2.4 THE ASSOCIATION RELATIONSHIPS AMONG BUBBLES, PRECIPITATES, AND GRAIN BOUNDARIES IN DUAL BEAM IRRADIATED NANO-STRUCTURED FERRITIC ALLOYS

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OBJECTIVE

The objective of this work is to characterize the relationship between start-of-life alloy and irradiation-induced features in nano-structured ferritic alloys, with emphasis on bubbles and bubble associations, as a foundation for microstructurally informed helium transport, fate and consequence models.

SUMMARY

Transmission electron microscopy (TEM) was used to characterize the associations between various microstructural features, including helium bubbles, in nanostructured ferritic alloys, following dual ion irradiations at 650°C. Almost all of the nm-scale oxide precipitates are associated with one and, in some cases a few, interface bubbles. The distribution of precipitates and bubbles along dislocations and small angle grain boundaries are not significantly different than in the matrix. However, the precipitates on large angle grain boundaries are larger and often associated with more bubbles.

PROGRESS AND STATUS

Introduction

Nano-structured ferritic alloys (NFA) are dispersion strengthened by nm-scale Y-Ti-O oxide features (NF), resulting in outstanding high temperature creep strength and remarkable radiation damage tolerance [1-3]. Therefore, NFA are good candidates advanced fission and fusion energy applications. In particular, NFA manage low solubility helium by trapping it in the form of small bubbles at the interface between NF and the Fe-Cr matrix [2-5]. Very small, high-pressure (≈ 2g/r) bubbles efficiently store helium in a way that prevents its deleterious effects with respect to void nucleation and various manifestations of helium embrittlement [2-6]. For example, both in situ He injection and dual ion irradiation studies show that, in contrast to tempered martensitic steels (TMS) with bi-modal distributions of cavities composed of small bubbles and larger growing voids, only small nm-scale bubbles are observed in NFA [2-6].

In addition to the NF, NFA contain high dislocation densities and fine grains [2,3]. It is well established that bubbles and voids in many other irradiated alloys, including TMS and austenitic stainless steels, are often associated with various microstructural features predominantly dislocations, precipitates and grain boundaries. These associations and bubble sites are critical to the consequences of helium as well. For example, larger bubbles on precipitates and grain boundaries are favored void and creep cavity nucleation sites, respectively [2,3,6]. Helium on grain boundaries also leads to severe degradation of fracture toughness [6]. However, the NF associated bubbles are more numerous and smaller in NFA. Thus characterizing such associations is critical to developing helium transport, fate and consequence models.

Dual beam (helium plus heavy) ion irradiation coupled with transmission electron microscopy (TEM) is a powerful method to study helium behavior [6]. In this study, we clarify the associations relationships that exist among various features in dual ion irradiated NFA. To the

best of our understanding, this is the first systematic and comprehensive evaluations of bubble-boundary-interface-precipitate associations in NFA.

Experimental Procedure

MA957 was irradiated by dual 6.4 MeV Fe^+ plus 1.0 MeV He^+ ion beams at 650°C using the DuET facility at Kyoto University in Japan, to a nominal condition of 48 dpa at 2200 appm at a depth of 600 nm. The actual dpa, He, and He/dpa vary with depth. TEM specimens were prepared by in-situ lift out in a FEI Helios-FIB; a low final low energy, 2 KV at 5.5 pA minimized the gallium ion beam damage. TEM was performed using a FEI Titan at 300 KV. Conventional TEM Frensnel contrast imaging at defocuses of ±1.0-1.5 μm was used to image the helium bubbles. Bubbles image with bright contrast in the under-focus images and dark contrast for over focus. It is especially important to compare under-focus and over-focus images from the same location observing for small bubbles with d<2 nm. The NF oxide precipitates were imaged in-focus. Adobe Photoshop was used to overlap the in-focus and under-focus images to simultaneously reveal the precipitates and bubbles. Finally, high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and energy dispersive X-ray (EDX) techniques were used to investigate the composition of the lager features with bright contrast (bubbles) in under-focus images.

Results and Discussion

The under-focused (≈-1500 nm) bright field image in Figure 1 shows the distribution of He bubbles in the irradiated region. A large angle grain boundary (LAGB) runs diagonally from the top to the right side of the image. The white features are bubbles. The bubbles located on the LAGB appear to be larger than in the matrix. However, as shown in Figure 2, further detailed investigation shows that the apparent size of boundary bubbles is misleading. Figure 2a shows that lager precipitates are also located on the LAGB. The under- and over-focus images in Figure 2b and c show that bubbles on the larger and smaller precipitates are similar, but they appear larger in the former case due to overlap locally and through the foil thickness. Further, the larger LAGB precipitates are associated with more numerous bubbles than on the smaller oxides in the matrix. Figure 2d illustrates that while bubbles are essentially always associated with the precipitates, the latter appear to be bubble free in some cases (see arrows).

