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Sample Preparation Methods for Optimal HS-AFM Analysis: Duplex Stainless Steel

Stacy Moore^{1*}, Alexander D. Warren¹, Robert Burrows², Oliver D. Payton^{1,3}, Loren Picco^{3,4}, Freddie S. Russell-Pavier¹, Peter G. Martin¹, and Tomas L. Martin¹

¹Interface Analysis Centre, HH Wills Physics Laboratory, University of Bristol, Bristol, BS8 1TL, UK.

²National Nuclear Laboratory, Building 102B, Stonehouse Park, Sperry Way, Stonehouse, Gloucestershire, GL10 3UT, UK.

³Bristol Nano Dynamics Ltd., Bristol, UK.

⁴Department of Physics, Virginia Commonwealth University, VA, USA.

*Corresponding author. Tel.: +44 117 33 17684 - Email: stacy.moore@bristol.ac.uk

The contact mode high-speed atomic force microscope (AFM) operates orders of magnitude faster than conventional AFMs. It is capable of capturing multiple frames per second with nanometre-scale lateral resolution and subatomic height resolution. This advancement in imaging rate allows for microscale analysis across macroscale surfaces, making it suitable for applications across materials science. However, the quality of the surface analysis obtained by high-speed AFM is highly dependent upon the standard of sample preparation and the resultant final surface finish. In this study, different surface preparation techniques that are commonly implemented within metallurgical studies are compared for samples of SAF 2205 duplex stainless steel. It was found that, while acid etching and electrolytic etching were optimal for the low resolution of optical microscopy, these methods were less suited for analysis by high resolution high-speed AFM. Mechanical and colloidal silica polishing was found to be the optimal method explored, as it provided a gentle etch of the surface allowing for high quality topographic maps of the sample surface.

Keywords: sample preparation; contact mode high-speed atomic force microscopy; duplex stainless steel; acid etching; electrolytic etching; focussed ion beam etching

1 Introduction and Background

High-speed atomic force microscopy (HS-AFM) is a novel materials analysis technique capable of rapid nanoscale resolution topography mapping of material microstructure. However, in order to realise the full potential of HS-AFM, it is of vital importance to suitably prepare the sample surface under investigation. In the study presented here various sample preparation methods are compared with the aim of identifying an optimal method for HS-AFM analysis.

Atomic force microscopy (AFM) is a scanning probe microscopy (SPM) technique developed by Binnig, Quate, and Gerber in 1986 [1]. Since its invention, AFM has come to be considered as one of the most versatile tools in nanoscience, capable of high-resolution mapping of surface microstructures, and the measuring of mechanical properties at nanometre scales in a range of environments [2–8].

In comparison with other microscopy techniques, AFM has a number of advantages. AFM is not limited to low pressure or vacuum environments, nor is the sample required to be conductive [5, 6, 9]. In this way, AFM offers a multitude of applications in materials, surface, and biological sciences. However, a significant limiting factor of AFM is its long collection times. A typical image is collected over minutes. This renders AFM unsuitable for observing shorter timescale dynamic processes or mapping macro-sized areas across a surface [5–7, 10–12]. The clear potential of AFM quickly gave rise to considerable effort to enhance the image rate and address its other limitations, ultimately resulting in the development of HS-AFM [6, 13].

Contact mode HS-AFM is orders of magnitude faster than a conventional AFM, with the ability to image multiple frames per second [4, 6]. The high frame rate of the contact mode HS-AFM makes it capable of imaging dynamic processes in real-time, allowing for new insight into nanoscale mechanisms for a range of phenomena, such as corrosion processes [14]. The increase in speed allows the HS-AFM to quickly analyse the topography over millimetre length scales to nanometre precision, making observations of specific features present on the sample surface considerably easier. The high throughput also allows for the analysis of surface statistics over large areas with a high degree of confidence. These capabilities are particularly important for materials which have large microstructural differences, such as welds or coatings. HS-AFM has considerable potential for materials science applications. By optimising the specimen preparation technique, this potential may be realised.

