OXIDE AND NITRIDE PROTECTIVE LAYERS FORMED ON STAINLESS STEEL BY THERMAL TREATMENT: SEM, AES, WDS AND CORROSION MEASUREMENTS

Protective oxide and/or nitride layers on AISI 321 stainless steel were prepared by thermal treatment in air and two controlled atmospheres in a laboratory simulation of an actual technological procedure. Samples' surface was imaged by Scanning Electron Microscopy (SEM), elemental composition of the substrates was checked by Wavelength Dispersive Spectroscopy (WDS) and depth profiles of the samples were measured by Auger Electron Spectroscopy (AES). Since protective layer thicknesses were found to be of the order of hundreds of nanometers an attempt was made to obtain some fast averaged information about layers composition by Wavelength Dispersive Spectroscopy (WDS) with appropriately adjusted primary beam energy. Electrochemical corrosion testing was also performed on samples.

Key words: stainless steel, thermal treatment, surface, AES, WDS

SEM, AES, WDS i korozijsko testiranje oksidnih i nitridnih zaštitnih slojeva oblikovanjih toplinskom obradom nerđajućeg čelika. Zaštitne oksidne i/ili nitridne slojeve na AISI 321 nerđajućem čeliku pripremljen toplinskom obradom materijala na zraku i u 2 kontrolirana tipa atmosfera kao laboratorijsku simulaciju stvarnog tehnološkog procesa. Slike površine uzoraka dobijene tehnikom SEM, sastav substrata metodom WDS a za profilnu analizu upotrijebljena je spektroskopija Augerovih elektrona (AES). Kako je ustanovljeno, da su debljine formiranih zaštitnih slojeva reda veličine nekoliko stotina nanometara pokušalo se doći do ocjene o prosječnom sastavu unutar sloja upotrijebom tehnike WDS uz odgovarajuće odabranu energiju primarnog elektronskog snopa. Na uzorcima je provjereno i korozijsko testiranje.

Ključne riječi: nerđajući čelik, toplinska obrada, površina, AES, WDS

INTRODUCTION

Protective layers on stainless steels under high temperatures should exhibit adequate mechanical properties as well as resistance to chemical degradation due to reaction with the environment. Simplicity of producing the coating is also important. AISI 321 with its high chromium content offers a possibility of a chromium compound based protective layer. Surface modification of the base material in a form of a protective surface layer has become a standard manufacturing practice to increase the chemical resistance of the base materials (tribological properties can also be significantly influenced in this way, especially by so-called hard coating type films [1-3]). There is number of technologies to induce and control protective layer growth. The simpler, like metallurgical thermal treatments are typically easy-to-use resulting in a lower quality layers while high quality layers are usually prepared in a somewhat more complex way by specialized thin films growth techniques through precise control of the growth parameters. In this study protective layers grown by thermal treatment of the AISI 321 stainless steel in a laboratory simulation of a technological process used in a manufacturing plant are studied. These constraints notwithstanding, different atmosphere compositions during thermal treatment do significantly influence protective layers composition, structure and corrosion resistance.

It is desired for the protective layer to be adequately stoichiometric so the transport of metal or oxygen ions in the oxides lattice is slow. Cr_2O_3 oxide protective layer, for example, is reasonably protective in oxygen or air to about 900 °C. At higher temperatures this oxide reacts further with oxygen to form CrO_3 [4]. Some continuous concentration change, however, as contrasted to abrupt concentration change at the protective layer / substrate interface may be preferable from the point of view of the layer's adhesion to the substrate and is sometimes introduced into layer's structure on purpose [5]. Also, if metallic nitride protective layer is implemented, thin pure metallic interlayer is sometimes fabricated onto metallic substrate to improve adhesion [6].