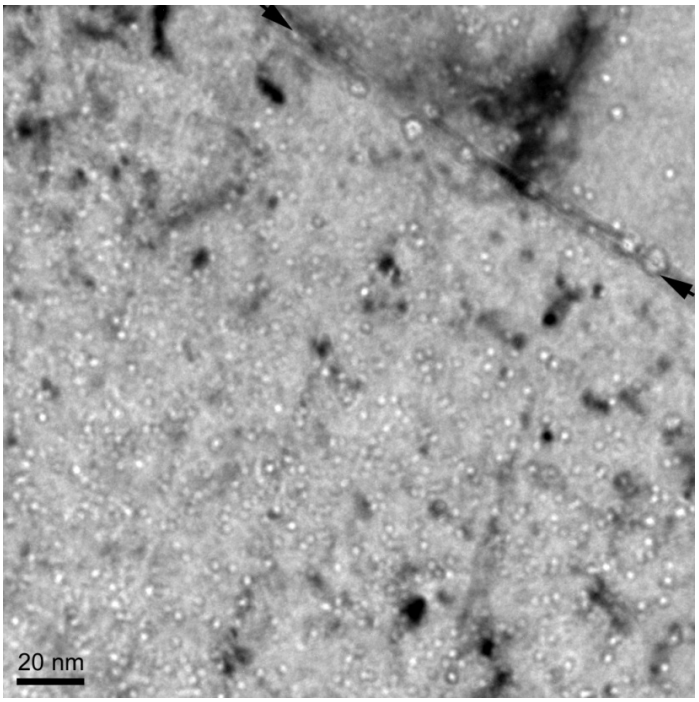

Figure 1. An under focus bright field image showing larger features with bright contrast lie along the LAGB, while the smaller features with bright contrast reside in the matrix.

Energy dispersive X-ray (EDX) spectroscopy was used to measure the composition of the larger features lying along the LAGB's in the under-focus bright field images. Figure 3 shows the EDX results. Figure 3a is an under focus bright field image of a triple junction area and Figure 3b shows the corresponding HAADF STEM image (Z-contrast image). The bright spots in the bright field images appear as dark spots in the HAADF image indicating the presence of lower-Z elements. In order to optimize the experimental condition for recording EDX signals, the HAADF image is tilted at 10° from the bright field image; therefore, the dark spots in the HAADF images may not appear at exactly at the same locations as in the bright field image. EDX on 12 large features showed that they all are enriched in Ti and Y. Examples of EDX spectra from the larger LAGB Y-Ti-O precipitates are shown in Figures 3c and d, for dark regions 10 and 11, respectively. These results are consistent with many previous observations of bubble precipitate associations at both matrix and grain boundary sites [6]. Figures 1 and 4 shows that the bubbles are distributed more unevenly on LAGB compared to those on SAGB that are again highly associated with precipitate features.

The possible enhanced association of bubbles and dislocations was also examined. Lines drawn along a random segment of dislocations were compared to parallel lines of the same length in the adjoining matrix. No significant differences in the number of bubbles along the dislocation and matrix lines were observed. In the example shown in Figure 5, there are 6 bubbles in the matrix and 5 easily visible along the dislocation.

