doi:10.1017/S1431927621000714
Microsc. Microanal. 27 (Suppl 1), 2021

Fast Automated Phase Differentiation in Industrial Stainless Steel by Combining Low-Loss EELS Experiments with Machine Learning-based Algorithms

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Introduction. Duplex stainless steels (DSSs) constitute a family of steels made of chromium-nickel-molybdenum-iron bi-phased alloys in which α ferrite and γ austenite fractions are present in relatively large separate volumes. Due to their bi-phased microstructure, they possess higher mechanical strength and better corrosion resistance than standard austenitic stainless steels and are used for a wide range of applications including thermal desalination plants, pipes and storage tanks for the oil & gas industry [1]. However, during aging, a large variety of phases, including the Cr-Mo-rich σ phase which is often observed at the α/γ interface boundary, are known to precipitate in DSS and lead to a dramatic deterioration of their mechanical and corrosion properties [2]. Characterizing and mapping in a timely manner the phases present in aged DSS for industrial applications if thus of high-importance. Because of the high intensity of the signal, low-loss EELS allows us to obtain large dataset with short acquisition time. However, interpretation and analysis of such data is not straightforward. Low-loss EELS spectra contain many excitation processes including volume plasmon which can be used for fingerprinting approaches but requires to use a catalogue of reference spectra and laborious fitting procedures [3]. In the present work, we developed a new and fast method based on low-loss EELS experiments to automatically separate the phases present in as-cast and aged industrial DSS. It allows us, not only to map α and γ phases, but also intermetallic phases such as the σ phase.

Experimental. As-cast (2205, 2304 and 2001) and aged DSS (after thermomechanical treatment at 1090 or 1270ºC) were fabricated at the ACERINOX EUROPA SAU plant of Campo de Gibraltar. TEM samples were prepared by electropolishing and were studied by using a FEI Titan Cubed Themis 60-300 microscope at the University of Cádiz which was operated at 200 kV. The Themis is equipped with a double Cs aberration-corrector, a monochromator, an X-FEG gun, an Ultra High Resolution Energy Filter (Gatan Quantum ERS) which allows working in dual-EELS mode and a Super X EDS detector. Phase determination was based on the prior results of EDS quantification. Absorption correction for EDS quantification was performed by taking into account the thickness of the probed area. For this purpose, low-loss EELS measurements were used to determine the t/λ ratio (t the thickness of the analyzed crystal and λ the inelastic mean free path) and the modified Iakoubovskii formula [4] was used to determine λ. EELS data were acquired with a dispersion of 0.1eV/pixel and an energy resolution of 0.8 eV. Dataset of about 18 µm × 18 µm (100 pixels × 100 pixels) were acquired with a dwell time of 0.05s. After multiple scattering removal, EELS datasets were clustered by using the "kmeans++" algorithm. The only parameter needed was the number of clusters which was determined by using the silhouette metric [5] before clustering. To compare with more classical approaches, EELS dataset were also fitted pixel per pixel by using the Drude model in order to map the plasmon energy and plasmon width parameters. In order to interpret the results, EELS experimental spectra were also compared with calculated spectra based on the density-functional theory.

Results. Figure 1a and **1b** shows the annular dark field (ADF) image and EELS spectra acquired on an as-cast DSS along an α/γ interface boundary. The plasmon of the α and γ phases are well separated by about 2 eV**,** the plasmon of the alpha phase being situated at lower energy**. Figure 1c** and **1d** shows the results of the k-means clustering. The clustering reproduces really well the α and γ domains and there is a nearly perfect match between the cluster centers and the representative EELS spectra. It should be noted that classical approaches by using pixel by pixel fit leads to a plasmon map which can also be used to discriminate the α and γ domains. However, this approach is much more computational demanding. For comparison, k-means clustering on the same dataset and computer was performed in about 30s whereas the pixel by pixel fitting was performed in about 10 minutes. In addition, the fitting approach is also time-consuming for the user as it requires a fine pre-tuning of the fitting parameters. **Figure 2a** shows the superposition of Cr elemental map and dark field image (DF) along an α/γ interface boundary of an aged sample. Precipitates rich in Cr belonging to the σ phase can be observed along the interface with a size of about 200 nm. The silhouette metric indicates that three clusters for this dataset are needed whereas only two were highlighted for the as-cast dataset. **Figure 2c** and **2d** shows the cluster centers and clusters maps, respectively. There is an excellent agreement between the results of the clustering and the EDS mapping and electron diffraction analyses. It should be noted that the classical fitting approach did not success to separate the three phases because of the proximity between the plasmon energies. All these results show that automatic phase separation in DSS can be successfully performed by combining low-loss EELS experiments and k-means clustering. If time allows, comparison with hierarchical and spectral clustering will also be presented.

