THE INFLUENCE OF ISOTHERMAL ANNEALING ON DEGRADATION OF MECHANICAL PROPERTIES OF HOMOGENEOUS WELDMENT OF THE 9Cr-Mo STEEL

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Keywords: 9Cr-Mo creep-resistant steel, homogeneous weldment, hardness, impact toughness, fracture mode

1. Introduction

The weldments of 9Cr-Mo martensitic/ferritic creep-resistant steels are commonly used in construction of steam boilers of power generating plants [1,2]. It is well-known that the microstructure of individual regions of weldments, namely weld metal (WM), fusion zone (FZ) and heat-affected zone (HAZ), depends on location (distance from weld center-line) and reached peak temperature during welding. The thickness of HAZ basically depends on heat input and thermal conductivity of base material (BM). The weldments of 9Cr-Mo steels require the application of post-weld heat treatment (PWHT), typically in the range from 720 to 760 °C. Requirements on the weldments of creep-resistant steels include besides their high creep-strength also suitable hardness and sufficient toughness [3].

The aim of present work is to study the influence of isothermal annealing on the mechanical properties and fracture behaviour in the individual locations of homogeneous weldment of the 9Cr-Mo „CB2“ steel.

2. Experimental material and procedure

Two bulk pieces (wall thickness 92 mm) of the weldment of CB2 steel were obtained in the Post Weld Heat Treatment (PWHT) state (730 °C / 24 h / furnace cool) within the framework of COST Action 536 project. The chemical composition of CB2 steel BM and WM is shown in Tab. I. The weldments of 9Cr-Mo steels require the application of post-weld heat treatment (PWHT), typically in the range from 720 to 760 °C. Requirements on the weldments of creep-resistant steels include besides their high creep-strength also suitable hardness and sufficient toughness [3].

The aim of present work is to study the influence of isothermal annealing on the mechanical properties and fracture behaviour in the individual locations of homogeneous weldment of the 9Cr-Mo „CB2“ steel.

3. Results and discussion

Typical microstructural gradient of the studied weldment is shown in Fig. 1.

With respect to the existence of microstructural gradient, the hardness profiles were determined to characterize the individual regions in all experimental states (see Fig. 2).

The highest hardness in the coarse-grained HAZ region next to WM can be attributed to the presence of „fresh“, carbon-enriched martensite, formed during the
welding. The lowest hardness was measured in the intercritical HAZ close to BM as a result of "double-tempering effect" of original martensite and back transformation of unsaturated austenite to the fine-grained ferrite.

Apart from hardness tests, Charpy V-notch impact toughness tests (CVN) were carried out (see Tab. II).

Table II
Results of CVN impact toughness tests

<table>
<thead>
<tr>
<th>Notch location</th>
<th>Average CVN [J·cm⁻²] (material state / testing condition)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(AR / RT)</td>
</tr>
<tr>
<td>BM</td>
<td>48</td>
</tr>
<tr>
<td>HAZ</td>
<td>40</td>
</tr>
<tr>
<td>WM</td>
<td>67</td>
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</table>

The coarse-grained HAZ region exhibits the lowest CVN values in all experimental states which can be ascribed to the presence of coarse prior austenite grains in this location. In contrast, the highest CVN values were measured in WM due to the presence of oxide inclusions which promote the formation of dimples during deformation. Compared to the AR state, CVN values rapidly decrease after the long-term annealing which can be attributed to the thermal degradation of microstructure.

However, the small differences in CVN values between the annealed states are caused by the similar level of their microstructure degradation.

Fig. 3 compares the fracture characteristics of CVN samples with notch in WM after RT impact test, in the AR state (Fig. 3a) and after the annealing (Fig. 3b).

The fracture in Fig. 3a can be characterized by a presence of cleavage facets and ductile dimples. In contrast, the fracture in Fig. 3b is almost fully formed of transgranular cleavage.

Fig. 4 compares the fracture characteristics of CVN samples in the annealed state after the impact test at 100 °C with notch location in WM (Fig. 4a) and in coarse-grained HAZ (Fig. 4b). The fracture mode in Fig. 4a is characterized by ductile dimple tearing. Such manifestation of fracture behaviour at increased temperature can be generally related to the thermally enhanced plasticity via increasing mobility of free dislocations in the lattice. The appearance of fracture surface of the CVN sample tested at 100 °C indicates that the impact test was carried out above the brittle-to-ductile transition temperature (BDTT). However, the brittle character of fracture from the HAZ region (Fig. 4b) tested also at 100 °C indicates the strong influence of local thermal degradation on the resulting mechanical behaviour.

4. Conclusion

The determination of local mechanical properties such as hardness and impact toughness of the studied welded joint of CB2 steel revealed significant differences in the individual locations in different experimental states after thermal exposure.

The present work was supported by the European international collaborative project COST Action 536 and the Slovak national project VEGA 2/0128/10.

REFERENCES


This paper deals with characterization of hardness (HV10), impact toughness (CVN) and fracture behavior in the individual locations of thermally exposed weldment of 9Cr-Mo creep-resistant steel. The variation of mechanical properties strongly depends on the duration of thermal exposure and testing temperature. The observed differences in fracture characteristics of the individual regions and material states correspond well with their different local mechanical properties.
INDENTATION TOUGHNESS OF Si$_3$N$_4$ REINFORCED WITH GRAPHENE PLATELETS

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Keywords: ceramic composites, GPLs, toughness

1. Introduction

Recently graphene, a monolayer of sp2-hybridized carbon atoms arranged in a two-dimensional lattice, with exceptional thermal, mechanical, and electrical properties has attracted tremendous attention. This material exhibits exceptional electrical, mechanical and thermal properties. Recently a new cost effective, high quality carbon based filamentous was developed in the form of graphene platelets (GPL) also called graphene nanoplatelets (GNP) or multilayer graphene nanosheets (MGN), which is an alternative to the more expensive nanotubes and monolayer graphene. Walker et al. applied graphene to enhance the toughness of bulk silicon nitride ceramics. They found that the ceramics fracture toughness with 1.5% graphene increases from 2.8 MPa m$^{0.5}$ to 6.6 MPa m$^{0.5}$. The aim of this contribution is to investigate the influence of the addition of various kinds of graphene platelets on the fracture toughness and toughening mechanism of Si$_3$N$_4$ – GPLs composites.

2. Experimental part

Different types of GPLs/multilayer or few-layer graphene were used as reinforcement material for Si$_3$N$_4$ matrix as multilayer graphene (MLG) nanosheets prepared by mechanical milling method, commercial exfoliated graphite nanoplatelets (xGnP-M-5 and xGnP-M-25) and nano graphene platelets (Angstron N006-010-P). The specimens were processed by hot isostatic pressing (HIP) performed at 1700 °C by a two-step sinter-HIP method at 20 MPa, with 3 h holding time.

The tests of the microhardness (Leco Instruments) and hardness were performed by the Vickers indentation method at loads from 9.81 N to 150 N. The small specimen size did not allow to use standard fracture toughness test, therefore indentation fracture toughness was performed at loads of 147 N using a Vickers indenter, and the $K_{IC}$ was calculated using the Shetty equation:

$$K_{IC} = 0.0899 (H.P/4l)^{0.5}$$

where H is the hardness, P is the indentation load, 1 = c-a is the length of the indentation crack.

Serial sectioning has been used for the characterization of indented crack systems. Microfractography was used to study the fracture lines and surfaces of the specimens and to identify the fracture micromechanisms in the monolithic material and in the composites. This study was realised by SEM analysis (Jeol JSM 700).

3. Results

Fractography study showed that in the present Si$_3$N$_4$ – GPLs composites no clusters were found with globular shape and the GPLs are relatively homogenously distributed in all systems, Fig. 1a. Beside separated platelets there are often two or more platelets stuck closely together on the plane parallel with the plane of the graphene sheets, Fig. 1b.

![Fig. 1. Distribution of the multilayer graphene nanosheets in the Si$_3$N$_4$ matrix – a, stuck nanosheets – b](image)

The hardness and indentation fracture toughness of the investigated materials are illustrated in Tab. I. According to the results beside the system reinforced by multilayer graphene nanosheets all composites exhibit lower hardness in comparison to the hardness of monolith. The lower hardness of these composites compared to the monolithic material is mainly dependent on the residual porosity that remains in the material after the sintering, similar to that observed in other investigations. The highest hardness for the mentioned system can be explained by the lowest porosity and lower grain size of the matrix in comparison to the other composites and to the monolith.

All composites exhibit higher indentation fracture toughness compared to the monolith, thanks to the more frequently occurred toughening mechanisms during the crack propagation. These are very similar for all systems reinforced by different GPLs, only the frequency of their
occurrence during the crack propagation or their effectiveness in toughening process is different.

The main toughening mechanisms are: crack branching Fig. 2, crack deflection Fig. 3a,b and crack bridging Fig. 3c,d.

The origin of this mechanism is the interaction of the propagating crack and GPLs with smaller size. The length of the secondary cracks is several micron and the frequency of occurrence of this mechanism is very high.

### 4. Conclusion

The GPLs are relatively well distributed in the Si₃N₄ matrix of all systems however we often found that two or more platelets are stuck closely together. These single or multi platelets are located at the Si₃N₄/Si₃N₄ grain boundaries and are often connected with a presence of pores. The indentation fracture toughness of the composites is significantly higher compared to the monolithic silicon nitride with the highest value of 9.92 MPa m⁰.⁵ in the case of composite reinforced by multilayer graphene nanosheets. The toughening mechanisms were similar in all composites in the form of crack deflection, crack branching and crack bridging.

### Would like to thank

Ľubomír Čaplovíč, Karol Iždinský and Jerzy Morgiel for the help with SEM and TEM measurement. The work was supported by NANOSMART, Centre of Excellence, SAS, by the Slovak Grant Agency for Science, grant No. 2/7914/27 by the APVV 0171-06 and LPP 0203-07 and by the KMM-NoE EU 6FP Project.

### REFERENCES


The aim of the present contribution is to study the influence of graphene platelets additives on the fracture toughness of Si₃N₄-graphene system. The experimental materials were silicon nitride with various types of graphene additives, multilayer graphene, exfoliated graphene nanoplatelets and nano graphene platelets. The indentation toughness was measured using indentation fracture method and was calculated using the Shetty’s equation. According to the result the composites exhibit higher fracture toughness in comparison to the monolithic material. The highest fracture toughness was found in the case of composite with multilayer graphene platelets. Scanning electron microscope was used for the characterization of toughening mechanisms.

### Table I

<table>
<thead>
<tr>
<th>Composition of investigated materials [wt%]</th>
<th>Type of GPL additives</th>
<th>Hardness HV1 [GPa]</th>
<th>Toughness KIc [MPa m⁰.⁵]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₃N₄ Al₂O₃ Y₂O₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90 4 6</td>
<td>xGnP-M-5</td>
<td>14.6</td>
<td>7.8</td>
</tr>
<tr>
<td>90 4 6</td>
<td>xGnP-M-25</td>
<td>15.1</td>
<td>8.6</td>
</tr>
<tr>
<td>90 4 6</td>
<td>Angstrom N006-010-P</td>
<td>14.6</td>
<td>8.8</td>
</tr>
<tr>
<td>90 4 6</td>
<td>Multilayer graphene</td>
<td>16.4</td>
<td>9.9</td>
</tr>
</tbody>
</table>

**Fig. 2.** Crack branching during the propagation of crack in nanographene platelets reinforced composite

**Fig. 3.** Toughening mechanisms in the form of crack bridging and branching on the fracture line
NANOINDENTATION PROPERTIES OF PHASE PARTICLES IN AUSTENITIC CAST STEEL

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Keywords: nanoindentation, microstructure, mechanical properties

1. Introduction

Austenitic cast steels assigned for operation at high temperatures are enriched with titanium or niobium mainly to improve the creep resistance or to reduce the carburising effect. Introducing niobium or titanium to 0.3%C-30%Ni-18%Cr cast steel causes the formation in the as-cast structure of niobium or titanium MC carbides instead of chromium carbides of M23C6 type. During annealing at 900 °C the MC carbides undergo transformation into an intermetallic G phase of formula Ni16(Nb,Ti)6Si7. This transformation is accompanied by the precipitation of chromium carbides of the M23C6 type, due to carbon being liberated from the MC carbides. As a result of changes caused by partial or total replacement of the chromium M23C6 carbides with simple MC carbides, the transformation of MC carbides into the G phase and secondary precipitation processes due to annealing, the complex precipitates composed of several phases appear in the alloy structure. Each of the phases has its own hardness which makes their differentiation possible by the use of microhardness or nanoindentation method.