When preparing the sample surface, samples are required to be pristinely polished (free of scratches) to reveal any microstructures present, and free of loose matter such that resolution quality is maintained, and image artefacts are avoided [15]. In 2016, Warren *et al.* described a methodology for the preparation of AISI Type 300 series austenitic and SAF 2205 duplex stainless steels for optimised SPM analysis [15]. By mechanically polishing the surface, the resultant topography is hardness induced, highlighting harder features such as certain precipitates [16]. The investigation presented here follows on from this previous work by exploring the effects of additional sample preparation steps.

Within this study, samples of SAF 2205 stainless steel are prepared by methods described by Warren *et al.* [15] before undergoing one of three treatments:

- Acid etching
- Electrolytic etching
- Focussed ion beam (FIB) etching

Samples were then imaged under the HS-AFM and compared for signs of surface deformation and damage, preferential etching, and inhomogeneities. Electron backscatter diffraction (EBSD) analysis of the surface was also implemented for confirmation of phase identification. To give the most effective comparison

between the behaviours of different phases under surface preparation techniques, a dual phase (duplex) stainless steel was utilised - this comprises an approximate 1:1 ratio of austenite to δ -ferrite in a banded structure. The selected sample preparation methods are commonly implemented in metallurgy studies as well as for other analytical techniques, such as EBSD. The aim of this study is to identify a sample preparation method that is optimal for HS-AFM. This may be determined by whether high quality topographic images (with discernible microstructure and clear of surface debris or imaging artefacts) are produced from the prepared surface. By testing a selection of methods used within other disciplines and techniques, a sample preparation method may be identified that is versatile and suitable across a range of analytical methods without the requirement for re-preparation.

Acid etching and electrolytic etching are both common wet etching procedures for the examination of stainless steel microstructure. There are a multitude of recipes for both techniques; etchants are selected dependant on the chosen material as well as the purpose of study, such as revealing grain boundaries, phases, or precipitates [17–24]. This is achieved by preferential or selective etching, producing a contrast between certain microstructural features, such as different colours or etch patterns [17,18,22–24]. As such, these preparation techniques are typically implemented within optical studies of microstructure [17,21] and will likely produce surfaces that are considerably rougher than those typically prepared for analysis by HS-AFM.

FIB etching (or milling) is a dry etching method in which an ion beam (typically Ga^+ ions) is scanned over the sample surface, where upon material in the upper layers of the specimen are sputtered away [25]. Different grain orientations are etched at slightly differing rates, resulting in the crystallographic structure being revealed [26]. However, it is not known whether the grain contrast observed within the FIB microscope will be reflected within the small-scale topography measured across the resultant sample surface by HS-AFM. Previous studies by SEM and EBSD have found that FIB etching can result in damage to the upper layers of the surface [27–30]. This damage can be observed as ripples or dots that appear periodically across a surface [27]. Furthermore, ion-implantation can result in a reconfiguration of sample structure, resulting in a localised phase change [28,29]. These factors must be considered when interpreting the microstructures observed on the resultant surface.

2 Materials and Methods

2.1 Materials

Samples of SAF 2205 stainless steel (‘as received’ condition from Outokumpu Stainless AB, composition given in Table 1) were cut to size using an automated diamond disc cut-off saw (StruersTMAccutom) before being set into a resin (cold set, StruersTMClarocit) mount for polishing, as described below.

Table 1: Elemental composition (in wt%) of SAF 2205 duplex stainless steel as stated by the manufacturer.

C	Si	Mn	P	S	Cr	Mo	Ni	N	Cu	Ti	Ce	Fe
0.016	0.39	1.43	0.022	0.001	22.39	3.19	5.7	0.178	0.2	0.001	0.002	Bal.

2.2 Initial Sample Preparation

Initial sample preparation methods are outlined here, and described in detail by Warren *et al.* [15]. The upper layers of the sample surface were removed by progressively finer silicon carbide (SiC) papers using

an automatic polisher (StruersTM TegraPol-15 polisher) as follows:

1. 1 minute at 300 rpm on P320 SiC paper, with a force of 30 N.
2. 1 minute at 300 rpm on P800 SiC paper, with a force of 30 N.
3. 3 minutes at 300 rpm on P1200 SiC paper, with a force of 30 N.
4. 5 minutes at 300 rpm on P2500 SiC paper, with a force of 30 N.
5. 10 minutes at 150 rpm on P4000 SiC paper, with a force of 30 N.
6. 5 minutes at 150 rpm on P4000 SiC paper, with a force of 15 N.

