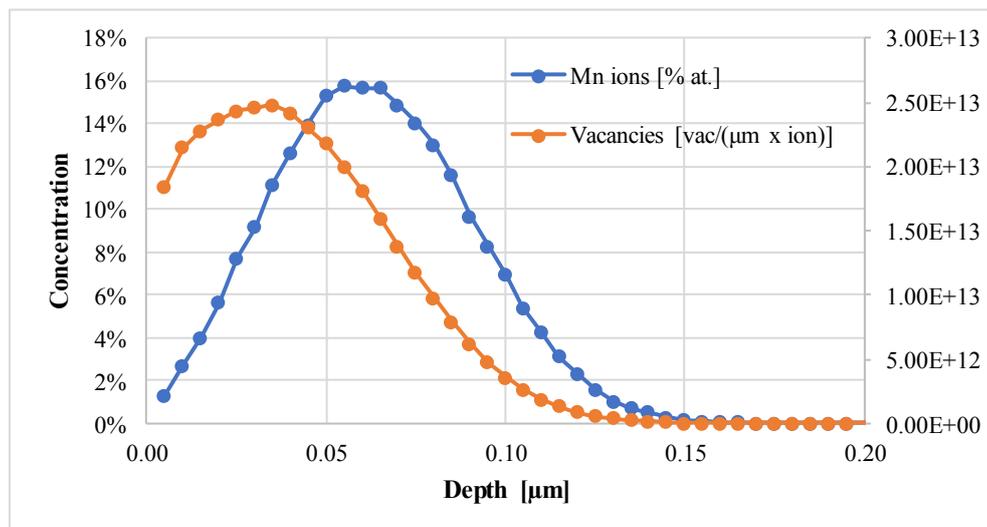


Figure 1. Calculated distribution of manganese ions implanted at energy $E = 175$ keV and a fluence of $D = 1 \times 10^{17} \text{N}^+/\text{cm}^2$ into the Stellite 6 cobalt alloy and vacancies generated thereby

The results of friction coefficient measurements obtained in the tribological test are presented in Figure 2. This parameter was evidently reduced by the manganese ion implantation, compared to the friction coefficient of the unimplanted sample. The increase in the friction coefficient with respect to the initial value in the unimplanted sample is noted already after approx. 60 rotations. In the sample implanted at a fluence of $D=5 \times 10^{16} \text{Mn}^+/\text{cm}^2$, the reduced friction coefficient value was maintained for approx. 220 rotations. In turn, upon sample implantation at a fluence of $D=1 \times 10^{17} \text{Mn}^+/\text{cm}^2$, the friction coefficient began to increase substantially only after 500 cycles. The value was nearly 10-fold higher than in the case of the unimplanted sample. Noteworthy, the implantation with manganese ions resulted in a 10-fold longer friction working time accompanied by reduced values of its coefficient. In turn, in the case of implantation with nitrogen ions at energy 65 keV and fluences of 5×10^{16} and $1 \times 10^{17} \text{N}^+/\text{cm}^2$ in the same work conditions, the friction coefficient started to increase after 1900 and 3500 cycles, respectively [7].