In the recent years the nanoindentation method has become a valuable tool for the evaluation of materials mechanical properties. The method allows to determine the hardness and the Young’s modulus from the nanoindentation load displacement data. The main advantage of this method is that the load applied can be very small and therefore the dimensions of measured microstructure elements (phase, particles) can be small and it is possible to determine their individual contributions in multiphase alloys.

In the present work the changes of the microstructure 0.3C-30Ni-18Cr cast steel due to titanium and niobium additions were investigated in relation to mechanical properties of microstructure phase constituents. Nanoindentation experiments were carried out to determine the hardness and Young’s modulus of matrix and phase particles of cast steel with and without additions of Ti or Nb.

2. Material and tests

The austenitic 0.3C-30Ni-18Cr cast steel was used for investigations. The content of individual elements was varying within the chemical composition of the tested alloys and is shown in Tab. I. The investigated alloys were in the same heat treatment condition – after annealing in air at 900 °C for 500 hrs and then cooling down together with furnace.

<table>
<thead>
<tr>
<th>Alloy no</th>
<th>Ti</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td>1.00</td>
<td>0.03</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>1.84</td>
</tr>
</tbody>
</table>

The phase composition was investigated by X-ray diffraction method. Detailed analysis of XRD diffraction patterns is presented in work. The microstructure investigations were carried out with use of optical microscope, SEM and AFM microscopy.

Nanoindentation tests were performed using Nanoindenter XP with a diamond pyramidal-shaped Berkovich type indenter. The experiments were carried out by the CSM method at a constant depth of 300 nm. For each alloy a set of 100 indentations was performed. The measurements were taken on polished metallographic cross-sections of etched specimens.

3. Results and discussion

Microstructure

Austenite matrix and phase precipitates compose the microstructure of tested alloys. Titanium and niobium
(alloy 2 and 3 respectively) induce the refinement of microstructure of the base cast steel (alloy 1) – Fig. 1. Parameter SDAS (secondary dendrite arm spacing) is lower in cast steels with Nb or Ti additions.

By changing the type of solidified carbides both the elements Ti and Nb change the morphology of primary precipitates. The shape and distribution of carbides in the alloy varies depending on kind of element, as in Fig. 1. Annealing of cast steel causes the secondary precipitation processes. The small secondary precipitates are visible in the matrix of alloy 1, as in Fig. 1.

Chromium carbides of M_23C_6 type are the only precipitates in alloy 1. They form almost continuous network at boundaries of dendrites. Chromium carbides M_23C_6 are present in alloys 2 and 3 as well. Mostly they appear at the precipitate-matrix boundary, but the small precipitates of chromium carbides can also be seen in the matrix, as in Fig. 2.

The main phase constituents in alloy 2 are titanium carbides TiC and in alloy 3 niobium carbides NbC. Additionally carbonitride TiN which forms the center of TiC precipitates was found in very small quantities in alloy 2. In both alloys 2 and 3 the phase G of formula Ni_{16}Ti_{6}Si_{7} and Ni_{16}Nb_{6}Si_{7}, respectively, was also indentified. Phase G rich in silicon and nickel was found surrounding the primary precipitates of MC carbides, as in Fig. 2.

Nanoindentation

The indentations were done in the vicinity of interdendritic boundaries. The aim was to encompass the region of both the austenite matrix and eutectic carbides precipitates. Indentations of 100 points were performed with a step of 7.5 µm what gave 90 × 55 µm of measured area. Indentations were mostly located in the matrix. The indentations grid in alloy 3 is shown in Fig. 3.

The obtained load – displacement curves for alloys 1, 2 and 3 are shown in Fig. 4. The minimal load was 7 mN.

![Fig. 2. Microstructure and mapping of elements in alloy 2, SEM](image)

![Fig. 3. Indentation grid on the cross section of alloy 3](image)

![Fig. 4. Load-displacement curves in alloys 1, 2 and 3](image)
To reach the indentation depth of 300 nm the maximal load increased to about 14, 38 and 21 mN in alloys 1, 2 and 3 respectively.

The hardness value is known to be strongly dependent on the indentation depth\(^7\). To enable the values of hardness and Young’s modulus to be comparable between the alloys the constant maximal depth equal to 300 nm was chosen for nanoindentation measurements. According to ISO 14577-1 the nano range is limited to the maximum nanoindentation depth \(h_{\text{max}}\) less/equal to 200 nm (ref.\(^6,7\)). It means that the measurements in terms of depth were done on nano-micro scale. However, the maximal load of the indentations was below the value of 100 mN, which is considered as the nano force limit.

Fig. 5 shows the images of the single indentations performed in matrix and precipitates of alloys 2 and 3.

![Fig. 5. AFM and SEM images of indentations: a) alloy 3, screenshot from the optical alignment microscope of the AFM, b) alloy 2, AFM amplitude image, c) 3D surface plot of indentation in b), d) alloy 3, indentation in austenite matrix, SEM e) alloy 3, indentation in NbC carbide, SEM](image)

Fig. 6. Modulus as a function of indentation depth. Curves for precipitates and matrix in alloy 1

![Fig. 6. Modulus as a function of indentation depth. Curves for precipitates and matrix in alloy 1](image)

The curves of Young’s modulus and hardness versus displacement into surface are presented in Fig. 6–8.

![Fig. 7. Modulus vs. indentation depth curves: a) for precipitates in alloy 2, b) for matrix and precipitates in alloy 3](image)

![Fig. 7. Modulus vs. indentation depth curves: a) for precipitates in alloy 2, b) for matrix and precipitates in alloy 3](image)

![Fig. 8. Hardness curves as a function of indentation depth, alloy 3](image)

![Fig. 8. Hardness curves as a function of indentation depth, alloy 3](image)
Alloy 1, in which only two phase constituents were identified in the microstructure, was the first alloy analysed on the basis of the parameters obtained from nanoindentation test for individual precipitates in alloys. Taking into account the fact that the number of indentations performed in the matrix was several times higher than the number of indentations in precipitates, the modulus (E) and hardness (H) of the matrix were the first parameters, which were determined, Fig. 6, Tab. II. The highest values of E and H were attributed to chromium carbides. As the number of indentations was small, only the approximate values of E=300 GPa and H=10 GPa were determined. The values of modulus and hardness between the matrix and carbides were attributed to indentations taken partly from the matrix and partly from the carbides, Fig. 6.

The values of E and H for the matrix of the investigated alloys are shown in Tab. II. The differences among alloys are minor and, taking into account the standard deviation value, they are practically irrelevant.

The modulus and hardness for phase precipitates are given in Tab. III. As the number of indentations corresponding to individual precipitates was small, the standard deviation from the mean value was not evaluated and only approximate values are presented.

### 4. Conclusions

On the basis of nanoindentation measurements of alloys based on austenitic cast steel 0.3C-30Ni-18Cr with different content of niobium and titanium, the values of Young’s modulus E and hardness H of phase constituents identified in alloys were evaluated.

The value of modulus (E ~ 200 GPa) and hardness (H ~ 4.5 GPa) of the matrix were similar for all three alloys. So, the conclusion can be drawn that the additions of niobium 1.84 wt.% and titanium 1 wt.% do not influence precipitation processes occurring in the matrix of austenitic cast steel during annealing in air at 900 °C for 500 hrs. However, the big difference in properties of other phase constituents (E=300–450 GPa, H=10–38 GPa) having diverse morphology can suggest that in macro scale the investigated alloys will exhibit different mechanical properties. In presented investigations the quantitative contribution of individual phases was not analysed. However, taking into account a good repeatability of results for individual phases (E and H for the matrix), the quantitative contribution seems to give a possibility of investigation of the kinetics of phase transformations taking place in investigated alloys.

Nevertheless, in order to use the nanoindentation measurements to statistic analysis of phase contribution, the number of indentations should be increased. Moreover, it is not only important to carry out the representative quantitative test for individual phases, but first of all to increase an area subjected to measurements, what is essential for dendritic structures.

*This work was supported by the SK-PL-0019-09 project.*

### REFERENCES


**M. Garbiak and B. Piekarski (West Pomeranian University of Technology, Szczecin, Poland): Nanoindentation Properties of Phase Particles in Austenitic Cast Steel**

The nanoindentation measurements performed on three cast steels of 0.3C-30Ni-18Cr type with different content of niobium and titanium were presented and results compared between the tested alloys annealed at 900 °C/500 hrs. The phase constituents (austenite, NbC, TiC, M_{23}C_6, G phase) were identified with X-ray and SEM analysis and distinguished by nanoindentation measurements. It was found that the additions of 1.84 Nb or 1 Ti wt% did not change the precipitation processes occurring in austenite matrix. The value of hardness and Young’s modulus for the matrix were similar within the alloys. Essential differences (E=300–450 GPa, H=10–38 GPa) were found between the phase constituents of alloy.

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### Table II
Mean values of E and H for matrix, GPa

<table>
<thead>
<tr>
<th>Alloy no</th>
<th>E</th>
<th>Std dev</th>
<th>H</th>
<th>Std dev.</th>
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<td>1</td>
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<td>10</td>
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<td>197</td>
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<tr>
<td>3</td>
<td>203</td>
<td>10</td>
<td>4.3</td>
<td>0.56</td>
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### Table III
Approximated values of E and H for precipitates indentified in alloys, GPa

<table>
<thead>
<tr>
<th>TiC (TiCN)</th>
<th>NbC</th>
<th>G phase</th>
<th>M_{23}C_6</th>
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<tbody>
<tr>
<td>E</td>
<td>450</td>
<td>400</td>
<td>350</td>
</tr>
<tr>
<td>H</td>
<td>38</td>
<td>28</td>
<td>18</td>
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</table>
DEPENDENCE OF INDENTATION PROPERTIES OF ELECTROTECHNICAL STEEL ON TEMPERATURE AND GRAIN ORIENTATION

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Keywords: non-oriented electrotechnical steel, high-temperature nanoindentation, nanohardness measurement

1. Introduction

Electrical steels are soft magnetic materials1,2. Electrical engines use a variable magnetic field, parallel to the sheet surface. For this kind, the ideal steel would be the non-oriented grain electrical steels (NO steels)3. The highest quality of these steels is achieved using the advanced technology of the very clean steels production with precise control of both the chemical composition and the microstructure of the steels. Taking into account the directional anisotropy of physical properties in crystallographic lattice of ferrite (bcc) and fact that NO steels are mainly used in circuit electromagnetic field, particularly in electrical motors as a core material, it is necessary to provide crystallographic isotropy in the plane of the sheet in order to achieve good final magnetic properties. The "rotating" cube or {100} <0vw> crystallographic orientation in the sheet plane is ideal for the NO steels. However this texture is not achieved in the practise so far1.

Nanoindentation has proven to be an effective and convenient technique of determining the mechanical properties of solids, especially Young’s modulus and hardness. The most popular method of extraction of hardness and modulus from experimental load-displacement response relies on an analysis of the unloading part which is assumed to be elastic, even if the contact is elastic-plastic8,9.

High-temperature or elevated-temperature nanoindentation testing represents an additional capability in nanoindentation techniques, which have demonstrated tremendous potential in the study of nanoscale mechanical behaviour. The use of the elevated-temperature nanoindentation enhances our ability to study nanoscale behaviour of microstructure since by using temperature as a variable the observation of additional and/or new mechanisms is expected10.

In this study, nanoindentation tests were conducted to determine the difference in hardness and Young’s modulus between the grains possessing three predefined orientations (with (100); (110); and (111) planes perpendicular to the loading) in dependence on temperature up to 250 °C.

2. Experimental material and procedure

The investigated sample of NO electrical steel with dimensions of 2x4 mm was taken from industrial line after hot rolling. The chemical composition of studied material is presented in Tab. I and the microstructure of the investigated steel is presented in Fig. 1. It is apparent that the average grain size is about 150–250 μm.

Crystallographic orientation of single grains was examined using Electron Backscatter Diffraction commonly used for microstructural-crystallographic analysis.

Nanoindentation experiments were performed using NanoTest NT600 instrument equipped with the calibrated Berkovich indenter at the maximum force of 25 mN. Loading as well as unloading lasted 20 s and the hold period was 10 s. The indentation experiments were performed at room temperature (RT) and at elevated temperatures of 100, 200, 250 °C using load control system.

The NanoTest system was equipped with a computer-control heating stage for measurement at elevated temperatures. Heating was applied to both indenter and the sample utilizing separate temperature control. This isothermal contact ensures that there is no heat flow during indentation process. The sample was fixed to the heated holder using a special cement paste.

Hardness \( H_T \) and indentation modulus \( E_T \) were determined from load-displacement curves using Oliver-Pharr method8. The presented data here were acquired during a single continuous heating sequence. Each grain was measured at target temperature after stabilization (typically 2 hours). When all grains were measured at specific temperature the sample was heated to the next

Table I

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>N</th>
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<tr>
<td>%wt</td>
<td>0.004</td>
<td>0.23</td>
<td>2.8</td>
<td>0.008</td>
<td>0.005</td>
<td>0.48</td>
<td>0.004</td>
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</table>
temperature, without intermediate cooling. When all of the experiments were completed, the specimen was cooled down to room temperature. Heating as well as cooling rate was 1.6 °C min⁻¹.