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In this study surface morphology of the protective layers formed on AISI 321 stainless steel was studied by SEM and profile analysis of the layers was performed by AES. WDS of appropriately chosen primary beam energy was performed in an attempt for fast estimation of the averaged elemental compositions of the protective layers. WDS was also used to check the elemental composition of the AISI 321 stainless steel substrate. Electrochemical corrosion tests were used to determine corrosion resistance of the layers.

EXPERIMENTAL

Protective layers on the walls of the stainless steel tubes with diameter of approximately 10 mm were formed, as they would be formed during the actual technological process, by heating the material of the approximate thickness of the 0.1 mm at 1060 $^{\circ}$C in air and 2 types of controlled atmosphere (N_2 and $N_2 + H_2$ with 1 : 3 atomic ratio) at ambient total pressure. In all cases temperature was linearly increased to its maximal value during 2 minutes, kept there for 8 minutes and slowly cooled down after switching off the heaters. Tubular furnace was used with different atmosphere types circulated through it. Sample types prepared in air, nitrogen and nitrogen-hydrogen mixture were labelled as "1060AIR", "1060N2" and "1060ZA", respectively. Parameters were constrained according to particulars of the technological process involved in the protective layers formation. From these stainless steel surfaces with protective layers samples for AES and WDS analysis of approximately 3 - 5 × 10 mm^2 were cut out. In a same manner, several approximately half-length samples were prepared for SEM and WDS measurements, to facilitate mounting onto a multi-sample holder.

WDS of the prepared samples was performed by JEOL JSM 5610 and AES by VG Microlab 310F. The former was operated at higher primary beam energy of 20 keV in WDS mode, with probing depth of the order of approximately 1 μm [7] in layers with predominantly Mn/Fe/Cr/Ni composition. In some samples layer thickness was below 1 μm and average layer density considerably decreased, due to oxide and/or nitride nature of the layer, thus lower primary beam energy was advised. WDS at 5 keV primary electron beam with roughly estimated 0,3 - 0,4 μm probing depth in metal oxide / nitride type materials [7] was considered more appropriate to obtain some fast volume averaged information about protective layers composition.

Primary electron beam energies of 10 keV were used for AES depth profiling. Ar$^+$ was used of 3 keV energy and order of magnitude of 1μA ion current over the area of 3 × 4 mm^2. Rough estimate for sputtering rate at these parameters is approximately 1 nm/min. This is roughly in agreement with some calibration measurements performed on metallic and oxide type samples as well as with some reference data for sputtering rates for Fe and Cr and their oxides [8]. However, sputtering rates may have been severely influenced by the depth-dependant stoichiometry of the samples. Thus all information provided on depth or layer thickness must be viewed upon as an estimate at best, based on rough 1 nm/min sputtering rate estimate.

VG Microlab acquisitioned data were processed by the Eclipse V2.1 ver07 software produced and supplied by the manufacturer of the instrument and by the CasaXPS commercially available software for processing of the XPS and AES spectra.

Electrochemical corrosion tests were performed with EG&G PAR 352 Soft Corr computer-assisted electrochemical corrosion measurement equipment in 3,5 % solution of NaCl.

RESULTS AND DISCUSSION

Average composition of approximately top 1 μm [7] of AISI 312 stainless steel surface with no protective layer applied, as obtained by WDS is presented in Table 1 compared to manufacturers compositional data for the same material. Also, values in Table 1 were obtained from measurement on the sample of thickness large compared to the probing depth of the WDS.

