

## The influence of nitrogen ion implantation on microhardness of the Stellite 6 alloy

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**Abstract.** Cobalt alloys known as Stellite used to produce or surfacing machine elements subjected to combustion gases and heat. They are used a currently in the manufacture of valves and valve seats in internal combustion engines. Because of the small thermal conductivity, stellite may not be subjected heat treatment. In order to improve the mechanical properties of cobalt alloys, samples were implanted with nitrogen ions with 65 keV energy and ion dose of  $1 \cdot 10^{16}$ ,  $5 \cdot 10^{16}$ ,  $1 \cdot 10^{17}$  N<sup>+</sup>/cm<sup>2</sup>. The influence of ion implantation on properties of strength was determined by measuring microhardness using a Vickers hardness test. The measurement results allowed to determine the increase in the microhardness of 20% with dose  $5 \cdot 10^{16}$  N<sup>+</sup>/cm<sup>2</sup> compared to the sample not implanted. Implantation of nitrogen ions can increase the strength of the valves and the valve seats having Stellite without changing the external dimensions of the final element, and without interfering with its inner structure by low-temperature of modification the surface layer.

### 1. Introduction

Current internal combustion engines competing with electric motors must be characterised by high efficiency and performance. Manufacturers strive to reduce engine displacement in order to lower the weight of the engine, simultaneously increasing their generated power. This necessitates application of light and extremely durable materials for construction of engines. The efficiency of internal combustion engines depends on their capability to generate and maintain high pressure in the combustion chamber. Besides the piston-ring-cylinder system, valves and valve seats are largely responsible for the tightness of the combustion chamber. They are elements of the valve timing in four-stroke engines designed to facilitate supply of fresh air or the air-fuel mixture to the cylinder; next, they have to ensure tightness during compression and combustion of the load and facilitate removal of exhaust gas from the cylinder [12].

Valves and valve seats are exposed to direct contact with high temperature while sealing the combustion chamber and fuel flow around the valves and valve seats in the exhaust stroke, in particular in the case of exhaust valves [9]. This results in considerable thermal loads during heat exhaust through the valves and valve seats into the cylinder head. Also, the work of the valves causes high mechanical loads associated with the impact of the surface of the valve heads against the surface of valve seats.



Additionally, exhaust valves should exhibit high thermal conductivity, heat resistance, a low coefficient of thermal expansion, and resistance to tribological wear and corrosion [11].

Damage to the contact surface between the valve face and the valve seat face induces loss of tightness of the combustion chamber, which is associated with reduction of the efficiency of the engine. To prevent their rapid wear, valves and valve seats are made of materials that are resistant to substantial changes in temperature and to cyclic impact loads related to valve opening and closure. The intake valves are usually made of low alloy steels or chromium steels in the case of highly loaded engines. In turn, exhaust valves are produced from various types of steel, e.g. ferritic-pearlitic, austenitic, and silchromesteels. Given the relatively low hardness of valves and valve faces made of austenitic steels, their strength is improved by hard facing [2], with stellite as the main welding material [1].

The name “stellite” denotes cobalt alloys with chromium, tungsten, carbon, and others. These alloys have a multiphase structure. In the microstructure, the metallographic sections of these alloys exhibit star-like regions (stella –the Latin name for “star”), hence their name. These alloys are resistant to abrasion and activity of organic acids; they are also creep-resistant and heat-resistant materials [2]. They are widely used in aviation, space, and automotive technologies as well as biomedical engineering as implant materials. Stellites are used for production of the highest quality tools and parts of combustion engines and other elements operating in extreme heat conditions. The alloy was developed in the early 20<sup>th</sup> century and its mechanical properties are still being improved.