3. Results and discussion

Investigated grains of the examined material are characterized by single crystal orientation in space with low defects (dislocation) density.

The map describing the spatial orientation of single grains (Inverse Pole Figure – IPF) is in Fig. 2.

In order to study the effect of crystallographic orientation on indentation properties three grains with different crystallographic orientation were chosen; G1 (111), G2 (001), G3 (011). These grains were subjected to the nanoindentation measurements. 20 indentations have been carried out for each grain at each temperature in array of 2 ×10 with spacing of 25 μm. Fig. 3 shows the residual indents in the grain G2 with (001) crystallographic orientation.

Typical nanoindentation results from NO steel are illustrated in Fig. 4. Since we are interested primarily in the presence or absence of serrated flow at elevated temperature in the present work, the loading portion of the F-h curve was analysed and two important observations apparent from Fig. 4 were found.

First, we observed that the maximum depth of the indentations does not change very much as temperature increases up to 100 °C. Further increase to 200–250 °C leads to a sudden increase in the indentation depth. Second, one can see that as the temperature increases, there is a clear accentuation of serrated flow due to a thermal activation of dislocations. This phenomenon becomes pronounced especially at higher temperature 200 and 250 °C.

This effect with the load drops/serrated flows at elevated temperature was observed in all three grains. Schuh et al.⁹ observed a similar trend during the elevated temperature Berkovich indentation of metallic glasses, or Leipner et al.¹⁰ observed the „pop-in“ effect as homogeneous nucleation of dislocations during nanoindentation. This process is related to a sudden displacement shift in the load-depth curve (F-h curve).
Hardness and modulus analysis

Indentation hardness $H_{IT}$ slightly decreases with increasing temperature for grains G1, G2 and G3 from RT up to 250 °C from 2.7 to 2.3 GPa, from 2.7 to 2.1 GPa and from 2.8 to 2.1 GPa, respectively, Fig. 5.

As one can see in Fig. 5 there are some differences in hardness values between particular grain orientations. Decrease of hardness with increasing temperature for grains G1, G2 and G3 was about 15, 22 and 26 %, respectively. This differences between individual grains can be related to various number of active slip systems in grains11.

Similarly to hardness, the differences in indentation modulus of particular grains are also observed, $E_{IT}$ decreases with increasing temperature as illustrates Fig. 6, however, not so pronounced as for $H_{IT}$.

The average value of indentation modulus for grains G1, G2 and G3 decreases by the temperature change from RT up to 250 °C from 198 to 185 GPa, from 193 to 171 GPa and from 204 to 201 GPa, which expressed in % is 6.7, 11.2 and 1.5 %, respectively.

These results, when the values of both hardness and indentation modulus decreases with increasing temperature are in agreement with other research paper12.

Conclusions

In situ high temperature nanoindentation experiments were performed in order to study the influence of temperature on indentation properties of grains with different crystallographic orientation.

On the basis of results from elevated temperature nanoindentation measurements in each of particular grain orientations it was observed following:

- Analysis of the load drops/ serrations in the load – displacement curves allowed for the identification of onset of serrated flow during elevated temperature nanoindentation. This pop-in effect or the transitions from smooth to serrated flow were observed at 200–250 °C. The pop-in effect could be related to homogeneous nucleation of dislocation during nanoindentation or with increasing temperature so that the transition is temperature-dependent.

- Hardness was found decrease for all investigated grain orientations G1 (111), G2 (001) and G3 (011) with increasing temperature from room temperature up to 250 °C. The differences of hardness values were observed also between particular grain orientations. This can be explained with various number of active slip systems in the individual grains.

- The values of indentation modulus are slightly decreasing with increasing temperature. These results are in agreement with other research papers. The presented results proved that high temperature indentation is a promising technique which extends the possibilities of studying of local mechanical properties.

This work was realized within the frame of the project „New Materials and Technologies for Energetics“, ITMS: 26220220037, which supported by the operational Program „Research and Development financed through European Regional Development Fund.

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P. Gavendová a, R. Čtvrtlík b, F. Kováč a, L. Pešek c, and I. Petryshynets a
(H) Institute of Materials Research, Slovak Academy of Sciences, Košice, Slovakia, b Palacky University, Faculty of Science, Regional Centre of Advanced Technologies and Materials, Joint laboratory of Optics of Palacky University and Institute of Physics of Academy of Sciences of the Czech Republic, Olomouc, Czech Republic, c Department of Materials Science, Technical University of Košice, Faculty of Metallurgy, Košice, Slovakia): Dependence of Indentation Properties of Electrotechnical Steel on Temperature and Grain Orientation

The elevated temperature response of NO electrical steel was examined using a nanoindenter Nano Test NT 600 with tip and sample heating. Hardness was found to decrease with increasing temperature in each of tested grain orientation. The similar situation occurred in the case of elastic modulus. It was shown some differences in values of hardness and indentation modulus between particular grain orientations. Conversely, the magnitude of the load drops/ serrated flow in the load displacement curve was found to increase with temperature.
INDENTATION TESTING OF HUMAN ENAMEL

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Keywords: human enamel, nanoindentation, AFM

1. Introduction

As the hardest and one of the most durable load bearing tissues of the body, enamel has attracted considerable interest during the last decade from both material scientists and clinical practitioners due to its excellent mechanical properties1,2. Knowledge of the mechanical and wear properties of human teeth is of importance as they act as a mechanical device during masticatory processes such as cutting, tearing and grinding of food particles. In the last years, depth-sensing indentation has become a useful technique for mechanical characterization of mineralized biological tissues, including enamel and dentin3,4. Due to its small probe size, nanoindentation is suited to measure local material properties in small, thin samples and allows characterizing the properties of individual constituents within composite tissues, such as enamel and dentin, or mapping their mechanical properties across a sample surface5.

The aim of this investigation is to characterize the hardness and elastic modulus of human teeth using instrumented indentation.

2. Experimental materials and methods

2.1. Sample preparation

The used samples were fresh intact human premolars extracted due to orthodontic reasons. The samples were collected with the patients’ informed consent with professional dentist (team of dentists from UPJS Košice). Teeth were stored in salt solution after removal and before testing, were embedded in EpoFix20 epoxy cold-mounting compound (Buehler Ltd., Lake Bluff, IL). Samples were cut with a precise diamond saw so that the teeth were divided into two halves. Cutting parameters were: low speed rotation (150 rt./min) and cooling with water to protect dehydration and heating.

The sample surface was polished sequentially with 6-, 3-, 1- µm diamond paste and 0.25 – µm alumina suspension. Between polishing steps, the sample was ultrasonically cleaned in de-ionized water to remove any polishing debris and stored in a saline solution at 4 °C. Effect of the epoxy compound on the measured hardness is minimal, due to the used low indentation load.

2.2. Nanoindentation

The nanoindentation experiments were performed using instrumental hardness tester (TTX/NHT by CSM Instruments) equipped with Berkovich indenter using the indentation load of 5 mN. The indents have been applied to the area of enamel, dentin and dentin-enamel junction (DEJ). The number of indents was 20 in three rows. The first indents were located near the occlusal surface, followed by indents toward dentin across DEJ, with the distance of 0.25 mm between the indents. The indentation hardness, HIT, and reduced modulus, EIT, were calculated by Oliver-Pharr method 6. The average values of hardness and reduced elastic modulus were calculated at least from three independent measurements. Light microscopy (LM) and atomic force microscopy (AFM) was used for the characterization of indents.

3. Results and discussion

In Fig. 1 characteristic indents are illustrated located in different parts of human tooth. The hardness of enamel is significantly higher (Fig. 2a) than that of the dentin with values different for the area close to the surface ~ 5 GPa and area close to the DEJ (~ 3 GPa). The hardness of dentin is significantly lower in comparison to the enamel with the average value of ~ 0.4 GPa. Similar behaviour was found in the case of reduced modulus (Fig.2b), however the decrease in its value from the enamel surface (~ 88 GPa) to DEJ (~ 81 GPa) is not so visible as in the case of hardness. There is a significant change in reduced modulus at the DEJ from ~ 81 GPa to ~ 20 GPa. Cuy et al.4 used nanoindentation for mapping mechanical properties of human molar teeth enamel. They found the enamel surface hardness, HIT > 6 GPa and reduced modulus, EIT > 115 GPa, while at the enamel–dentine junction HIT < 3 GPa and EIT < 70 GPa. He and Swain7 also used nanoindentation for characterisation of hardness of enamel. Their results are similar as the results of Cuy et al., but with slightly lower values of hardness and reduced modulus, which can be explain with the higher applied indentation load. Our results are in good agreement with these findings and can contribute to the design and development of functionally graded coatings.
4. Conclusion

The values of indentation hardness and reduced modulus of human teeth were characterized as a function of position on the cross-section of enamel/DEJ/dentin areas. The $H_{IT}$ and $E_{IT}$ of enamel exhibits a distinct decrease on traversing from the outer surface of enamel to the DEJ. According to the results at the enamel surface, $H_{IT} > 5.0$ GPa and $E_{IT} > 90$ GPa, while at the enamel – dentin – junction $H_{IT} < 3.0$ GPa and $E_{IT} < 80$ GPa. The indentation hardness and reduced modulus of dentin, $H_{IT} \sim 0.6$ GPa and $E_{IT} \sim 20$ GPa.

REFERENCES

R. Halgáš a,b, J. Dusza b, L. Kovácsová c, J. Kaiferová a, and N. Markovská a,b, c (a Faculty of Material Science and Technology of STU, Trnava, Slovakia, b Institute of Materials Research of SAS, Košice, Slovakia, c 1st Department of Stomatology of UPJS, Košice, Slovakia): Indentation Testing of Human Enamel

The aim of the present contribution was to investigate the local mechanical properties on cross-section of fresh extracted human molar teeth using nanoindentation method and Berkovich diamond indenter. The indentation hardness, $H_{IT}$ and reduced modulus, $E_{IT}$ in enamel decreased on traversing from the outer surface of enamel to the DEJ from $H_{IT} > 5.0$ GPa and $E_{IT} > 90$ GPa to $H_{IT} < 3.0$ GPa and $E_{IT} < 80$ GPa, respectively. The characteristics of dentin are; $H_{IT} \sim 0.6$ GPa and $E_{IT} \sim 20$ GPa.

4. Conclusion

The values of indentation hardness and reduced modulus of human teeth were characterized as a function of position on the cross-section of enamel/DEJ/dentin areas. The $H_{IT}$ and $E_{IT}$ of enamel exhibits a distinct decrease on traversing from the outer surface of enamel to the DEJ. According to the results at the enamel surface, $H_{IT} > 5.0$ GPa and $E_{IT} > 90$ GPa, while at the enamel – dentin – junction $H_{IT} < 3.0$ GPa and $E_{IT} < 80$ GPa. The indentation hardness and reduced modulus of dentin, $H_{IT} \sim 0.6$ GPa and $E_{IT} \sim 20$ GPa.

REFERENCES

R. Halgáš a,b, J. Dusza b, L. Kovácsová c, J. Kaiferová a, and N. Markovská a,b, c (a Faculty of Material Science and Technology of STU, Trnava, Slovakia, b Institute of Materials Research of SAS, Košice, Slovakia, c 1st Department of Stomatology of UPJS, Košice, Slovakia): Indentation Testing of Human Enamel

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CHARACTERIZATION OF INDENTATION INDUCED MARTENSITIC TRANSFORMATION BY SCANNING ELECTRON MICROSCOPY AND ELECTRON BACK-SCATTERED DIFFRACTION

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Keywords: nanoindentation; stainless steel; martensitic transformation

1. Introduction

Instrumented indentation with spherical indenter is widely used for characterization of local mechanical properties of various materials including metals, ceramics or polymers and offers several advantages comparing to the indentation with sharp indenters. Using spherical indenter, plastic deformation under the indenter is gradually changed as the indentation depth increases$^{1-3}$. This can appropriately be utilized for characterization of the deformation-induced phase transformation during indentation$.^4$ On the other hand, the triaxial stress-strain field under the indenter differs substantially from tensile stress-strain field.

2. Experimental details

Recrystalized metastable austenitic stainless steel (AISI 301) was chosen as an experimental material. The chemical composition is given in Tab. I. Surface of samples was electro-polished to avoid the subsurface layer affected by mechanical grinding and polishing.

