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Reference:

Ramachandran Dhanya, Egoavil Escobar Ricardo Juan, Crabbe Amandine, Hauffman Tom, Abakumov Artem M., Verbeeck Johan, Vandendael Isabelle, Terryn Herman, Schryvers Dominique.- TEM and AES investigations of the natural surface nano-oxide layer of an AISI 316L stainless steel microfibre

Journal of microscopy - ISSN 0022-2720 - (2016), p. 1-8

Full text (Publishers DOI): <http://dx.doi.org/doi:10.1111/jmi.12434>

TEM and AES investigations of the natural surface nanooxide layer of an AISI 316L stainless steel microfibre

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Abstract

The chemical composition, nanostructure and electronic structure of nanosized oxide scales naturally formed on the surface of AISI 316L stainless steel microfibres used for strengthening of composite materials have been characterised using a combination of scanning and transmission electron microscopy with energy-dispersive X-ray, electron energy loss and Auger spectroscopy. The analysis reveals the presence of three sublayers within the total surface oxide scale of 5.0 – 6.7 nm thick: an outer oxide layer rich in a mixture of FeO.Fe₂O₃, an intermediate layer rich in Cr₂O₃ with a mixture of FeO.Fe₂O₃ and an inner oxide layer rich in nickel.

Introduction

Stainless steel microfibre reinforced polymers are gaining considerable attention because of their remarkable flexural strength, fatigue resistance and the ability to tailor directional mechanical properties. When a stainless steel surface is thermally treated or even simply exposed to natural atmospheric conditions, a thin layer of oxide is instantaneously formed at the surface. This oxide layer not only plays an important role in protecting the steel from further corrosion, but also acts as the

interface with any possible sizing applied to the microwires or with the polymer matrix when using these fibres in composite materials. The present study was performed in order to properly characterize the outer surface of the steel microfibres to better understand the bonding of the fibres with the sizing or the epoxy matrix. Detailed knowledge about the structure, chemical composition and bonding of these surface oxide-layers is essential in understanding the interface bonding characteristics and thus the mechanical behaviour of the composite.

There are several literature reports that explain the effect of high temperature annealing in aqueous environment on the thickness, morphology, composition, electronic and crystallographic structure of the oxide layer formed on the surface of stainless steel [Robertson (1991), Stellwag (1998), Sun et al. (2009)]. Exposure to such an environment results in the formation of a thick duplex oxide layer [Miyazawa et al. (2006), Sun et al. (2009), Soulas et al. (2013)], which generally consists of an outer layer rich in iron or iron-nickel spinel and an inner layer rich in chromium or chromium-iron spinel. In addition to that, nickel enrichment was observed in some cases at the oxide/metal interface [Olsson et al. (1994)]. For as-received stainless steel, this layer is only a few nanometres thick, making it difficult to characterize with nanoscopic detail. Conventional optical and spectroscopic techniques such as Auger electron spectroscopy (AES) [Pons et al. (1977), Lister et al. (1987)] and X-ray photoelectron spectroscopy (XPS) [Hashimoto et al. (1979)] have been used to investigate natural as well as passivated surface oxide layers.

Recently, scanning transmission electron microscopy (STEM) in combination with energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) has been used to characterize the electronic structure and chemical composition of the surface oxide layer formed on a type 304 stainless steel [Murayama et al. (2006), Hamada et al. (2010)]. These measurements demonstrated an enrichment of chromium in the lower part of the surface oxide layer and an enrichment of nickel and depletion of chromium at the surface oxide layer/alloy interface. The goal of the present study is to investigate the chemical composition and electronic structure of the protective layer formed on the surface of AISI 316L type stainless steel microfibres, using aberration corrected STEM-EDS and STEM-EELS under ambient temperature. Field Emission Auger Electron Spectroscopy (FE-AES) [Briggs et al. (2003), Hofmann (1987)] combined with controlled argon

sputtering will be used to validate the lateral resolution of the STEM-EDS and STEM-EELS techniques. The layered structure of the surface oxide layer and the valence states of iron, chromium and nickel in the oxide layer are discussed in detail.