Acknowledgements Authors acknowledge the use of instrumentation provided by the National Facility ELECMI ICTS ("Division de Microscopia Electronica", Universidad de Cadiz). This work has been partially financed by the Andalusian regional government (FEDER-UCA-18-106613), the European Union's Horizon 2020 research and innovation program (grant agreement 823717 – ESTEEM3) and the Spanish Ministerio de Economia y Competitividad (PID2019-107578GA-I00).

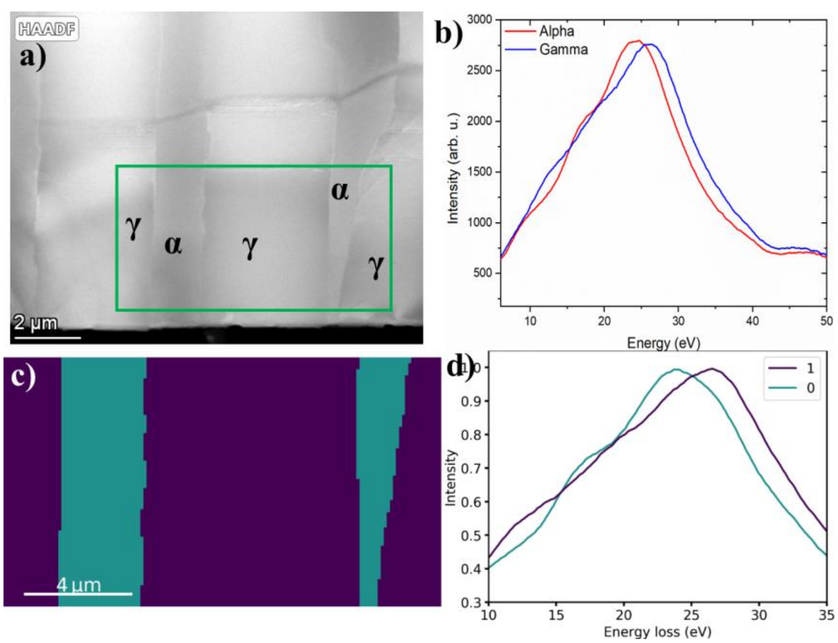

Figure 1. As-cast sample a) ADF image acquired simultaneously as the EELS dataset b) EELS spectra acquired on the α and γ phases. c) Results of k-means clustering and d) corresponding cluster centers

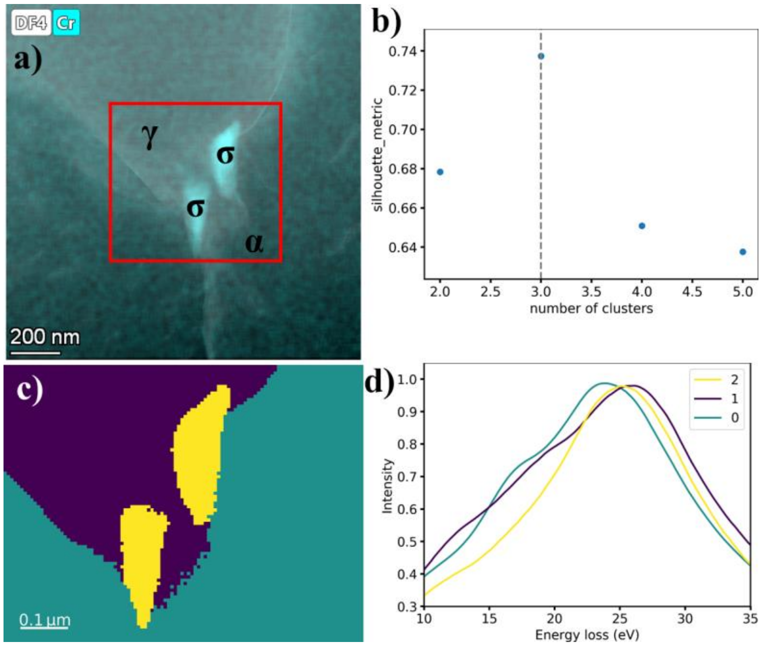

Figure 2. Aged sample a) Superposition of Cr elemental map and DF image. b) Estimation of the number of clusters c) Results of k-means clustering and d) corresponding cluster centers.

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https://doi.org/10.1017/S1431927621000714 Published online by Cambridge University Press