Table 1: **Composition of stainless steel substrate as given by manufacturer and as measured by WDS.**

Element	N	O	Al	Si	Cr	Fe	Ni
C_{MNF} / at%	–	–	–	2,0	18,0-19,4	68,3	8,4-10,8
C_{WDS} / at%	2,1	1,9	0,2	0,6	17,2	68,8	8,1

Surface morphologies of protective layers prepared under different thermal treatment parameters are shown in SEM images in Figures 1a – 1c. Surface of the samples prepared in air is nearly completely covered with submicron-sized crystallites, possibly of oxide nature (Figure 1a). However, these crystallites are not very small compared to the thickness of the protective layers (typically tenths of a μm compared to a μm), therefore protective layers prepared in air may be considered to be of a very poor homogeneity. Somewhat similar Cr_2O_3 crystallites in size range of 0,03 – 0,15 mm can be formed on a stainless steel 316L of an equally high chromium content as AISI 321 by electrochemical anodic roughening [9]. Crystallites on the surface of the samples prepared in N_2 atmosphere are larger on the average and much less numerous (Figure 1b), suggesting that actual protective layer is a homogenous one with few oxide-type crystallites at the top. Samples that were prepared in hydrogen-nitrogen atmosphere (Figure 1c) have virtually no oxide-type crystallites on the surface due to reductive properties of the atmosphere.

AES concentration profiles for the stainless steel layers with 3 different protective layers are shown in Figure
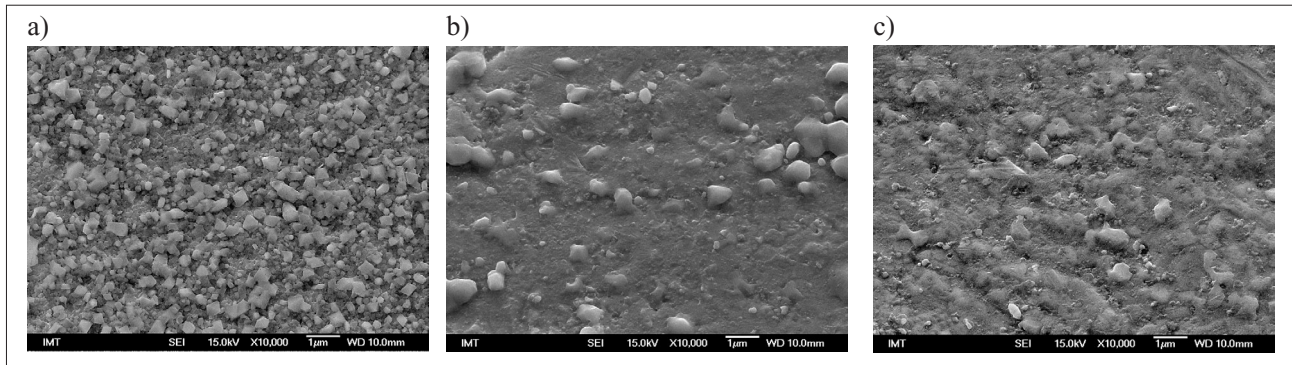
Figure 1: High-magnification SEM images of protective layers prepared in air, nitrogen and nitrogen-hydrogen atmosphere.
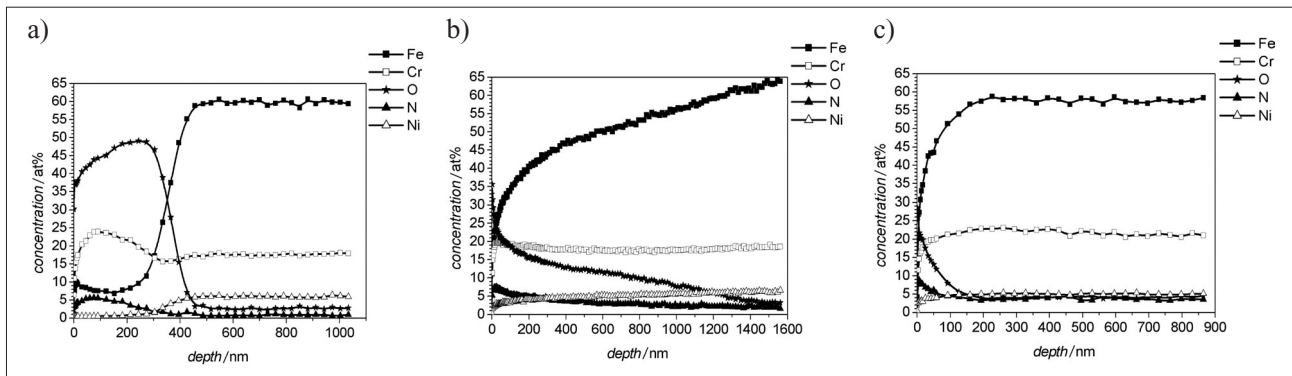