Material and Methods

Annealed AISI 316L microfibrils of 30 μm diameter were received from N.V. Bekaert S.A., Belgium. These microfibrils are produced by packing several 100 μm thick copper-coated steel wires in an iron casing which is then drawn through a drawing die of well-defined dimensions in several cold deformation and annealing steps. The drawing process reduces the diameter and increases the length of the wire. The casing and the copper coating are then dissolved in various acids to obtain individual fibrils of 30 μm thickness. The microfibrils obtained by this method were ultrasonically cleaned in ethanol for 15 minutes and rinsed with demineralized water. Since no further treatment was performed in order to intentionally create an oxide surface layer, the present observations are considered to show the oxide layer naturally grown under ambient conditions during storage after the above treatments.

The surface morphology of the microfibril was examined with a FEI Quanta FEG 250 SEM operating at 10 kV. The EDS attachment to the SEM probe was used to obtain the chemical composition of large particles found on the surface of the microfibril. Detailed cross-section characteristics were further investigated using TEM and STEM. Thin axial cross-sections for TEM and STEM measurements were prepared using Focused Ion Beam (FIB) with gallium ion sputtering using a FEI Nova 200 SEM/FIB dual system. After identification of the region of interest on the surface of the steel microfibril, electron beam assisted platinum deposition is performed in order to protect the outer surface from the ensuing FIB thinning and without damaging the thin oxide layer, followed by ion thinning with gallium ions to make a cross-section lamella with a thickness of 80 nm. The lamella was then lifted out with a nanomanipulator and transferred onto a TEM grid and welded with platinum. High-resolution TEM (HRTEM) observations were performed with a FEI Tecnai G2 TEM operated at 200 kV. STEM-EDS and -EELS experiments were performed on a probe aberration-corrected FEI Titan operated at 200 kV and equipped with a SuperEDX system and an

ENFINA spectrometer. The selected probe size is appr. 0.1 nm diameter. Quantification of the EDS maps was performed using the Cliff-Lorimer method [Cliff et al. (1975)]. The electronic structure of iron and chromium was measured using a monochromated and double aberration-corrected FEI Titan microscope equipped with a QUANTA spectrometer and operated at 300 kV using a probe size of appr. 0.15 nm diameter.

The atomic composition depth profile was confirmed by using argon ion sputtering combined with FE-AES surface analyses. Wide and narrow scan spectra were recorded using a JEOL-JAMP 9500F scanning Auger Microprobe with a Hemi Spherical Analyser (HSA). An electron beam of 10 kV and 10 nA ($\Delta E/E$: 0.06%) at angle of 30° was applied. The depth profile was obtained by alternating measurements and sputtering of the surface. The sputtering is performed using an Ar^+ gun at 1000 eV for 7 s per cycle, in these conditions the obtained sputtering rate is 6.1 nm/min on silicon dioxide reference material according to the manufacturer. A total of 40 cycles is performed. The acquisition conditions for the different chemical elements for the narrow scan spectra of the depth profile are listed in the Table 1.

Results and Discussion

Figure 1a shows a low magnification SEM image of an AISI 316L stainless steel microfiber, confirming the 30 μm fibre thickness. The surface of the fibre is uneven and rough which is expected to be due to the cold drawing process [Ghosh et al. (2013), Fang et al. (2014)]. SEM-EDS analysis on an as received microfibre reveals the following chemical composition: Fe (69.8 ± 0.7 wt. %), Cr (16.6 ± 0.5 wt. %), Ni (10.4 ± 0.5 wt. %), Mo (2.2 ± 0.5 wt. %), Si (0.4 ± 0.5 wt. %), N (0.2 ± 0.5 wt. %), Mn (0.3 ± 0.5 wt. %), P (0.05 ± 0.5 wt. %), S (0.02 ± 0.5 wt. %) and C (0.03 ± 0.5 wt. %), corresponding with the composition range of AISI 316L stainless steel. A magnified SEM image showing a grooved surface and 20 – 40 nm sized particles present on the surface of the microfibre is shown in Figure 1b. SEM-EDS analysis of these particles, but probably including an important contribution from the steel below, yields: Fe (63.5 ± 0.5 wt. %), Cr (30.0 ± 0.5 wt. %) and Ni (6.5 ± 0.5 wt. %), which still indicates a chromium enrichment in the particle. These chromium enriched particles on the surface could have been formed during the high temperature processing of the steel

fibres [Terachi et al. (2005)] and might strongly affect the mechanical strength of the bonding with the epoxy composite matrix.