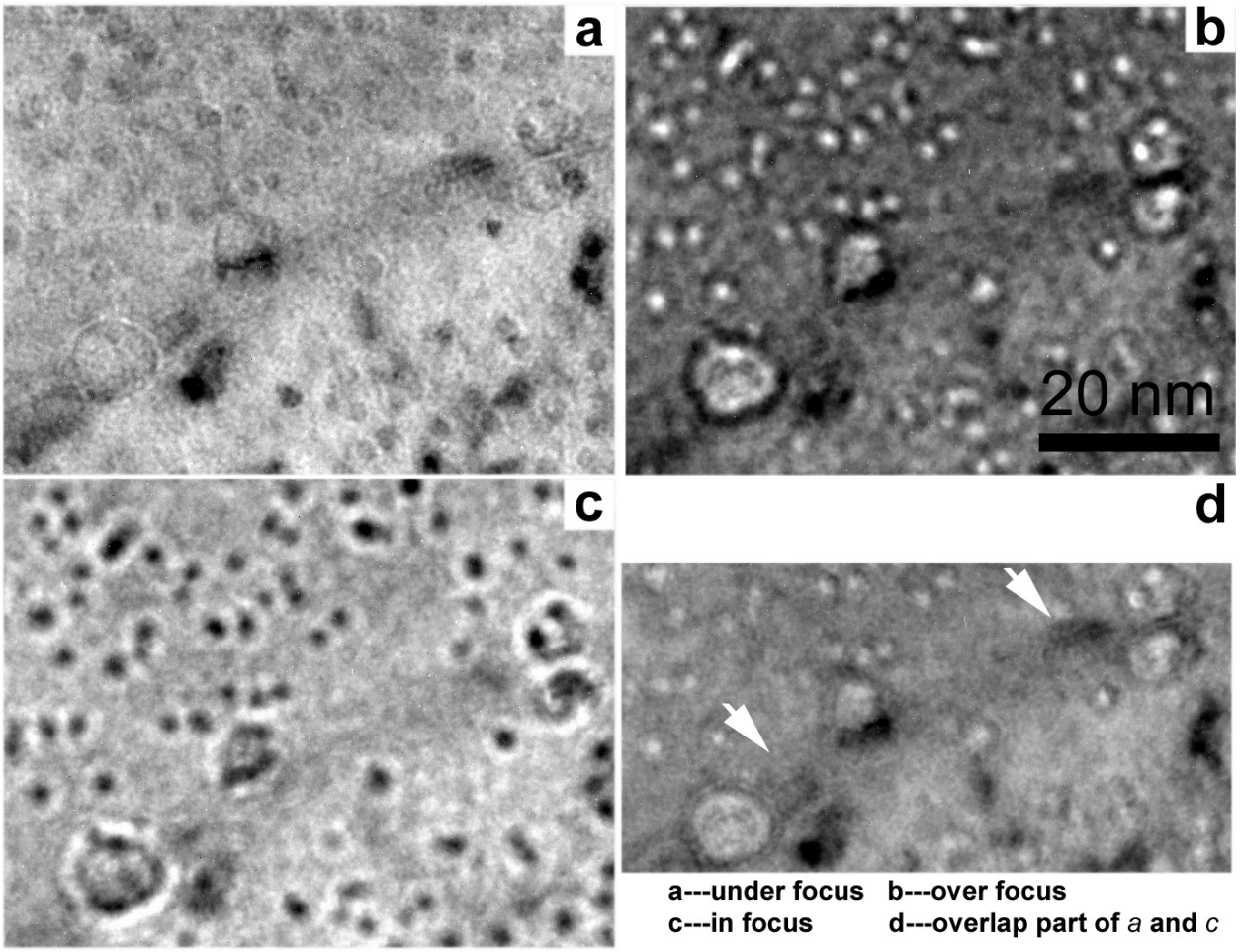

Figure 2. a) In-focus bright field image; b) under focus bright field image; c) over focus bright field image; and, d) overlapping a and b images.

A similar evaluation of precipitates-dislocation associations was also carried out. Again the matrix and dislocation precipitate populations are similar. In the example shown in Figure 6, there are 10 precipitates along the dislocation segment compared to 9 in the adjoining matrix. Thus, neither bubbles nor precipitates show a strong preference to be associated with dislocations.

Summary and Conclusions

The results of this study can be summarized as follows:

Bubbles are always associated with oxide NF precipitates;

Bubbles are observed on most, but not all, precipitates;

The precipitates on LAGB are larger;

The size of the bubbles on the larger NF along LAGB is similar to those on smaller matrix features;

Matrix features typically are associated with one bubble while the larger LAGB precipitates often contain several bubbles;

SAGB are decorated with smaller NF similar to this found in the matrix; and

The NF along SAGB typically is associated with one bubble that is similar in size to those in the matrix and on LAGB.

