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<Graphical abstract>

- (1) Transmission Kikuchi diffraction
- (2) Atom probe tomography
- (3) Y:Ti:O ratio of individual oxides

(a) ODS steel with low interstitials

(b) ODS steel with high interstitials

Non-stoichiometry oxides
Higher O level in oxides
High strength and low ductility

- (4) Y-Al rich core promoting oxide particle coarsening

Al

volume of $10 \times 12 \times 8 \text{ nm}^3$

- Y iso-surface 0.7 at.%
- Ti iso-surface 2.0 at.%
- O iso-surface 1.5 at.%

Influences of interstitial and extrusion temperature on grain boundary segregation, Y–Ti–O nanostructures, and mechanical properties of ferritic steels

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Abstract

Doping with interstitials influences the grain boundary (GB) composition of metallic alloys, enabling changes in elemental GB enrichment, grain size, and mechanical properties or even promoting nanoparticle formation. Yet, little efforts on these doping effects have been made in oxide dispersion-strengthened (ODS) steels. Here, by combining advanced microscopy techniques, we studied the impact of interstitial concentration and extrusion temperature on the GB structure-dependent solute segregation, Y–Ti–O nanostructures, and mechanical properties of ferritic Fe–14Cr (wt%) ODS steels fabricated by ball milling. We found that doping with high carbon and oxygen contents causes the GB to be decorated with the interstitials and promotes nanoparticle formation along the GBs, thereby retarding capillary-driven grain coarsening. This effect performs twofold, through grain size refinement and particle hardening. For samples with low interstitial contents, altering the extrusion temperature does not significantly change the

material's mechanical properties and microstructure or the nonstoichiometric chemistry of nanoparticles, which are highly stable at high temperatures. Further, for all the samples, Y–Al oxides in the initial precipitation stages rapidly become coarsened at high temperatures, as Al weakens the thermal stability of nanoparticles, thereby transforming them to core-shell structures with Y–Al-rich cores and Ti–O-rich shells in the later precipitation stages.

Keywords: ODS ferritic steel; grain-boundary segregation; nanoparticles; Atom probe tomography.

1. Introduction

The growing interest in and demand for cleaner energy has led to the development of high-performance structural alloys exhibiting outstanding stability in severe environments. The core components of advanced fusion and fission reactors must be able to withstand high levels of radiation damage [1-4]. Oxide dispersion-strengthened (ODS) steels exhibit remarkable creep and radiation resistance and hence provide enormous promise in meeting these requirements. Moreover, the combination of an ultrafine ferritic structure with highly dense Y–Ti–O nanofeatures having <5 nm bridges allows these steels to withstand high-temperature stress and high neutron dose environments expected in future fusion and Generation IV reactors operating at elevated temperatures.

In ferrite-based ODS steels, Y–Ti–O rich nanometer-sized clusters (shortly, NCs) are regarded as the key component for improving the material's mechanical properties. The superiority of NCs over their non-NC counterparts with the same matrix size has been discussed earlier [5,6]. For example, the NCs enable self-healing against radiation damage and trap any insoluble helium produced during transmutation reactions, thereby suppressing void swelling

and loss of creep rupture strength [3,7]. It is also widely known that NCs are highly stable upon high neutron irradiation doses [1].

ODS steels are fabricated via ball milling 14YWT alloys, i.e., Fe–9 to 14 Cr–1 to 3 W–0.1 to 0.4 Ti (wt.%) with Y_2O_3 oxide powders [1-6]. The Y_2O_3 powders decompose into yttrium (Y) and oxygen (O) atoms and are dissolved into the ferritic 14YWT steel's matrix during ball milling due to the generation of a large amount of energy [8]. Subsequently, the concentrations of dissolved Y and O in the mechanically alloyed powders is far greater than the concentrations introduced during typical near-equilibrium solidification processes [9]. During the hot consolidation stage after ball milling [10], the Y–Ti–O rich NCs, which are highly stable at high temperatures and high neutron doses, form very rapidly. Hence, the choice of milling parameters, especially milling environment and consolidation temperature, influences the stability, structural, and chemical states of highly dispersed and extremely fine NCs because other impurities can be incorporated, and as a result, affecting the mechanical response of the materials [5,11,12]. For instance, near-stoichiometric NCs with a cubic pyrochlore structure of $Y_2Ti_2O_7$ have been observed in ODS steels fabricated at consolidation temperatures of ≥ 1000 °C [13]. On the contrary, non-stoichiometric NCs have been observed in ODS steels fabricated at consolidation temperatures of < 850 °C.

Despite such intensive studies on NCs, to date, no consensus has reached its structure. The transmission electron microscopy (TEM) results indicated that the NCs had a crystal structure of cubic pyrochlore $Y_2Ti_2O_7$ [3]. Wu et al. [10], who employed high-resolution TEM, proposed a size-dependent composition of NCs, i.e. NCs with a diameter of < 5 nm showed only a near-stoichiometric $Y_2Ti_2O_7$ structure. These efforts are in line with the studies of Ohnuma et al. [14] and Hoelzer et al. [15] who performed fast Fourier transform (FFT) analysis on coarse NCs in 14YWT steels and identified them to have a pyrochlore $Y_2Ti_2O_7$ structure. However, Brandes et al. [16] reported that in 14YWT steels the NCs with a diameter of 2–4 nm manifested a high

degree of disorder and lacked an identifiable crystal structure. Also, Hirata et al. [17,18] claimed that in the same alloy the NCs consisted of small defected crystalline oxides with a NaCl-type rock salt structure. It is noteworthy here that the foregoing observations on the crystal structure of NCs is only relevant to intergrain NCs in 14YWT steels, not to the NCs formed along grain boundaries (GBs).

Less experimental efforts have been expended on investigating the NCs formed along GBs (shortly, GB-NCs) and on revealing the GB segregation of alloying elements. The importance of GB-NCs and associated solute GB decoration originates from a fact that interfacial regions separating different grains in polycrystalline materials, while occupying only a small fraction of the total volume, largely control the material's properties, including mechanics and radiation resistance [19,20]. Furthermore, the impact of GBs on blocking lattice dislocations has become more important because of the Hall-Petch effect. Therefore, an accurate determination of the chemical composition of GB-NCs and of the GBs themselves is of great interest.

