Electron spectroscopic study of passive oxide layer formation on Fe–19Cr–18Ni–1Al–TiC austenitic stainless steel

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A R T I C L E   I N F O

Article history:
Received 4 June 2010
Received in revised form 6 September 2010
Accepted 13 September 2010
Available online 19 September 2010

Key words:
XPS
XAS
Austenitic stainless steel

A B S T R A C T

Surface oxidation of a TiC-enriched austenitic stainless steel alloy was investigated at 50 °C by X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). It was found that a passive oxide layer started to form on the alloy surface after 5 L of oxygen exposure. Further oxidation of the alloy was suppressed after 500 L of oxygen exposure when a stable passive layer was formed. It was found also that Ti and Ni did not oxidize and Ti remained in a carbide form during whole oxidation. The oxidation kinetics of different metals were investigated as well.

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1. Introduction

Stainless steel materials are widely used in a number of modern applications thanks to their excellent corrosion resistance in oxidizing environments, good physical and mechanical properties. The key issue related to the corrosion resistance is the protective chromium-rich surface oxide layer, which suppresses the ion diffusion between the alloy and the ambient environment. This extremely thin layer, under appropriate conditions, is also self-repairing. A passive oxide layer usually consists of more elements than iron and chromium.

Impurities are added to stainless steel to enhance the passive layer and to obtain certain properties for specific applications. For example, nickel is added to Fe–Cr alloys to obtain an austenitic structure (the respective material is called austenitic stainless steel). Austenitic stainless steel is a non-magnetic material and has great resistance to corrosion. It is a most-produced and widely-used stainless steel. In some specific applications even a more advanced passive oxide layer on the surface of austenitic stainless steel is needed. For example, in biocompatible steels Al and Si are added to prevent the harmful release of metal cations (especially nickel) near the tissue [1]. In the applications where an enhanced resistance to inter-granular corrosion is needed, carbide-forming elements such as Ti or Nb are added to stainless steel [2].

To achieve a better understanding of the passive oxide layer formation and its property dependence on the additives, detailed studies in well-defined experimental conditions are needed. Predominantly the surface analytical studies of the oxidation of stainless steel materials are made ex situ and at high temperatures. There are only a few exceptions, where the onset of the oxidation process of austenitic stainless steel alloys is studied in situ at 323 K [3,4].

In the present work, besides the well-defined experimental conditions, also surface-sensitive methods have been applied. A common technique of obtaining information about the electronic structure and the chemical state of a solid surface is X-ray photoelectron spectroscopy (XPS). XPS is based on photoelectric effect, where absorbed photons liberate photoelectrons, which are analyzed with respect to their kinetic energy. XPS is surface sensitive method due to small escape depth of the excited electrons, which is typically in the range of a 5–20 Å [5]. Besides XPS, surface sensitive method is X-ray absorption spectroscopy (XAS). XAS is known as a highly versatile tool for determining the local electronic structure and the chemical state of matter [6,7]. This method is based on a local nature of X-ray absorption process, where an electron is excited from a core state to an unoccupied empty state. In a total electron yield (TEY) mode, absorption cross section is measured by detecting and counting electrons with all kinds of kinetic energies, which escape from the surface after the decay of the core hole [8]. XAS in TEY mode has the probing depth of 40 Å and deeper for transition metal 2p edges [9,10], which is deeper than in XPS. Thus, XAS in TEY mode permits an adequate study of a protective oxide layer with a typical thickness of 10–30 Å [11].

In the present work, we investigated the formation of a passive oxide layer on the surface of a specially prepared titanium carbide enriched austenitic stainless steel alloy at 50 °C by using XPS and...
XAS. These methods were comparably applied to investigate the metal's 2p edges. XPS peak area analyses were carried out to investigate the changes in proportion of alloy major elements in surface layer after every oxidation experiment. XAS was applied also to oxygen's 1s edge. Furthermore, XPS with the excitation energy of 400 eV was used to study gradually the low binding energy region (<120 eV) and C 1s band.