High-angle annular dark field (HAADF) STEM micrographs from the FIB cross-section of the top surface of a steel microfiber, as indicated by a white line in Figure 1a, are presented in Figures 2a and 2b. The intensity contrast in the HAADF images is very sensitive to the projected atomic number of the atomic species as well as the thickness. These images clearly show a very thin natural surface oxide layer of approximately 5 nm width (thin dark layer in Figure 2a) and a larger single particle on the surface of the fibre (Figure 2b) in both cases covered by the protective electron beam deposited Pt layer. No distinction between top, middle and lower regions of the surface oxide layer can be made from the HAADF image. As this layer is responsible for protecting the steel from corrosion its chemical and electronic structure play an important role for understanding this protective nature.

A cross-sectional EDS map of the surface oxide layer of this microfibre is shown in Figure 3. From this EDS map it can be concluded that the 5 nm thick layer consists of a three-layer oxide structure. The quantitative results of the EDS analysis are listed in Table 2. The outer layer (A) consists of mainly iron and oxygen. A small percentage of chromium (2.9 ± 0.5 wt. %) is present in this layer. In the intermediate layer (B), the content of chromium increases sharply to 37.8 ± 0.5 wt. % and that of iron decreases to 24.2 ± 0.5 wt. % (Table 2). When compared with the steel (D) (19.1 ± 0.5 wt. % Cr), this layer contains a higher chromium content. Since iron and chromium possess a higher affinity to oxygen than nickel, the rate of incorporation of the nickel in the outer and intermediate oxide layers is much slower than that of iron and chromium [Tian et al. (2001)], which corresponds with the fact that only the inner layer (C) is enriched with nickel. The nickel content in this layer is nearly three times the bulk concentration. Nickel enrichment at the interface not only promotes the adherence of the oxide scale to the steel but also reduces porosity at the interface upon further oxidation [Olefjord et al. (1990)]. In addition, the content of chromium was found to be higher in the intermediate and inner layers than in the outer layer, hence these two layers are likely to be more

protective than the outer one. These results are in good agreement with the EELS map presented in the Supporting Information (SI Figure 1).

The FE-AES depth profile of the microfibre is shown in Figure 4, in which every profile is normalised w.r.t. its maximum value in order to reveal the respective maxima for each element separately. The analysed lateral surface is between 8 to 10 nm² ensuring a selected area smaller than the roughness of the microwire surface. This map confirms that the outer layer is enriched in iron. The chromium signal reaches a local maximum after the first maximum of the iron signal confirming the distinction between the two layers as observed with EDS and EELS. The third layer is enriched in nickel and is clearly distinct from the two outer ones, which still show some degree of overlap. The oxygen maximum coincides with the outer (Fe-rich) and intermediate (Cr-rich) layers and gradually decreases from the onset of the Ni-rich layer. At the same depth the iron and chromium signals start to increase till they reach their respective values of the steel bulk material. In conclusion, and although exact values of layer thickness cannot be given due to a variation of sputtering efficiency in the various layers, the FE-AES results confirm the three-layer scheme concluded from the EDS (and EELS) cross-sectional mapping on the stainless steel microwire.

Figure 5 shows the cross-sectional EDS map of the particle from Figure 2b on the surface of the microfibre. The chemical compositions of iron, chromium, nickel and oxygen in the surrounding layers (A, B, C, D) and in the particle (E) are listed in Table 3. The particle (E) has a much higher content of chromium than measured by SEM, indeed indicating a strong signal from the underlying steel in the latter measurement. The particle is embedded in a layer (D) enriched in iron (which could also have contributed to the SEM spectra). Layers A, B and C show a chemical composition similar to that of the outer, intermediate and inner layers of the surface oxide shown in Figure 3.

