



## Regular Article

# Atomically resolved chemical ordering at the nm-thick TiO precipitate/matrix interface in V-4Ti-4Cr alloy



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## ABSTRACT

We have used advanced analytical electron microscopy to characterise the local structure and chemistry at the interface between nm-thick TiO precipitates and the V-based matrix in a V-4Ti-4Cr alloy. Our results reveal the presence of an intergrowth between the fcc TiO and bcc vanadium structures, with a repeat lattice distance that equals 2.5 times the vanadium lattice parameter along the c-axis. Our atomic resolution analysis of the interface will impact the mechanistic understanding of its interaction with interstitials and radiation-induced lattice defects, and consequently trigger the development of improved alloy structures with interfaces engineered for enhanced radiation tolerance.

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Vanadium-based alloys constitute advanced structural material candidates for the first wall of future magnetically-confined fusion reactors, due to their relatively low cross section for neutron activation [1,2]. Consequently, the targeted tritium breeding ratio will be achieved without the need of an additional neutron-multiplier material such as beryllium. The high strength and creep resistance of V-based alloys, enhanced by the addition of Cr, will allow these materials to withstand temperatures up to 750 °C without compromising reactor operability and safety [3]. In addition, the body-centred cubic (bcc) nature of the V matrix, with additions of Ti, provides these materials with good resistance to radiation-induced void swelling [4,5]. These considerations have led to the V-4Cr-4Ti alloy being identified as the prime V-based candidate material for fusion reactor applications [2,6,7].

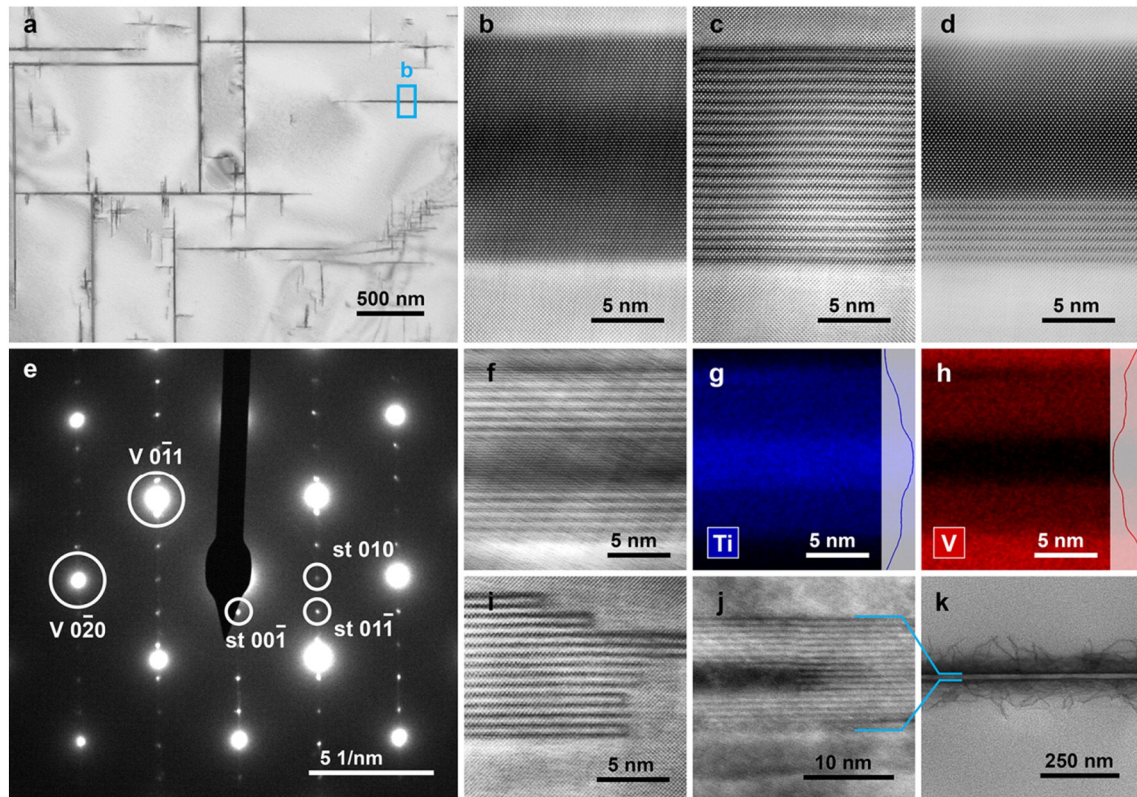
However, the presence of H, C, O and N as ‘free interstitials’ in the V-matrix causes the detrimental shift of the ductile-to-brittle transition temperature from –200 °C to values well above room temperature [8–10]. Ti was identified as an effective scavenger for interstitials [11], by forming plate-like oxycarbo-nitride precipitates [12–15]. The additional benefit is that the precipitate/matrix interface could potentially act as an effective sink for radiation-induced lattice defects, such as vacancies, vacancy clusters or dislocation loops, or for transmutant helium

atoms [16,17]. Unfortunately, a unified view about the local structure and chemistry of these nano-precipitates is still lacking. In this paper, we have addressed this by characterising, with atomic resolution, the chemical distribution and local structure inside the precipitates and within the precipitate-matrix interface region.

