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Atomic-scale Investigation on the Structure Evolution of the $MnCr_2O_4$ Nano-octahedron in a Stainless Steel in Corrosion Environment by *in situ ex-environment* TEM Observations

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Stainless steels are widely used in our daily life because of their excellent corrosion resistance. The unique property is attributed to the protection of the oxide thin film naturally formed on the surface. In the presence of non-metallic inclusions, however, the oxide film becomes discontinuous. Such areas are often susceptible to localized degradation in an aggressive liquid environment, which is well known as pitting corrosion. During the past decades, it has confirmed that the manganese sulphide (MnS) is such kind of weakness whose dissolution is a critical event triggering the pitting of stainless steels.

Due to the resolution limitation of conventionally used analytical approaches, the link between the local structure/chemistry of MnS and pitting corrosion has not been successfully established so far. By our recently developed *in situ ex-environment* TEM characterization techniques, some atomic-level understanding on such issue has been achieved [1-3]. For example, we found that the nano-sized $MnCr_2O_4$ spinel particles inside the MnS inclusions play a significant role in catalyzing the cathodic reaction and hence the anodic dissolution of MnS [1]. As the place where the cathodic reaction occurs, the surface of $MnCr_2O_4$ particle is worthwhile to concern, since its atomic structure is closely related to the catalytic capability of the particle. In this study, the surface reconstruction of the nanoparticle in the corrosion process is observed. The reconstructed structure is unraveled by aberration-corrected high resolution STEM imaging combined with electron energy loss spectroscopy (EELS).

A commercial 316F stainless steel (Nippon Steel and Sumikin Stainless Steel Corporation) was chosen in this study. TEM samples were prepared by conventional ion milling process. The atomic resolution HAADF-STEM images were acquired by a Titan G^2 Cube 60-300 aberration-corrected TEM.

Fig. 1(a) shows a low-magnification STEM image of a MnS section in the stainless steel sample. Two $MnCr_2O_4$ nanoparticles embedded in the sulphide are clear seen. Each particle has a specific geometric shape, which has been identified by our previous research to be an octahedron enclosed by eight {111} surfaces [1]. Fig. 1(b) shows the same area as that in Fig. 1(a) but suffered corrosion test in 1 mol/L NaCl electrolyte for 30 minutes. Localized dissolution of MnS inclusion in stainless steels is found to nucleate at the $MnCr_2O_4$/MnS interfaces and develops a small pit as indicated by the black contrast around the nanoparticles. The two particles remain undissolved.

Viewing along the [110] zone axis of the particle allows us to image the atomic structure of the {111} surfaces. Fig. 2(a) shows a HR-STEM image of the surface profile of a $MnCr_2O_4$ nano-octahedron. The MnS has no definite orientation relationships (ORs) with the randomly orientated $MnCr_2O_4$ nanoparticles. When the particle is tilted to a low-index zone axis, the MnS crystal does not show lattice fringe in the HR-STEM image. The atomic model of the spinel is inset in the image. When the MnS dissolved, a reconstructed surface was observed on the same nanoparticle. The surface profile of the particle is displayed in Fig. 2(b). The newly formed crystalline layer has a rock-salt structure whose lattice matches well with the (111) plane of the pristine $MnCr_2O_4$. The EELS analysis under STEM mode was further performed on both the bulk $MnCr_2O_4$ and the reconstructed layer. The $L_{2,3}$-edges of elements Mn, Cr and the K-edge of O are shown in Fig. 2(c)-(e), respectively. It indicates that the surface layer is mainly composed of manganese, oxygen and a small amount of chromium. Judging from the characteristics of the Mn $L_{2,3}$-edges as well as the O K-edge [4], we can conclude that the reconstructed layer corresponds to MnO crystal.

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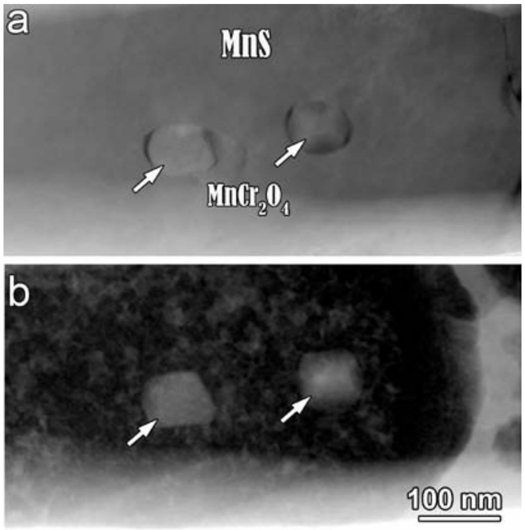

Figure 1. (a) HAADF STEM image of a section of the MnS inclusion in a stainless steel. Two nano-sized $MnCr_2O_4$ particles embedded in MnS are marked by arrows. (b) the same area as that in (a) but experienced corrosion test. A dissolution pit in MnS appears around the particles. The two oxide particles remain undissolved.

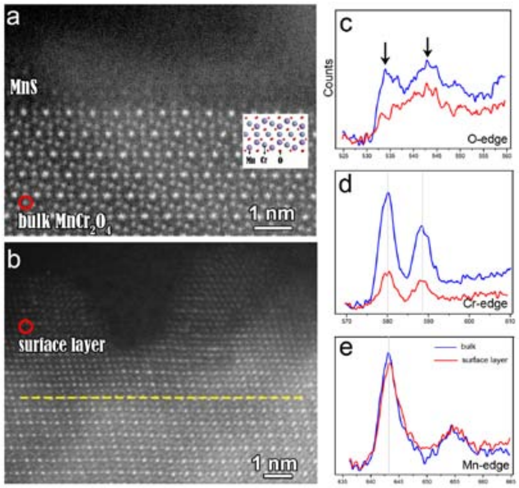

Figure 2. (a) The atomic structure of the {111} surface of a $MnCr_2O_4$ particle viewed along its [110] zone axis. (b) the surface of the particle exhibit a reconstructed feature when the MnS dissolved. (c)-(e) the EEL spectra of the O K-edge, Cr $L_{2,3}$-edges and Mn $L_{2,3}$-edges of the bulk $MnCr_2O_4$ and the surface crystalline layer.