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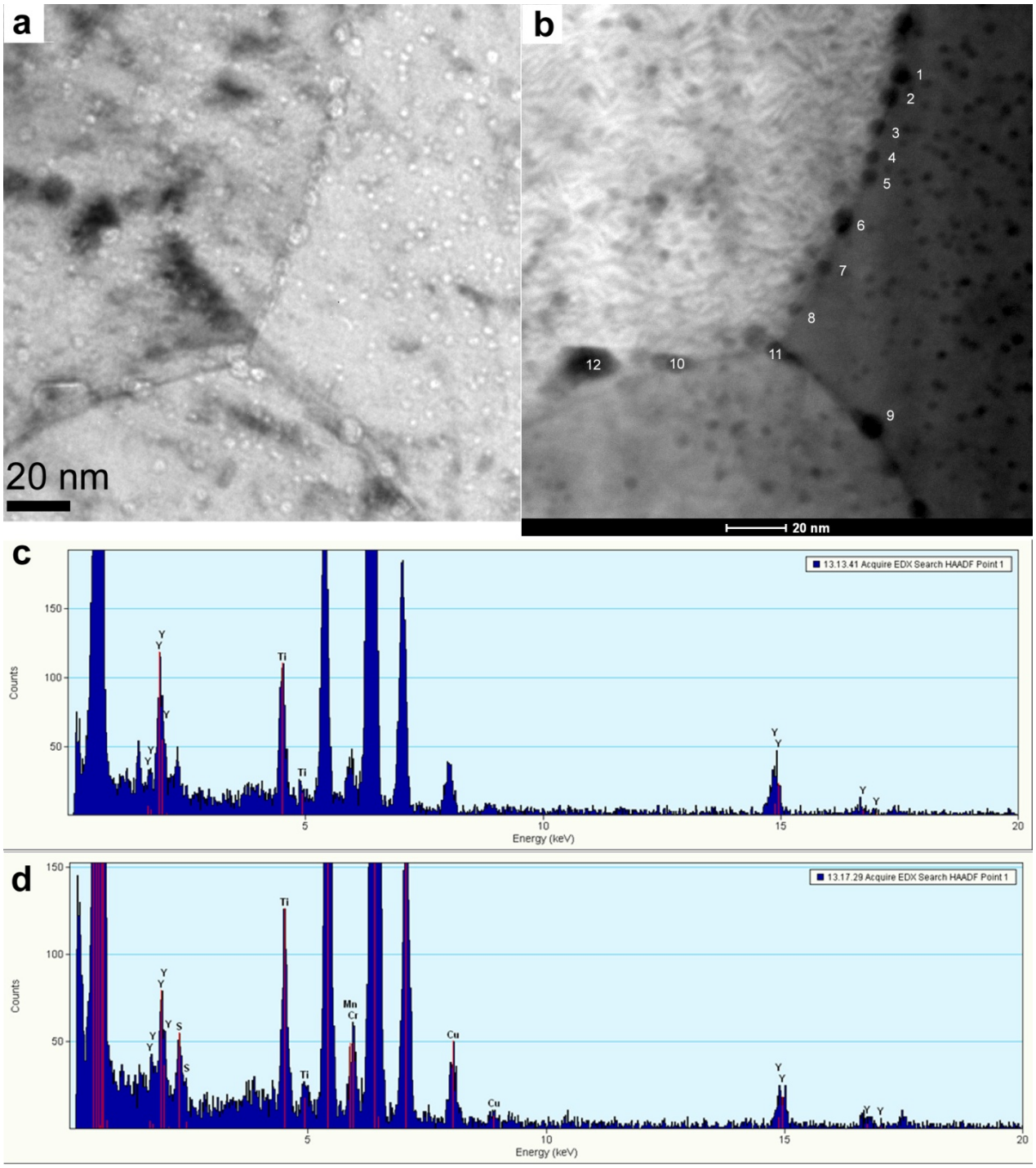

Figure 3. a) An under focus bright field image of a triple junction; b) the corresponding HAADF STEM image; c, d) EDXS spectra for features labeled 10 and 11, respectively.