This study aims at revealing the influence of interstitial doping content and different extrusion temperatures on the GB structure-dependent solute segregation, GB-NCs, intergrain NCs, and mechanical properties of a series of Fe–14 wt.% Cr ODS alloys. The ferritic steels are fabricated by mechanical alloying at different extrusion temperatures. We subject the steel samples to multi-scale analytical characterization using TEM and atom probe tomography (APT). Indeed, APT has been rapidly gaining prominence over the past decade as a key tool for determining the chemical composition and crystallographic orientation information of GBs and nanofeatures of a range of material systems [21–23]. It also offers near-atomic spatial resolution and equal detection sensitivity for all alloying elements in ODS steels [16,24]. Moreover, for studying GBs relevant to complex site-specific sample preparation more accurately, transmission Kikuchi diffraction (TKD) is performed jointly with APT on the samples, with a focus on identifying the structure and chemical compositions of GBs and NCs or visually correlating them

with APT reconstructions of the same steel sample at the same GB position. Since TKD using an on-axis detector provides higher lateral resolution than electron backscatter diffraction (EBSD), a combined TKD and APT analysis allows for a deeper understanding of the structure-composition relations at GBs [25,26].

We expect that determining the precise solute occupancy in GBs will provide insight into the formation mechanisms of GB-NCs and into the underlying mechanism responsible for solute dissolution during ball milling, thereby shedding light on the hardening mechanisms of ODS steels.

2. Experimental

A pre-alloyed metal powder with a chemical composition of Fe-14Cr-3W-0.4Ti (wt%) prepared by gas atomization was supplied by Special Metals. The pre-alloyed powder was mixed with 0.3 wt.% Y_2O_3 powder with a crystallite size of 17–31 nm. Three 1 kg batches of the blended powder were ball milled for 40 h under static Ar atmosphere using a Zoz Simoloyer CM08 machine. After several cycles of vacuum operation and Ar gas purging, Ar gas was supplied to the chamber, and the chamber was sealed using valves. The three 1 kg batches of ball milled powder were blended together and filled in three steel cans (~0.75 kg of powder per can). These cans were degassed at 300 °C in vacuum and sealed. Pre-extrusion annealing at 850 °C for 1 h was performed on the three sealed cans. The cans were then extruded at three different temperatures, 850, 1000, and 1150 °C, using a rectangular die to form bars, which were referred to as SM85, SM100, and SM115, respectively. To further study the effects of high interstitial contents, such as C and O, on GB segregation, we synthesized a high C- and O-containing ODS steel powder by applying a higher O partial pressure in an Ar atmosphere during milling of higher C containing pre-alloyed powder. The ODS steel powder was extruded at 850 °C using

the same process. The produced high C- and O-containing ODS steel is referred to as SM85H. The chemical compositions of all hot-rolled samples are shown in Table 1. The host metallic elements were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES), C content was analyzed by combustive analysis, and O content was determined by inert gas fusion.

Tensile strength tests were performed at room temperature, 500 °C, and 700 °C using screw-driven machines equipped with a high temperature vacuum furnace at a nominal strain rate of 10^{-3} s^{-1} . The vacuum level in the furnace was maintained at about 10^{-4} Pa during the testing at elevated temperatures. Specimens were heated to the target temperature at a heating rate of 10 °C s^{-1} , and the temperature was maintained for 10 min before testing. A sub-size flat specimen with a gage section of $7.62 \times 1.52 \times 0.76 \text{ mm}^3$ was used for the tensile strength testing. All specimens were machined such that their length direction aligned with the extrusion direction. Engineering strain was measured from the stroke displacement.

Samples for TEM observation were fabricated by a dual-beam focused ion beam (FIB, Helios Nano-Lab) instrument to observe the microstructures of the specimens. A low-angle (4°) and low-energy (5 kV) Ar-ion milling step was used to remove the damage caused by the FIB. TEM and scanning TEM (STEM) observations of the extruded samples were performed using a JEOL 2010F microscope equipped with a Cs-aberration corrector, operating at an accelerated voltage of 200 kV.

Samples for TKD and APT analysis, taken from the GBs of the four ODS samples, were prepared by a combined method of focused ion beam (FIB) milling and TKD scans, as described in detail by Babinsky et al. [25]. This was accomplished by a dual-beam FIB instrument (FEI, Helios Nano-Lab 650i) equipped with a TKD system using an OPTIMUSTM TKD detector head (Bruker Nano GmbH, Quantax CrystAlign 400). The TKD scans were recorded at a voltage of 20 kV in analytical mode, a working distance of 10 mm, and a step size of 5 nm. The TKD data

were post-processed using the Quantax Esprit software. The GBs with a misorientation angle $\geq 15^\circ$ were defined as high-angle GBs, while a misorientation angle $< 15^\circ$ for low-angle GBs.

After TKD observation on APT tips, APT was performed with a local electrode AP (LEAP 4000X HR) microscope in the voltage-pulsing mode, operating at 200 kHz pulse repetition rate and 20% pulse fraction. Measurements were conducted at a base temperature of 50 K. The APT data were visualized using the IVAS software. To determine the concentration of the particles accurately, specific attention was paid to identifying the overlapping mass peaks of $\text{TiO}^{++}/\text{O}_2^+$ at 32 Da and $\text{TiO}^+/\text{Fe}_2\text{O}^{++}$ at 64 Da using the peak decomposition algorithm of IVAS. This algorithm considers all the obtained APT data sets to provide the compositional data. When chemical compositions of the oxide particles were analyzed, the total number of atoms for all oxide particles in a given analyzed volume was used for average composition calculation to improve counting statistics. We used nearest-neighbor identification to extract clusters, and the method given in [27,28] to determine a distance d_{max} by performing repeated d_{max} analysis on the original and a randomized (mass-charge redistributed over the data points) dataset. This procedure considered a wide range of d_{max} and N_{min} (the minimum cluster size) values to ensure that the false-positive rate was below the selected threshold value, which was set to <0.01 , allowing for the computation of the maximum false-positive rate. Thus, parameters could be selected as objectively as possible by minimizing the false-positive rate, as established by Williams et al. [29] Further, the information loss could be minimized by selecting a large N_{min} value. Consequently, for all APT data sets obtained for the SM115, SM100, and SM85 samples, $d_{\text{max}} = 0.8$ nm and $N_{\text{min}} = 5$ atoms were selected, while $d_{\text{max}} = 0.4$ nm and $N_{\text{min}} = 5$ atoms were selected for the SM85H sample.

