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NANOINDENTATION STUDY OF CHROME LAYER

Maroš Eckert[1*] – Michal Krbaťa[1]

[1]Design and Special Technology Department, Faculty of Special Technology, Alexander Dubcek University of Trencin, Ku kyselke 469, 911 06 Trencin

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Abstract:

The article focuses on the analysis of chromium layers applied in various companies on the base material in the form of a tube of AISI 304 material. The measurement of the thickness of the chromium layer was performed by optical microscopy on samples formed by cross section. The quality of the chromium layer was evaluated using two different methods of measuring hardness. One was the classical method of measuring microhardness (Hv0.1) from the surface part of chromium. The second method was nanoindentation analysis, in which the nano-hardness was measured along the thickness of the chromium layer. The results show that the surface hardness has increased more than 3-fold by using a chromium layer. It has also been shown that a layer with greater thickness does not show the greatest microhardness. From the nanoindentation results, it was confirmed that the layer with the highest surface hardness also shows the highest nanoindentation hardness after the layer thickness, and this hardness decreases in the direction away from the surface of the base material in all layers.

1 Introduction

The rapid development of materials physics and its successful application in various industries has led to an increase in requirements for the study of the mechanical properties of thin films. These are quantified, inter alia, by mechanical quantities such as hardness, modulus of elasticity, fracture toughness, stress, viscoelastic parameters, ductility, creep or stiffness. The most used method for the study of local mechanical properties is nanoindentation - indentation with penetration depth in the nanometer scale. This is a relatively simple method, which consists in injecting a material with known mechanical properties with a known force into a material whose mechanical properties are unknown, as shown in Figure 1.5. The advantage is that it is a non-destructive method, and it is possible to determine the mechanical properties of a wide range of materials such as metals, ceramics or alloys [1]. Methods based on measuring the contact area from residual indentation have been used in the past to study mechanical properties. However, since the nanoindentation is performed with small loads, the resulting residual area is very small. That is why it was necessary to replace the light microscope, electron microscope or microscope with a scanning probe, which would greatly complicate the measurement. For this reason, the DSI (Depth-sensing indentation) method was developed, which is based on recording the instantaneous values of the applied force and the depth of indenter formation, from which the contact area can be calculated. The

* Corresponding author. Tel.: +421 32 7400 246
E-mail address: maros.eckert@tnuni.sk

measured dependence of the applied force L on the penetration depth h is known as the load-depth curve. Nanoindentation analysis began to be significantly applied in determining the hardness and mechanical properties of thin films, where measurement by standard methods would not be possible. An example of such a layer is electrolytic chromium plating. Chromium is a blue-white and shiny metal resistant to corrosion in most environments. Mainly for its resistance to external influences together with its aesthetic appearance, it is widely used as the last finishing operation for the surface treatment of metal parts [2]. In general, there are two types of chromium plating, namely decorative, in which the thin coating serves as a glossy and durable surface treatment. The second type is industrial or hard chromium, in which it uses a chromium coating for its advantageous properties such as resistance to heat, wear, corrosion and erosion, abrasion and low coefficient of friction. The difference between decorative and hard chrome is not only in the purpose of its use, but also in the different thickness of the chrome layer. In the case of decorative chromium, this layer ranges from 0.5 to 2 μm, in the case of hard chromium, the standard layer thickness is from 10 to 250 μm [3]. The use of hard chromium is used not only on steel, but preferably also on other metallic materials to form a durable surface layer [4]. Electrolytic chromium plating is an important means of extending the life of all types of metal parts that are exposed to wear, friction, abrasion, and corrosion. Such components may have protected functional surfaces with a chromium layer, whereby after wear of such surfaces it is possible to re-form a chromium layer which either immediately or after further processing meets the original properties and tolerances. Because hard chromium has a low surface energy, it is often used on sliding or rotating parts of motors, pumps, compressors and hydraulic or pneumatic piston rods [5]. Another advantage is its high corrosion resistance, which makes it widely used to protect the surfaces of parts exposed to various highly corrosive environments [6]. Another advantage is that the chromium plating process is relatively cold and can therefore be used to increase the hardness of the surfaces of very small parts without the risk of thermal deformation or a change in the properties of the base material. Hard chromium coatings achieve a hardness in the range of 56 to 74 HRC depending on the electrolytic bath used. In most cases, the greater the hardness, the longer the life of the component. Therefore, it is best to use a plating process that provides the highest hardness. A component with a hardness of up to 70 HRC will provide the longest possible service life. Decorative chrome plating provides the same hardness values as industrial chromium, but these tend to be harder only for a thicker layer of chrome. For the surface of the component to reflect only the properties of the metallic chromium and not the base material, the layer thickness must be at least 50 μm. However, all types of chromium plating tend to lower the fatigue limit of components [7].

