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Intermediate stages of CrN precipitation during PIII nitriding of austenitic stainless steel

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ABSTRACT

The formation of metastable expanded austenite in austenitic stainless steel after energetic nitrogen insertion is a well established fact. While the initial formation of CrN precipitates and the longterm evolution towards a continuous layer containing Cr_xN and a bcc-phase have been known for several years, no information about the intermediate stage beyond XRD data indicating an X-ray amorphous phase is available. Here, this intermediate stage is investigated with a temperature series of nitrogen plasma immersion ion implantation (PIII) experiments using austenitic steel 316Ti. Scanning electron microscopy (SEM) viewgraphs of cross sections clearly show a very corrugated interface between the already transformed zone and the original expanded austenite. This interface is growing towards the interface between the substrate and the expanded austenite and simultaneously becoming more and more flat. The competition between nucleation of precipitates and growth of these transformed regions is governed by the much faster dynamics of the latter process at higher temperatures (respective longer times).

1. Introduction

The formation of an expanded austenitic lattice in austenitic steel has been attracting considerable interest from a scientific and a commercial viewpoint [1–3]. As a metastable, a supersaturated phase with nitrogen on interstitial sites at surface concentrations between 20 and 40 at.% is observed in the temperature range from 300 to 500 °C [4,5], and a very large increase in the wear resistance is obtained while the surface hardness increases to values of 15–18 GPa. The mechanical properties are very similar even for completely disparate preparation methods, e.g. including plasma nitriding, low energy ion implantation or PIII plasma immersion ion implantation [6–9].

The advantage of retaining the excellent corrosion resistance of the base material even after surface modification is, however, only preserved as the expanded phase is being present. It is known that the metastable expanded austenite, similar to the metastable FeN phase [10], is decomposing for long times and elevated temperatures [11], as CrN and Cr_2N are energetically more favourable. Consequently, the matrix is depleted of Cr, thus destabilising the (metastable) austenite phase and allowing the formation of a ferritic or martensitic iron phase [12]. While the final stable state is readily observed by XRD (however, with a rather low scattering intensity), the initial start of precipitates appearing is only visible in transmission electron micrographs [13,14]. Information on the intermediate process stage is rare or nonexistent.

In this presentation, the evolution of the Cr_xN containing zone is examined for a temperature series – corresponding to time series at fixed temperature assuming a thermally activated process – for PIII experiments with steel 316Ti using SEM images of metallographic cross sections. Another advantage of these experiments is a comprehensive characterisation detailing elemental depth profiles, XRD scattering information and the microstructure of the modified zone as a function of temperature yielding more than single snapshots.

2. Experiment

Polished austenitic stainless steel coupons of AISI 316Ti (corresponding to EN 1.4571, respective X6CrNiMoTi17-12-2) with a diameter of 15 mm were used for a series of PIII experiments at a fixed time of 1 h while the temperature was varied between 325 and 575 °C. The experiments were performed in a UHV chamber with a base pressure of $<10^{-7}$ mbar without auxiliary heating. Afterwards, a nitrogen plasma was ignited with an ECR source operating at 150 W at a pressure of 5 μbar. The PIII process was started at a fixed pulse frequency of 5 kHz and a voltage of 10 kV. After reaching the processing temperature, the pulse frequency was reduced to maintain the respective temperature. The heating time between 10 and 25 min is included in the total processing time.

Secondary ion mass spectrometry (SIMS) was employed to obtain nitrogen depth profiles. By measuring the crater depth the thickness of the nitrided layers was determined assuming a constant sputter

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rate within the implanted layer with no degradation of the profile edges due to sputter roughening within the crater. The phase formation was investigated with X-ray diffraction (XRD) in Bragg–Brentano geometry. Metallographic cross sections were prepared by cutting, embedding, grinding and polishing the implanted samples. Physical etching for contrast improvement was done by SIMS using 2 keV oxygen ions under 45°. As chemical etching will be much more effective for the CrN containing regions, this physical etching allows details to be visible for both phases in the SEM viewgraphs.

3. Results

Fig. 1 shows nitrogen depth profiles for the lower temperature samples as obtained from SIMS. Absolute quantification of the concentration has been obtained by comparing with GDOS and SIMS data of similar samples [15]. With rising temperature, an increase in the nitrogen surface concentration as well as a fast growth of the nitrogen containing layer is occurring. However, at 475 °C a relatively minor change compared to 425 °C is present, which could be explained by a change from diffusion limited to supply limited growth [16]. As a large, combined nitrogen uptake from the plasma and from the high energy ions is achieved, the retained nitrogen content for this sample is very large, around $1.6–1.7 \times 10^{19}$ at./cm^2. While the low energy ion flux arriving from the plasma at the surface is constant, the higher pulse frequency for increasing the temperature is not sufficiently increasing the high energy ion flux to account for the fast diffusivity at higher temperatures. A similar tendency for the layer thickness is observed from the SEM viewgraphs (depicted in the inset of Fig. 1), which are in good agreement with the SIMS data (for the thicker samples, the necessary sputtering time in SIMS becomes prohibitively long). For the lower temperatures, a thermally activated diffusion with an activation energy of 0.8–1.0 eV is obtained, in agreement with literature values with no supply limitations.