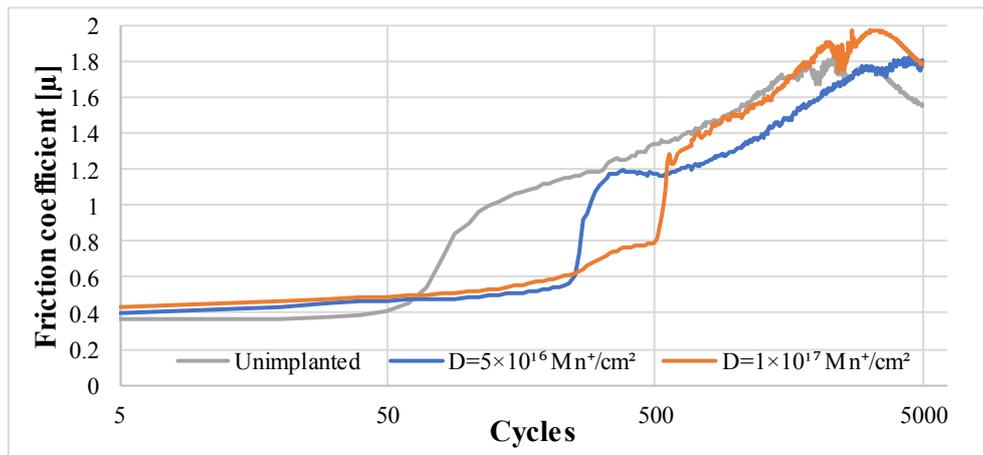


Figure 2. Results of measurements of the friction coefficient for the Stellite 6 sample before and after implantation of manganese ions

Figure 3a) and b) shows a microphotograph of the wear track. It suggests an adhesive nature of the sample wear process. As demonstrated by the analysis of the wear profile, the presence of excess material at the margins of the wear track, visible in the profiles presented in Figure 4, indicated adhesive wear.

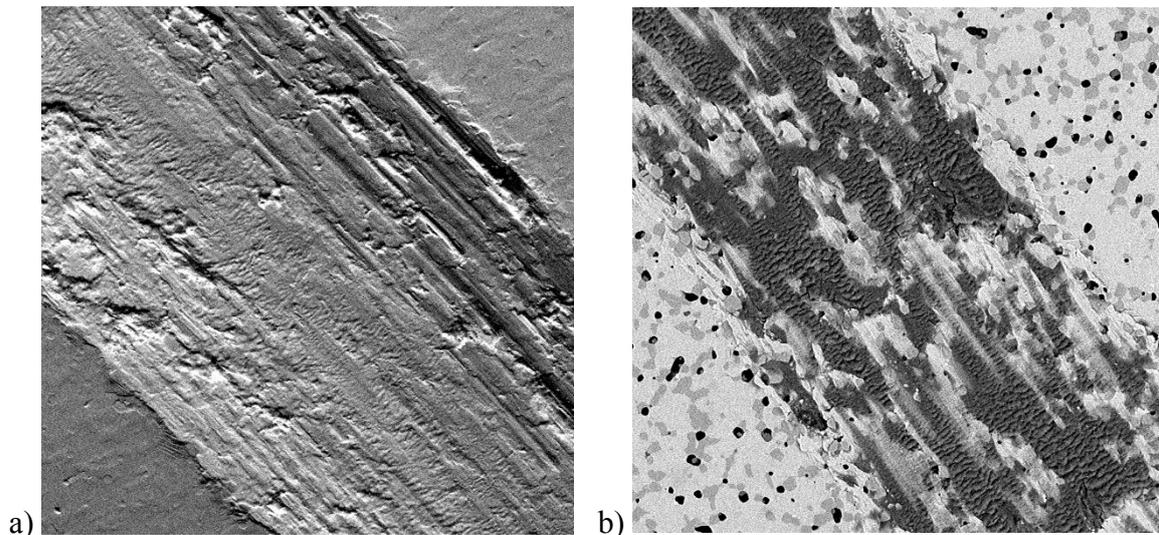


Figure 3. Microphotographs of a track fragment with magnification 2000x worn on the Stellite 6 samples implanted with a) $D=5 \times 10^{16} \text{ Mn}^+ / \text{cm}^2$; b) $D=1 \times 10^{17} \text{ Mn}^+ / \text{cm}^2$

The mean value of the cross-sectional area of the track calculated from the measured profilograms was adopted as the measure of wear. The results are shown in Figure 5.