2 Material and Methods

2.1 Experimental material

Stainless steel AISI 304 was used as a substrate material supplied in the form of cold drawn tubes tempered to 850 MPa. The outer diameter of the pipe 12.3 mm was then ground to a diameter of 12 ± 0.005 mm and the same roughness value max. Rz = 3 μm, inner diameter was 9.3 mm. Nominal chemical composition is in Tab. 1. Electroplated hard-chrome coatings with a thickness of min. 30 μm were applied to the outer surface of the pipe in three different industrial plants according to the specific company procedure and the experience of a particular company. However, in order to achieve a uniform layer, the tubes had to be placed during chromium plating in a preparation which rotated in an electrolytic bath for about 1 rev / min. The chromium layers were designated as A, B, and C. 3 tubes were selected from each type of chromium, which were cut to a length of 30 mm, each from the center of the tube. Subsequently, the surface microhardness was measured on them using an AFFRI Microhardness DM2D device at a load of 100 mN (Hv0.1). 10 indents were performed on each sample. The cross-sectional thickness of the chromium layer on the polished and etched samples was determined by optical microscopy.

Tab. 1 Chemical composition of AISI 304 stainless steel tube used as a substrate material

Element	Cr	Ni	Mn	Mo	Si	C	Co	P	S	Cu	V	Fe
Wt %	17.35	8.52	0.98	0.18	0.45	0.03	0.21	0.02	0.003	0.19	0.08	Re-main

2.2 Nanoindentation study

Nanoindentation tests were performed by quasistatic nanoindentation method on the device Bruker Hysitron TI-950. Quasistatic nanoindentation has become the standard technique used for nanomechanical characterization of materials. A quasistatic nanoindentation test is performed by applying and removing a load to a sample in a controlled manner with a geometrically well-defined probe. During the nanoindentation a force is applied by the transducer and the resulting displacement is observed to produce a traditional force versus displacement curve (Fig. 1). Hysitron measures the force and displacement of the nanoindentation probe with a unique patented three-plate capacitive transducer design. This transducer design provides an unsurpassed noise floor and ultra-low working force.
The nano hardness (H) was measured in the cross section of the specimen along the thickness of the chromium layer up to the substrate material. Two columns of dots with a spacing between indents of 5x15 µm were measured on each sample. The load parameters were the same for each measurement, namely the trapezoid load curve with a maximum load of 1000 µN. To obtain the hardness with negligible creep effect, experiments were carried out under the single loading and unloading cycle with a 2 second hold at the maximum load [8]. A diamond cube corner tip with an included angle of 90 ° and a radius of curvature of 40 - 100 nm was used as an induction tip.

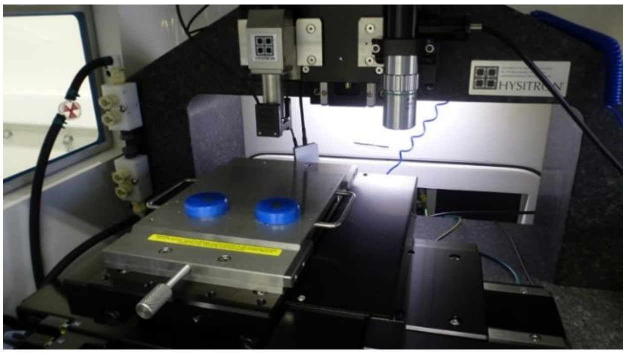
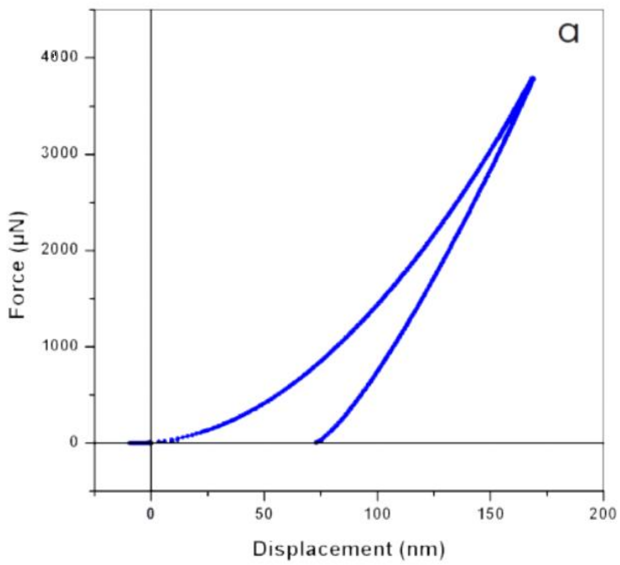