3. Results

3.1. Grain size and particle diameter

High-angle annular dark-field (HAADF) TEM micrographs of the SM85, SM100, and SM115 samples and bright-field images of the SM85H sample are shown in Fig. 1. All the samples have fine equiaxed grain structures. When performing dark-field imaging, GBs show a bright contrast and NCs exhibit a dark contrast. The mean grain sizes of the SM85, SM100, and SM115 samples possessing low O and C contents are ranged similarly with 800~900 nm. On the other hand, fine grains (mean size of 200 nm) are seen in the SM85H samples including high-C and high-O contents, Fig. 1(d). Some GBs in the SM85H sample are not pristine and appear to be decorated with many dislocations and particles. The grain size measurement on the four different samples indicates that ferrite grain sizes are irrespective of the employed extrusion temperatures: instead, they depend on the steel compositions, especially interstitial doping content. The GB-NCs with ~5 nm, as indicated by yellow arrows, are also visible in the magnified HAADF-TEM images of all samples. Some large particles with > ~10 nm are identified as Cr_2O_3 or TiO_2 , which are not considered in this study. More interestingly, the particle size of GB-NCs and intergrain NCs considered does not seem to be much affected by both extrusion temperatures and interstitial doping contents: rather, their number density in the SM85H sample is higher than that of others samples. Details of particle density measurement will be addressed in the next subsection.

3.2 APT of GB concentration and nanofeatures

For analyzing the GB misorientation angles and their effects on the GB-NCs, a correlative analysis using TKD and APT was performed on the SM85 samples. Two GBs are imaged using TKD in Fig. 2(a) and cross-correlated with the solute decoration observed by APT in Fig. 2(b). The TKD pattern, inverse pole figure, and misorientation angle maps from one APT tip reveal that the two GBs have different misorientation angles. The upper GB (GB #1) corresponds to a low-angle GB with 13.8° , whilst a high-angle GB with 64.3° for the lower GB

(GB #2). We imaged a set of Y–Ti–O rich NCs highlighted in terms of isoconcentration enveloped in W reconstructions with a volume of $30 \times 30 \times 180 \text{ nm}^3$. In this study, 0.7 at.% Y (magenta), 2.0 at.% Ti (green), and 1.5 at.% O (blue) were chosen as the threshold values to display nanoparticles. In the APT reconstructions of Cr, W, Y, Ti and O, the TKD-scanned GBs are clearly visible with decoration of Cr (violet), W (black), and Ti (green), Fig. 2(b). More fractions of NCs per unit volume are populated with GB #2 than with GB #1. As shown in Fig. 2(c), the compositional profiles probed along 2-nm-diameter cylinders across GB #1 and GB #2 quantify the GB segregation. To avoid edge effects due to the small precipitate sizes [30], 2-nm-cylinders were chosen for all profiles. Figure 2(d) shows the resulting profiles of W, Ti and Cr, demonstrating their accumulation along both GBs. Three key features are revealed: (i) GB #2 (misorientation angle of 64.3°) has greater accumulation of W, Ti, and Cr than GB #1 (misorientation angle of 13.8°); (ii) GB segregation for other NC-forming elements, like Y and O, is negligible; and (iii) more GB-NCs are present at the GB #2, compared to those at the GB #1. These results demonstrate that GB structure determines both solute composition at GBs and number density of GB-NCs.

For the SM115 sample, one single GB is visible in the APT result (Supplementary Information Fig. S1). Also, despite no clear GB decoration for Y and O, more Cr, W, and Ti atoms are detected along the GBs than in the intergrain space. Considering the elemental compositions at the high-angle GB for the SM85 sample (Fig. 2), the APT-observed GB for the SM115 sample is likely to be a high-angle random GB. Although the APT data sets considered here were acquired from three or more APT tips of the samples, we attained only one successful APT result, including a single GB, for the SM115 sample. Thus, the APT technique had a major drawback: small sample volume.

For the high-C and high-O containing SM85H (grain size $\sim 200 \text{ nm}$) samples subjected to hot extrusion at 850°C , the high- and low-angle GBs are clearly rendered by a combined

analysis of EBSD or TKD with APT (Fig. 3). The EBSD grain distribution map in Fig. 3(a) reveals that the area fractions of the high- and low-angle GBs are 62% and 38%, respectively. These values for the SM85H sample are identical to those of the low-C and low-O containing SM85 samples subjected to the extrusion at the same temperature. In the corresponding misorientation map, GBs with a misorientation angle $\geq 15^\circ$ are defined as high-angle GBs (blue), and those with a misorientation angle $< 15^\circ$, as low-angle GBs (red). The high-angle GBs were further analyzed to clarify the relation between the GB structure and the chemical identities of individual alloying atoms. Figure 3(b) illustrates the TKD results of the APT tip taken from the high-angle GB (enclosed by the brown box in the misorientation map in Fig. 3(a)). In the TKD grain map, the orientation of the red-colored grain is close to the [001] orientation of ferrite, while that of the blue-colored grain, to the [111] orientation. Interestingly, the tip includes triple GBs (denoted as GB #1, GB #2, and GB #3) consisting of high- and low-angle GBs, as highlighted by the brown conical outline. TKD results reveal that both GB #1 and GB #3 are high-angle GBs, whereas GB #2 is a low-angle GB with $< 15^\circ$. Furthermore, GB #3 has the highest misorientation angle among the detected GBs. As evident from APT reconstructions in Fig. 3(c), most of Cr, C, W, and Ti atoms are detected at all the GBs, rather than at the intergrains. We imaged a set of Y-Ti-O rich NCs highlighted in terms of isoconcentration envelopes, which were superimposed to the W reconstruction with a volume of $40 \times 40 \times 150 \text{ nm}^3$. This APT result clearly presents the distribution of GB-NCs as well as intergrain NCs. The compositional profiles in Fig. 3(d), which are obtained along the 2 nm-diameter cylinders across the GBs, reveal the greatest accumulation of Cr, W, and C at the GB #3 among the detected GBs. More importantly, this trend is also visible for the NC-formers, like Y, Ti and O. The high concentration of the NC-formers at the GBs is believed to be responsible for the high number density of GB-NCs in the SM85H samples. At the GB #2 with the lowest misorientation angle, only Cr, Ti, and O are clearly distinguishable from the intergrains, whereas the GB accumulation