2. Experimental

The chemical composition of the bulk alloy used in the present work resembles closely (but not fully) grade UNS S33400 [12] and consists of 60.1 at.% Fe, 19.4 at.% Cr, 17.5 at.% Ni, 1.0 at.% Al, 0.5 at.% Mn, 0.7 at.% Si, 0.4 at.% Ti and 0.24 at.% C. Furthermore, the alloy contains a very low concentration of non-metals and traces of metals typical to industrial melts (mainly O, N, S, P, K and W).

The TiC-enriched surface was prepared by annealing the bulk alloy to 1000 K. After this treatment the amount of TiC remained constant through several cleaning cycles. The relative atomic surface concentrations of minor alloy constituents after each cleaning were 12–20% Al, 8–18% O, 7% C, 7% Ti and 1–2% Si within the XPS analysis depth when using a photon energy of 400 eV [3]. In spite of the fact that the surface composition differs from the bulk composition, in further discussion we refer to the alloy by its relative bulk atomic content, i.e. Fe–19Cr–18Ni–1Al–TiC. Before every oxidation experiment the alloy surface and reference Fe, Cr, Ni foil surface were cleaned in situ by 2.0 keV argon ion sputtering in ultra high vacuum (UHV) conditions and a subsequent annealing at 900 K for 10 min, followed by a slow cooling (within 1 h) to 323 K. Before the oxidation experiment the substrate cleanliness was checked by XPS. Oxidation experiments were performed by backfilling the UHV chamber (base pressure $1 \times 10^{-10}$ mbar) with $2.7 \times 10^{-6}$ mbar of O$_2$ (99.9999%), while maintaining the sample temperature 50 °C throughout the exposure duration. The investigated O$_2$ exposure range was 0–3000 L (1 L = $1 \times 10^{-6}$ Torr s).

The experiments were carried through at a beamline D1011 of MAX II storage ring (Lund, Sweden). The beamline is equipped with a modified SX-700 plane grating monochromator. XPS spectra were measured by an electron energy analyser SCIENTA SES-200 in a fixed analyser transmission (FAT) mode with 200 eV pass energy. XAS spectra were measured in the TEY mode by using a microchannel plate detector. The photon energy resolution was about 0.1 eV. The sample was positioned at a normal emission with 40° incident angle for the incoming photon beam.

XPS and XAS spectra were normalized to the synchrotron ring current to account for the variations in the photon beam intensity. The binding energy scales for XPS experiments were referenced to the Ni 3p$_{3/2}$ (66.3 eV), 3s (110.7 eV) and 2p$_{3/2}$ (852.7 eV) transitions. The photon energy scale for XAS experiments was calibrated from the measured Fe 3p ($52.8$ eV) and Ni 3p$_{3/2}$ (66.3 eV) bands in first and second order excited with photon energy of 400 eV. The XAS spectra of metal 2p edges were normalized by a reference signal from a gold mesh. O 1s edge spectra were normalized by a cleaned alloy spectrum. For reference, cleaned Fe, Cr, Ni foils and oxidized Fe, Cr foils XAS spectra were measured.

Changes in XPS peak areas of the alloy main components were determined from XPS spectra (excitation energy 1486.6 eV). Fe 2p, Cr 2p, Ni 2p, Ti 2p and O 1s photopeaks were fitted by asymmetric Gaussian–Lorentzian lineshapes after subtracting a Shirley background. An analysis was carried out by using CasaXPS software (version 2.3.13) [13].