Fig. 2 Nanoindentor measuring chamber with sample locations (blue disks) [9]

3 Results and Discussion

In Fig. 3 are cross-sectional images of individual coatings, which were also used to measure their thickness. The largest thickness was in the case of coating B, where it reached values of up to 45 µm. The quality of the surface layer is best in the case of coating A, where there are the least surface and volume cracks



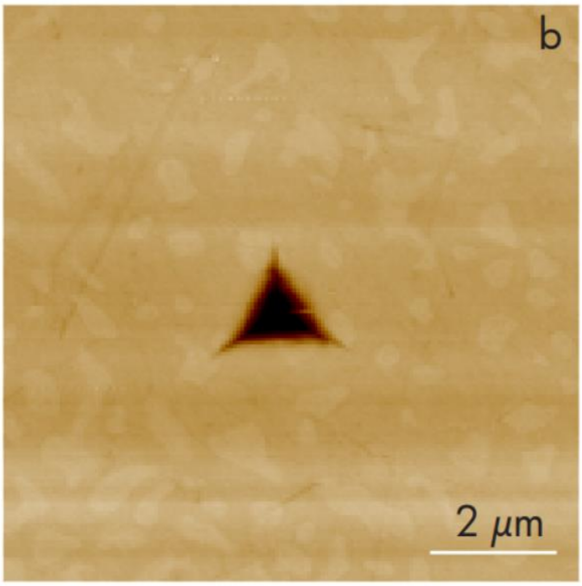
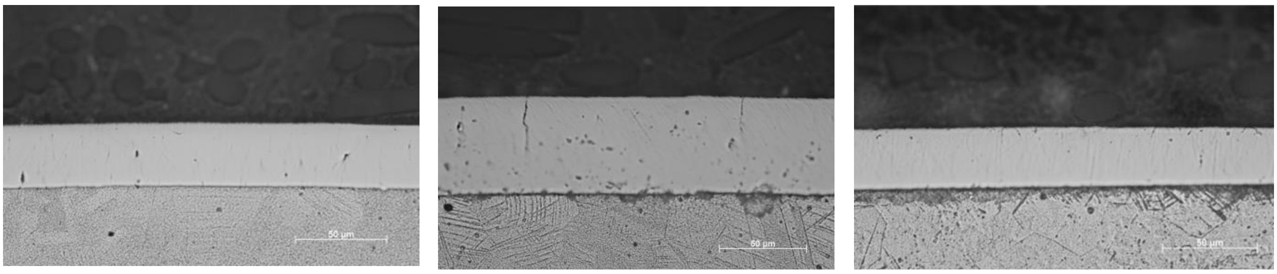


Fig. 1 a) *Typical force versus displacement curve during nanoindentation test, b) SPM image of quartz surface after quasistatic indentation showing residual indent impression*