of W, C, and Y is negligible. Note that although molecular ions of CrO, YO, and TiO were often detected in the APT data sets of ODS steels [30], they are, in this study, detected only at the intergrains, not at the GBs (Supplementary Information Fig. S2).

3.3. Particle size and density distribution

Particle size measurements, determined from TEM images and APT data (Fig. 4), indicate that the Y–Ti–O rich NCs at the intergrains (i.e. intergrain NCs) for all samples have a mean diameter ranging between 2 ~ 6 nm. There is good consistency between the two analyses: for SM85 and SM100, mean diameters of the NCs are ~2.6 nm, while ~3.9 nm for SM115 sample and ~3.6 nm for SM85H sample. This result confirms that both different extrusion temperatures and interstitial doping content lead to a minor change in the particle diameter.

Besides the particle size, the resulting particle number density per unit volume is listed in Table 2. From the results of TEM and APT, we counted the number density of the GB-NCs separated from the intergrain NCs for all samples. For the low-C and low-O containing samples (i.e. SM85, SM100, and SM115), the number density of GB-NC is irrespective of the extrusion temperatures. Also, although the density ratio of GB-NCs to intergrain NCs in each sample increases with increasing extrusion temperature, its value remains below 12%. Interestingly, the density ratio of GB-NCs to intergrain NCs is much higher (~23.0%) for the SM85H (grain size of 200 nm) sample containing high C and O contents than for the SM85 (grain size of 827 nm) sample (~3.3%), although both samples are produced at the same extrusion temperature (850 °C). This finding is consistent with the result from Cunningham et al. [31] who reported that the bulk O content is quite important for determining the density of the NCs.

3.4. Compositional variation of nanoparticles

To determine the atomic ratios of Y, Ti, and O in all detected NCs with respect to the applied extrusion temperatures, we used the maximum separation method of APT. Figure 5 shows the average Y/Ti/O atomic ratios inside all probed NCs observed in all individual APT data sets. The sum of Y, Ti, and O equals one. The data points on the Gibbs ternary triangle for Y, Ti, and O, acquired from all of samples, represent the individual cluster compositions with the normalized O content along the left-hand edge, with the normalized Y content along the bottom, and with normalized Ti content along the right-hand edge. The outlined marker size by different colors presents the number of solute atoms of each NC. We note that the Fe and Cr atoms are detected inside the NCs, owing to the matrix atoms being focused; this leads to overlapping of their trajectories with those of the NC-forming atoms [30], so that the Cr and Fe atoms are extruded when calculating the Y/Ti/O atomic ratios. For the SM115, SM100, and SM85 samples, the resulting mean ratios of Y/Ti/O in the NCs ranged between 11/21/58 and 10/26/64 (Fig 5(a)–(c)). These values are not close to the stoichiometric ratio of $\text{Y}_2\text{Ti}_2\text{O}_7$. Also, the analyzed ratio of Y/Ti/O in the NCs for the SM85H sample is remarkably scattered (Fig. 5 (d)). Compared to the measured Y/Ti/O ratios of the NCs for samples containing low C and O contents (SM85, SM100, and SM115), three distinct features of the SM85H sample are revealed: (i) most NCs have a much higher O fraction with a lower Ti fraction and no significant change in the Y fraction; (ii) the deviation between Y/Ti/O ratios of the NCs and the stoichiometric ratio of $\text{Y}_2\text{Ti}_2\text{O}_7$ is large; and (iii) the compositional deviation of NCs becomes more prominent with decreasing NC size.

3.5. Tensile properties

Uniaxial tensile stress–tensile strain curves of the present steels, acquired at 25 °C, 500 °C, and 700 °C, are shown in Fig. 6. As expected, the tensile strength of all samples increases dramatically with decreasing tensile loading temperatures. This is the general mechanical response for other metallic alloys, because all impediments to dislocation motion for the given

materials are lowered by thermal activation. More importantly, all stress–strain curves, in this study, demonstrate the enormous effects of the interstitial doping contents rather than those of the applied extrusion temperature. For the SM115, SM100, and SM85 alloys including low interstitials, similar values of the tensile strengths at uniform elongations of 20–25 % are estimated with respect to the different extrusion temperatures, Fig. 6(a)–(c). These results are not very surprising, when considering microstructural similarities such as grain sizes and interstitial content for the three SM heats. On the contrary, the high-O and high-C containing SM85H materials show ultrahigh strength and poor ductility at all tensile-tested temperatures (Fig. 6(d)). Also, the strain hardening of the SM85H alloy is negligible, so that uniform elongation measurements do not exceed 1.0% when mechanically loaded at room temperature and 500 °C.

4. Discussion

4.1. Effects of interstitial doping on GB segregation and grain size

Despite applying the same extrusion temperature (850 °C) for the SM85 and SM85H samples, APT analysis revealed that high-angle GBs in the SM85H (Fig. 3) sample included more Cr, O, and Y atoms than those in the SM85 sample (Fig. 2). This compositional discrepancy between the two sets of APT observations is probably due to the difference in the C and O contents doped on the two samples in the as-milled powder state. Atomic-scale observations of GBs show that doping with interstitials influences the grain sizes of the considered steels as follows. The GBs are decorated with high concentrations of C and O. Because of strong attractive binding energy between Y–O or Cr–O, many O atoms readily attract Y and Cr atoms to the GBs (Fig. 3(d)). Through a great GB decoration of Y, Cr, and O atoms, the energy barrier for the nucleation and growth of Y–Ti–O-rich NCs along the GBs can be thermodynamically lowered. Such a conducive environment at the GBs promotes the

formation of GB-NCs (see Table 2), thereby retarding the capillary-driven grain coarsening and leading to grain size reduction.