Fig. 2 shows the XRD data obtained from the samples with the substrate visible only for 325 and 375 °C. A clear identification of the expanded phase is possible between 325 and 425 °C for both the (111) and (200) oriented lattice planes with an expansion of 5–9% for the former and 8–12% for the latter. While a slight narrowing of the reflexions from the expanded phase is observed for increasing temperature, rather symmetric peaks with no obvious tail indicating probing across regions with strongly decreasing nitrogen content are obtained [17]. At the same time, the anisotropic expansion can be observed directly from the figure as the absolute lattice expansion is decreasing for 475 °C only for the (200) orientation while remaining identical to the 400 °C sample for the (111) orientation.

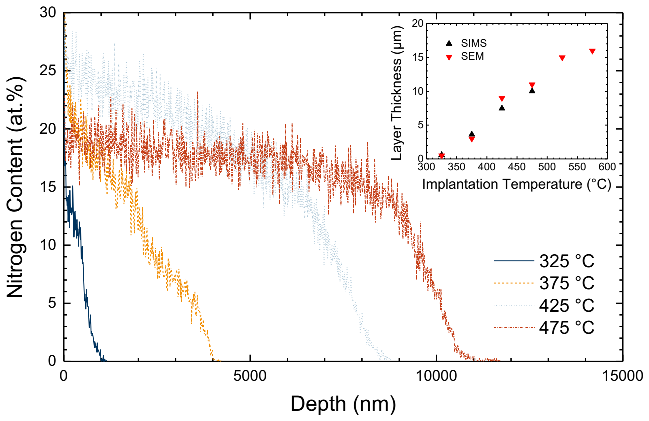

Fig. 1. Nitrogen depth profiles for stainless steel 316Ti after PIII for different temperatures. The inset shows a comparison of the layer thickness from SEM and SIMS.

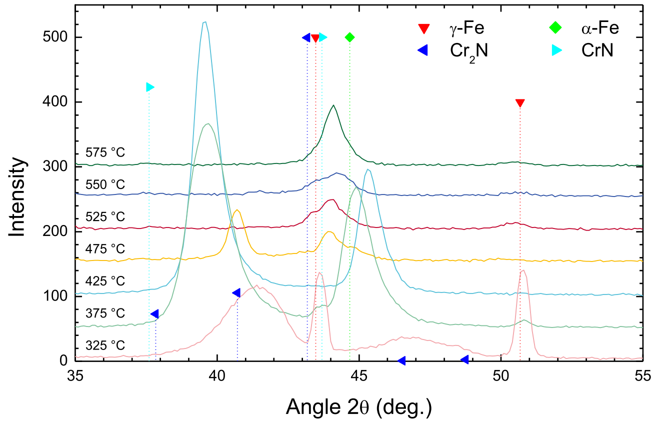

Fig. 2. XRD spectra for the temperature series of PIII treated steel 316Ti.

With increasing temperature, the information from the XRD measurements is strongly reduced as the structure of the original austenitic phase is lost and replaced by a microstructure with a very small coherence length, e.g. nanoscale precipitates. At 475 °C, a remnant of the expanded phase may be identified for the (111) oriented planes (narrow and more symmetric), at 43.17°, while the peak structure near 44–45° (very broad and very weak) could be identified by some mixture of CrN, Cr_2N, expanded ferrite or distorted martensitic phase. Although no direct calculation of the grain size from the Debye–Scherrer equation is possible, estimates lead to values smaller than 50 nm. For even higher temperatures, this structure becomes more pronounced, together with a hint of some intensity near the original (200) peak, which is also a very broad structure.

Summarising the XRD data, a layered structure of the expanded phase on top of the substrate can be inferred for 325–425 °C with a layer thickness less than about 5 µm, as calculated from the information depth of the X-ray radiation [18]. For 475 °C, a decayed phase on top of the expanded phase may be present while higher temperatures show only a decayed phase within the information depth. It has to be pointed out that the purpose of this manuscript is not a time and temperature evolution of the growth and decay of the expanded phase where *in situ* measurements are much more suited [19].

Here, the focus is on metallographic cross sections allowing a detailed investigation without being restricted to a small group of crystallites (despite a highly oriented material after the rolling process, most of the crystallites cannot be probed in Bragg–Brentano geometry) and

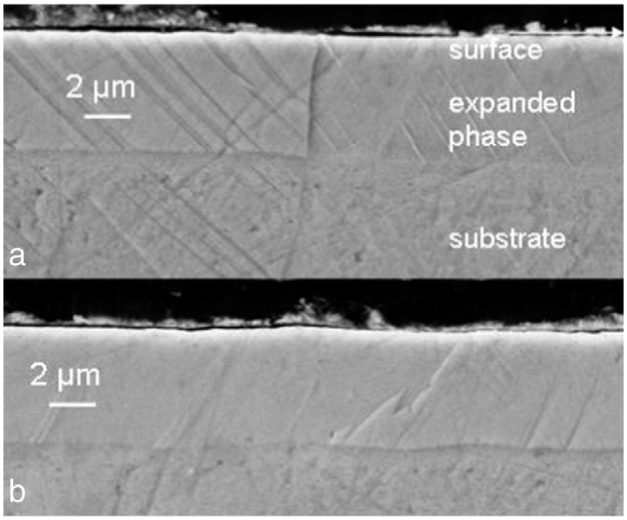

Fig. 3. SEM viewgraphs of the sample implanted at 425 °C.