Also the microhardness of the surface layer was the largest in the case of coating A and reached values up to 1178 Hv0.1. The lowest microhardness values were measured in the case of coating B, although this layer was the thickness, from Fig. 3 can be seen to contain the most internal pores and cracks, which can cause lower microhardness values. The microhardness of the substrate material is about 3 times smaller than the hardness of the chromium layers. All results of layer thickness and microhardness of individual layers and base material are given in Table 2. The position of the individual nanoindentation indent for each coating is shown in Fig. 4. On each coating, 21 indents were created in two columns with a gap between the columns of 15 µm and between the rows of 5 µm. The smoother chrome layer is always in the picture on the top, the base material on the bottom. Nanoindentation hardness of individual points was determined from load-displacement curves as [8, 10]:

$$H = \frac{P}{A_C} \tag{1}$$

where H is nanohardness, P is maximum load and AC is contact area [11, 12, 13]. The course of nanohardness after the thickness of individual coatings is shown in Fig. 5. Coating A shows the highest nanohardness, as was the case with microhardness. For coatings B and C, the course and values of nanohardness are similar, but in contrast to microhardness, where coating B was especially soft, it is harder in individual layers than coating C. All samples show a slight strengthening of the layer along its thickness. This was followed by a jump, which represents the difference in nanohardness between the chromium layer and the base material. In all cases, it had almost the same value, which was of course expected. From these results, it can be also seen that coating B is thicker than the other two layers.

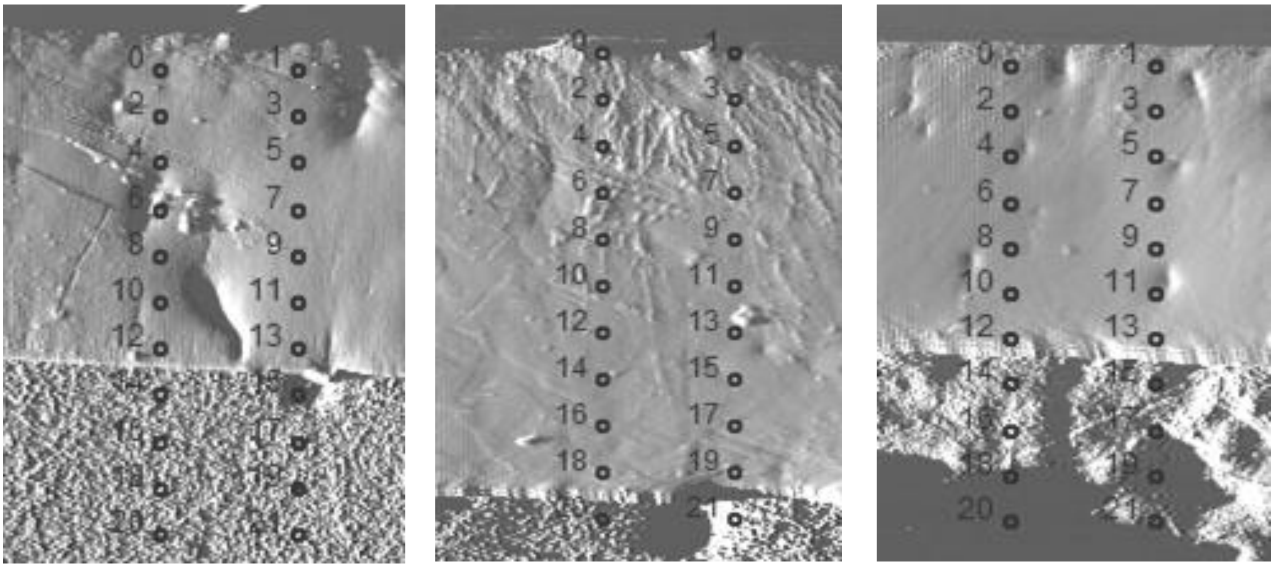


a) *b)* *c)*

Fig. 3 Cross-section of (a) coating A, (b) coating B, (c) coating C

Tab. 2 Specimens coating thickness and roughness

Coating	Coating thickness [µm]	Microhardness [$Hv_{0,1}$]
A	34.56 ± 5.12	1178.49 ± 244.40
B	45.12 ± 12.98	933.86 ± 89.70
C	32.67 ± 7.55	965.27 ± 118.16
Substrate	-	319.91 ± 169.44



a) *b)* *c)*

Fig. 4 Position of individual indents in the thickness of the chromium layer, a) coating A, b) coating B, c) coating C