In order to investigate the atomic structure of the surface oxide layer, HRTEM images of a cross-section of the steel microfibre were obtained. The images shown in Figure 6 (a, b) confirm the presence of the 5.0-6.7 nm thick uniform surface oxide layer. The fast Fourier transformations (FFT) of regions 1 and 2 (red boxes) in the surface oxide layer reveal the crystalline nature of this layer consisting of randomly oriented particles of a few nanometer in diameter. Although the EDS map

shows a clear separation between the three sub-layers, HRTEM imaging does not reveal different crystalline phases within the surface oxide layer. Unfortunately, although the crystallinity of the oxide layer is clear, the actual crystal structures could not be determined due to the similarity of the lattice parameters and symmetries of the potentially occurring systems. The FFT from regions 3 and 4 (red boxes) confirms the crystalline nature and ferritic bcc structure of the steel fibre.

In order to investigate the electronic structure of the different phases of the surface oxide layer, EELS measurements were carried out. The oxidation states of Fe and Cr in this oxide layer were estimated by (i) analyzing the spectral induced differences in the fine structures of L_3 and L_2 edges, also referred to as energy loss near edge structures (ELNES), and comparing those with reference spectra for Cr^0 , Cr^{2+} and Cr^{3+} as well as for Fe^0 , Fe^{2+} and Fe^{3+} reported in the literature [Daulton et al. (2006), Tan et al. (2012)] and (ii) using a linear combination fitting procedure [Egoavil et al. (2015)] of these reference spectra to estimate their relative percentage composition as indicated in Table 4. Figure 7a shows the Cr- $L_{2,3}$ edge spectra collected from different regions in the surface oxide layer (A, B, C) and from the steel fibre (D) as indicated in Figure 3 along with the reference spectra of metallic Cr^0 , Cr^{2+} and Cr^{3+} . No significant Cr signal was detected in the outer surface layer (A), as expected from the EDS results in Table 2. The fine structure of the Cr- L_3 edge from the intermediate layer (B) shows a major peak at 578.8 eV and a pre-peak at 576.7 eV. The shape and the energy position of the dominant L_3 peak mainly matches with the reference spectrum of Cr^{3+} (pink curve) estimated as 99.9 % of the Cr content, while the pre-peak at 576.7 eV and the slight deviation of the shape of the L_2 edge suggests the presence of a very small amount of Cr^{2+} (0.1% of the Cr) in this layer. This reveals essentially the presence of the Cr_2O_3 phase in this layer. The change in the shape as well as the increased width of the L_3 peak in the inner (C) layer seem to indicate a gradual increase of Cr^0 content to 20.7 % when compared with the middle layer (B). However, the dominant peak in C remains at 578.8 eV suggesting still the dominant presence of Cr_2O_3 with 73.5 % content in this inner layer. The spectrum collected from the steel fibre (D) resembles quite well the reference spectrum of Cr^0 (91.7 %) confirming its nominal metallic electronic state in the bulk of the material.

Figure 7b shows the Fe-L_{2,3} edge spectra collected from the surface oxide layer (A, B, C) and from the steel fibre (D) of Figure 3. The fine structure of the Fe-L₃ edge collected from the outer layer (A) shows a major peak at 710.4 eV and a pre-peak at 709.1 eV. The shape and energy position of the major peak are in good agreement with the Fe³⁺ oxidation state (pink curve) of Fe₂O₃ for up to 70.3 % content and with a 29.6 % contribution of Fe²⁺. This suggests the presence of a mixture of FeO and Fe₂O₃ or most likely, at least partially, the formation of an oxide (e.g., Fe₃O₄) with an equivalent iron electronic state. For the intermediate (B), inner (C) layers and steel fibre (D), the spectral shape and the position of the major peak at 709.1 eV are found to match well with the reference spectra of Fe⁰ and Fe²⁺. Note that no remarkable spectral differences are observed between the Fe⁰ and Fe²⁺ states in these reference spectra. Moreover, the shoulder of the L₃ peak in (B) can be attributed to the presence of a higher amount of Fe³⁺ (27.1 %) when compared with C (6.5 %) and D (1.1 %). This suggests the presence of Fe²⁺ and Fe³⁺ states, again indicating the occurrence of the mixed oxide FeO·Fe₂O₃ in the intermediate layer and metallic Fe⁰ up to 93.4 % of the Fe content in the inner layer and to 98.9 % in the steel fibre substrate, as expected. The oxygen signal was detected only in the regions A, B and C and none was detected in the steel fibre while the Ni signal clearly increased in the layer in between the Cr-rich one and the steel (see Figs. S1 & S2 of the Supplementary Information). The rapid drop of oxygen in the inner layer, also observed in the FE-AES profiles, could indicate the existence of metallic Ni, although the EELS signal was too low to determine the Ni valence state. Finally, the compiled chemical composition within each layer is proposed in Table 4.