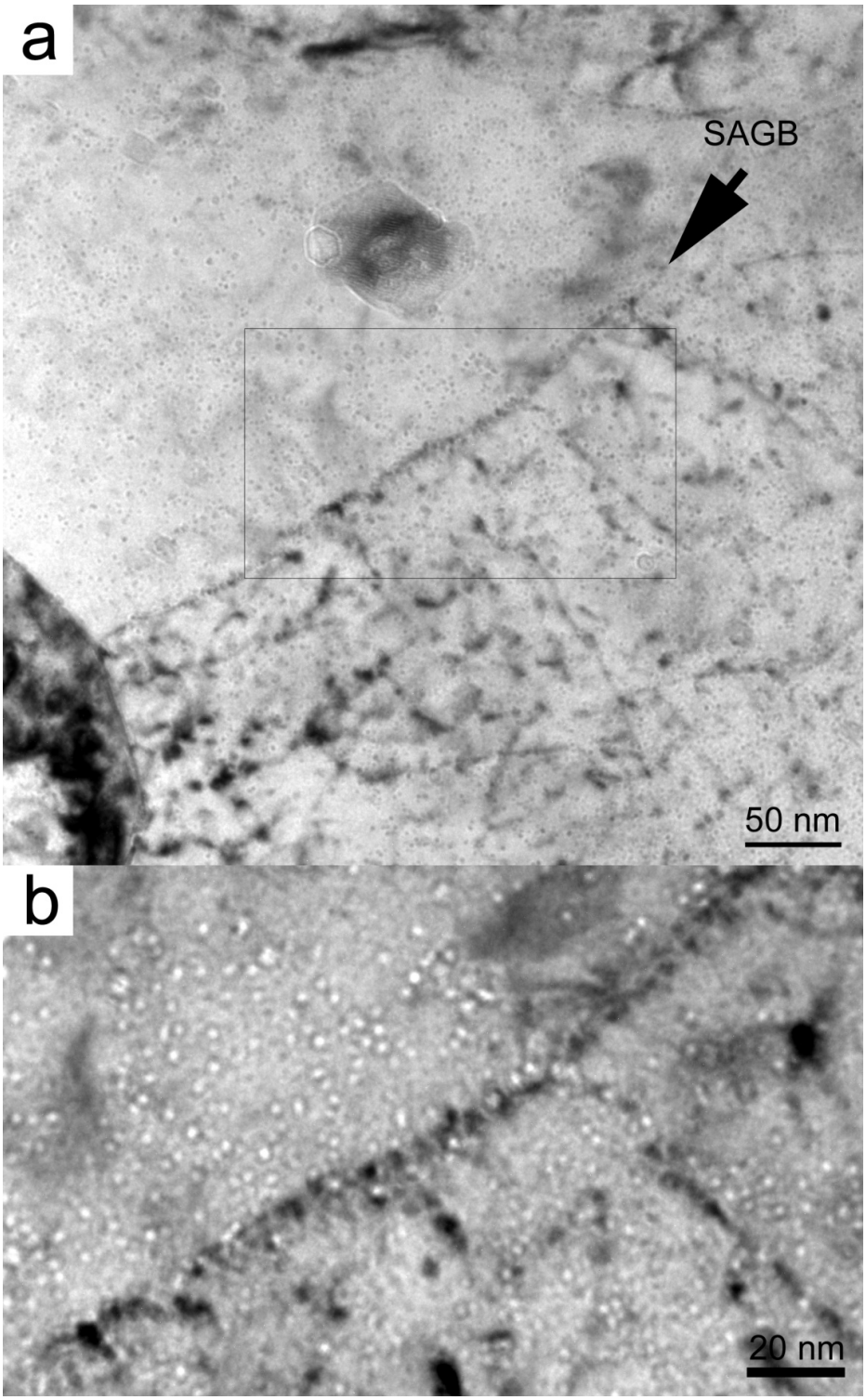

Figure 4. a) An over focus bright field image showing a SAGB, indicated by an arrow; and, b) an under focus image of the rectangular area in a.