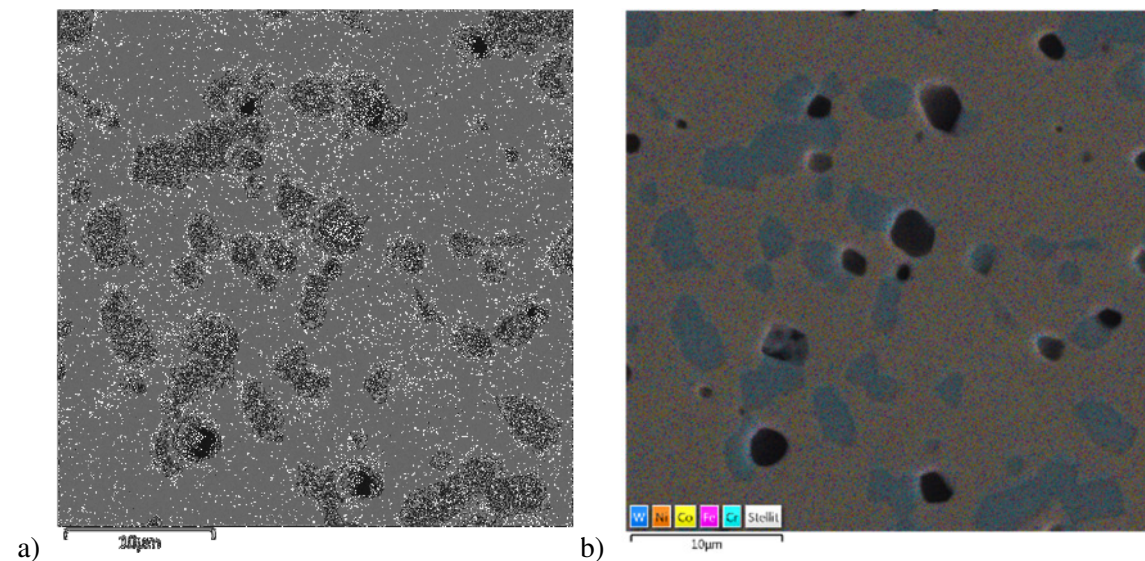
The strength properties of stellite-welded valve faces and valve seats can be improved using ion implantation. This process facilitates implantation of ions of any element into the structure of materials, which changes their tribological, chemical, and mechanical properties. There are many well-known examples of improvement of material properties by application of ion implantation described e.g. in publications [4] and [5]. A great advantage is the negligible effect of ion implantation on the dimensions of the treated element; hence, the process can be applied in the final stage of manufacturing of products that already have their final dimensions [3].

Besides improvement of tribological properties, ion implantation contributes to an increase in mechanical strength. This is associated with an increase in the microhardness of the implanted element. The implantation process is accompanied with appearance of compressive stresses and inclusions of nitrides, carbides, and borides. The implantation-induced hardening process depends on the type and dose of implanted ions and the temperature of the implanted material [7]. It has been proven that the increase in the microhardness of the implanted material is a permanent change, retained even in the heating process [10].

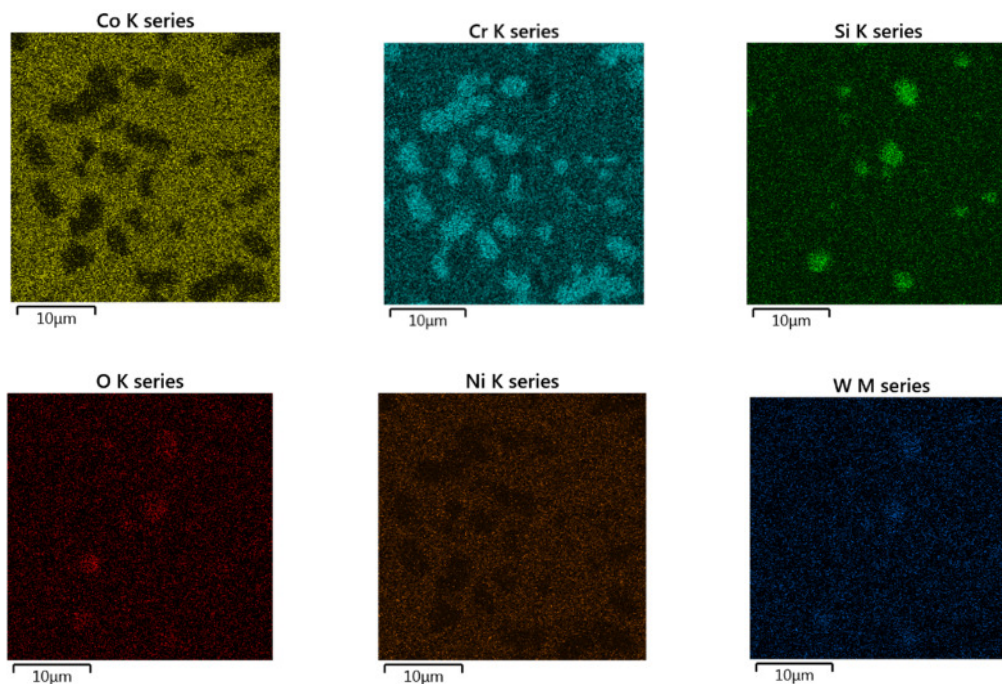
This paper presents investigations of the effect of nitrogen implantation on the microhardness of a selected stellite type.