These steps were carried out using a water lubricant and with the sample holder orientated in such a way that it rotated in the same direction as the grinding pad. The surface was then polished to a mirror finish by hand using 1 μm , 0.25 μm , and finally 0.1 μm diamond pastes (Kemet International Ltd., KD Diamond Pastes) on a nylon cloth lubricated with StruersTM DP-Lubricant (Brown). These steps were performed for the time required to remove all polishing lines from the previous steps. The sample was washed thoroughly with detergent and deionised water between each step to avoid cross contamination, and direction of polishing was varied throughout polishing stages.

Following polishing steps, each sample was placed onto a vibrational polisher (VibroMetTM, Buehler) with colloidal silica (MasterMet[®], Buehler), an oxide polishing suspension (OPS), for a duration of 12 hrs to provide a deformation free surface [19]. This step may be extended to longer durations, such as 24 hrs as suggested by Warren *et al.* [15]. Longer durations may result in greater preferential etching across the surface. Once removed from the vibrational polisher the sample was rinsed thoroughly with detergent and deionised water.

Once these steps were completed, the samples were removed from the resin mount and cleaned. Each sample was sonicated for two minutes in several organic solvents a total of six times - twice with acetone, twice with ethanol and finally twice with isopropanol, changing for a fresh solution each time. The sample was then thoroughly rinsed with deionised water and dried with dry air to avoid drying marks or salt growth [15].

The surface was then marked with a razor blade to create a fiducial such that specific areas on each sample could be revisited. Samples then underwent one of three surface preparation techniques: acid etching, electrolytic etching, or FIB etching. The sample surface was imaged before and after each technique such that comparable measurements and observations could be made. Imaging was performed by HS-AFM as well as by EBSD. Samples were stored on pin stubs secured within sample boxes to prevent any contact with the sample surface, as this can result in surface residue.

2.3 Acid Etching

The duplex sample was acid-etched by immersion in a Carpenter's reagent (a mixture of ethanol and hydrochloric acid) [21, 23, 31]. This technique is reported to reveal grain and phase boundaries in duplex stainless steels [21, 31]. The etchant was prepared by mixing 85 mL of ethanol with 15 mL of 35% hydrochloric acid, and the sample was immersed for a duration of 35 minutes [21, 31]. Experimental work was performed in ambient conditions.

2.4 Electrolytic Etching

Electrolytic etching offers a number of advantages over other etching techniques. It is capable of uniform polishing and deburring of samples without direction lines and without the requirement of a flat surface [32–34]. In particular, when compared to acid etching, electrolytic etching is easier to control and produces more reproducible results [19, 33, 35]. This method implements a two electrode electrolytic cell for etching, where the sample acts as the anode (positive electrode) and the etchant solution acts as the electrolyte [32–34, 36]. By supplying a DC voltage across the cell, oxidation reactions are driven at the anode and metal ions from the sample are conducted away, entering into the etchant solution [32–34, 36].

In this study, the sample was electrolytically etched with an etchant solution of 10 g of oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) dissolved in 100 mL of water (H_2O) [20]. This etch is reported to reveal grain structure in austenite and outline δ -ferrite [22]. The sample acted as the anode, with 0.87 cm^2 of surface exposed to the solution facing towards the cathode, separated by approximately 1 cm. The cathode consisted of a stainless steel wire (3.5 cm immersed). A DC voltage of 6 V was applied across the cell using a TENMA[®] 72-10480 Digital-Control DC power supply for a duration of 1 minute [20]. During electrolytic etching a current of 0.4 A was measured. Experimental work was carried out in ambient conditions.

2.5 Focussed Ion Beam (FIB) Etching

FIB etching removes the upper layers of the sample surface by sputtering. This is a process that occurs when energetic ions collide with the sample surface. The ion imparts energy to the electrons and atoms present in the sample resulting in the ejection of particles from the surface [25]. The ion beam is generated by applying a strong electric field across a liquid-metal ion source [25]. By increasing or decreasing the beam energy, the amount of material removed can be increased or decreased, respectively.