Nanoindentation measurements were performed on CSM Instruments NHT Nanoindentation Tester with spherical indenter (with radius of 50 $\mu$m) using instrumented indentation technique$^{5-7}$. Increasing load was applied up to maximum load of 400 mN. The indents were subsequently characterized by light microscopy using differential interference (Nomarski) contrast, scanning electron microscope (SEM) JEOL JSM5510LV using back-scattered electron channeling contrast and by three-dimensional reconstruction (Alicona™) using stereopair technique.

Local analysis of martensite transformed in the vicinity of the indents was carried out by electron back-scattered diffraction (EBSD) HKL™ system mounted on scanning electron microscope JEOL JSM 7600F equipped with field emission gun (FEG).

Table I

<p>| Chemical composition of AISI 301 steel (in wt.%) |</p>
<table>
<thead>
<tr>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Mn</th>
<th>Mo</th>
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<td>7</td>
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</table>

3. Results and discussion

Light and SEM micrographs are shown in Fig. 1. It can be seen that AISI 301 steel undergoes at room temperature deformation-induced phase transformation of face-centered cubic $\gamma$ austenite to body-centered cubic $\alpha'$-martensite$^{8-10}$.

Fig. 1. Deformation-induced martensite in the vicinity of spherical indent - light microscopy (Nomarski contrast), SEM back-scattered electron channeling contrast and 3D stereopair reconstruction
Martensitic transformation is accompanied by volume change which results in a significant relief on the surface sample in the vicinity of indent (see Fig. 1).

Non-transformed austenite and deformation-induced martensite in the vicinity of spherical indents were characterized by EBSD. The crystallographic orientation of the transformed martensite is in the relation to the parent austenite grain according to the Kurdjumov-Sachs (K-S) orientation relations (see Fig. 2). The transformation is significantly influenced by the stress state. The transformation texture arises because not all possible martensite crystallographic variants grow when the austenite is subjected to external stress; i.e. the total number of selected martensite variants within a γ-grain is much lower than 24 theoretically allowed by K-S orientation relation.

4. Conclusions

The results of the study can be summarized as follows:

- High internal stresses are generated due to an incompatible transformation strain accompanying the γ → α’ transformation.
- Multiaxial stress-strain field under the indent has a significant effect on the orientation of the martensite variants.
- Combining nanoindentation with scanning techniques such as SEM and EBSD brings more insight into the whole indentation process.

*This work was carried out in the frame of research project GACR 101/09/0702.*

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P. Haušilda and J. Nohava b (a Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Czech Republic, b CSM Instruments, Switzerland): *Characterization of Indentation Induced Martensitic Transformation by Scanning Electron Microscopy and Electron Back-Scattered Diffraction*

Local analysis of martensite transformed in the vicinity of the spherical indents was carried out by light and scanning electron microscopy, 3D stereopair reconstruction and electron back-scattered diffraction. Multiaxial stress-strain field under the indent has a significant effect on the orientation of the martensite variants. Combining nanoindentation with scanning techniques such as SEM and EBSD brings more insight into the whole indentation process.
CAUSES OF INCONEL 622 WELD CRACKING

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Keywords: inconel, weld, fractography, nanohardness, impact test

Introduction

This paper is dealt with the topic of welding of duplex steel with Ni alloy Inconel 622 being used e.g. in aerospace, offshore and chemical industry. The welding procedure for Ni based alloys typically requires a cautious control over parameters outlined by the Welding Procedure Specifications (WPS) and using high quality filler metals. Even if the welding procedure matches the WPS requirements, the random occurrence of weld defects may cause the failure initiation.

Experimental

By evaluating the weldment, a tendency to cracking was indicated in the SMAW region of the weld metal and at a fusion zone during the bend test. In order to estimate causes of undesired behaviors of the weld metal, a metallographic evaluation was applied. Light and electron microscopy have been used for a structural analysis of the weld. Furthermore, the Charpy impact testing and fractographic analysis of the fracture surface was used. For the mechanical properties of discrete material areas, the nanoindentation method was applied. Carl Zeiss Neophot 32 metallographic microscope, Jeol 7600F High Resolution Scanning Electron Microscope with EDS analyzer (Oxford) and Nanohardness Tester was used.

Results and discussion

The welding procedure used for the joining of thicker plates had two steps. The root of the joint was prepared using the Gas Tungsten Arc Welding (GTAW) method. In next, filing passes were made by Shielded Metal Arc Welding (SMAW). Tab. I shows the typical chemical composition of Inconel 622.

Metallographic evaluation carried out on polished samples showed a significant disproportion in micropurity in different weld regions. The root of the weld, produced by the TIG method (GTAW), had a relatively low content of inclusions (Fig. 1a). The SMAW region shown in Fig. 1b exhibited a large number of spherical inclusions of various dimensions.

The microstructure of both weld regions was similar. The weld metal had a typical dendritic form (Fig. 2 and Fig. 4). Fig. 3 shows that the microstructure of the filler metal rod was oxide-less. On the other hand, Fig. 4 shows the SEM image demonstrating that the presence of inclusions was significantly higher in SMAW region. Table II displays the example of a chemical composition measured by EDS on large spherical inclusions.

![Microstructure of weld metal, unetched](image1)

![GTAW region, Beraha III etched](image2)

![Filler metal rod, Beraha III etched](image3)

**Table I**

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>S</th>
<th>P</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.01</td>
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<td>0.03</td>
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<td>Si</td>
<td>0.2</td>
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<td></td>
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</tr>
<tr>
<td>Cr</td>
<td>20.0 – 22.5</td>
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<td>12.5 – 14.5</td>
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</tr>
<tr>
<td>Mo</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
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</tr>
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<tr>
<td>Fe</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>V</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>0.5</td>
<td>2.5</td>
<td>2.0 – 6.0</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Fig. 1. Microstructure of weld metal, unetched

Fig. 2. GTAW region, Beraha III etched

Fig. 3. Filler metal rod, Beraha III etched
The Charpy impact test was conducted on samples from different areas of the weld. The 2 mm V notches of samples were positioned to the weld metal, fusion edge and root. The orientations of the notch in the root area permitted a simultaneous fracture analysis in both weld regions (GTAW and SMAW).

The average impact energy $KV$, measured at room temperature on samples with different positions in the weld region, was $55 \pm 4$ J. This value was lower than the material standard value declared by the weld wire supplier.

Following the Charpy impact test, fracture surfaces were analyzed. The priority was given to a sample specially oriented to the weld notch region. The fracture surface typical for GTAW and SMAW regions is documented in Fig. 5. Fractographic analyses revealed an increased number of oxide particles in GTAW region in accordance to the microstructural evaluation.

The surface morphology of both weld regions indicated a predominantly ductile fracture. The dendritic arrangement of microstructure was evident. Sporadically, a brittle transgranular fracture was observed in small isolated areas. In SMAW region a large amount of particles was monitored. Predominantly, spherical inclusions with various diameters were observed. Approximately 5% of the present particles were fine angular shaped.

Fig. 6 shows the distribution of selected chemical elements in the fracture surface. The inclusions had an oxide origin of varied chemical composition. The predominantly detected elements were Al, Mn and Ti.

The increased number of the oxide particles had negative influence on toughness. The crack initiation and propagation was easier due to the presence of the described particles.

![Fig. 5. Fracture surface after Charpy impact test](image)

![Fig. 6. SMAW region – oxide particles, distribution of selected chemical elements](image)
The standard methods for testing of mechanical properties as the Charpy impact test, hardness and micro-hardness measurements have not been sufficiently sensitive to indicate the difference between both monitored weld regions (GTAW and SMAW). The nanoindentation method was then used for the evaluation.

Indentation was performed in line and in grid form in both evaluated regions. Parameters applied were summarized in Tab. III. Indents map of line profile measurements and corresponding indentation curves were documented in Fig. 7 (GTAW region) and Fig. 8 (SMAW region).

![Fig. 7. GTAW region indents and indentation curves](image)

![Fig. 8. SMAW region indents and indentation curves](image)

Tab. IV compares the hardness of GTAW and SMAW regions. The measurement conditions have been identical (Tab. III). The hardness and reduced modulus of GTAW were lower than that of SMAW region. It was evident that the indentation plastic work of GTAW region was higher by about 12%. It could be assumed that the GTAW matrix was more ductile than that of SMAW.

However, certain interaction has been indicated between the indenter and the particles dispersed in the matrix (see the indents map in Fig. 7 and related indentation diagrams in Fig. 8). The deviation was affected by the heterogeneity in chemical composition of the dendritic structure. As expected, interdendritic regions had slightly higher hardness values then the dendrite axis. The presence of oxide particles was observed only in the interdendritic spaces.

**4. Conclusions**

It was demonstrated that the weld microstructure contained hard particles, mostly of an oxide origin. The volume fraction of these particles was significantly higher in the SMAW than in GTAW region of the weld. Nanoindentation proved a high hardness of oxide particles and the proper toughness of the matrix. As expected, the plasticity of the GTAW region was higher. An increased volume fraction of oxide particles caused a decrease of the toughness of the weld metal in SMAW region. Oxides played the role of the crack initiators and facilitated the crack propagation.

The oxide presence was probably caused by a technological discrepancy.

This paper has been supported by the CTU project: SGS number SGS10/258/OHK2/3T/12, MEYS project FRVŠ number 2610/2011, OPPA project number CZ.2.17/1.1.00/32213 and OPPK project number CZ.2.16/3.1.00/21037.

**REFERENCES**

J. Horník, P. Hájková, E. Anisimov, and J. Rybníček (CTU in Prague, Faculty of Mechanical Engineering, Department of Materials Engineering, ICDAM, Prague, Czech Republic): Causes of Inconel 622 Weld Cracking

Problems related to the welding of duplex steel with Ni alloy Inconel 622 are described. The GTAW welding procedure was used for the root and SMAW of the main weld. The weldment was characterized by a tendency of the weld metal to cracking in the SMAW region during the bend test. Microstructural analysis of the weld was performed and supplemented by nanohardness measurements. The Charpy impact test and fractographic analysis were carried out. Microstructure of the weld exhibited the presence of hard particles, mostly of an oxide region in SMAW region. Their presence had a negative effect on the ductility of the weld. The oxide presence was probably caused by a technological discrepancy.
AN OPTICAL SENSOR FOR LOCAL STRAIN MEASURING OF AN OBJECT
BY MEANS OF A SPECKLE CORRELATION METHOD

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Keywords: non-contact measurement, strain, speckle, speckle correlation

1. Introduction

Measuring of object deformation is a frequent measurement used in mechanics. There are several methods allowing to obtain the needed information as strain or stress. However, most of them are based on close contact of a measuring tool with a measured object what often leads into destructive effect. Optical methods offer one of suitable solutions since light in optical region can serve as a non-destructive agent.

Speckle interferometry forms an important group of the optical methods. Speckle is the peculiar appearance, which is generated, if an object with a rough surface is illuminated by a coherent beam. The speckle interferometry utilizes optical interferometers for the coherent addition of speckle fields diffracted by object and reference fields. This method have achieved intense progress during last decades in consequence of development of modern optoelectronic components and converted to their electronic or digital modification.

Currently correlation methods join the speckle interferometry in the speckle metrology. In these methods linear or matrix detectors detect the speckle field generated by the object under investigation during its deformation. Their output signals are then mutually correlated by means of computer or hardware correlators. The results of correlation enable to get the information about behaviour of deformation of the object.

The measurement method presented in this paper uses the same principle as aforementioned correlation methods. Deformation of an elementary area of rough surface of an object responsible for the speckle character of reflected coherent light in a general way results in shift of the corresponding speckle pattern in the detection plane and partial modification of its chaotic structure. The position of the global maximum of a cross-correlation function of two intensity sets (speckle patterns) recorded before and after the surface deformation determine the speckle pattern displacement. The displacement is then used for evaluation of small deformation tensor components describing the deformation state of the elementary area of object’s surface. The theoretical study of speckle displacement and decorrelation in the diffraction and image fields was made by Yamaguchi.

The aim of this paper is to present a design of an optical sensor and its experimental verification in non-contact detection and quantitative evaluations of a local strain of a rubber specimen used in tire manufacturing by a speckle correlation method.

2. Theory

For measurement of strain of a surface element of an object it is convenient to use an optical set-up with the symmetrical arrangement of two detection planes and one illumination source (see Fig. 1). Observation directions form the angles – and illumination direction. There are placed thin lenses with identical focal lengths between the object and detectors to magnify the speckle field.

The equation for evaluation of strain is valid for this case of the sensor arrangement

\[ \Delta A_x = A_x (\theta_1, \theta_0) - A_x (\theta_1 - \theta_0) \]

where \( \Delta A_x \) represents the difference between the displacements of speckle fields detected in the planes \((X_1, Y_1)\) and \((X_2, Y_2)\), \( L_x \) and \( L'_{p} \) are the distances of the thin lens from the object plane and detection plane, respectively.