## **2. Characteristics of the material and research methodology**

Given the multiple applications of stellite as a material for construction of valves and valve faces, this material was chosen for analysis and assessment. 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  $\phi 25$  mm-diameter rod. Sample surfaces intended for the analysis were polished in order to achieve a roughness value of  $R_a=0.01$ .



**Figure 1.** Microphotograph of the sample surface (a); analysis of the content of the main elements on the sample surface (b).



**Figure 2.** Contents of elements exhibiting the highest heterogeneity of distribution per unit area of the sample surface.

After preparation of the samples, microphotographs of their surfaces were taken with a scanning electron microscope TESCAN Vega 3LMU. The sample surface topography is shown in Figure 1a, and Figure 1b shows the content of the major alloy components. The microphotographs reveal a mosaic and heterogeneous structure characteristic for stellite. The heterogeneous distribution of the alloy components is shown in Figure 2.



The samples were subjected to the ion implantation process. Nitrogen was the implanted element. The implantation was carried out evenly over the entire surface of the sample at energy 65 keV. The dose of the implanted ions varied between the samples; the values of the fluences of the implanted nitrogen ions are presented in Table 1.

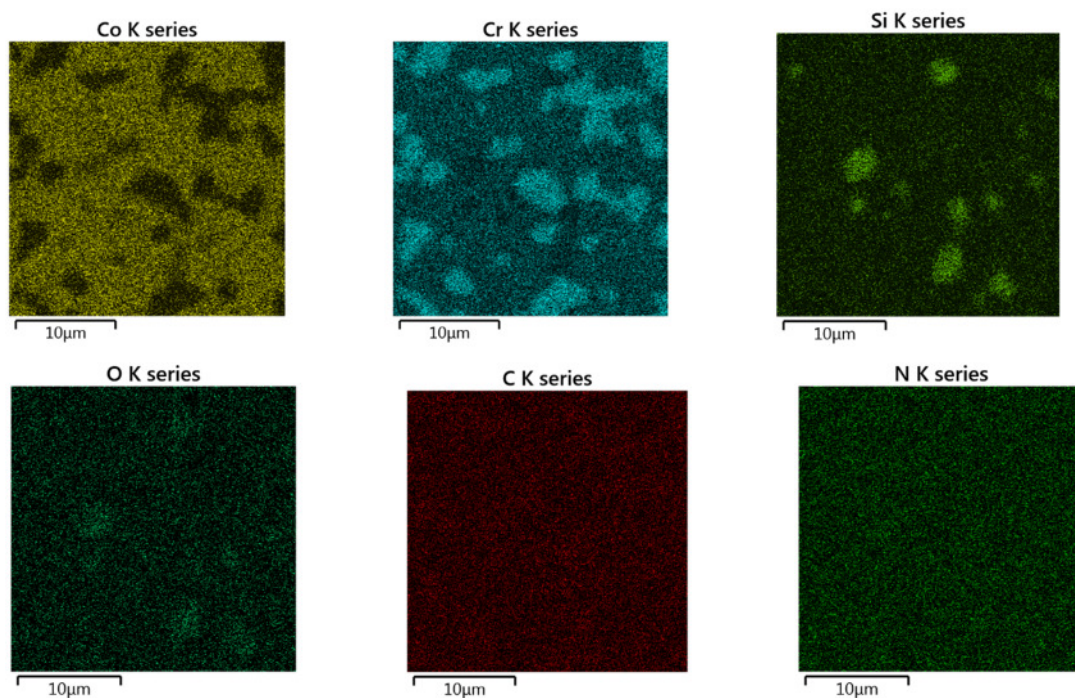
**Table 1.** Fluences of the implanted ions for individual samples.

Sample	Fluences of implanted ions (N <sup>+</sup> /cm <sup>2</sup> )
S6.1	$1 \cdot 10^{16}$
S6.2	$5 \cdot 10^{16}$
S6.3	$1 \cdot 10^{17}$
S6.4	unimplanted

After ion implantation, the samples were again analysed under the scanning electron microscope and next microhardness was assessed. The measurement was performed using a microhardness meter FM-800 from Future-Tech. Hardness was assessed with the Vickers method, and the load of 5g (0.049 N) was applied. A microhardness value of HV<sub>0.005</sub> was determined based on the measurements. The implanted samples and the unimplanted sample were analysed in order to compare the microhardness results.