FIB etching was performed with a FEI FIB-201 focussed ion beam instrument. FIB etching was undertaken using a Ga^+ ion beam at 30 kV and 11 nA for a duration of 20 seconds over an area of $120 \mu\text{m} \times 100 \mu\text{m}$ at 0° from flat. Material was removed at a rate of approximately $0.5 \mu\text{m}^3 \text{ nC}^{-1}$, this corresponds to $5.5 \mu\text{m}^3 \text{ s}^{-1}$ for a beam current of 11 nA. The beam was scanned over an area of $12,000 \mu\text{m}^2$, thus giving an etch rate of 0.46 nm s^{-1} , which, for a 20 second period, translates to the removal of approximately 9.2 nm of the upper material.

2.6 Techniques for Analysis of Final Surface

2.6.1 High-Speed Atomic Force Microscopy (HS-AFM)

For HS-AFM analysis, the sample was mounted onto a 12.5 mm pin stub and secured in a custom piezo flexure stage; this stage translates the surface under the sharp probe in a raster pattern. The area of interest was located on the surface using $20\times$ optical objective equipped to the HS-AFM. A contact mode MSNL-10 cantilever (Bruker, USA) was lowered such that the probe tip engaged with the surface. The contact mode HS-AFM developed at the University of Bristol and Bristol Nano Dynamics Ltd. (UK) measured the cantilever’s z-displacement using a laser Doppler vibrometer (LDV) detector system, focussed above the tip of the probe. This information was collected using Bristol Nano Dynamics Ltd. software, which built and displayed a 3D topographic map of the surface in real-time. This data was analysed further post-collection using Gwyddion SPM data processing software, version 2.53 [37].

2.6.2 Electron Backscatter Diffraction (EBSD)

Quantitative microstructural data about the crystallographic nature of the specimen can be analysed by EBSD, such as grain size and orientation, phase identification, and the mapping of surface texture [38]. EBSD analysis was conducted on each sample, before and after the selected sample preparation techniques, using a Zeiss SIGMATM Variable Pressure (VP) Field Emission Scanning Electron Microscope (FE-SEM) (Oberkochen, Germany. Serial: 03-72) equipped with a GeminiTM electron source. EBSD instrumentation from EDAX-AMETEK Inc. (Mahwah, NJ, USA) comprised a DigiviewTM high-speed digital camera as well as the associated OIMTM Data Collection and Analysis software. The sample was tilted at 70° to the horizontal at a working distance of 10 mm. EBSD scans were performed at a constant beam voltage of 30 kV, 120 μm aperture, with a step size of 0.5 μm .

3 Results

3.1 Mechanical and OPS Polishing

Following initial sample preparations steps described in Section 2.2, HS-AFM maps were collected in the area adjacent to a fiducial on the sample surface, seen in Figure 1. Optically the austenite and δ -ferrite phases could only be faintly differentiated, with one appearing somewhat lighter than the other. By correlating EBSD measurements with optical images it was possible to determine that the darker phase was ferrite, and the lighter austenite.

Figure 1: a) and b) show optical images of the surface following mechanical and OPS polishing steps during HS-AFM measurements, where b) is an enhanced contrast version of the image outlined in blue in a), with labels indicating areas of austenite and ferrite phases. The fiducial is seen to the right of the cantilever beam.

Topographic maps of the sample surface are shown in Figure 2. The high throughput of the HS-AFM allowed for measurements to be performed in several different areas on the sample for higher confidence in phase identification. For this sample preparation method, HS-AFM analysis was performed over approximately 14,700 μm^2 . Topographic maps were compared to optical images where it was found that the higher phase (lighter in Figure 2) is ferrite and the lower phase (darker in Figure 2) is austenite. The step height between the two phases was measured during post processing as between 1.4 nm and 2.4 nm, with a mean step height of 1.9 nm (calculated from 15 measurements).