Knowledge of strain enables to state local stress according to the known relation \( \sigma_x = E \varepsilon_x \) valid in the case of one axis elastic tension of the object, where \( E \) is modulus of elasticity of isotropic material of the object.

In general case of study of object’s surface stress state it is necessary to carry out the measurement of specific elongation in three different directions in the plane of object’s surface. There is a direct analogy with the usage of resistance strain gauges and the term of an optical speckle strain gauge appears.
3. Description of an optical sensor

There is a designed optical sensor for measuring of strain $\varepsilon_{xx}$ in $x$-axis outlined in Fig. 1 and Fig. 2.

A He-Ne laser is chosen as a source of coherent light. Its beam is directed perpendicularly on the surface of a measured object. The investigated object is represented by a rubber specimen. It is a specific type of black rubber that is convenient for tire manufacturing. The specimen has form of a thin tape that is 118.3 mm long and 6.6 mm wide. Its thickness is 2.1 mm. The specimen is firmly fastened at its both ends into two clamping jaws. One is static and the other movable. The position of the adjustable clamping jaw is actuated by means of an electronic linear actuator. Therefore specimen loading or unloading can be controlled very exactly. Besides an electronic transducer touching the movable jaw supervises the jaw displacement.

The reflected speckle field is captured with a pair of monochrome cameras containing matrix CMOS image. The sensors have resolution of $1288 \times 1032$ pixels with pixel size of $7.5 \times 7.5 \mu m^2$ and bit depth of 8 bits per pixel. Since for the measurement by the speckle correlation method only linear detectors are sufficient the scanning area of the CMOS detectors is reduced in order to obtain only one row from the whole matrix.

Geometrical and optical parameters of the designed sensor are $L_p' = 181$ mm, $L_c = 111$ mm, $\theta_s = 45^\circ$, $f' = 19.96$ mm.

4. Measurement process

The measurement process is divided into two stages. First the electronic linear actuator elongates the rubber specimen with required constant loading rate and accuracy of 0.1 $\mu$m. The maximum deformation is $2100 \cdot 10^{-6}$. This value corresponds to linear expansion of 200 $\mu$m while the initial pitch of the jaws is 95 300 $\mu$m. In the second stage the linear actuator unloads the rubber specimen into the reference state. The initial pitch of the jaws is 95 500 $\mu$m and the unloading actuator displacement is 200 $\mu$m. The unloading rate is the same as the one used in the first stage.

During each stage of the measurement process both cameras capture $N + 1$ times the developed speckle field with defined capturing frequency. So that $N$ measurement steps are obtained in each stage of the measurement process. The selection of the constant rate of the specimen loading/unloading and the capturing frequency defines value of strain $\varepsilon_{xx}$ for each measurement step. Then the maximum deformation in the corresponding stage of the measurement process is given as $N\Delta\varepsilon_{xx}$.

In our case of measurement both the loading and unloading rate is 7.6 $\mu$m/s and the capturing frequency is 4 Hz. Exposure time is 40 ms. With these conditions the strain $\varepsilon_{xx} = 20 \cdot 10^{-6}$ is achieved for each of 105 measurement steps in every stage of the measurement process over the maximum deformation $2100 \cdot 10^{-6}$.

Each capture of the developed speckle field is represented by a set of 8-bit numbers. The 8-bit number represents an intensity level of light detected by the corresponding pixel of the row of the CMOS matrix. Obtained sets are numerically processed in the PC by a program that determines the maximum position of the normalized cross-correlation function and next the deformation components $\varepsilon_{xx}$ are evaluated using Eq. (1).

5. Experimental results

The example of reached results of measurement is plotted into a graph shown in Fig. 3. Since the measurement process consists of two stages there are two lines in the graph. A straight line corresponds to the
specimen elongation. A dashed line represents the results of the following specimen unloading. On the horizontal axis there is strain $\Delta l/l$ measured by means of the electronic transducer where $\Delta l$ is longitudinal increment to the initial specimen length $l$ determined by the jaws pitch. On the vertical axis there are results of strain $\varepsilon_{xx}$ obtained by means of the presented speckle correlation method.

6. Conclusion and discussion

The paper shows good agreement of results obtained with the electromechanical and optical measurement instruments. In the ideal case the results should be the same and both lines in Fig. 3 (the solid line and the dashed one) should merge into one line with the slope equaled to unity. However presented real case shows small difference from the ideal case. The results obtained using the speckle strain gauge differ from those obtained with electronic transducer no more than 5%. Hysteresis in the results can be related to the measurement in real time and to the expected inertia of the rubber specimen during its unloading.

The sensor has advantages: measurement is non-contact and non-destructive, sensitivity and accuracy of measurement is defined through geometrical and optical parameters of the sensor and measurement runs in quasi-real time. On the contrary there are limiting factors of the sensor: source of coherent light needs to be used and low level of background light has to be secured because of the reason of use of CMOS (CCD) cameras.

The supports of the grant of the Academy of Sciences of the Czech Republic (No. KAN301370701) and the grant of the Ministry of Education, Youth and Sports of the Czech Republic (No. LG11044) are acknowledged.

REFERENCES

THE MECHANICAL PROPERTIES OF HVOF SPRAYED Cr$_3$C$_2$-25%CoNiCrAlY COATING DETERMINED BY INDENTATION

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Keywords: HVOF, coating, CrC-based, depth sensing indentation, indentation fracture toughness

1. Introduction

The Cr$_3$C$_2$-25%CoNiCrAlY HVOF (High Velocity Oxy-Fuel) sprayed coating belongs to the group of hardmetal coatings intended for wear protection of highly mechanically and thermally stressed components. The hardmetal based HVOF coatings benefit from the combination of hard particles, embedded in tough matrix. While the hard particles ensure the high hardness, the tough matrix is responsible for lowering the brittleness, usual for hard materials. Compared to WC-based, the CrC-based coatings have lower inner cohesion, thanks to the lower bonding of Cr$_3$C$_2$ grains into the metallic matrix, typically found in coatings of this composition. On the other hand, they offer the resistance to high temperatures due to the content of Cr in the carbides and matrix. Two CrC-based types of cermet are commercially available: CrC in NiCr matrix and CrC in CoNiCrAlY matrix. The used CoNiCrAlY matrix offers better sliding properties and thermal resistance.

In the case of thermally sprayed coatings, the quality and properties of coatings are strongly influenced by spraying parameters. The not optimal choice of parameters can significantly deteriorate the qualities of sprayed materials.

The most common way of coatings evaluation is the microstructure analyses (presence of tensile or adhesion cracks, amount of porosity, oxides, shape of individual splats), surface hardness (HR15N) measurements and microhardness (HV0.3) measurements. It is usually sufficient for confirmation of coatings quality.

In the paper, the results of measurement of coating hardness and elastic modulus by continuous stiffness measurement (CSM) method and Vickers indentation fracture toughness (IFT) of Cr$_3$C$_2$-25%CoNiCrAlY are presented. The results are compared with the results of previously measured Cr$_3$C$_2$-25%NiCr coating. From the comparison, the deterioration of Cr$_3$C$_2$-25%CoNiCrAlY coating cohesive strength due to used parameters are apparent, even if the coating microstructure and surface hardness measurement does not show any imperfections. The lower coatings cohesion became evident analyzing the results of corrosion and abrasion wear tests.

2. Experimental

The HVOF coatings were sprayed by the HVOF TAFA JP5000 spraying equipment onto a grid blasted steel surface in Výzkumný a zkušební ústav Plzeň, s.r.o., using the standard spraying procedure. While the spraying parameters for Cr$_3$C$_2$-25%NiCr were previously optimized, the Cr$_3$C$_2$-25%CoNiCrAlY coating was sprayed by the same spraying parameters. The thickness of the coatings varied from 350 to 400 µm. The cross sections of the samples, embedded in an epoxy resin, were mechanically grinded and polished using the Struers automatic polishing machine.

The instrumented microhardness and Young’s elastic modulus in dependence on the depth of indentation was measured by the MTS Nanoindenter. For each coating, more than 50 measurements were done. The methodology, described in ref. was used for determination of properties of carbides, matrix and coatings.

The superficial coating’s hardness was measured on the as-sprayed coating surface by HR15N method to avoid the influence of the substrate. For the IFT measurements, the CSEM Scratch Tester, equipped with the Vickers indenters, was used. The indentations in to the coatings cross sections were done using 25, 50, 75, 100, 125, 150, 175 and 200 N loads, for each load 16–20 indents were made in dependence on their size. The space between the individual indents equaled at least 3 indents diagonal to avoid their mutual affecting. The methodology, recommended by Chicot was used to determine the value of $K_i$. The equation of Chicot enables to incorporate the Meyer’s index, characterizing the Indentation Size Effect, in to the equation for $K_i$, and exclude the Indentation size effect from the IFT evaluation.

The lengths of indents diagonals, as well as the lengths of cracks (Fig. 1), were measured by NICON EPIPHOT 200 microscope with software LUCIA. For the $K_i$ calculations, the equation proposed by Chicot was used:

$$K_i(M-M) = (0.0074 - 0.0043q)\left(\frac{E}{H^2}\right)\frac{L}{a^{1.5}e^{0.75}}$$

as an average value of the E/H ratio in the range defined from the depth of indentation 2–8.5 µm.

The wear tests were realized according to ASTM G-65 – Dry sand rubber wheel test (DSRW). The wear rate $K_{abs}$ [mm$^3$/m] was calculated from measured volume loss
of the coatings material and the length of abrasive distance.

2. Results and discussion

The results of instrumented hardness and Young’s elastic modulus of the hard particles, matrix and coatings is shown in the Fig. 2 and Fig. 3 and summarized in the Table I.

The H and E values of Cr-based carbides, embedded in 25%CoNiCrAlY matrix is significantly lower compare to the values, measured for CrC-based carbides in 25% NiCr matrix (published elsewhere\(^3,6\)).

This effect can be caused by not sufficient amount of measurement in the case of Cr\(_3\)C\(_2\)-25%CoNiCrAlY coating. But with respect to the previous experiences with measurements of coatings with comparable hard particles size the set of 60 measurements is sufficient to hit several of them.

The other explanation can be found in coating worse inner cohesion, indicated in particular by the IFT measurements.

The results of the IFT measurements are shown in the Fig. 4 and Fig. 5.

In the Fig. 4, the \(K_{IC}\) values calculated according to formula Chicot\(^4\) for Palmqvist cracks mode (P), Radial-median cracks mode (R-M) and mixed cracks mode are shown in dependence on used indentation load. It can be seen, that while for Palmqvist cracks mode and Radial-median cracks mode formulas the indentation size effect (ISE) is significant, it is successfully excluded using the formula for mixed cracks mode proposed by Chicot\(^4\).

In the Fig. 5 the comparison between \(K_{IC}\) of Cr\(_3\)C\(_2\)-25%CoNiCrAlY and Cr\(_3\)C\(_2\)-25%NiCr coating is displayed. The average value of \(K_{IC}\) was calculated to be 0.395 ± 0.045 for Cr\(_3\)C\(_2\)-25%CoNiCrAlY, while for Cr\(_3\)C\(_2\)-25%NiCr it was 0.763 ± 0.059.

The difference in the toughness of two coatings can be seen also from the measured length of cracs. In Fig. 6 and 7, the dependence of cracks length on the indentation load is demonstrated for Cr\(_3\)C\(_2\)-25%CoNiCrAlY and Cr\(_3\)C\(_2\)-25%NiCr resp. In the Ponton-Rowlings work\(^7\), the Palmqvist and Radial-median cracking mode was recognized according to ratio c/a (c/a < 2.8 for Palmqvist cracks and c/a > 2.8 for Radial-median cracks). The slopes of the length of the crack – load of indentation dependencies measured in this work confirm the Ponton – Rowling rule.

The tougher Cr\(_3\)C\(_2\)-25%NiCr coating reached the transition between the Palmqvist and Radial-median cracks mode at higher load, than the coating with lower inner cohesion. The transition between the two cracks mode in the material in dependence on used load was described by Rios\(^8\). For thermally sprayed coatings it was observed in Lima’s

<table>
<thead>
<tr>
<th></th>
<th>CrC-25%CoNiCrAlY</th>
<th>CrC-25%NiCr</th>
</tr>
</thead>
<tbody>
<tr>
<td>H carbides [GPa]</td>
<td>19.5 ± 1.7</td>
<td>30.2 ± 0.8</td>
</tr>
<tr>
<td>E carbides [GPa]</td>
<td>293 ± 58</td>
<td>398 ± 7</td>
</tr>
<tr>
<td>H matrix [GPa]</td>
<td>9.3 ± 1.1</td>
<td>10.7 ± 1.2</td>
</tr>
<tr>
<td>E matrix [GPa]</td>
<td>167 ± 13</td>
<td>280 ± 47</td>
</tr>
<tr>
<td>H coating [GPa]</td>
<td>8.5 ± 0.4</td>
<td>15.1 ± 1.2</td>
</tr>
<tr>
<td>E coating [GPa]</td>
<td>135 ± 12</td>
<td>259 ± 26</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic picture of the Vickers indent

Fig. 2. Cr\(_3\)C\(_2\)-25%CoNiCrAlY hardness values in dependence on indentation depth

Fig. 3. Cr\(_3\)C\(_2\)-25%CoNiCrAlY Young’s elastic modulus values in dependence on indentation depth

Table I

Hardness and Young’s elastic modulus of the CrC-based coatings
The WC-12%Co coating was found to have the transition load between Palmqvist and Radian-median cracks load about 150 N.