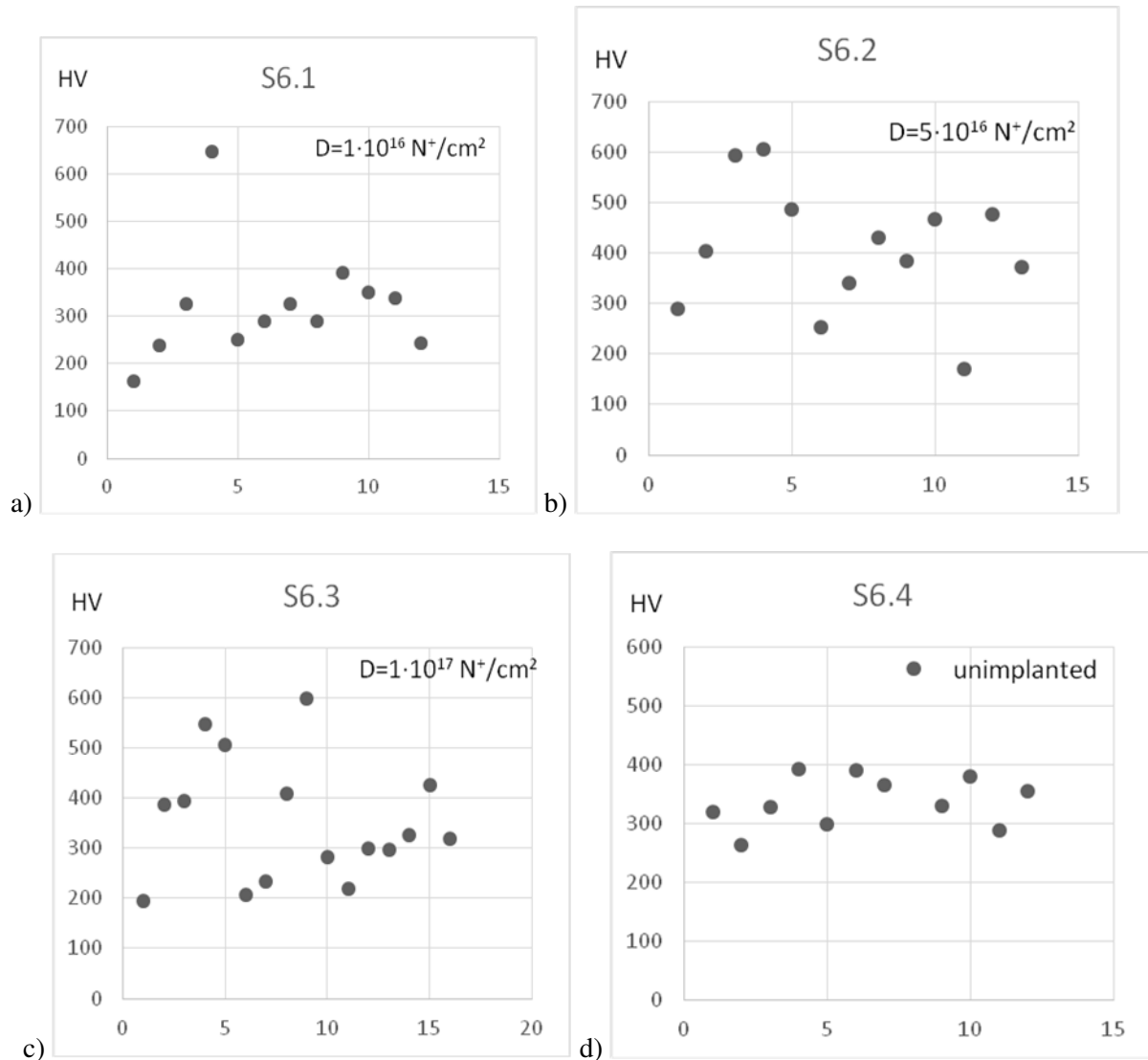
### 3. Results and discussion

The reassessment of the surface structure revealed that the distribution of the implanted nitrogen ions was uniform over the entire surface (Figure 3), in contrast to the other alloy components.



**Figure 3.** Density of elements per unit area of the analysed sample after nitrogen ion implantation at energy 60 keV and a fluence of  $5 \cdot 10^{16}$  ions/cm<sup>2</sup>.