The height difference between the two phases is a result of preferential mechanical polishing combined with the effects of colloidal silica on each phase. In previous work colloidal silica has been found to preferentially etch austenite in comparison to ferrite, resulting in the ferrite grain appearing higher

Figure 2: A composite topographic map of the sample surface following mechanical polishing steps with two frames, a) and b), selected, with coloured versions highlighting ferrite in green and austenite in red. Frame a) shows austenite and ferrite phases with an orientation change within the austenite phase, as indicated by a dotted line. Frame b) shows austenite and ferrite phases. This data was collected from the region adjacent to the fiducial.

topographically [39, 40]. This agrees with the observations made in this study. Topographic maps may be collected before polishing with colloidal silica; however, this step is required for a scratch free finish on the nanoscale which is vital for acquiring good quality HS-AFM maps.

Figure 2 also shows an orientation change in austenite, highlighted in Figure 2a. Within Figure 2a the austenite phase contains two areas that appear to have polished anisotropically: this is likely due to differences in the orientation between grains in austenite. This affect was less clear within the ferrite phase, though it may be the case that no ferrite grain boundaries were present in the areas analysed by HS-AFM.

3.2 Acid Etching in Carpenter's Reagent

Etching the surface using Carpenter's reagent (a mixture of ethanol and hydrochloric acid described in Section 2.3) clearly revealed austenite and ferrite regions, visible by optical microscope, as seen in Figure 3. This result is expected as Carpenter's reagent is known to identify grain and phase boundaries in duplex stainless steels [21, 31]. Following comparison with EBSD results, the lighter, smoother looking areas were identified as austenitic, and the darker areas as ferritic.

Topographic maps collected by HS-AFM in the region adjacent to the fiducial are shown in Figure 4. HS-AFM analysis for the acid etched sample was performed over approximately $8,320 \mu\text{m}^2$. Within these images two different phases are distinct from one another, as each phase has been affected differently by the etch. The flatter, lower (darker) phase was identified as austenite, and the higher (lighter) phase as ferrite. The step height between the two phases was measured to be between 22 nm and 47 nm, with a mean step height of 35 nm (calculated from 15 measurements), considerably larger than that measured following mechanical and OPS polishing.

HS-AFM topographic maps show that areas of ferrite contain deep pits (Figure 4a). These microscale pits are likely the cause of the rough looking texture on the macroscale. The ferrite regions exhibit

Figure 3: An optical image of the surface following acid etching with Carpenter's reagent, with fiducial. With labels indicating regions of austenite and ferrite phases.

some variation in pit size and distribution, the cause of this is unknown, though may be due to changes in orientation. However, there are no obvious boundaries between different orientations due to etching within the ferritic areas, nor in the austenitic areas.

Figure 4: A composite topographic map of the sample surface following acid etching with Carpenter's reagent with two frames, a) and b), selected, with coloured versions highlighting ferrite in green and austenite in red. Frame a) shows austenite and ferrite phases. Frame b) shows an area with majority austenite phase. This data was collected from the region adjacent to the fiducial.

3.3 Electrolytic Etching in an Oxalic Acid Solution

Optical images were collected of the sample surface in the region of the fiducial following electrolytic etching within an oxalic acid solution, Figure 5a. The surface appeared very rough, with some areas appearing more etched than others. It was evident that a large portion of top surface had been removed

by electrolytic etching, and a shadowing effect was observed within EBSD maps due to the uneven surface. As such, phase identification by EBSD in the region of the fiducial was not conclusive. However, for these particular etch conditions (described in Section 2.4), the rougher, darker-looking areas are expected to be austenite, with the grain structure outlined, and the smoother areas δ -ferrite [22].

Figure 5: Optical images of the surface following electrolytic etching in an oxalic acid solution showing: a) an area adjacent to fiducial mark, and b) an area next to the partially covered section.

Analysis by HS-AFM was performed in the area adjacent to the fiducial, shown in Figure 5a. The uneven surface within the austenite regions resulted in challenging imaging conditions; this was particularly evident while traversing large areas. Figures 6a-c were collected from regions of austenite. By tracking the cantilever optically during imaging, it was deduced that the large pit structures occurred around the visibly etched regions on the surface. These pits likely mark austenite grain boundaries and gave rise to the structures seen optically on the macroscale. Figures 6d and 6e were collected from a region on the surface identified as ferrite. In contrast to the austenite regions, the ferrite regions on the surface were much flatter. This was evident in the reduced height range.