In this study we annealed V-4Cr-4Ti (wt.%) sheet material for 2 h at 1200 °C in an inert atmosphere, followed by water-quenching to room temperature. For transmission electron microscope (TEM) imaging and analysis discs were prepared by mechanical pre-thinning, followed by electro-polishing using an electrolyte of 60 vol.% methanol–35 vol.% 2-butoxyethanol–5 vol.% perchloric acid (60%) at a temperature of –35 °C. Advanced scanning transmission electron microscope (STEM) imaging, coupled with Energy-dispersive X-ray Spectroscopy (EDS) and Electron Energy Loss Spectroscopy (EELS) measurements performed in a STEM microscope, was used to obtain structural and chemical information with atomic resolution. A High Angle Annular Dark Field (HAADF) detector was used to collect the Rutherford-like scattering signal while the subnanometre-sized electron probe was scanning the sample. The intensity in the HAADF images is proportional to  $Z^{\nu}$ , where  $Z$  denotes the atomic number and  $\nu = 1.6–1.9$  [18]. The HAADF data therefore yielded information about the atomic positions and local arrangements inside the Ti-rich precipitates present in the V-4Cr-4Ti alloy. For the chemical identification we used (1) STEM-EDS to detect elements with high atomic number, and (2) STEM-EELS suitable to detect low-Z elements, and also to determine the chemical environment of a specific element.

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**Fig. 1.** (a) TEM BF image of the V-4Ti-4Cr alloy microstructure with the plate-like precipitates viewed along the [001] zone axis. (b–d) HAADF images showing precipitates with (b) a uniform atomic structure, (c) a superstructure and (d) both uniform and superstructure regions. (e) The corresponding SADF of (a) with the V matrix and simple tetragonal (st) superstructure reflections highlighted. Precipitates with different proportions of superstructure fringes: (f) with superstructure at both long sides with the relative EDS spectrum images for (g)  $K_{\alpha}$  Ti and (h)  $K_{\alpha}$  V, (i) with superstructure at the short edge of the precipitates, and (j) with superstructure surrounding a region of uniform atomic structure. (k) BF image of a precipitate with dislocations pinned at the precipitate–matrix interface.

Fig. 1a shows a TEM bright-field (BF) image of the V-4Cr-4Ti specimen after the annealing treatment. A significant number of plate-like precipitates, with lengths of up to a few microns and only a few tens of nanometres in width, were observed in this material. The selected area electron diffraction pattern (SADP) in Fig. 1e shows the [001] zone axis of the V matrix with additional reflections due to the presence of one of the plate-like precipitates. The lattice parameter of bcc V ( $a_v$ ) is  $\sim 3.02$  Å. The pattern clearly shows that the plates are lying on the V{100} family of planes. Additionally, we have observed the presence of diffraction spots corresponding to a superstructure with a spacing of  $\sim 7.56$  Å, which corresponds to  $\sim 2.5$  times the lattice parameter of the matrix.

High resolution STEM imaging of the precipitates (Fig. 1) revealed a range of atomic structures within different plate-like precipitates: uniform (b), showing a superstructure through the thickness (c), or showing a superstructure localised on one (d) or both (f) long sides of the precipitates. The spacing determined in the high resolution STEM data for the superstructure corresponds to the value obtained from the SADP. Fig. 1g and h are the related background-subtracted EDS spectrum images for the  $K_{\alpha}$  Ti and  $K_{\alpha}$  V lines, respectively. The EDS data show that the uniform area of the precipitate mainly contains Ti, whereas both Ti and V are present in the superstructure regions. Cr has not been detected in significant amounts inside any of the precipitates. Two additional cases are also reported in Fig. 1: superstructure at the short edge of the precipitates (i), and surrounding a region of uniform atomic structure (j). Interestingly, the interface between the precipitate superstructure and the matrix acts as an effective trap for dislocations present in the matrix (k).

In order to obtain further information about the local chemical distribution and the origin of the interfacial superstructure phase, we recorded the EELS core loss and low loss spectra [19] at representative

locations of the matrix, the superstructure and the uniform structure of the precipitate (Fig. 2). The EELS core loss spectrum of the matrix is dominated by the  $L_{2,3}$  edges of vanadium (in the region of 440–590 eV). A relatively weak  $L_{2,3}$  edge from the substitutional Cr atoms can also be observed close to 580 eV. When profiling from the matrix to the superstructure of the precipitate, the vanadium edge is still visible but decreases in intensity, whereas the  $L_{2,3}$  edge of Ti starts to appear at characteristic peak energies of 457 and 462 eV. The edge consists of  $L_3$  and  $L_2$  ‘white lines’ which originate from electron transitions from the inner  $2p_{3/2}$  and  $2p_{1/2}$  orbitals respectively to empty 3d orbitals of Ti [20]. Those characteristic Ti lines constitute the main feature of the EELS spectrum in the uniform structure of the precipitate. Additionally, we can also observe the appearance of the K-edge of oxygen at 530–550 eV, with the most distinctive maximum located just above the edge onset at 532 eV. The lower-energy features of this peak are known to originate from transitions between oxygen 1s and  $2p$   $\sigma^*$  states that are hybridised with empty Ti 3d orbitals [20]. The intensity of the 532 eV peak increases when moving the beam from the matrix into the superstructure and further into the uniform structure of the precipitate. We have not observed any significant signal in the EELS spectrum at around 280 and 400 eV which suggests the absence of C or N within the precipitate. These results would point to the precipitates consisting of a titanium oxide phase. To confirm this, we have also examined the EELS low loss or valence spectrum below 35 eV (Fig. 2c), which is dominated by plasmon excitations. The main plasmon peak of the matrix at 21.6(1) eV can be attributed to metallic vanadium [19]. The position of the maximum consistently shifts to a value of 23.8(1) eV inside the precipitate. An equivalent peak shift is observed for the superstructure and the uniform structure in the precipitate, see Fig. 2a–II. The main plasmon peak of metallic Ti would be located at 18 eV [19], and is expected to shift to  $\sim 20$  eV when forming Ti hydrides

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