The transition between the Palmqvist and Radial-median crack mode is characterized by a significant increase of cracks length. The sudden decrease of $K_{Ic}$ value calculated according to the formula for Palmqvist crack mode is induced by the increase of cracks length. For the $K_{Ic}$ value calculated according to the formula for Radial-median crack mode the decrease is less pronounced, while it has no influence on the $K_{Ic}$ value calculated according to the Chicot formula for the mixed crack mode.

The Dry sand rubber wheel wear test according to Fig. 6.

The transition between Palmqvist and radial-median cracking mode for Cr$_3$C$_2$-25%CoNiCrAlY coating Fig. 5.

The dependence of $K_{Ic}$ on the indentation load for Cr$_3$C$_2$-25%CoNiCrAlY and for Cr$_3$C$_2$-25%NiCr coating Fig. 4.

The dependence of HV and $K_{Ic}$ on the indentation load for Cr$_3$C$_2$-25%NiCr coating

The transition between Palmqvist and radial-median cracking mode for Cr$_3$C$_2$-25%NiCr coating Fig. 7.

The Vickers indent in Cr$_3$C$_2$-25%CoNiCrAlY coating made at 100 N Fig. 9.

The transition between Palmqvist and radial-median cracking mode for Cr$_3$C$_2$-25%CoNiCrAlY coating Fig. 8.

The Vickers indent in Cr$_3$C$_2$-25%CoNiCrAlY coating made at 75 N Fig. 7.

The transition between Palmqvist and radial-median cracking mode for Cr$_3$C$_2$-25%NiCr coating made at 100 N
ASTM G-65 showed the wear rate 0.01 mm³/m for Cr₃C₂-25%CoNiCrAlY and 0.08 mm³/m for Cr₃C₂-25%NiCr. For the abrasive wear, the hardness and microhardness of material is the crucial property. The fracture toughness does not play such a significant role in the case of abrasive wear, but is essential in erosive and cavitation conditions.

In our case, the superficial hardness HR15N was measured to be 85.3 ± 0.9 for Cr₃C₂-25%CoNiCrAlY and 84.0 ± 0.5 for Cr₃C₂-25%NiCr resp. In contradiction to that, the measured microhardness HV₀.₃ was 848 ± 30 for Cr₃C₂-25%CoNiCrAlY and 1030 ± 114 for Cr₃C₂-25% NiCr resp.

The higher microhardness and fracture toughness of Cr₃C₂-25%NiCr coating is responsible for its better abrasive wear resistance.

In the Fig. 10, the appearance of the Cr₃C₂-25% CoNiCrAlY and Cr₃C₂-25%NiCr after the 150 h exposition to the steam environment (550°C, 245 bar) can be seen.

It is obvious, that the corrosion of Cr₃C₂-25% CoNiCrAlY is much more pronounced compare to Cr₃C₂-25%NiCr coating, although the CoNiCrAlY was expected to increase the corrosion resistance of CrC-based coating. The poor corrosion resistance is believed to be caused by coatings low intersplat cohesion.

3. Conclusions

The indentation test measurements pointed to the necessity of optimization process of spraying parameters for Cr₃C₂-25%CoNiCrAlY. The parameters, successfully used for Cr₃C₂-25%NiCr, have to be modified for using CoNiCrAlY matrix to reach coating’s expected mechanical properties. The lower microhardness of coatings components as well as coating’s itself and significantly lower fracture toughness lead to the deterioration of coating’s wear and corrosion resistance.

The methodology of fracture toughness determination according to Chicot’s mixed cracks mode excludes the indentation size effect, and enables to compare the values measured at different load. More to that, it enables do determine the load, representing the transition between the Palmqvist and Radial-median cracks mode. On the other hand, it requires creating and measuring a big amount of indents, which although it’s not experimentally demanding, is time-consuming. This fact is limiting for its common, routine use in parameters optimization process.

The paper was prepared thanks to the project of Ministry of Industry and Trade of Czech Republic no. FR-TI1/273.

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Š. Houdková, O. Bláhová, and M. Kašparová (University of West Bohemia): The Mechanical Properties of HVOF Sprayed Cr₃C₂-25%CoNiCrAlY Coating Determined by Indentation

In the paper, the experimental evaluation of basic mechanical properties such as hardness, Young elastic modulus and fracture toughness of HVOF sprayed Cr₃C₂-25% CoNiCrAlY coating are presented. The continuous stiffness measurement method was used to determine the coatings hardness and Young elastic modulus of single microstructure phases as well as the composite properties. The Vickers indentation with high loads was then used to evaluate the coatings indentation fracture toughness. The methodology of Chicot was used to calculate the indentation fracture toughness independently on used load, excluding the ISE effect.

The measured results are compared with previously determined behavior of other CrC-based coating. Compared to them, the Cr₃C₂-25%CoNiCrAlY coating shown poor results considering the coating microstructure, cohesion strength and hard particle instrumented indentation hardness, but not the superficial hardness and overall coating microhardness. The not optimal spraying parameters were indentified to be responsible for the deteriorated coating properties.
EFFECT OF FINE CLAY FRACTION ON FUNCTIONAL PROPERTIES OF VITREOUS ENAMEL COATINGS

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Keywords: coating, clay, glass, nano indentation test

1. Introduction

Vitreous enamels are glazes formed on a metallic undercoat by burning at temperature exceeding 800 °C (ref.1–4). Final brittle-fracture properties of the coatings are dependent on the structure, texture and chemical composition. Clay is one of the most important inorganic components of enamel slurry used in the technique of wet enamel coating. The addition of clay in suspension prevents sedimentation of particles milled glassy frit. The resulting quality of the coating is influenced by the use of components with different particle size. The main goal of this paper is to compare brittle-fracture properties of vitreous enamel coatings made by using commonly-dimensioned and nano-dimensioned inorganic particles.

2. Sample preparation

For experimental testing, as a substrate was used steel plate Kosmalt E 300T (produced by U.S. Steel Košice), thickness 3 mm, with the following chemical composition (wt.%): C: 0.041; Si: 0.02; S: 0.007; N: 0.006; Mn: 0.241; P: 0.010; Al: 0.052; Ti: 0.067; Cr: 0.023; Mo: 0.005; V: 0.005. The surface of hot-rolled steel plate was treated by mechanical shot blasting to obtain the surface cleanliness of Sa 2.5 (ČSN EN ISO 12944-4 Paints and varnishes – Corrosion protection of steel structures by protective paint systems – Part 4. Types of surface and surface preparation) and degreased for 5 minutes in the degreasing alkaline liquid Simple Green (pH 9.4) with the concentration 1:10. The 24 hours-old enamel slurry was applied on degreased steel substrate by pneumatic spraying, dried at the temperature 100 °C for 5 minutes, and subsequently burned at the temperature 820 °C for 8 minutes. Finally the samples were cooled in air at room temperature. In accordance to the colour of enamel slurry two types of enamels were distinguished: the grey under-coat and the green top-coat. Density of both enamels is 1400 kg m–3 and main chemical composition (wt.%): quartz ground: 25; clay MIC: 8; boric acid: 0.4; Sb2O3: 0.3; K2CO3: 0.05; NaNO2: 0.15; colouring pigments:10,1 and water: 56. Undercoat enamel layer forms the function interlayer in enamel-metal system. Increasing content of elements (Si, Ni, Ca, K …) causes improving adhesion of glassy phase to the substrate and strongly influences a surface design of final product. MIC clay is a valuable kind of clay and has a quite favourable plasticity and it is suitable for the enameller’s purposes. Chemical composition of the MIC Clay (wt.%): mineralogical pure clay: 83.5; admixtures: feldspar: 8; silica from feldspar 8.5 (of which SiO2: 60; Al2O3: min 30; Fe2O3: max 3; TiO2: max 1.5; CuO: max. 0.2; MgO: max. 0.4). MIC clays used for surface enamel coatings: MIC coarse clay fractions – average size of particles 15 μm, MIC fine clay fraction – average size of particles 1.85 μm with a 1D dimension of 400 nm. Fine clay had been prepared using jet vertical mill STURTEVANT. The enamel slurry was applied on steel substrate after mechanical shot blasting and degreasing processes. The thickness of both layers of enamel coatings (under-coat and top-coat) is 200 μm. Sample 1 is the substrate covering by grey under-coat with MIC coarse clay fractions. Sample 2 is the substrate covering by grey under-coat with MIC fine clay fractions. Sample 3 is the substrate covering by grey under-coat and green top-coat enamel layers with MIC coarse clay fractions. Sample 4 is the substrate covering by grey under-coat and green top-coat enamel layers with MIC fine clay fractions.

3. Results and discussions

To realize these experiments number of modern experimental methods were applied kinematic viscosity (ČSN EN ISO 2431–Paints and varnishes – Determination of flow time by use of flow cups), microhardness measurements and fracture toughness, resistance to shot (shot firing test), surface roughness – (ČSN ISO 4287 Geometrical product specifications – Surface texture: Profile method – Terms, definitions and surface texture parameters), scratch, static and nano-indentation test.

On the basis of the kinematic viscosity measurements: enamel slurry with fine clay showed higher viscosity than enamel slurry with classic coarse clay (usage of fine clay at the same weight content as coarse clay), and therefore its rheological properties are different. Finally milled clay (with average size of particles 1.85 μm) shows more uniform structure and the fraction. By measuring the
brittle-fracture properties was proved a significant positive effect of fine clay fraction in enamel slurry.

For sample 2 can be observed increasing the parameter Hv and analogue fracture toughness in comparison with sample 1. Higher microhardness comparable to the fracture toughness is obvious for sample 3 (in comparison with the sample 4). Increased levels of bursting force Fp for fine-clay coatings represent an increase in enamel adhesion to the steel substrate. The most significant damage at minimal perpendicular force arises to the sample 2. There is rapid penetration of the indenter to the volume of coating. On the edges a large expansion of the cohesive crack is visible. Significant damage of coating is also evident on sample 1. Similar to sample 2 there is a great damage on the incision edges. These results correspond with the lowest values of the parameter Hv (see Table I). For samples 3 and 4 there is a distinct shift in the beginning of damage to higher loading forces. At the scratch edges the expansion and cohesion damage is lower. Sample 4 also shows significant wear of surface on the bottom of the scratch. Set of nano-indentation curves with the maximal normal loading of 200 g displays the highest nano-hardness for sample 1–610 DHV, which is related to damage during scratch indentation test. The significantly lower value of nanohardness is recognized for the sample 2–480 DHV, but in total it achieves the lowest value for sample 3–460 DHV. The higher hardness due to brittle cracking is apparent for the fourth sample. Decreasing acoustic emissivity at high perpendicular forces can be seen for sample 1. This corresponds to deeper penetration into the enamel volume. The significant stress generation occurs deep in the volume of the coating, which corresponds to the morphology of the crack. Increase of acoustic emission (at high perpendicular forces) for sample 3 corresponds to a slower rate of damage in the morphology of the rift.

4. Conclusion

The use of clay with different particle size affects the cohesive and adhesive degradation of metal – vitreous enamel coating, leading to significant changes in the deformation processes as well as the initiation of damage of the surface enamel layer. On the basis of experimental tests significant positive affect of fine clay onto the brittle-fracture and functional properties of the coat have been shown. Tendency to defect formation is also substantially reduced. These benefits can be used in practice especially in assembling of enameled segments.

Acknowledgments – MŠMT ME 08083, MSM6198910016, SP2012/78, CZ.1.05/2.1.00/01.0040.

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"aInstitute of Physics, "bFaculty of mechanical Engineering, RMTVC-606, VŠB - Technical University of Ostrava, "cFaculty of mechanical Engineering, University of West Bohemia in Pilsen, Czech Republic). Effect of Fine Clay Fraction on Functional Properties of Vitreous Enamel Coatings

Final brittle-fracture properties of vitreous enamel coating are dependent on its structure, texture and chemical composition. The most important inorganic components during production of this coating are clay and fritted glass. Usage of various sizes of these components influences final quality of the coating. The main goal of this thesis was to compare functional properties of vitreous enamel coatings made by using commonly-dimensioned and nano-dimensioned particles.