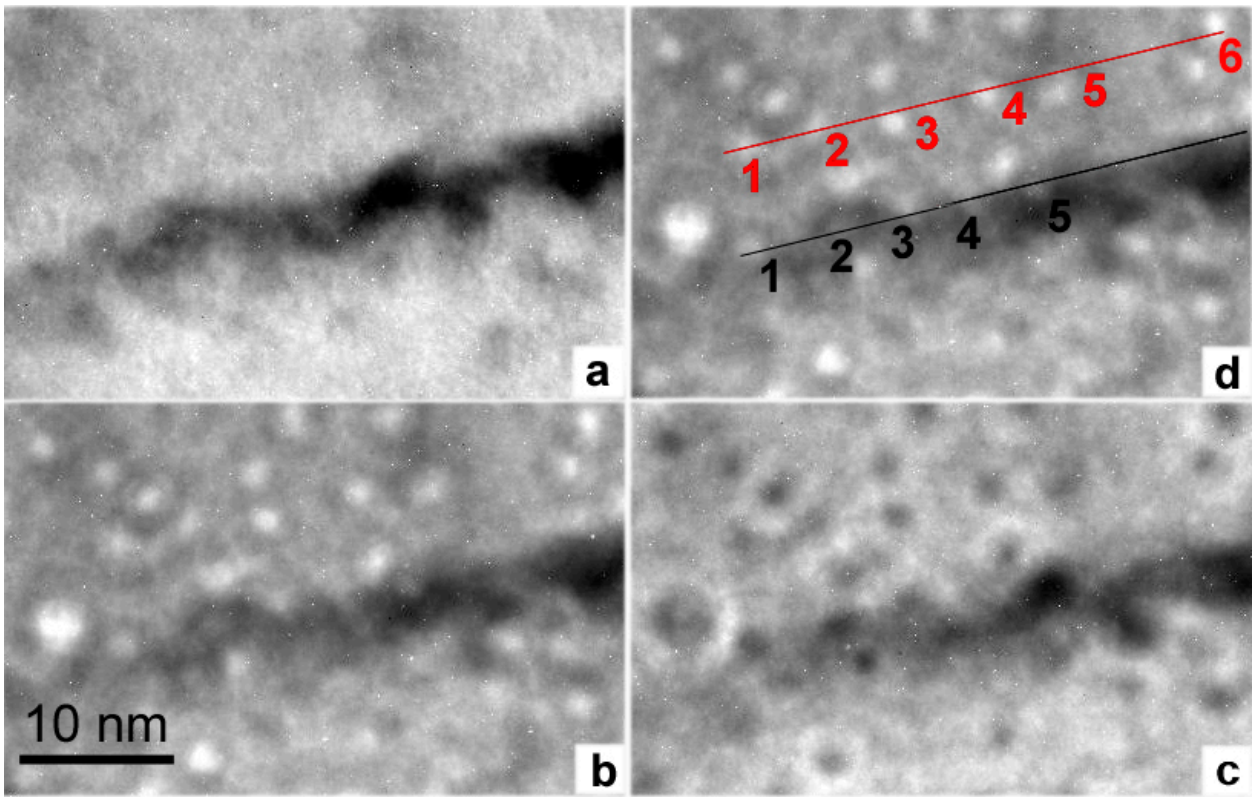

Figure 5. a) An in focus bright field image showing precipitates; b) an under focus bright field image of bubbles lying along dislocations vs. those residing in the matrix; c-d) under and over focus bright field images showing bubbles.

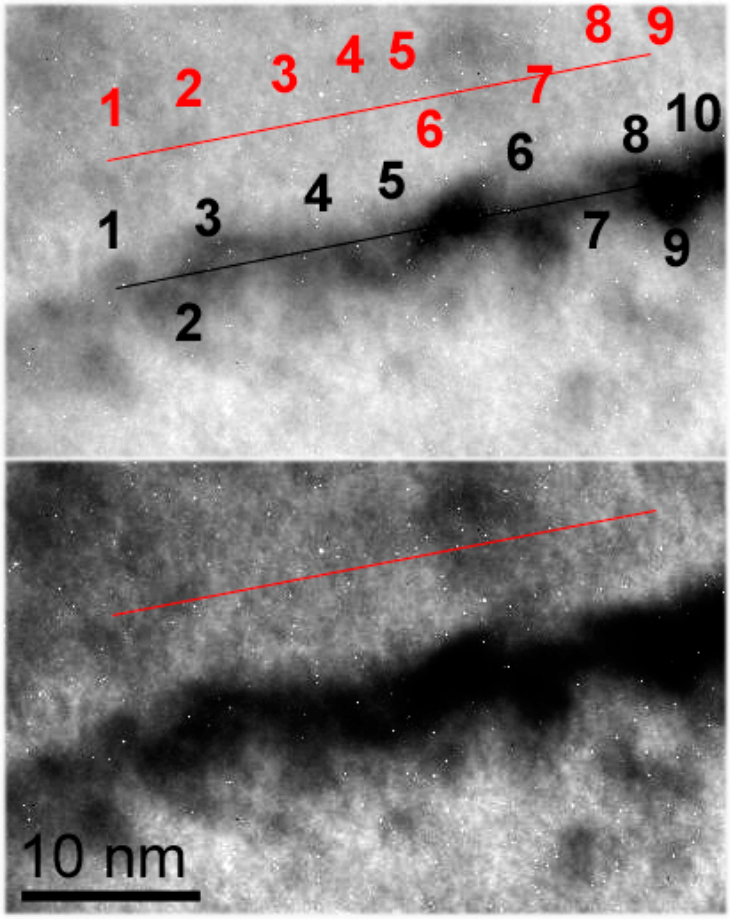

Figure 6. a-b) Bright field images showing the relationship between precipitates and dislocations where the brightness and contrast have been adjusted to be favorable for counting precipitates along the dislocation and in the matrix, respectively.