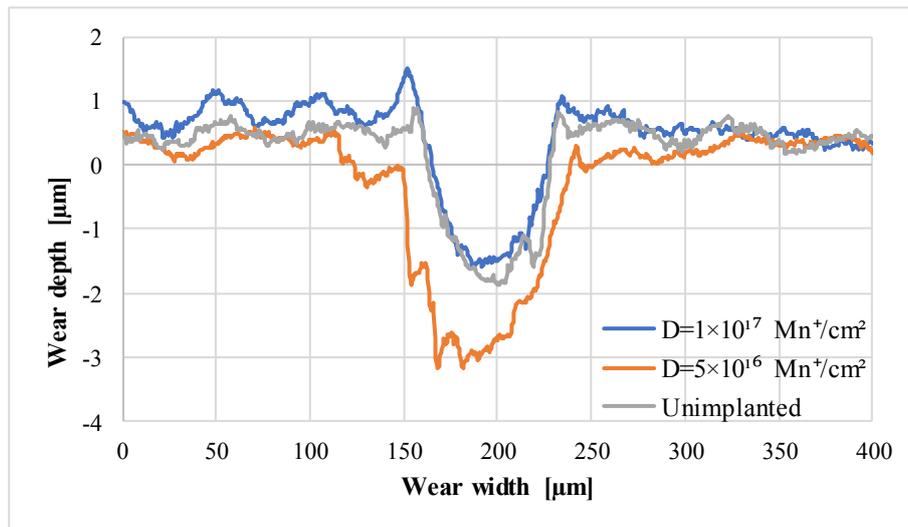


Figure 4. Profilograms of a track worn by the ball on the Stellite 6 sample in a 5000-cycle test

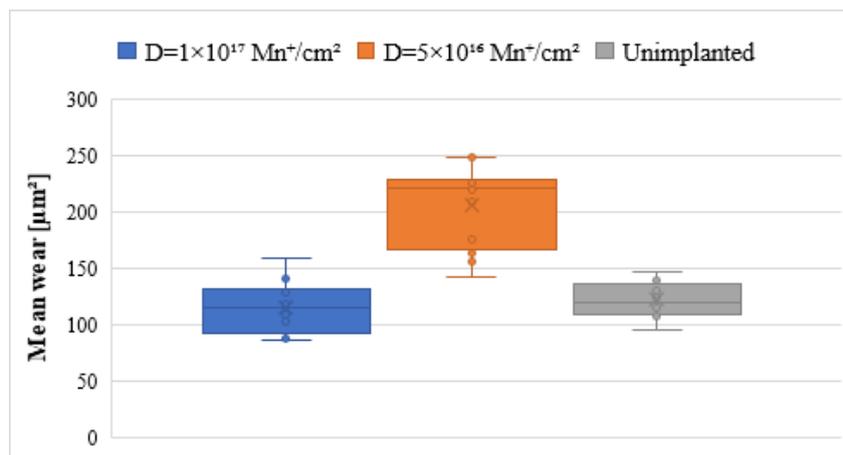


Figure 5. Mean sample wear after 5000 measurement cycles

The implantation of manganese ions induced changes in the tribological wear of the analysed samples. However, the effects of manganese doping are not as satisfactory as in the case of nitrogen ion implantation [14]. Implantation of manganese at a fluence of $D=1 \times 10^{17} \text{ Mn}^+ / \text{cm}^2$ slightly decreased the wear value, which may be related to the prolonged work time at a low friction coefficient. In turn, the manganese implantation at a fluence of $D=5 \times 10^{16} \text{ Mn}^+ / \text{cm}^2$ contributed to an increase in the sample wear, compared to the unimplanted sample. The absence of an evident increase in the tribological wear resistance upon manganese doping may be related to the fact that implanted manganese is part of the solid alloy solution [15] and does not form separate compounds, as in the case of nitrogen [16], boron [17], or carbon [18] implantation.

4. Conclusions

The tribological test carried out in technically dry friction conditions demonstrated prolongation of the working time in a manganese ion-implanted Stellite 6 sample accompanied by a reduced friction coefficient value, compared to the unimplanted sample. This period was 10-fold longer in the sample implanted at a fluence of $D=1 \times 10^{17} \text{ Mn}^+ / \text{cm}^2$; nevertheless, it was many times shorter than in the case of nitrogen ion implantation [7]. Despite the reduction of the friction coefficient, the manganese ion implantation did not induce a decline in tribological wear. The analysis of the microphotograph of wear tracks and profilograms revealed dominance of adhesive wear. Doping the structure of the Stellite 6

cobalt alloy with manganese ions can be used to change the tribological properties of valves and valve faces in internal combustion engines. Manganese implantation might improve corrosion resistance of Stellite 6, as is the case with steel and cast irons, but this will be the subject of further research.

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