3. Results

Fig. 1 represents the Fe 2p XPS and XAS spectra of cleaned and to a different extent oxidized stainless steel alloy, iron oxidation states are marked as Fe$^{0}$, Fe$^{2+}$ and Fe$^{3+}$; (b) Fe 2p XAS spectra of cleaned and to a different extent oxidized stainless steel alloy and reference spectra of cleaned and oxidized Fe foil, dashed line marks the feature related to metallic iron.
corresponding value for XPS spectra, 13.1 eV. This difference is due to circumstance that in comparison with XPS final state the XAS final state has additional d electron. This may lead to redistribution of intensities of different terms of multiplet.

A change in Fe 2p XPS spectrum was detectable after 40 L of oxygen exposure, when a higher background at 709.4 eV, related to the formation of FeO (marked as Fe$^{2+}$ in Fig. 1a) in the oxidation process, was observed. Another structure appeared in the XPS spectrum at 710.7 eV after 500 L of oxygen exposure. This was due to the formation of Fe$_2$O$_3$ (marked as Fe$^{3+}$ in Fig. 1a) in the surface layer of the alloy. Since the iron oxides were formed, the characteristic satellite peaks, related to Fe$^{2+}$ and Fe$^{3+}$ cations, at the high binding energy side of the main peaks were observed as well [14]. Comparably, the XAS spectra of the alloy showed a significant change after 500 L of oxygen exposure, when a clear shoulder appeared at 707.8 eV. This shoulder was related to the iron oxides formed in the alloy surface.

At the highest oxygen exposure used, 3000 L, a mixture of FeO and Fe$_2$O$_3$ besides the metallic iron was present in the XPS spectrum. The Fe–19Cr–18Ni–1Al–TiC Fe 2p XPS spectrum, after 3000 L of oxygen exposure, differed from the oxidized Fe foil XAS spectrum (Fig. 1b), which was identified as Fe$_3$O$_4$ (oxide containing both Fe$^{2+}$ and Fe$^{3+}$ cations) [8]. XPS spectra of alloy contained X-ray absorption of metallic chromium (Fig. 2b). After 5 L of oxygen exposure, shoulder appeared at 576.5 eV in the Cr 2p$_{3/2}$ band. When the oxygen exposure was increased, the shoulder in XPS and XAS spectra became stronger, having the maximum after 500 L of oxygen exposure. On a further increase of oxygen exposure the shoulder in XPS and XAS spectra slightly decreased.

The Ni 2p XAS and XPS spectra of cleaned and to a different extent oxidized Fe–19Cr–18Ni–1Al–TiC are shown in Fig. 3. For reference, an XAS spectrum of Ni 2p of a cleaned Ni foil was measured. Before oxidation the Fe–19Cr–18Ni–1Al–TiC Ni 2p XPS spectrum (Fig. 3a, 0 L) consists of two separate peaks Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ (due to the spin–orbit splitting), which were separated by 17.2 eV. Also, weak broad structures on the higher binding energy side of Ni 2p peaks were observed. This is typical for metallic nickel [15]. After oxidation Fe–19Cr–18Ni–1Al–TiC XPS spectra had the same structure as the cleaned alloy XPS spectrum. In the cleaned Fe–19Cr–18Ni–1Al–TiC XAS spectrum (Fig. 3b, 0 L) two spin–orbit–split components were also observed. The Ni 2p XPS spectra of a cleaned and oxidized alloy had the same structure as spectrum measured from a cleaned Ni foil. This confirms that nickel does not oxidize. The position of Ni 2p$_{3/2}$ peak indicates that Ni remains metallic (marked as Ni$^0$ in Fig. 3a) on the oxidation of the stainless steel surface, which justifies the use of Ni signals as a binding energy reference for XPS spectra.

For a better understanding how titanium acted as an additive, the XPS and XAS spectra of Ti 2p were measured from cleaned and to a different extent oxidized Fe–19Cr–18Ni–1Al–TiC (Fig. 4). Due to Ti 2p spin–orbit coupling two bands were observed in XPS and XAS spectra, Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$. The XPS spectra of a cleaned and oxidized sample had the same structure and no new features were monitored during the oxidation. However, the Ti 2p$_{3/2}$ photoline was located at 454.9 eV. This value is typical by the formation of TiC [16].