Figure 2: Concentration profiles for protective layers formed at 1060 ^{o}C in air (a), in nitrogen (b), and in nitrogen – hydrogen mixture (c).

2. In all samples it was intended to measure concentration profiles until all concentrations reach constant values, however, due to unexpectedly thick layers this could not be achieved in all samples. Total time of measurement (sputtering + data acquisition) for sample 1060N2 (estimated profiling depth of 1600 nm) was in excess of 50 hours. Depth profiles of protective layers show that only layer prepared in air is oxide-like (Figure 2a). Also, well-defined layer structure with at least moderately homogeneous stoichiometry inside the layer followed by an interfacial layer characterised by a steeper stoichiometry change can only be found in oxide-like layer prepared in air (Figure 2a). Depth profile of 1060AIR sample show that the protective layers prepared in air also contain nitrogen though in much lower concentration than oxygen (Figure 2a).

This lower concentration is still about 2 to 3 times bulk nitrogen concentration of the substrate material which indicates that nitrogen transport from the substrate into the layer may occur during the layer preparation.

Cyclic oxidation treatments [10] below 700 ^{o}C have been found to cause a co-formation of an oxide phase with cubic lattice of M_2O_3 type and spinel with cubic lattice of M_3O_4 type with good adhesion to the base metal. Above 950 ^{o}C diffusion of iron through the Cr_2O_3 layer intensifies, the Fe_3O_4 starts to form inside the Cr_2O_3 layer [11]. This mixture of 2 oxide phases is consistent with (Fe+Cr)/O atomic ratios presented in Figure 3 with theoretical values from 0,67 to 0,75 over the whole range of

Cr_2O_3 and Fe_3O_4 molar ratios. Average Cr_2O_3 and Fe_3O_4 molar ratio inside the layers prepared in air was roughly estimated from Cr and Fe concentrations in the corresponding depth profiles (Figures 2a and 2b) as approximately 2 : 1. Depth profiles in Figures 2b, and 2c show protective layers prepared in nitrogen and nitrogen-hydrogen atmospheres as prolonged interface layers with continuously changing stoichiometries along the depth of the layers. Cr concentration after prolonged sputtering decreases to approximately 17 – 20 at%, which is consistent with 17 at% value for non-processed material (Table 1). However, Fe concentration in some samples did not reach constant level and where it did concen-
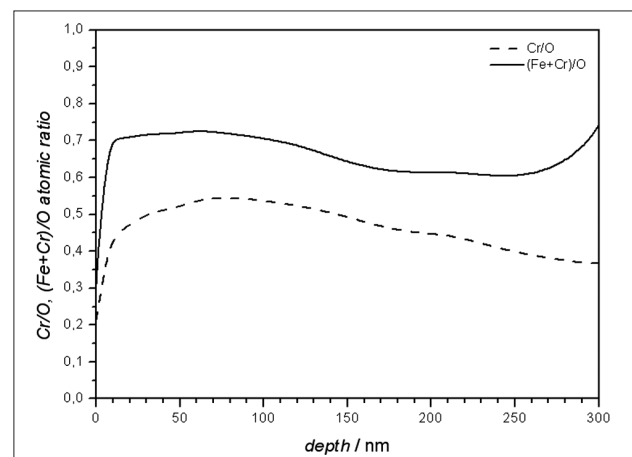

Figure 3: Metal - oxygen atomic ratios for protective layers formed in air.

trations were somewhat lower (48 – 58 at%) than for non-processed material (69 at%) (Table 1).