Measurements were collected while traversing areas on the surface identified as ferrite into regions identified as austenite. Figure 6f contains pitted structures on the left hand side and a smooth region on the right hand side. This may be an example of a boundary between ferrite and austenite, however this is purely speculative.

Due to the high aspect ratio of some of the pit structures within the austenite regions, it is possible that tip convolution artefacts are present in the resultant HS-AFM data [41]. Additionally, in some cases the depth of the pit structure exceeded 4 μm, and as such were deeper than the height of the probe tip [42]. To accurately measure the full extent of the pit would require another technique such as FIB cross-sectioning, or alternatively a higher aspect ratio cantilever may be used. However, in the context of gauging suitability of the etched surface for HS-AFM analysis it is deduced that these conditions are not suitable.

An area on the surface was identified where the surface was etched to a lesser degree, shown in Figure 5b. This area was not fully submerged during the etching process as it was partially covered. By comparing images collected from this region to the phases identified previously in Figure 1, the smoother areas were confirmed as ferrite, and the rougher areas as austenite.

HS-AFM topography measurements performed in the area in Figure 5b are shown in Figure 7. Figure 7 shows two distinct phases. Areas identified as ferrite were generally uniformly etched, whereas austenite had irregular clusters of pits. In contrast to the results from the previous sample preparation methods (Sections 3.1 and 3.2) the austenite phase was topographically higher than the ferrite phase. The step

Figure 6: Topographic maps of each phase identified on the surface following electrolytic etching in an oxalic acid solution collected in the region adjacent to fiducial mark, where a), b) and c) show austenite regions, and d) and e) show ferrite regions. e) shows a region possibly containing a phase boundary, with austenite on the left hand side and ferrite on the right.

edge between the two different phases in this area was measured as between 11 nm and 54 nm, with an average step height of 25 nm (calculated from 10 measurements). This is a much larger range than that measured on the acid-etched or mechanically polished samples, this is likely the result of sampling in the partially covered area, where the etch conditions vary. this was the only etch investigated that preferentially etched ferrite, as such ferrite regions appeared lower within topographic maps. The step height between each phase varied considerably and was dependent upon the location at which measurements were collected. For this sample preparation method, HS-AFM analysis was performed over a total surface area of approximately $28,400 \mu\text{m}^2$.

Comparing the data collected in the region of the fiducial to that collected in the partially covered region indicates how the surface changes as the etch progresses. The pits present within the austenite regions became much larger and deeper, as indicated by the large change in height values, from 48.2 nm (Figure 7a) up to 381 nm (Figure 6c). In contrast to this, the ferrite region became flatter and smoother as the etch progressed.

Figure 7: A composite topographic map of the sample surface following electrolytic etching in an oxalic acid solution collected in the area adjacent to the covered area with two frames, a) and b), selected. Frame a) shows an area identified as austenite. Frame b) shows an area identified as ferrite.

3.4 FIB Etching

The final sample preparation method was FIB etching of the surface. The area adjacent to the fiducial was etched, as outlined by a blue box in Figure 8a. Following FIB etching, the surface appeared somewhat darker in the region of the etch, making phase identification difficult optically. FIB images of the etched region before and after 20 seconds of etching are shown in Figures 8b and 8c, respectively. Figure 8c shows grain contrast, where different orientations of grain are etched at different rates [26]. This was confirmed by comparing this image with EBSD maps collected from the same region. It was found that, generally, the lighter grains within the FIB image were austenitic, and the darker grains were ferritic.

Figure 8: a) An optical image of the surface following FIB etching, with the etch area outlined in blue, also FIB images showing the area outlined in blue after etching for: b) 0 seconds, and c) 20 seconds.

Topographic maps were collected in the etched region, as shown in Figure 9. The different orientations within each phase were etched at varying rates, allowing for observations of grain structure but conversely

making phase identification somewhat challenging. By comparing these maps with those collected by FIB and EBSD it was found that ferritic areas had higher topography, whereas austenitic areas were generally lower. However, phase boundaries were not obvious or consistent. HS-AFM analysis for the FIB etched sample was performed over a total area of approximately $14,700 \mu\text{m}^2$. A step height between the two phases was not measured as it varied depending on which orientations were adjacent to one another.