Table I

| Average values of kinematic viscosity, microhardness, fracture toughness, bursting force by the shot firing test, nanohardness and surface roughness of the vitreous enamel (Ra, Rq, Rt parameters from CSN ISO 4287) |
|---|---|---|---|---|
| Sample | Sample | Sample | Sample |
| 1 | 2 | 3 | 4 |
| **Kinematic viscosity [m² s⁻¹]** | 5.10⁻⁶ | 60.10⁻⁶ | 10.10⁻⁶ | 80. 10⁻⁶ |
| HV₀.1 [MPa] | 4042 | 4227 | 5136 | 4376 |
| KIC [MPa m¹/₂] | 0.88 | 0.87 | 1.01 | 1.04 |
| Bursting force Fp [N] | 50 | 55 | 50 | 70 |
| Nanohardness | 610 | 480 | 460 | 530 |
| DHV | DHV | DHV | DHV |
| Surface Roughness | Ra = 1.02 | Ra = 0.87 | Rq = 0.56 | 0.52 |
| [µm] | Rq = 1.31 | Rq = 1.06 | Rq = 1.83 | 0.67 |
| Ra = 25.75 | Ra = 13.64 | Ra = 15.21 | Ra = 16.42 |

s433
PARTICLE SWARM OPTIMIZATION FOR AUTOMATIC HARDNESS MEASUREMENT

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Keywords: particle swarm optimization, hardness measurement, image processing

1. Introduction

Hardness measurement enables fast and reliable identification of low quality material and helps to prevent its use in the production process. Automatic hardness measurement can speed up the measurement process and provides repeatable results in contrast to manual measurement that is time consuming and always affected by a human factor. On the other hand, the automatic measurement often fails, when the specimen surface is not well prepared. This article introduces an algorithm that enables measurement of rough polished specimens and minimizes the effect of specimen surface properties.

2. Hardness measurement

Hardness is one of the important mechanical properties of construction materials and therefore it is very often measured in the technical practice. The main advantage of hardness tests is their easiness, repeatability and also the fact that in many cases the measurement can be performed directly on a product or on samples produced and designed for other types of mechanical tests.

Hardness can be defined as the resistance of material (surface of the material in the measured spot) against local deformation caused by pressing indenter of a specific geometrical shape at a defined load. The degree of hardness is determined by the size of the permanent plastic deformation.

Hardness tests can be divided according to different criteria: In terms of principle, we can recognize a scratch test, indentation test, impact test and rebound test. In terms of the loading force we can recognize static and dynamic tests for hardness.

The most frequent methods of measuring microhardness are static methods of Brinell (ČSN EN ISO 6506), Rockwell (ČSN EN ISO 6508), Vickers (ČSN EN ISO 6507) and Knoop (ČSN EN ISO 4545). The article focuses on Vickers test.

Test of hardness according to Vickers is prescribed by European standard, for three different ranges of testing load (Tab. I).

The penetrating body – made of diamond shaped as a regular tetragonal pyramid with the square base and with preset vertex angle (136°) between opposite walls – is pushed against the surface of testing body. Then, the diagonal size of the indent left after load removal is measured (Fig. 1).

Vickers’ hardness is then expressed as the ratio of the testing load applied to indent area in form of regular tetragonal pyramid with square base and the vertex angle equal to the angle of penetrating body (136°) as:

\[ HV = \frac{0.1891 \times F}{d^2} \]  

Where \( HV \) – Hardness according to Vickers, \( F \) – Testing load in N, \( d \) – Arithmetic average of two diagonals \( d_1, d_2 \) in mm.

Table I

<table>
<thead>
<tr>
<th>Ranges of testing load ( F ) [N]</th>
<th>Symbol of hardness</th>
<th>Previous marking (ISO 6507-1:1982)</th>
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</thead>
<tbody>
<tr>
<td>( F \geq 49.03 )</td>
<td>( HV \geq 5 )</td>
<td>Test of hardness according to Vickers</td>
</tr>
<tr>
<td>( 1.961 \leq F &lt; 49.03 )</td>
<td>( 0.2 &lt; HV &lt; 5 )</td>
<td>Test of hardness according to Vickers with low load</td>
</tr>
<tr>
<td>( 0.0980 \leq F &lt; 1.961 )</td>
<td>( 0.01 &lt; HV &lt; 0.2 )</td>
<td>Test of micro-hardness according to Vickers</td>
</tr>
</tbody>
</table>

Fig. 1. The basic principle of hardness testing according to Vickers
Evaluatd sample has to have smooth and even surface, without flakes, lubricants and foreign particles. The sample is thus prepared as a metallographic scratch pattern. Generally, the preparation is done by wet grinding and then by polishing on diamond pastes or by electropolishing. Exact method of sample preparation is chosen according to respective materials. Thickness of testing body or layer has to be at least 1.5-6 times longer than the diagonal length of the indent.

3. Automatic hardness measurement

Several different approaches to automatic hardness measurement were presented in the past. Straightforward technique of indentation vertex calculation is presented in ref\(^3\). It uses the least square method for the average diagonal length calculation. Key issue of the threshold determination is discussed there as well. Region growing technique is presented in ref\(^2\). More sophisticated method that utilizes thick line Hough transform is discussed in ref\(^3\). In ref\(^6\), the hardness measurement process is divided in three steps: image preprocessing, indentation recognition and indentation measurement. Different techniques for each stage are briefly introduced. Another advanced approach that utilizes wavelet functions is discussed in ref\(^5\),\(^6\).

The proposed algorithm is based on a parametric description of indentation. The indentation is described by the following parameters: centre of horizontal and vertical axes, horizontal and vertical diagonal length and rotation of the axes with respect to the image axes

\[
\Theta = \{x, y, a, b, \varphi\} \in \mathbb{R}^5. \tag{2}
\]

Using these parameters we are able to compute vertices of the indentation in the frame of the image. The final edge is constructed by connecting the vertices with lines in the proper order. In digital images the lines are composed of pixels and we will denote the set of the pixels that form the edges as \(E_i\). The goal is to find such values of the parameters that match a processed camera image of indentation the best. Testing of all combinations of values is numerically overwhelming and therefore some of the global optimization techniques can be employed. Our article describes the usage of the particle swarm optimization.

The first step of the algorithm is filtering of the original image that is depicted in Fig. 2. The goal is to highlight important objects in the image. In the case of hardness measurement, we focus on filtration of indentation edges. To process the image we use a bank of filters for gradient estimation. General form of the filters’ kernels which respect the diagonal direction of the indentation edges is the following

\[
F_i = \begin{bmatrix}
0 & -1 & 0 \\
-1 & 0 & 1 \\
0 & 1 & 0 \\
1 & 0 & -1
\end{bmatrix}
\tag{3}
\]

The image \(I\) is filtered four times. Each time we use a different kernel \(F_i\)

\[
IF_i(x, y) = (I * F_i)(x, y) = \sum_{m=-h}^{h} \sum_{n=-w}^{w} I(x-m, y-n) \cdot IF_i(m, n) + 2) \tag{4}
\]

where \(IF_i(x,y)\) can be seen as an indication of a match between the filter \(F_i\) and the image \(I\) at position \((x,y)\). Thus, for each pixel we obtain four responses from four filters. For each pixel we choose the largest response as the approximation of the gradient magnitude (Eq. (5)). The filtered gradient image is denoted as \(I_g\)

\[
I_g(x, y) = \max_i IF_i(x, y). \tag{5}
\]

In our calculations we use wider kernels which respect the character of the visual data. The result can be seen in Fig. 3. Since the image is too noisy we do not use any post processing of the gradient image to obtain thin edges. We are interested in the magnitude of the gradient. The larger the magnitude is for a pixel the larger is the certainty of the edge in the position of the pixel.

When the gradient magnitude in the image is estimated we can begin to search for the best set of the model parameters. One set of the model parameters is called a particle. We consider a constant number of particles during iterations of the algorithm. The set of particles is defined as

\[
\Pi = \{x_k \in \Theta : k = 1...N\}, \tag{6}
\]

where \(N\) is the number of particles. At first, the set of particles is initialized by values that cover the parametric space reasonably, as in Fig. 4. Each particle generates an edge model of the indentation. We fit each edge model to the gradient image and we compute the sum of the magnitude of the gradient field in positions defined by the model.
The sum is the score $s_k$ for the given particle. $E_k$ is the set of coordinates of the edge defined by the particle $x_k$. In the next step we do the re-sampling. This means that the particles that achieved the highest score have the highest probability of being re-sampled (used in the next iteration of the algorithm). Since we use a constant number of particles we draw each particle independently from the distribution given by the particles’ scores. All particles that are passed to the next iteration are shifted towards the particle that achieved the best score in the current iteration

$$x^* = \arg \max_{x_k \in \mathcal{E}} s_k$$

The shifting of the particle means that we compute a vector

$$v_k = x^* - x_k$$

and the particle in the next iteration (denoted as $x_k^{+}$) is given as

$$x_k^+ = x_k + c \cdot v_k + \sigma$$

where the $c \in (0;1)$ constant defines the extent of the shifting towards the best particle. A small Gaussian noise $\sigma$ is added to the shift, so that the particles cover larger volumes in the parametric space.

Correspondence of particle set is evaluated by the weighted average based on the score of all particles

$$E_{\text{weighted}} = \sum_{k=1}^{N} x_k^* \cdot x_k.$$  \hfill (11)

$$S = \sum_{(x,y) \in \mathcal{E}_{\text{complex}}} I_k(x,y).$$  \hfill (12)

If the score is the highest achieved so far it is remembered as the best result. The algorithm iterates until the score of the weighted particle decreases below a given value or the maximum number of iterations was achieved. Then the intermediate result with the highest achieved score is chosen as the final result. In Fig. 5 and Fig. 6 we show specific iterations of the algorithm. The final result is shown over the original image in Fig. 7.

4. Conclusion

A novel technique of automatic hardness measurement was described in the paper. The goal was to automatically measure the length of indentation diagonals. The algorithm is based on the particle swarm optimization. It enables to measure hardness even if the specimen is etched or rough polished. Employment of the automatic algorithm speeds up hardness measurement process and increases measurement repeatability.

On a standard PC (Intel® Core™ 2 Quad @ 2.83 GHz) with four CPU cores the algorithm runs ~0.3 sec. The algorithm is optimized for multi-core CPU.
This work was supported by the grant MPO No. FRTI1/487 Development of the hardness measurement system with focus on research of the new possibilities in the area of polymer properties analysis and its application in the market.

REFERENCES

M. Hrúz, J. Široký, and D. Maňa (University of West Bohemia, Faculty of Applied Sciences, Department of Cybernetics, Tomas Bata University in Zlín, Faculty of Technology, Department of Production Engineering, Czech Republic): Particle Swarm Optimization for Automatic Hardness Measurement

Hardness measurement enables fast and reliable identification of low quality material and helps to prevent its use in the production process. Automatic hardness measurement can speed up the measurement process and provides repeatable results in contrast to manual measurement that is time consuming and always affected by a human factor. On the other hand, the automatic measurement often fails, when the specimen surface is not well prepared. This article introduces an algorithm that enables measurement of rough polished specimens and minimizes the effect of specimen surface properties.
MEASURING OF MECHANICAL PROPERTIES OF ELECTROCHEMICALLY DEPOSITED ZrO$_2$, Ce$_2$O$_3$-CeO$_2$ AND La$_2$O$_3$ FILMS BY NANOINDENTATION

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Keywords: thin films, cerium oxide, zirconium oxide, lanthanum oxide, mechanical properties, nanoindentation

1. Introduction

Zirconia is proving an exciting novel material which is gaining in popularity due to its specific key advantages over other more traditional ceramics. It does not have the malleability of metals but does have significantly high fracture toughness. Zirconia is wear resistant and inert and can therefore be utilised in areas where traditional metallic systems would not be able to function. That’s why zirconia is widely used in the oil and gas industry. In sub-sea systems where metallic systems would corrode, zirconia excels. Zirconia has great wear resistance, which, combined with its high fracture toughness makes it an ideal material for pumps and turbines. As zirconia is so hard, it is the perfect material from which to manufacture knives and blades – cutting edges remain sharp for much longer. Zirconia is also used for femoral head components in hip implants. Now it is successfully applied in dental medicine too. Zirconium dioxide is used for making single crowns and bridges with 4 elements, veneers and laboratory-made fillings. These have high aesthetic qualities because they do not have the grey metallic color that is often shown through the porcelain in metal-porcelain constructions. Zirconium constructions are distinguished by unique resistance to breakage, perfect biocompatibility, good transmittance, low heat conductivity by showing no darkish borders of the crown towards the gum; and by color stability over time.