TiC in the sample was identified from Ti 2p XAS spectra, the observed structure of this edge (Fig. 4b) fits well with the respective XAS structure for TiC from literature [17]. XAS spectra did not show any change through the oxidation. This confirms that Ti stayed in the same stable compound, like it was before oxidation experi-
ments. The XPS spectrum of C 1s shown in Fig. 5 (measured with the excitation energy of 400 eV) also confirmed that TiC was formed as C 1s band has binding energy value at 281.9 eV, which is close to respective typical value in case of TiC [18].

The O 1s XAS spectra of 5 and 3000 L oxidized Fe–19Cr–18Ni–1Al–TiC with the spectra of oxidized Fe and Cr foils are shown in Fig. 6. The spectra originate from electronic transitions into unoccupied states with an O 2p character hybridised with metal states [19]. The interpretation of the O 1s XAS is only qualitative due to the presence of different oxides, which cause the XAS peaks overlap. O 1s XAS spectra can be divided into two parts. The first part at 527–533 eV corresponds to the oxygen 2p states hybridised with 3d transition metal states. The second part, at 533–545 eV, is attributed to the oxygen 2p states hybridised with metal 4s and 4p states [19].

The O 1s XAS spectrum of oxidized Fe–19Cr–18Ni–1Al–TiC has similarities with the oxidized Cr foil and the oxidized Fe foil spectrum in 3d related band. As we can see, the peak of the oxygen 2p state hybridised with a Fe 3d band is located at lower photon energies as compared to the oxygen 2p state hybridised with a Cr 3d band. This suggests that the observed structures in the alloy spectrum at 529.3 eV and 531.3 eV are related to the formed Fe$_3$O$_4$ and Cr$_2$O$_3$, respectively, confirming that the oxide layer consists of both Fe and Cr oxides.

**Fig. 3.** (a) Ni 2p XPS spectra of clean and to a different extent oxidized stainless steel alloy, metallic nickel is marked as Ni$^0$; (b) Ni 2p XAS spectra of clean and to a different extent oxidized stainless steel alloy and reference spectra of cleaned Ni foil, metallic nickel is marked by a dashed line.

**Fig. 4.** (a) Ti 2p XPS spectra of clean and to a different extent oxidized stainless steel alloy; (b) XAS spectra of Ti 2p edge of clean and to a different extent oxidized stainless steel alloy.
For a better understanding of the oxidation kinetics, changes of Fe 2p, Cr 2p, Ni 2p, Ti 2p and O 1s peak areas (which are proportional to respective changes of relative concentrations in surface layer) were evaluated. Changes in peak areas were determined from XPS spectra measured with excitation energy of 1486.6 eV. Fe 2p, Cr 2p, Ni 2p, Ti 2p and O 1s photopeaks were fitted by asymmetric Gaussian–Lorentzian lineshapes after subtracting a Shirley background.

Changes of Fe 2p (Fe\(^0\)), Cr 2p (Cr\(^0\)), Ni 2p (Ni\(^0\)), Ti 2p and O 1s peak areas (marked as Fe(met.), Cr(met.), Ni(met.), Ti(carb.), oxygen) as a function of oxygen exposure are shown in Fig. 7a. The changes were significant already after 5 L of oxygen exposure as the oxygen proportion in the surface increased, the Fe\(^0\), Cr\(^0\) and Ni\(^0\) proportion decreased. The alloy surface oxidation slowed down after 100 L of oxygen exposure. After 500 L of oxygen exposure a stable protective layer in the surface of the alloy was formed. No further significant changes in the composition of the alloy surface were observed. It should be noticed that the amount of TiC stayed mostly unchanged during oxidation.