Cr/N ratios of protective layers grown in nitrogen and nitrogen-hydrogen mixture can be roughly described as slowly linearly increasing while the corresponding ratio for layer grown in air increases sharply around layer-substrate interface (Figure 4).
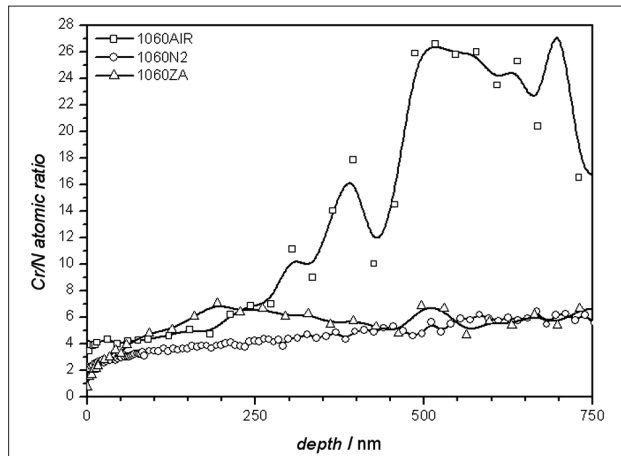

Figure 4: Cr/N atomic ratios vs layer depth for different protective layers.

This increase suggests the substrate-to-layer nitrogen transport and is consistent with nitrogen depletion from the top of the substrate that can be observed if nitrogen concentration values in substrate from Figures 2b and 2c are compared to unprocessed substrate value (Table 1). Conversely, nitrogen concentrations in substrate for protective layers grown in air mixture are larger than unprocessed substrate nitrogen concentration (Figure 2a, Table 1), which suggests that nitrogen in these protective layers derives from the nitrogen and nitrogen-hydrogen mixture atmosphere. Average value of Cr/N ratio over first 300 nm for this layer is between 2,5 and 3. This is in agreement with preliminary results from X-ray Photoelectron Spectroscopy (XPS) depth profiling of sample 1060ZA that chromium is in a chemical state close to Cr_2N [12].

2 primary beam electron energies, 5 and 20 keV, were used for WDS fast compositional information averaged over the probing depth. Results, as well as comparison with average values calculated from the AES depth profile data are presented in Table 2. Low Fe concentrations in Table 2 for samples prepared in air show that probing depth of WDS analysis at 5 keV primary electron beam energy is predominantly limited to protective layer which makes WDS probing depth estimates roughly consistent with depth profiling depth scale estimates. Table 2 shows that while average concentrations measured by WDS at 5 keV primary beam energy and calculated from AES depth profiles are of the same orders of magnitude and sometimes agree very well, average concentration values analysis of a protection layer obtained by WDS can be considered only

Table 2: Average compositions of the protective layers derived from the WDS measurements at 2 different electron beam energies and averaged compositions obtained from the first 300 nm of the AES depth profiles in Figure 2.

	c(N) / at%	c(O) / at%	c(C) / at%	c(Fe) / at%	c(Ni) / at%
1060 AIR					
5 keV	3,9	76,1	12,4	6,8	0,9
20 keV	2,9	33,0	16,3	38,1	4,7
<AES300>	4,0	42,5	18,8	8,8	0,6
1060N2					
5 keV	10,0	7,7	17,7	54,9	9,8
20 keV	9,9	0,0	20,8	60,4	7,6
<AES300>	5,7	19,8	18,5	32,8	3,3
1060ZA					
5 keV	5,4	6,9	16,6	61,0	10,2
20 keV	4,6	0,0	19,6	66,5	8,2
<AES300>	5.5	13,5	18,5	42,2	3,8

orientational. This is due to only very approximate probing depth assessment in samples of estimated composition. An iterative approach could improve results, however, some of the advantages compared to time consuming profiling techniques would be lost. At 20 kV primary beam energy probing depth of the WDS is approximately $1.0 – 1.5\ \mu$m [7]. This strongly influences average concentrations in Table 2 with the substrate influence becoming considerable, as seen from large decrease in oxygen concentration and large increase in iron concentration in air prepared samples. Such a sharp drop is not observed in nitrogen concentration in samples prepared in nitrogen and nitrogen-hydrogen atmospheres. This means that in these samples even below 1 μm depth there is still slowly decreasing nitrogen concentration of the order of 1 atomic percent.