Overall, despite the rough surface of the microwires, these findings confirm existing knowledge on the nanostructure of naturally grown oxide layers on the surface of various types of steel [Terachi et al. (2004), Higginson et al. (2015), Isao et al. (1998), Ziemniak et al. (2008)]. The quantification of the type of oxides and their ratios using EELS provides more detail than most other techniques and especially for microwires used as strengthening component in metal-polymer composites, these details are essential for understanding the bonding with the matrix material. Despite the extremely thin nature (appr. 5 nm) of the entire oxide layer, and although some interference from neighbouring layers can never be excluded, still three different sub-layers could be identified. The Fe-rich outer layer mainly consists of a mixed oxide of FeO and Fe₂O₃ (or Fe₃O₄) while the Cr-rich

middle layer suggests the prime occurrence of a heterogeneous mixture of Cr_2O_3 possibly combined with FeO and Fe_2O_3 phases. In the inner layer the oxide content sharply decreases and possesses essentially the Cr_2O_3 phase. This could indicate that the enrichment in Ni primarily corresponds with its metallic form as for Fe and Cr in the steel. Fe_2O_3 , commonly known as rust, forms a weaker bond with the inner layer of the surface oxide layer, which can result in the delamination of any polymer coating or matrix from the steel surface. This could in turn lead to the nucleation of cracks in the composite material due to the formation of other corrosion products at the unprotected steel surface. Therefore, in order to enhance the performance of the composite, extra passivation steps removing the Fe_2O_3 or extra coatings on the microwire surface might improve the performance of the composite.

Conclusions

The chemical composition, crystallinity and electronic structure of the surface oxide layer formed under ambient conditions on the surface of a commercial stainless steel type AISI 316L microwire was characterized using aberration corrected STEM-EDS and EELS and supported by FE-AES. The EDS maps clearly demonstrate a nanosized three-layer oxide structure. The EELS analysis reveals the major presence of $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ (or Fe_3O_4) in the outer layer, a mixture of Cr_2O_3 and $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ in the intermediate layer and a mixture of Cr_2O_3 with metallic elements in the inner layer. A gradual increase in Cr^0 and Fe^0 was also observed in the intermediate and inner layers. FE-AES spectra combined with controlled argon ion sputtering confirmed the presence of this three-layer structure. All these details are essential in understanding the properties of the bonding between the matrix and the strengthening microwires and thus the overall behaviour of the composite.

Acknowledgements

This work was supported by SIM vzw, Technologiepark 935, BE-9052 Zwijnaarde, Belgium, within the InterPoCo project of the H-INT-S horizontal program. The authors are also thankful to Stijn Van den Broeck for help in FIB sample preparation, to Hamed Heidari for useful comments and to the N.V. Bekaert S.A. company for providing the microfibrils. RE acknowledges funding by the European Union Council under the 7th Framework Program (FP7) grant nr NMP3-LA-2010-246102 IFOX.

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Figure captions

Figure 1. SEM image of (a) AISI 316L stainless steel microfibre and (b) Chromium-rich nanoparticles on the grooved surface of the microfibre. The white line in (a) shows a typical site for a cross-sectional FIB sample.