Zirconium oxide thin films are excellent candidates for hard and protective coating applications where transparency is required. They may be used as diffusion barrier coatings in nuclear energy reactors, as protective layers on metal cutting tools, as insulating layers in microelectronics and in optical filters.

Excellent chemical stability, mechanical strength, wear resistance as well as some peculiarities of electron conductance allow zirconia layers to be used as catalysts or catalyst supports in exhaust-gas purifying devices where high thermal, mechanical and corrosion stability are required.

Cerium oxide is a technologically important material with remarkable properties that is used in a number of applications such as oxygen storage – in automobile exhaust catalytic converters thanks to its ability to uptake and release oxygen under oxidizing and reducing conditions. The cause of this effect is the continuous transformation between two Ce oxides: the oxygen-rich CeO$_2$ and the oxygen-deficient Ce$_2$O$_3$ depending on the external oxygen concentration. Other important properties such as high dielectric constant and good epitaxy on Si, make Ce oxide a promising material for future microelectronic applications. In particular, CeO$_2$ is considered candidate for replacing silicon dioxide in electronic applications. Cerium oxide layers deposited on metals and alloys offer also excellent corrosion-protection against various aggressive media. This explains the present intensive attention that is drawn to this oxide and its properties.

La$_2$O$_3$ is used to make optical glasses, to which it provides increased density, refractive index, and hardness. Together with oxides of tungsten, tantalum, and thorium, La$_2$O$_3$ improves the resistance of the glass to attack by alkali. La$_2$O$_3$ is an ingredient for the manufacture of piezoelectric and thermoelastic materials. Automobile exhaust-gas catalytic converters contain La$_2$O$_3$ (ref.8). La$_2$O$_3$ is also used in X-ray imaging intensifying screens, phosphors as well as dielectric and conductive ceramics. La$_2$O$_3$ has been examined for the oxidative coupling of methane.

The broad spectrum of applications of zirconium, cerium and lanthanum oxides and the fact that properties of thin films are typically very different from the properties of bulk material make investigation of properties of ZrO$_2$, Ce$_2$O$_3$-CeO$_2$ and La$_2$O$_3$ films very important.

There are many studies of their electrochemical properties, numerous SEM and XPS studies of these films, but little information is available on their mechanical properties. That’s why the aim of the present work is to investigate mechanical properties of these films by means of instrumented indentation testing.

2. Theoretical

Instrumented-indentation testing (IIT) has been developed over the last decade for the purpose of probing mechanical properties of very small volumes of material. IIT is ideal for exploring mechanical properties of thin films, coatings, and surface layers. Because indents can be positioned to within about 1 micron, IIT also enables one to map the spatial distribution of surface mechanical properties with a good resolution. For example, one could map the mechanical properties within and around a weld. Even if a sample is spatial-large enough to be tested by other means, IIT often remains the method of choice because it requires little sample preparation. At its most basic
level, IIT employs a high-resolution actuator to force an indenter into the tested surface and a high-resolution sensor to continuously measure the penetration. One of the great advantages of this technique is that the contact area under load can often be inferred from the continuous load-displacement data alone. In other words, the residual hardness impression does not have to be directly imaged, thus facilitating property measurement at the sub-micron scale. Hardness \( (H_{IT}) \) and indentation elastic modulus \( (E_{IT}) \) are the properties most frequently measured by IIT using Oliver&Pharr approximation method\(^4\).

The fundamental relationships, from which \( H_{IT} \) and \( E \) are determined, are:

\[
H_{IT} = \frac{P}{A} \tag{1}
\]

where \( P \) is the load and \( A \) is the projected contact area at that load, and:

\[
E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A}} \tag{2}
\]

where \( E_r \) is the reduced elastic modulus, \( S \) is the slope of the upper portion of the unloading curve \( (S = dP / dh) \) and \( \beta \) is a constant that depends on the geometry of the indenter. For indenters with triangular cross section like the Berkovich one \( \beta = 1.034 \).

A reduced modulus, \( E_r \), is used in Eq. (2) to account for the fact that elastic displacements occur in both the indenter and the sample. The elastic modulus of the test material, \( E_{IT} \), is calculated from \( E_r \) using:

\[
\frac{1}{E_{IT}} = \frac{1-v^2}{E_i} + \frac{1-v_i^2}{E_i} \tag{3}
\]

where \( v \) is the Poisson’s ratio for the test material, and \( v_i \) and \( v_i \) are the elastic modulus and Poisson’s ratio, respectively, of the indenter. For diamond, elastic constants \( E_i = 1141 \text{ GPa} \) and \( v_i = 0.07 \) are often used. While it may seem counterintuitive that one must know the Poisson’s ratio of the material in order to compute its modulus, even a rough estimate, say \( v = 0.25 \pm 0.1 \), produces only about a 5% uncertainty in the calculated value of \( E \) for most materials\(^5\).

3. Experiment

3.1. Deposition of films

The samples/substrates from stainless steel (SS) (SS OC 404, containing 20 % Cr, 5 % Al, 0.02 % C and up to 100 % Fe) were plates with sizes 20×20 mm, which were cut from a steel foil with a thickness of 50 μm. Films of \( \text{ZrO}_2 \), \( \text{Ce}_2\text{O}_3-\text{CeO}_2 \) and \( \text{La}_2\text{O}_3 \) with thickness 0.5 μm were electrodeposited from non-aqueous electrolytes using the compositions and schedules, described in ref.\(^{10-13}\).

3.2. Nanoindentation experiments

Mechanical properties of \( \text{ZrO}_2 \), \( \text{Ce}_2\text{O}_3-\text{CeO}_2 \) and \( \text{La}_2\text{O}_3 \) films were investigated by nanoindentation experiments, using Nano Indenter G200 (Agilent Technologies). These films were electrochemically deposited on stainless steel substrate (SS OC 404) with a thickness of 50 μm. The nanoindenter is equipped with a Berkovich three-sided diamond pyramid with centerline-to-face angle 65.3° and a 20 nm radius at the tip of the indenter. The minimum allowed load is 10 mN, and the maximum load is 500 mN. Displacement recording resolution is 0.01 nm and the load recording resolution is 50 nN. The device is equipped with an optical microscope with 2 objectives with magnifications of 250× and 1000×. We made series of 25 indentations on each sample probe in order to have better statistics. We used an indentation method which prescribes series of 10 loading/unloading cycles in a single indentation experiment. Hardness and modulus are determined using stiffness calculated from the slope of the load-displacement curve during each unloading cycle. Basic input parameters used in this indentation method are given in Tab. I.

### Table I
Input parameters for nanoindentation experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent To Unload</td>
<td>[%]</td>
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</tr>
<tr>
<td>Surface Approach Velocity</td>
<td>[nm/s]</td>
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</tr>
<tr>
<td>Delta X For Finding Surface</td>
<td>[μm]</td>
<td>-50</td>
</tr>
<tr>
<td>Delta Y For Finding Surface</td>
<td>[μm]</td>
<td>-50</td>
</tr>
<tr>
<td>Maximum Load</td>
<td>[gf]</td>
<td>50</td>
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<td>Load Rate Multiple For Unload Rate</td>
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<tr>
<td>Number Of Times To Load</td>
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<td>10</td>
</tr>
<tr>
<td>Allowable Drift Rate</td>
<td>[nm/s]</td>
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<tr>
<td>Peak Hold Time</td>
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<td>Time To Load</td>
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<td>Surface Approach Sensitivity</td>
<td>[%]</td>
<td>40</td>
</tr>
<tr>
<td>Poisson Ratio</td>
<td>[-]</td>
<td>0.3</td>
</tr>
</tbody>
</table>

4. Results and discussion

As a result of nanoindentation experiments, load-displacement curves were obtained and two mechanical characteristics of substrate and investigated films – indentation hardness \( (H_{IT}) \) and indentation modulus \( (E_{IT}) \) were calculated using Oliver&Pharr approximation method\(^6\). Dependence of indentation modulus and inden-
tation hardness on depth of indentation was investigated as well.

Dependences of indentation modulus $E_{IT}$ and indentation hardness $H_{IT}$ on depth of indentation for the stainless steel substrate are shown on Fig. 1 and Fig. 2.

Fig. 1 and Fig. 2 clearly show that with increasing depth of indentation the indentation hardness and indentation modulus of the substrate decrease. In our opinion, this effect is associated with the presence of a thin natural passive film on the surface of the stainless steel. The chemical and phase composition of the film are quite different from those of the bulk steel. XPS investigations showed that the film’s thickness is about 1.5 nm and that consists of FeO, FeO$_2$, FeOOH, CrO$_2$, Cr$_2$O$_3$, AlO and Al$_2$O$_3$. At the same time, the concentrations of the metallic Cr and Al, their oxides respectively, in it are higher than concentrations of metallic Fe and its oxides, when compared with the ratio of metallic Fe, Cr and Al in the bulk steel$^{17,18}$. Results for stainless steels presented in ref. $^{19}$ suggest that in this case, a passive film may form that will contain Fe$^{3+}$, Cr$^{3+}$ and Al$^{3+}$; most probably an Al$^{3+}$-containing spinel of the type of Fe$^{2+}$(Fe$^{3+}$,Cr$^{3+}$)O$_4$. In this case, a Cr$^{3+}$:Fe$^{3+}$ ratio of about 3 is attained. Obviously, the surface passive film consist vastly highest concentration of metallic Cr, Cr oxides and Al oxides will determine measuring of considerably highest indentation hardness and indentation modulus in beginning stages of nanoindentation. The average values of indentation hardness and indentation modulus of the substrate obtained are $H_{IT} = 2.67$ GPa, $E_{IT} = 119.13$ GPa.

They were calculated using Eq. (4) and Eq. (5), where $H_{IT}$ and $E_{IT}$ are measured hardnesses and modulus at 10 different depths of indentations, shown on Fig. 1 and Fig. 2.

$$H_{IT} = \frac{\sum_{i=1}^{10} H_{IT,i}}{10} \quad (4)$$

$$E_{IT} = \frac{\sum_{i=1}^{10} E_{IT,i}}{10} \quad (5)$$

The dependences of indentation modulus $E_{IT}$ and indentation hardness $H_{IT}$ on depth of indentation for investigated films are shown in Fig. 3 and Fig. 4. It’s evident from Fig. 4 that the hardness of zirconium and lanthanum films decreases with increasing depth of indentation, due to the influence of the soft substrate. At one point, it becomes close to the hardness of the substrate. The reason is that below the depth of indentation of 500 nm, the substrate is reached. This boundary is marked with a vertical dashed line in Fig. 4. The hardness of the cerium film increases with increasing of depth of indentation, due to the influence of the soft substrate. Below the depth of indentation of 500 nm hardness becomes equal to the hardness of the substrate. Moreover, the cerium film has the highest hardness (3.09 GPa). Hardnesses of zirconium (2.69 GPa) and cerium films (1.11 GPa) follow. Fig. 3 shows that the hardness of zirconium and lanthanum films decreases with increasing depth of indentation, due to the influence of the soft substrate. They were calculated using Eq. (6) and Eq. (7), where $H_{IT}$ and $E_{IT}$ are measured hardnesses and modulus at first 5 depths of indentations (only inside the films), shown on Fig. 3 and Fig. 4.

$$H_{IT} = \frac{\sum_{i=1}^{5} H_{IT,i}}{5} \quad (6)$$

$$E_{IT} = \frac{\sum_{i=1}^{5} E_{IT,i}}{5} \quad (7)$$

Authors gratefully acknowledge the financial support of Bulgarian National Science Fund under grant No. TK01/0185.
REFERENCES

S. Cherneva a, D. Stoychev b, and R. Iankov a (a Institute of Mechanics, Bulgarian Academy of Sciences, Sofia, b Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria): Measuring of Mechanical Properties of Electrochemically Deposited ZrO2, Ce2O3-CeO2 and La2O3 Films by Nanoindentation

Mechanical properties of ZrO2, Ce2O3-CeO2 and La2O3 films with thickness of 0.5 µm were investigated by means of nanoindentation using Nanoindenter G200 (Agilent Technologies), equipped with Berkovich diamond indenter. These films were electrochemically deposited on stainless steel substrate – SS OC 404 with a thickness of 50 µm. Two mechanical characteristics of investigated films: indentation hardness (HIT) and indentation modulus (EIT), were determined by means of instrumented indentation and Oliver&Pharr approximation method. We used an indentation method that prescribes series of 10 loading/unloading cycles in a single indentation experiment. Hardness and modulus are determined using stiffness calculated from the slope of the load-displacement curve during each unloading cycle. The dependences of indentation modulus and indentation hardness on depth of indentation were also investigated.