While in protective layer prepared in air Fe concentration is very low in accordance to AES profiling as well as WDS measurements data, this is not so in layers prepared in nitrogen and nitrogen-hydrogen atmosphere. However, probability for iron nitride formation is rather low since formation enthalpies for Fe and Cr oxides in the temperature range 1000 - 1100 °C are from -800 to -200 kJ/mol [13] and for Fe nitrides around 15 to 20 kJ/mol [13]. Possibility of iron nitride formation can not be totally excluded, especially since interpretation of Fe $2p_{3/2}$ at 707.0 eV in preliminary XPS data remains ambiguous: metallic Fe or Fe nitride [12].

Potentiodynamic polarisation scans were measured for three samples prepared at 1060 °C in different atmospheres. Tafel calculations were used to determine corrosion current and corrosion rate for each sample (Table 3). Corrosion resistance of the sample prepared in air is significantly better than corrosion resistance of the sam-

Table 3: **Tafel calculations for samples heated at 1060 °C in air, N$_2$+H$_2$ and in N$_2$, tested in 3.5 % NaCl.**

Atmosphere	Air	N$_2$+H$_2$	N$_2$
Corrosion Rate / mpy	53,35E-3	105,9E-3	124,1E-3
E(I=0)/ mV	-233,1	-209,1	-218,2
Icorr / nA	118,5	235,2	275,5
Beta Anodic / (V/decade)	101,9E-3	218,8E-3	95,38E-3
Beta Cathodic / (V/decade)	70,03E-3	128,4E-3	141,2E-3

ples prepared in nitrogen and nitrogen-hydrogen atmospheres as can be seen from its low corrosion rate and corrosion current values compared to other two samples. This may be due to well defined oxide layer of rather homogeneous composition exhibited by the air-prepared sample but not by the other two.

CONCLUSIONS

Surface morphologies of the samples prepared at 1060 $^{\circ}$C in three different atmospheres are significantly influenced by the atmosphere composition. Well-defined protective layers developed only in air and seem to be a mixture of Cr$_2$O$_3$ and Fe$_3$O$_4$, with Fe percentage increasing towards substrate. Average Cr/N atomic ratio in protective layers prepared in nitrogen and nitrogen hydrogen atmospheres is between 2.5 and 3 if thickness of these ill-defined layers is considered as comparable to layers prepared in air. Chromium nitrides seem to be most likely compound candidates for these layers. Iron-nitrogen phases can not be excluded with certainty though they do not seem thermodynamicaly probable. An attempt was made to roughly estimate the average compositions of the layers by WDS. Obtained values were compared to the average values calculated from the AES profiling measurements. It can be concluded that while quantitative results obtained by WDS measurements are rather limited, qualitative conclusions about the system can be reached independently of or corroborative to other techniques. Corrosion testing showed protective layer prepared in air to be of superior corrosion resistivity to the layers prepared in nitrogen and nitrogen-hydrogen atmosphere.

In further investigations of these protective layers tribological tests will be performed. Full scale XPS depth profiling of the layers prepared in nitrogen and nitrogen-hydrogen atmosphere may reveal dependence of ratio of nitride chromium and solid solution metallic chromium on depth. Thin films X-Ray Diffraction (XRD) may also be used to help with and corroborate phase determination.

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Note: Authors are responsibles as language lecturers for English language.