Based on our results (Fig. 1 and Table 2), we focus on the grain growth mechanism. We found that the change in grain sizes of current ODS steels is directly linked to the formation of GB-NCs, but not intergrain NCs. This implies that GB-NCs, mostly precipitated along high-angle GBs during the pre-extrusion annealing or extrusion stages, are more efficient for preventing grain growth than intergrain NCs. Hence, we suggest that the suppression of capillary-driven grain coarsening via GB-NCs is more preferable for grain refinement than the GB pinning effect (i.e., a pre-existing particle hampers grain coarsening). Besides the suppression effect of GB-NCs, we suggest that the “solute drag effect” due to high segregation of C and O at the GBs are effective in preventing GB migration, thereby hindering grain growth in the SM85H sample.

Further, TEM and APT analyses of the SM85, SM100, and SM115 samples showed no carbide precipitation along the GBs. While this result is reasonable for samples doped with a low C content (0.03 wt%), carbide formation is expected at the GBs of the SM85H sample, which contains 0.11 wt% C. This hypothesis is confirmed by a previous study [32], where high C content (over 0.06 wt%) led to precipitation of $M_{23}C_6$ -type carbide at the GBs of ODS steels. In another study, Kim et al. [33] proposed that the segregation of C at the GBs could weaken the GB bonding because of carbide formation at the GBs. Hence, it is highly probable that the carbide precipitation at the GBs of the SM85H sample contributes to its enhanced yield strength and low fracture toughness.

4.2. Temperature effects on GB segregation and grain size

Through combined TKD or EBSD and APT analysis of the SM115, SM100, and SM85 samples, the amount of Cr, W, and Ti accumulated at the GBs of each sample is found to be

independent of the extrusion temperature; on the contrary, the higher the GB misorientation angle, the greater the accumulation of Cr, W, and Ti in the given sample. Also, considering that there are no significant changes among the tensile strengths and grain sizes of samples containing low C and O contents, the variation in the density ratio of GB-NCs to intergrain NCs with respect to extrusion temperature (Table 2) is a minor factor for improving a material's tensile strength and modifying its grain size.

4.3. Variation of NCs with respect to interstitial content and temperature

We found that manipulating the interstitial (C and O) doping content controls the Y/Ti/O ratios of nonstoichiometric NCs at a given extrusion temperature. This observation originates from two effects: First, the compositional deviation can be attributed to the APT artifacts resulting from either multiple evaporation events of weakly bonded elements such as Y and O [10,23,34,35], leading to a decreased Y content in the NCs [27], or local magnification effect due to the remarkable difference between the evaporation fields of the NCs and the ferritic matrix [21]. Second, according to present APT findings of particle size-dependent deviation and previous findings [15-17], it is plausible that very fine NCs would have inherently nonstoichiometric features with intrinsic defects. Indeed, the nonstoichiometric Y–Ti–O NCs were observed in a previous study by London et al. [36], who mentioned that ~60 at.% O was detected in ODS precipitates. Hence, it is highly improbable that such a nonstoichiometric feature would be attained by the APT artifacts alone; rather, it is much more likely that the nonstoichiometric chemistry of Y–Ti–O NCs is an actual characteristic.

When focusing more on the compositional variation in NCs in response to different extrusion temperatures, the Y/Ti/O ratios in all detected NCs of the samples containing low C and O contents (SM115, SM100, and SM85) are identical. The reason for this compositional similarity is the high thermal stability of NCs at a given temperature [37,38]. For further clarity,

Y/Ti ratios of the NCs do not significantly change with NC locations (intergrain or GBs). For example, the Y/Ti ratios of intergrain NCs and GB-NCs were 0.47 and 0.40 and 0.44 and 0.39 for SM115 and SM85, respectively. Generally, GB-NCs have a slightly higher Ti concentration than intergrain NCs. However, when clipping GB-NCs using the APT software, it is difficult to distinguish the GB-NC atoms from the GB atoms. Therefore, the Ti atoms detected in the GB-NCs may inevitably contain Ti atoms decorated on the GBs without NCs, thereby increasing the Ti concentration in the GB-NCs. Hence, a slightly lower Y/Ti ratio of GB-NCs might be partially due to the Ti segregation at the GBs.

4.4. Mechanical response

During tensile tests at elevated temperatures, low-interstitial SM heats (i.e. SM115, SM100, SM85 samples) exhibited the similar uniform elongations of 20–25%, while high-interstitial SM85H materials showed ultrahigh strength and poor ductility below a uniform elongation of 1.0% (Fig. 6). This mechanical response demonstrates that the high density of interstitials at GBs and GB-NCs or, if present, $M_{23}C_6$ -type carbides along the GBs could lead to a lowering of GB bonding strength for the SM85H sample [31]. Indeed, microcracks easily nucleate and propagate along the GBs of the SM85H sample (Supplementary Information Fig. S3). Hence, based on our result that doping with high C and O contents enables GB decoration of C, O, and Y, the effect of the formation of nonstoichiometric NCs is threefold: grain size refinement (resulting from GB-NCs), particle strengthening (resulting from intergrain NCs), and low tensile ductility (resulting from low GB bonding strength).