Figure 2. HAADF-STEM image of a FIB cross-section of an AISI 316L steel microfibre showing (a) the natural surface oxide layer (thin black layer) and (b) a single particle on the surface of the fibre.

Figure 3. EDS map of a FIB cross-section of AISI 316L steel microfibre showing the protective surface oxide layer.

Figure 4: FE-AES depth profile showing the three layers present in the oxide at the surface of the fibres.

Figure 5. EDS map of a FIB cross-section of AISI 316L steel microfibre showing a Cr-rich particle on the surface of the fibre.

Figure 6. (a, b) HRTEM and FFT images (1-4) of AISI 316 L stainless steel microfibre on which a natural surface oxide film has been formed.

Figure 7. (a) Cr-L_{2,3} and (b) Fe-L_{2,3} edge spectra collected from the surface oxide layer and the alloy (A, B, C, D labelling corresponds to Figure 3). The reference spectra for Cr⁰, Cr²⁺, Cr³⁺ and Fe⁰, Fe²⁺, Fe³⁺ were taken from Ref. [22] and [23], respectively.

Table 1: Auger electron spectral lines acquisition details.

Elements	Auger spectra line	Steps (eV)	Dwell time (ms)	Sweeps numbers
O	KLL	1.0	20	5
Cr	LMM	1.0	20	3
C	KLL	1.0	20	3
Fe	LMM	1.0	20	3
Ni	LMM	1.0	20	10
Cu	LMM	1.0	20	5

Table 2. Chemical compositions (wt. %) of the marked areas (A, B, C) in the surface oxide layer and (D) in the alloy by EDS analysis.

Elements	A (wt. %)	B (wt. %)	C (wt. %)	D (wt. %)
Fe	56.5 ±3.04	24.2 ±4.28	49.0 ±4.75	68.1 ±6.47
Cr	2.9 ±1.13	37.8 ±3.02	18.2 ±2.57	19.1 ±1.56
Ni	1.6 ±0.4	1.8 ±0.69	16.2 ±1.30	4.9 ±0.79
O	39.0 ±3.04	36.2 ±2.48	16.6 ±1.70	7.9 ±0.60

Table 3. Chemical compositions (wt. %) of the marked area (A, B, C, D) surrounding the particle and (E) on the particle by EDS analysis.

Elements	A (wt. %)	B (wt. %)	C (wt. %)	D (wt. %)	E (wt. %)
Fe	58.0 ± 5.74	24.5 ± 4.54	48.2 ± 6.79	64.0 ± 6.82	11.0 ± 1.66
Cr	2.5 ± 1.93	38.3 ± 3.12	22.5 ± 1.50	19.1 ± 1.49	70.5 ± 7.39
Ni	1.3 ± 0.66	2.0 ± 0.97	13.0 ± 0.85	4.6 ± 0.83	0.1 ± 0.14
O	38.2 ± 3.15	35.2 ± 2.82	16.3 ± 4.13	12.3 ± 4.14	18.4 ± 1.00

Table 4. Relative Cr and Fe electronic state compositions (wt. %) of the marked area (A, B, C, D) obtained by using a linear combination fitting procedure of the different (Cr^0 , Cr^{2+} , Cr^{3+}) and (Fe^0 , Fe^{2+} , Fe^{3+}) reference spectra [24].

Layer\Reference	Cr^0	Cr^{2+}	Cr^{3+}	Fe^0	Fe^{2+}	Fe^{3+}	Layer composition
A				0.1%	29.6%	70.3%	$\text{FeO} + \text{Fe}_2\text{O}_3$ (or Fe_3O_4)
B	0.0%	0.1%	99.9%	14.2%	58.7%	27.1%	$\text{Cr}_2\text{O}_3 + \text{FeO} + \text{Fe}_2\text{O}_3$
C	20.7%	5.8%	73.5%	93.4%	0.0%	6.5%	$\text{Cr}_2\text{O}_3 + \text{Ni-enrichment}$
D	91.7%	5.8%	2.5%	98.9%	0.0%	1.1%	FeCrNi steel-fibre