Figure 9: A composite HS-AFM topographic map of the sample surface following FIB etching with two frames, a) and b), selected, with coloured versions highlighting ferrite in green and austenite in red. a) and b) both show areas containing both austenite and ferrite phases.

4 Discussion

Within this study, four commonly implemented sample preparation techniques were performed on a duplex stainless steel and compared: mechanical and OPS polishing, acid etching, electrolytic etching, and FIB etching. A summary for each sample preparation method is given within Table 2.

As stated within Section 1, acid etching and electrolytic etching are commonly implemented for optical studies of microstructure as they preferentially etch or colour specific features of interest [17–24]. This can result in a rough surface that may be unsuitable for AFM studies, however this is highly dependent upon the etch conditions. In the work presented here it was found that acid etching and electrolytic etching of the surface allowed for optical identification of the austenite and ferrite phases. This was reflected within HS-AFM measurements where each phase was etched differently. However, topographic measurements had much larger height ranges than those measured following initial sample preparation steps. This can result in finer microstructural information being more difficult to identify.

HS-AFM measurements performed on the surface acid etched with Carpenter’s reagent were considered to be of good quality as images were clean and free of debris, with consistent and clear differences between phases allowing for confident phase identification. The austenite phase was lower topographically, whereas the ferrite phase was higher and pitted. These pits may coincide with precipitates. However, precipitates such as sigma phase are not expected to be present as the specimen was not aged [43]. It has been found in other works that ferrite is preferentially attacked by acidic-chloride solutions [23,24,44]. In particular, preferential pitting of the ferrite phase has been observed in other works [45]. It is possible that this is due to differences in chemical composition between the two phases [45], however this is beyond the scope

of this paper.

HS-AFM data collected from the surface electrolytic etched in an oxalic acid solution contained deep pit structures within areas identified as austenite. These pits likely formed at grain boundaries, thereby optically revealing grain structure [17, 22]. However, these large pits caused imaging artefacts during HS-AFM analysis. Furthermore, due to the lack of supporting EBSD data it is also of concern that electrolytic etching may have altered the phase fraction. Reflecting upon these results, the conditions explored within this work for electrolytic etching are not recommended for optimal analysis by HS-AFM. It is suggested that performing electrolytic etching for a reduced time, or at a lower etchant concentration, may result in better surface conditions for HS-AFM imaging. It must be stressed that these results are that of a specific etch recipe and is not true of all electrolytic etching. There are a wide range of recipes available, and other recipes have been successful in previous studies [46, 47]. In studies of duplex stainless steels by scanning Kelvin probe force microscope – a different type of SPM method – electrolytic etches have produced suitable surface finishes. For example, electrolytically etching in potassium hydroxide [46], which results in stained ferrite, or a nitric acid solution [47].

Following FIB etching of the surface, HS-AFM analysis revealed a topographic contrast from grain to grain allowing for clear observations of grain structure. However, as a result of this contrast, it was difficult to discern between different phases. The grains also appeared distorted, making microstructural characterisation particularly challenging. During FIB etching, it has been reported that micro-alloying of the near surface can occur as a result of ion implantation [28, 29]. In austenitic steels, Ga^+ implantation can lead to a phase change from FCC to BCC [28]. This may be the cause of the distorted microstructure observed by HS-AFM, however no clear phase change was measured by EBSD. Due to the difficulty of identification of features present on the sample surface, this method of sample preparation was found to be unsuitable for observations of microstructure by HS-AFM. However, this may not be the case for different materials or etch conditions. In other works, it has been found that lower acceleration voltage and shorter imaging times can reduce the effects of ion implantation [29, 30].

HS-AFM analysis performed of the surface following initial mechanical and OPS polishing produced high quality topographic maps with a consistent step height between the two phases, allowing for phase identification. However, each phase had a similar surface texture and so phase identification would require measurement of the step edge. This sample preparation method has been successfully implemented in other AFM studies of stainless steels [15, 39, 40], as well as for high resolution characterisation by EBSD [30, 39]. Mechanical and OPS polishing was the only sample preparation method that allowed for clear observations of grain boundaries within austenite. While grain boundaries were clearly observed within the FIB etched surface, phase identification was considerably more challenging.