Several different kinds of obstacles, such as a high number density of NCs and large area of GBs, can hamper dislocation motion during plastic deformation of ODS steels [39]. The proposed underlying strengthening mechanisms of ODS steels are GB strengthening (or Hall-Petch strengthening), particle strengthening, dislocation forest hardening, and matrix hardening

[40]. Nevertheless, according to our findings, the dislocation-related hardening and the matrix hardening seem to be marginal. Previously, Kim et al. [40] suggested the root-mean-square (RMS) method for summation of a large range of strengthening components (Eq. 1):

$$\Delta\sigma_{\text{tot}} = \sqrt{(\Delta\sigma_{\text{dis}})^2 + (\Delta\sigma_{\text{p}} + \Delta\sigma_{\text{gb}} + \Delta\sigma_{\text{m}})^2} \quad (1)$$

$$\Delta\sigma_{\text{p}} = 0.8M\alpha(r)Gb/\lambda, \quad (2)$$

where $\Delta\sigma_{\text{tot}}$ is the total yield strength, $\Delta\sigma_{\text{dis}}$ is the dislocation forest hardening, $\Delta\sigma_{\text{p}}$ is the particle strengthening via highly dispersed NCs, $\Delta\sigma_{\text{gb}}$ is the GB strengthening, $\Delta\sigma_{\text{m}}$ is the matrix hardening, M is the Taylor factor of 3.0, G is the shear modulus, $\alpha(r)$ is a barrier strength coefficient representing the strength of defect clusters as obstacles to dislocation motion, b is the Burgers vector of 0.25 nm, and λ is the mean planar center to the distance between NCs. Here, Eq. 2 is based on the dispersed barrier hardening model [41] which is established on the geometrical relations between dislocations and obstacles. In principle, $\alpha(r)$ is determined by the angle between adjacent dislocation segments at the point where the dislocation breaks free of the obstacle. If the critical angle is ϕ , $\alpha(r)$ is a function of $\cos(\phi/2)$. Alinger [42] found that $\alpha(r)$ increases approximately linearly with $\log(r/2b)$, by fitting the coefficient to the experimental dataset of several ODS steels, and proposed the function of $\alpha(r)$ as follows:

$$\alpha(r) = -0.017 + 0.374\log(r/2b), \quad (3)$$

where r is the mean planar radius of the cross-section of a particle. $\Delta\sigma_{\text{dis}}$ is expressed as $McGb\sqrt{\rho}$, where c is a material-dependent constant reported as 0.38 for polycrystalline iron, and ρ is the dislocation density. Bentley et al. examined the dislocation density of a 14YWT

specimen after tensile tests at room temperature and 700 °C. The room-temperature specimen has a dislocation density of $7 \times 10^{14} \text{ m/m}^3$, while the 700 °C specimen presented a value of $2 \times 10^{14} \text{ m/m}^3$. The term $\Delta\sigma_m$ includes both solid solution hardening and intrinsic lattice resistance to slip. Kim et al. [40] experimentally derived the data set of $\Delta\sigma_m$ as a function of temperature from Fe–14Cr–3W–0.4Ti (wt%) bulk samples containing no NCs inside. From this, a $\Delta\sigma_m$ of 255 MPa was obtained at room temperature. $\Delta\sigma_{gb}$ can be best expressed by the Hall–Petch relationship, $\Delta\sigma_{gb} = k_{hp} \times d^{-1/2}$. The Hall–Petch parameter k_{hp} was also derived as a function of $d^{-1/2}$ [40]. In their work, excellent agreement between experiment and calculation was observed, because the RMS method is preferred for alloy systems with a large range of strengths and high densities of different obstacles.

In the present work, the $\Delta\sigma_{tot}$ values of SM85 and SM85H were calculated and compared using an approach suggested by Kim et al. [40]. The values obtained from the experiments (TEM and APT) in this study were employed for evaluating the microstructural factors. It is assumed that only intergrain NCs contribute to particle strengthening. The values of $\Delta\sigma_{dis}$, k_{hp} , and $\Delta\sigma_m$ were adopted directly from Ref. [40], because of the microstructural similarity in the grain matrix and dislocation density between the studied samples. Table 3 is a summary of $\Delta\sigma_{dis}$, $\Delta\sigma_p$, $\Delta\sigma_{gb}$, and $\Delta\sigma_m$ values of SM85 and SM85H. The calculated $\Delta\sigma_{tot(cal.)}$ values are well matched with experimentally obtained ones, $\Delta\sigma_{tot(exp.)}$, at room temperature and 500 °C. In the SM85H sample, the $\Delta\sigma_{gb}/\Delta\sigma_{tot(exp.)}$ ratio is around 50%, whereas that of SM85 is around 40%. This indicates that a fine grain size of GB-NC constituents is very beneficial for the overall strengthening of ODS steel. However, the $\Delta\sigma_{tot(cal.)}$ value at 700 °C is considerably higher than the experimental value. This is because thermally activated mechanisms start to operate actively at this temperature. In practice, the temperature-dependent factor in Eq. (2) and (3) is only the shear modulus, which is not very sensitive to temperature change. Therefore, based on the Eq.

(2), the calculated contribution of NC strengthening to the total strengthening is somewhat exaggerated, resulting in a higher value of $\Delta\sigma_{\text{tot(cal.)}}$ compared to $\Delta\sigma_{\text{tot(exp.)}}$.

4.5. Coarse intergrain particles with core-shell structures

Representative APT reconstruction of the ferritic grain interior of the SM85H sample shows that the coarse intergrain NCs (with a size > 4 nm) have a core-shell structure with Y-rich (magenta) cores and Ti–O-rich (blue) shells (Fig. 7). A magnified view of the NCs marked by the purple box in Fig. 7(a) with respect to their different projections and corresponding compositional profiles for Y, Ti, and O across the interface between the matrix and the NCs are shown in Figs. 7(b) and 7(c) [24], respectively. The majority of the APT reconstructions show a wider lateral extent for O isoconcentration than for the metal ions (Fig. 7(b)). Further, the probed profiles intercepting the particles and oriented parallel to the analysis direction reveal that the analyzed Ti–O-rich shells of the intergrain NCs extend generally toward the analysis direction compared to the analysis of Y-rich core. These asymmetric reconstructions in the analysis direction are attributed to the APT artifacts, i.e., trajectory aberrations. The contribution of such artifacts to the reconstruction of core-shell particles has been previously studied [30], so we will not repeat the information here. Based on the results of our study and those reported previously [30], the length scale of the nanoparticles for the coarse NCs possibly exceeds that of the trajectory aberrations. Therefore, APT observations of the coarse NCs (especially, intergrain NCs) having a Y-rich core and Ti–O-rich shell are sufficiently pronounced to represent real effects, i.e., they are not APT reconstruction artifacts.