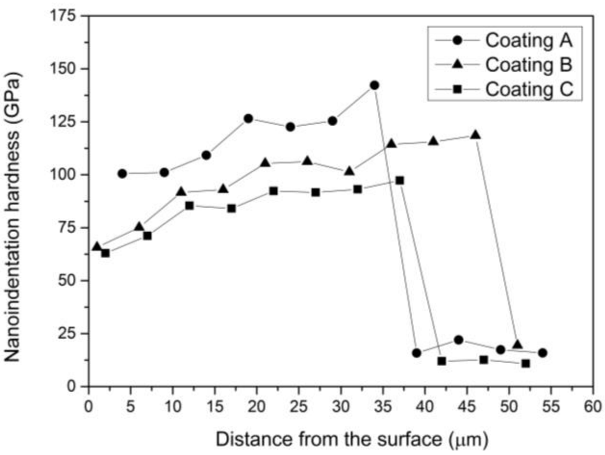


Fig. 5 Nanoindentation hardness of coatings through the thickness of coatings

4 Conclusion

This work was focused on determining the micro and nano hardness of different chromium layers on the same base materials AISI 304. From the results of microhardness it can be stated that the chromium layer increased the surface hardness by more than 3 times. In the case of the microhardness measured at the surface of the layer, it can be concluded that the thickness of the chromium layer did not affect the hardness, since the smallest hardness value was measured at the thickest layer, on the contrary

Measurement of the nanoindentation hardness over the layer thickness showed that it reflected to some extent the results of the surface hardness, and in the case of the chromium layer A layer the two highest hardnesses were achieved. Furthermore, it was found that the hardness of the chromium layer decreases with increasing thickness and is greatest at the surface of the base material.

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References

[1] Malzbender, J., den Toonder, J.M.J., Balkenende, A.R., de With, G.: *Measuring mechanical properties of coatings: a methodology applied to nano-particle-filled sol–gel coatings on glass*. Materials Science and Engineering: R: Reports. 36 (2002), p. 691–695.

[2] Schlesinger, M. Y., Paunovic, M. *Modern Electroplating*. Hoboken, N.J.: Wiley, 2010.

[3] Plating Resources. *DuraChrome Hard Chromium Plating*. Cocoa, Florida, 2006.

[4] Peciar, M., Fekete, R., Peciar, P.: *Agglomeration technologies of processing powder wastes*. In Solid State Phenomena. 244 (2016), p. 121-129.

[5] Fekete, R., Peciar, M., Peciar, P.: *Axiálny extrudér s rotujúcou hlavou (Axial extruder with*

rotatable die head): patentový spis 5014-2014. ÚPV SR 2015. PCT/IB2015/052668, WO2015159198A1.

[6] Peciar, P., Macho, O., Fekete, R., Peciar, M.: *Multifunkčný granulátor (Multifunctional granulator):* patentový spis 5047-2015. ÚPV SR 2017, PCT/IB2016/057081, WO2017089976A1.

[7] Lausmann, G. A.: *Current Industrial Practices Electrolytically Deposited Hardchrome*. Surf. Coating Technol., 86 (1996), p. 814-820.

[8] Oliver, W.C., Pharr, G.M.: *An improved technique for determining hardness and elastic-modulus using load and displacement sensing indentation experiments*. J. Mater. Res., 7 (1992), p. 1564-1583.

[9] Majerík, J., Barényi, Sedlák, J., Kusenda, R., Eckert, M.: *Microstructural analysis of examined 33NiCrMoV15 steel and investigation of its nanomechanical properties after machining*. Manufacturing Technology, 20 (2020), p. 72-77.

[10] Pharr, G.M., Bolshakov, A.: *Understanding nanoindentation unloading curves*. J. Mater. Res., 17 (2002), p. 2660-2671.

[11] Zeng, Z., Wang, L., Chen, L., Zhang, J.: *The Correlation between the Hardness and Tribological Behaviour of Electroplated Chromium Coating Sliding Against Ceramic and Steel Counterparts*. Surf. Coating Technol., 201 (2006), p. 2282-2288.

[12] Podgornik, B., Massler, O., Kafexhiu, F., Sedlacek, M.: *Crack Density and Tribological Performance of hard-chrome coatings*. Tribology International, 121 (2018), p. 333-340.

[13] Chen, S.: *The Coating Layer Structure of Commercial Chrome Plates*. Jour. of Electron Spectros. and Related Phen., 202 (2015), p. 1-6.