The implanted samples were analysed for microhardness. Several measurements were carried out to obtain a reliable result. The results of each measurement are shown in Figure 4.



**Figure 4.** Results of measurements of microhardness for individual samples

There is a noticeable dispersion of the values of microhardness assessed at different sites on the sample surface (Figure 4). This is related to e.g. the different contents of elements contained in the alloy in the different fragments of the sample. The varying microhardness is a result of the differences in the contents of alloy and structural components in the measured areas. In the analysed samples, the chromium, molybdenum, or tungsten solid solution in cobalt enhances the dispersion of hard carbides (primarily  $\text{Cr}_7\text{C}_3$ ), which determine the (macroscopic) hardness of the alloy.

During the implantation process, the microhardness of surface sections, which exhibited high hardness in the basic unimplanted material, was increased. The microhardness of weaker fragments exhibited a lower increase, hence the increasing coefficient of variation of the results.

The analysis of the results obtained indicated that some measurements for samples S6.1 and S6.4 (Figure 1a, 1d) apparently deviated from the other values. To determine whether these measurement points were significant for the results of the investigations, the results were analysed taking into account

the  $3S_x$  criterion. To this end, a mean value of the measurement results was established using equation (1), disregarding the overestimated value.

$$\bar{x} = \frac{1}{n} \sum_{k=1}^n x_k \quad (1)$$

In the equation,  $\bar{x}$  denotes the mean value and  $k=1 \dots n$  are values of each measurement in the series. After calculation of the mean value from all the measurements for each sample, equation (2) was used to calculate the standard deviation  $S_{\bar{x}}$ . Since the number of the measurements was greater than 10, a formula for calculation of the standard deviation from the mean value of Gaussian distribution was used.

$$S_{\bar{x}} = \left( \frac{\sum_{k=1}^n (x_k - \bar{x})^2}{n(n-1)} \right)^{\frac{1}{2}} \quad (2)$$

To meet the  $3S_x$  criterion the analysed measurement results must be within the range defined as (3)

$$\bar{x} - 3S_{\bar{x}} < k < \bar{x} + 3S_{\bar{x}} \quad (3)$$

Based on (3), it was found that the 647 HV value for sample S6.1 was not within the acceptable range. Similarly, the 563 HV value for sample S6.4 was discarded. The mean values of microhardness measurements for each sample as well as standard deviations and coefficients of variation are shown in Table 2.

**Table 2.** Averaged results of microhardness measurements for each sample

	Implanted ion fluence ( $N^+/cm^2$ )	Mean HV value	Standard deviation	Coefficient of variation (%)
S6.1	$1 \cdot 10^{16}$	292.02	64.02	22
S6.2	$5 \cdot 10^{16}$	405.75	125.33	31
S6.3	$1 \cdot 10^{17}$	353.13	122.13	35
S6.4	unimplanted	337.15	43.31	13

The highest coefficient of variation, i.e. 35%, which corresponds to an average variation, is noted in the sample implanted with the highest ion fluence. The lowest coefficient of variation was obtained for the unimplanted sample. There is a clear correlation between the coefficient of variations calculated for the measurements and the fluence of the implanted ions. The coefficient of variation increased with the increase in the ion dose.

As indicated by the results presented in Table 2, the ion implantation process had a positive effect on the value of microhardness in the analysed samples. The microhardness of the sample implanted with the  $1 \cdot 10^{16} N^+$  fluence was lower than that of the unimplanted sample. In the case of ion implantation at fluences of  $5 \cdot 10^{16}$  and  $1 \cdot 10^{17}$ , the microhardness value increased by 20% and 5%, respectively.

#### 4. Conclusions

Cobalt-based alloy steels, referred to as stellites, are widely used for improvement of the strength of valve faces and valve seats in internal combustion engines. They exhibit high resistance to mechanical damage as well as acid- and heat-resistance. Application of ion implantation contributes to an increase

in the average microhardness of stellite. Nitrogen implantation at a fluence of  $5 \cdot 10^{16} \text{ N}^+/\text{cm}^2$  proved the most effective, as it increased the mean microhardness of the sample by 20%, compared with the unimplanted sample. The structure of the stellite alloy largely differentiates the values of surface microhardness depending on where measurements are performed. This phenomenon is enhanced by ion implantation. Besides enhanced microhardness, ion implantation improves the tribological [6] and chemical [8] properties of implanted materials.

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