4.6. Al effect on coarsening of intergrain NCs with core-shell structures

Besides the SM85H sample, we found the presence of coarse intergrain NCs (size > 4 nm) comprising core-shell structures with Y-rich cores and Ti–O-rich shells for samples

containing low C and O contents. The magnified view of the APT results for the coarse NCs with core-shell structures, embedded in the SM115, SM100, and SM85 samples, is provided in Fig. 8. Two distinct features are observed: (i) significant Al (orange) incorporation in the coarse NCs of the different alloys, but no Al incorporation in the fine NCs (size < 4 nm) and (ii) more Al atoms in the Y-rich cores than in the Ti–O-rich shells. These atomic-scale observations suggest that Al, which is mostly present in the core regions of the coarse particles, leads to different initial precipitation stages for the fine (<4 nm) and coarse (>4 nm) particles, forming small NCs with a single structure and large NCs with core-shell structures of Ti–O@Y–Al, respectively.

Since Al is known to be a strong oxide-forming element, its presence significantly influences the coarsening of particles that exist in the ferritic grains. The reason why only coarse intergrain NCs have core-shell structures of Ti–O@Y–Al has been provided previously by Sakasegawa et al. [34,43,44], who reported that non-negligible Al content was detected in all $Y_2Ti_2O_7$ particles. Similarly, other Al-containing NCs have been observed in ferritic ODS steels including both Al and Ti, where Y–Al complex oxides are preferentially formed over Y–Ti complex oxides [45,46]. Hence, it is plausible that the Al-containing Y–Al complex oxides formed in the early precipitation stages can rapidly become coarse at high temperatures and that Al weakens the thermal stability of NCs, thereby inducing core-shell structures with Ti–O@Y–Al in the later precipitation stages due to the reduction in the interface energy between the nonstoichiometric core-shell NCs and the surrounding ferrite.

Among the several structures of Y–Al complex oxides reported, it is plausible from a thermodynamic point of view that intergrain NCs with Ti–O@Y–Al, as observed by APT, would have a $Y_4Al_2O_9$ -type structure due to both low formation enthalpy and low Al/Y ratio once they adopt a crystalline structure. The formation enthalpies of various oxide particles that may be produced during mechanical alloying are listed in Table 4. Most Al-containing oxides

had a higher formation enthalpy than the Y–Ti–O type oxides, except for $\text{Y}_4\text{Al}_2\text{O}_9$. In addition, the Al:(Y+O) ratio of $\text{Y}_4\text{Al}_2\text{O}_9$ was the lowest (0.15) among all Al-containing oxides. Since the Al concentration in the alloy composition was very low, it is likely that $\text{Y}_4\text{Al}_2\text{O}_9$ with the least Al content is most easily formed. Yet, determining the exact crystal structure of the Y–Al oxides, which can be formed at the very early stage of NC formation, is still unclear.

From assessments based on kinetics, we also propose the formation mechanism of the intergrain NCs comprising Ti–O@Y–Al. Figure 9 shows a schematic illustration of the Ti–O@Y–Al formation. In the incipient stage (stage I) of pre-extrusion treatment, the nucleation of NCs can be initiated by solute clustering, specifically O clustering with Ti, Y, Al, and V_a (vacancy) [4]. Laurent-Brocq et al. [47] reported that pre-annealing at 800 °C enhances NC nucleation during the first few minutes. However, the coarsening rate drops notably after a few minutes because a fast vacancy-based diffusion process lowers the activation energy by the annihilation of milling-generated vacancies. This hypothesis strongly suggests that the coarsening of NCs is mainly affected by the annihilation rate of milling-generated vacancies. Moreover, Fu et al. [48] proposed that the strong binding energy between O and V_a results in the formation of an O– V_a pair. The mobility of the O– V_a pair is very low because the O and vacancy must move together [4]. Instead, the Ti, Y, and Al solute atoms will diffuse to the O– V_a pairs to form NCs because these atoms have very high affinity for O. For the substitutional elements, the calculated diffusion of Al in the bcc phase at 1150 °C for 60 min is found to be much faster than that of other species. The diffusivity and diffusion length of the alloying elements are listed in Table 5.

Therefore, Al-enriched oxide can nucleate first, and then, the Y–Al complex oxide will grow as the NC core (stage II). Because of the higher interface energies, the Y–Al complex oxides grow faster than the Y–Ti–O oxides. The formation of the Y–Al oxides results in the trapping of Al at the oxides. Because the initial Al concentration of the matrix is extremely small

(below 0.04 at%), the trapping could lead to Al depletion in the adjacent matrix. Therefore, the growth of the Y–Al oxide core will stop soon after nucleation. Instead, the surrounding Ti atoms will diffuse more to the pre-existing Y–Al oxide and bind to the surface O (stage III). In this manner, Al partitioned Y–Ti complex oxide particles would nucleate and grow.

Assuming that the initial Y–Al–O core has a $Y_4Al_2O_9$ (YAM) structure, coherent strain can be deduced from the previous calculations [49]. From the specific orientation relationship between the YAM and the ferritic matrix, the coherent strain $\Delta\epsilon = \frac{(d_{004})_{Y_4Al_2O_9}}{d_{011}} - 1 = \sim 30\%$ was calculated using HRTEM analysis. Such a coherent strain is much larger than that from $Y_2Ti_2O_7$. Since the interface energy of Y–Al-terminated oxides is much higher than that of Y–Ti oxide, NCs having the Y–Al core can coarsen and grow faster by consuming the Y matrix due to the Gibbs-Thompson effect. Next, NCs having Y–Al rich cores surrounded by Ti–O rich shells can be formed based on the previous density-functional theory (DFT) clustering energy results reported by Jiang et al. [9], who stated that the solution energies for Ti were much lower than those for Y. These DFT calculations possibly rationalize the present APT observations of the core-shell NC structures with Y–Al cores and Ti–O rich shells (stage IV), because Ti or Ti-terminated oxides would afford more favorably bonded interfaces with the Fe matrix as compared to Y and YO [9].