Changes of Fe 2p (Fe\(^{2+}/Fe^{3+}\)) and Cr 2p (Cr\(^{3+}\)) peak areas (marked as Cr(ox.) and Fe(ox.)) as a function of oxygen exposure are shown in Fig. 7b. A clearly rapid oxidation of Cr was observed after 5 L of oxygen exposure, a significant amount of Cr\(_2\)O\(_3\) was formed. After 100 L of oxygen exposure a further oxidation of Cr was suppressed. Fe acted differently – at the beginning of oxidation there was only small amount of iron oxides in the alloy surface layer. The increasing rate of peak area related to Fe 2p (Fe\(^{2+}/Fe^{3+}\)) was rather balanced compared increasing rate of the peak area of Cr 2p (Cr\(^{3+}\)) (Fig. 7b). Peak area of Fe 2p (Fe\(^{2+}/Fe^{3+}\)) increased up to oxygen exposure 500 L and after that stayed stable.
In order to examine the lower binding energy region up to 120 eV in details, XPS with the excitation energy of 400 eV was used. In Fig. 8, the XPS spectra of a cleaned and a different extent oxidized Fe–19Cr–18Ni–1Al–TiC is shown. A broad valence band structure, Fe, Cr, Ni, Ti 3p and 3 s, Al 2p, Al 2s and Si 2p photolines were observed. Also, a small peak related to K 3p impurity was observed at 17.3 eV.

The valence band structure is difficult to analyse because overlapping of components with different origin in the alloy. However, some general ideas about valence band spectra could be brought out. In the valence band spectra of a cleaned and an oxidized alloy surface, two main structures are noticeable. The upper region of the valence band (0–3 eV binding energy) is mainly related to Fe, surface, two main structures are noticeable. The upper region of the valence band spectra of a cleaned and an oxidized alloy, a spectrum shape related to metal 3d dominates. After the oxidations, Si was in the oxidation state of SiO (binding energy 99 eV). When oxygen exposure was increased, the Si 2p (SiO2) peak area increased much faster than Fe 2p (Fe2+/Fe3+) peak area, but roughly at 100 L increase of Cr 2p (Cr3+) peak area stopped. This can be explained by a greater mobility of iron cations, which move to the surface when the oxygen exposure was increased.

Very sensitive to the formation of oxides in the alloy surface were O 1s XAS spectra, where changes were observed already after 5 L of oxygen exposure. However, the interpretation of the O 1s data is complicated because of the overlapping of different spectral bands. Therefore further analysis and calculations of the alloy O 1s XAS spectra are needed. Since Ni did not oxidize, no changes in XPS and XAS Ni 2p were observed. However, both methods showed a similar sensitivity to the presence of metallic nickel.

The alloy Ti 2p XPS and the XAS spectra did not show any change throughout the oxidation process. This confirmed that TiC, which was identified from Ti 2p XAS and XPS spectra, did not oxidize. A XPS peak area analysis confirmed that the amount of TiC was the same throughout the oxidation.

A stable protective oxide layer was formed on the Fe–19Cr–18Ni–1Al–TiC surface already after 500 L of oxygen exposure, when all elements in the composition of the alloy were oxidized and further oxidation growth was limited by a mass transport of oxygen and metal ions across the oxide film. Besides Cr2O3 and FeO/Fe2O3 also Al2O3 and oxidized Si were present in the passive layer. Aluminium was mostly in an oxidic form already in case of cleaned sample, Si oxidized when a small amount of oxygen was exposed to the surface.

Small changes in the chemical composition of the alloy surface related to the formation of iron oxides were more traceable in Fe 2p XPS than in XAS spectra. It was exhibited, when the 40 L oxidized Fe–19Cr–18Ni–1Al–TiC Fe 2p XPS and XAS spectra were compared, the changes were detectable in the XPS spectrum but not in the XAS spectrum (Fig. 1). From the XPS results we were able to draw a conclusion that when the oxygen exposure was increased, the Fe 2p (Fe2+/Fe3+) peak area increased (Fig. 7b). The changes in the alloy Fe 2p XAS spectra were significant only after 500 L of oxygen exposure. This was due to a relatively high amount of iron oxides present in the surface of the alloy as shown in Fig. 7b.