HS-AFM excels at imaging topography changes measured against an otherwise flat surface. This allows for observations of fine microstructure, such as small-scale precipitates, or subtle changes in surface texture. Sample preparation methods that result in the flattest surface possible, free of imaging artefacts or surface debris, will allow for the identification of these finer microstructures. It is on this basis that conclusions were drawn. Therefore, mechanical polishing followed by colloidal silica etching is recommended as an optimal surface preparation method for HS-AFM. This method is relatively fast and allows for initial observations of fine microstructure across the surface. Following these measurements further etches may be appropriate for observations of specific features. This may be applicable where surface chemistry may be of interest. Mechanical polishing alone produces a hardness induced topography, whereas various etchants provide information about the reactivity of the surface microstructures within specific environments. Iterative application of various etches may provide substantial information about the microstructures present and their properties.

Table 2: Summary of sample preparation techniques studied within this work. Example surfaces as measured by HS-AFM are given as 3D topographic maps. Identified phases are indicated within each image. *Please note that these phases were identified by optical and HS-AFM analysis and were not confirmed by EBSD analysis.

Method	Example Surface	Summary
Mechanical and OPS Polish		<ul style="list-style-type: none"> • Optical: Smooth, mirror-like surface. Phases could only faintly be differentiated. • HS-AFM: High quality topographic images with discernible phases with an average step height of 1.9 nm. Different grain orientations within austenite were also thought to be observed.
Acid Etch in Carpenter's Reagent		<ul style="list-style-type: none"> • Optical: Ferrite appeared darker than austenite allowing for identification. • HS-AFM: Clear topographic images, with discernible phases with an average step height of 35 nm. Austenite was flatter and smoother, whereas ferrite contained large pits likely giving rise to the macroscale appearance of the surface. Different grain orientations were not obviously distinguishable.
Electrolytic Etch in an Oxalic Acid Solution		<ul style="list-style-type: none"> • Optical: Etching of the grain and phase boundaries within austenite regions allowed for tenuous optical identification of the phases. • HS-AFM: The rough surface was not optimal for analysis by HS-AFM. Each phase was etched differently, with austenite containing deep pit structures, and ferrite appearing largely flat. There was no consistent step height between phases. • EBSD: Due to uneven surface, phase identification was not achieved.
FIB Etch		<ul style="list-style-type: none"> • Optical: Identification of the phases or microstructural features was not possible. • HS-AFM: Grains within ferrite and austenite observed, however difficult to identify each phase and no consistent step height between phases due to distorted grain appearance.

5 Conclusions

The importance of sample preparation in the process of acquiring high quality topographic data cannot be understated and must be considered carefully for accurate analysis. When considering sample preparation techniques, it is important to first consider what features on the surface are of interest and what imaging technique will be used to perform the analysis. This is particularly important when drawing conclusions from this study.

Within the work presented here, different surface preparation techniques that are commonly implemented within metallurgical studies were compared for samples of SAF 2205 duplex stainless steel using HS-AFM. It was found that, while acid etching and electrolytic etching were optimal for the low resolution of optical microscopy, these methods were less suited for analysis by high resolution HS-AFM. This was due to the large height changes across the surface, which can distort or hide any finer microstructures present. In contrast, mechanical and OPS polishing provided a gentle etch that allowed for high quality topographic measurements to be collected. Initial measurements may then be used to inform additional sample preparation methods that may be undertaken if appropriate. The results of this study are also applicable to conventional AFM.

This study extends beyond observations of duplex stainless steels. Mechanical and OPS polishing has been performed on samples of thermally sensitised AISI Type 304 stainless steels and has been found to be suitable for high resolution HS-AFM observations of nanoscale secondary phase precipitates within the grain boundaries [14]. Future work to be implemented will explore the extension to other more reactive or softer materials, such as pure metals, that pose a challenge when undertaking standard sample preparation steps.

In conclusion, a series of etchants have been used to prepare a duplex stainless steel for HS-AFM analysis. Mechanical polishing followed by vibropolishing with colloidal silica was identified as optimal for HS-AFM analysis and has been successful for the preparation of other single phase stainless steels.

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Declaration of Interests

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Oliver Payton and Loren Picco are shareholders in Bristol Nano Dynamics Ltd., a University of Bristol spin-out company.

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