XPS and XAS were similarly sensitive to changes of present system in case of Cr 2p bands. When a small amount of oxygen was present (5 L), a shoulder appeared in both XPS and XAS spectra. Since XAS showed some change, the amount of Cr2O3 should have been significant in the surface area. This was confirmed by an XPS peak area analysis (Fig. 7b). After 100 L of oxygen exposure, Cr oxidation slowed down. It has been shown before that in this certain system the thickness of the stable passive oxide layer is about 0.6 nm, which is formed when oxygen exposures are about 500 L.

When changes of Fe 2p (Fe2+/Fe3+) and Cr 2p (Cr3+) peak areas were compared (Fig. 7b), it was found that at the beginning of oxidation Cr 2p (Cr3+) peak area increased much faster than Fe 2p (Fe2+/Fe3+) peak area, but roughly at 100 L increase of Cr 2p (Cr3+) peak area stopped. This can be explained by a greater mobility of iron cations, which move to the surface when the oxygen exposure was increased.

The properties and the formation of a passive oxide layer on the surface of a TiC-enriched austenitic stainless steel was investigated in situ at 50 °C by XPS and XAS by using different oxygen exposures. When studying the alloy Fe 2p, it was found that XPS is more sensitive to small changes in the surface electronic structure than XAS. Both methods were similarly sensitive concerning the study of Cr 2p, Ni 2p and Ti 2p. Very sensitive to the formation of oxides in the alloy surface were O 1s XAS spectra, where changes were observed already after 5 L of oxygen exposure.

It was found that the formation of a passive oxide layer starts already in the case of very small oxygen exposures (5 L). Further

4. Discussion

The results of the investigation of TiC-enriched austenitic stainless steel oxidation at 50 °C by XPS and XAS revealed some general trends.
oxidation of the alloy is limited after 500 L of oxygen exposure when a stable passive layer is formed.

It was found that Ti and Ni did not oxidize. An amount of Ni decreased in the surface. Ti stayed in stable carbide form and amount of TiC in the surface layer stayed mostly same through the oxidation.

When changes of Fe 2p (Fe\(^{2+}/Fe^{3+}\)) and Cr 2p (Cr\(^{3+}\)) peak areas were compared (Fig. 7b), it was found that at the beginning of oxidation Cr 2p (Cr\(^{3+}\)) peak area increased much faster than Fe 2p (Fe\(^{2+}/Fe^{3+}\)) peak area, but roughly at 100 L increase of Cr 2p (Cr\(^{3+}\)) peak area stopped.

Besides FeO/Fe\(_2\)O\(_3\), Cr\(_2\)O\(_3\), TiC and Ni, it was found that Al\(_2\)O\(_3\) and oxidized Si were present in the passive oxide layer.

Acknowledgements

We are grateful to the staff of Max-laboratory especially for Alexei Preobrajenski for the assistance and co-operation during the measurements. Financial support by the Estonian Science Foundation (Grants 8216 and 7615) and Graduate School on Functional Materials and Technologies (ESF project 1.2.0401.09-0079) are gratefully acknowledged. Support by the European Community – Research Infrastructure Action under the FP6 “Structuring the European Research Area” Programme (through the Integrated Infrastructure Initiative “Integrating Activity on Synchrotron and Free Electron Laser Science”) is acknowledged as well.

The Academy of Finland (research Grant Nos. 5205296, 5213914, 5210276, and 5110328) and the National Technology Agency of Finland (research Grant Nos. 160951, 161035, and 161111) are acknowledged for their financial support.

Financial support by the Outokumpu Oyj Foundation, the Vaisala Foundation, and the National Graduate School in Materials Physics is also gratefully acknowledged.

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