Additionally, the GB structure and surrounding environment may influence the coarsening of GB-NCs as well as intergrain NCs. However, we found that the coarse particles (>4 nm) of the ODS samples were mostly observed inside the ferritic grains rather than at the GBs (see Figs. 2, 7, and 8). Therefore, the aforementioned calculations for the formation of coarse particles with core-shell structures are entirely relevant to intergrain NCs. However, further studies are required to fully understand the coarsening of GB-NCs.

5. Conclusions

By combining advanced microscopy techniques, we unveiled how small variations in the level of interstitial elements in the ball-milled powder could result in considerable changes in the distribution, size, solute GB decoration, and composition of NCs as well as the mechanical properties of ODS steels subjected to different hot-extrusion temperatures. The general conclusions drawn in the present study are summarized below:

1. High C and O contents at the high-angle GBs of the SM85H sample attract higher concentrations of Y and O than that attracted at the GBs of the SM85 sample. This effect promotes GB-NC formation, leading to a much higher density ratio of NCs to intergrain NCs for the SM85H sample. Hence, doping with high C and O contents enables decoration of GBs with C, O and Y, and the effect of this doping is threefold: particle strengthening, grain size reduction, and low tensile ductility.
2. The Y/Ti/O ratios of the nonstoichiometric NCs are dependent on the interstitial doping content, but are independent of extrusion temperature due to the high thermal stability of NCs at high temperatures. More interestingly, although NC-forming elements decorate the GBs, the difference in the Y/Ti ratio between the GB-NCs and the intergrain NCs is not significant.
3. No distinct changes in mechanical properties, solute GB decoration, and grain size were observed in the low-C and low-O containing SM115, SM100, and SM85 samples. On the contrary, the SM85H sample containing a high interstitial content shows enhanced tensile strength and lower elongation when mechanically loaded at 25 °C and high temperatures. This mechanical response is the consequence of highly segregated interstitials at GBs and highly dispersed GB-NCs or possible carbide precipitation along the GBs.

4. The atomic-scale observations suggest that the presence of Al at the core regions of coarse particles leads to different initial precipitation stages of fine (<4 nm) and coarse (>4 nm) particles, forming small NCs with a single structure and large NCs with core-shell structures of Ti–O@Y–Al, respectively. Based on formation enthalpy calculations and kinetics, the Y–Al complex oxide in the incipient stage of coarse intergrain NCs would energetically cause particle coarsening, where Al weakens the thermal stability of the NCs and makes them core-shell structure.

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Appendix A. Supplementary data

Supplementary data related to this article were uploaded separately.

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In the APT reconstructions, 0.7 at.% Y (magenta), 2.0 at.% Ti (green), and 1.5 at.% O (blue) were chosen as the threshold values to display nanoparticles (violet, Cr; green, Ti; black, W). In the reconstructions, Cr atoms were displayed only 20%. The concentration profiles across the GBs were obtained from the 2-nm-diameter cylinders chosen for each GB.

Figure 3. Combined analysis of (a) EBSD maps obtained from the SM85H samples, (b) TKD results of the APT tip acquired from the prior-EBSD scanned GB, (c) the corresponding APT reconstruction of Cr, C, and W, and (d) the compositional profiles of alloying elements. In the IPF map of Fig. 3(b), the marked brown concave line indicates APT analysis area. The 3D morphology of the C atoms was tilted along the arrow for better APT visualization of the amount of C segregated at the different GBs with two different projections. Using isoconcentration envelopes of 0.7 at.% Y (magnet), 2.0 at.% Ti (green), or 1.5 at.% O (blue), the nanoparticles were superimposed to the W reconstruction. All the compositional profiles across the three GBs were obtained from 2 nm-diameter cylinders.

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Figure 9. Schematic explaining the mechanism underlying the formation of coarse (over 4 nm) NCs with core-shell structures, i.e. Y-Al rich cores and Ti-O-rich shells. Red, O-V_a pair; Orange, Al; Green, Ti; Magnet, Y.

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Figure S1. (a) APT reconstructions of Cr and W for SM115 sample including isoconcentration envelopes of 0.7 at.% Y (magnet), 2.0 at.% Ti (green), or 1.5 at.% O (blue). The corresponding concentration profiles of (b) C, W, O, Ti, and Y and (c) Cr across the interfaces between matrix and GB. All the concentration profiles across the GB were obtained from 2-nm-diameter cylinders.

Figure S2. Representative atom maps of CrO (gold), YO (red), and TiO (cyan), taken from the matrix of the SM115 sample.

Figure S3. A side-surface photo of the SM85H sample after tensile testing at 700°C. Arrows indicate intergranular cracks.

Table 1. Results of chemical analysis of ODS steels, determined from ICP or inert gas fusion.

	Composition (wt.%)							
	Fe	Cr	W	Ti	Y	Al	O	C
SM85								
SM100	Bal.	14.33	2.17	0.27	0.09	0.04	0.10	0.03
SM115								
SM85H	Bal.	14.20	1.90	0.24	0.12	0.05	0.22	0.11

Table 2. Average number density of NCs per unit volume, formed at the GBs or inside the ferritic grains for the SM85, SM100, SM115, and SM85H.

Samples	GB-NCs (per m ²)	intergrain NCs (per m ²)	Ratio of GB-NCs to intergrain NCs (%)
SM85	2.2×10^{14}	6.6×10^{15}	3.3
SM100	1.6×10^{14}	2.4×10^{15}	6.7
SM115	2.4×10^{14}	2.0×10^{15}	12.0
SM85H	2.6×10^{15}	1.1×10^{16}	23.0

Table 3. Calculated $\Delta\sigma_{\text{dis}}$, $\Delta\sigma_{\text{p}}$, $\Delta\sigma_{\text{gb}}$, $\Delta\sigma_{\text{m}}$, and $\Delta\sigma_{\text{tot}}$ (calculated) values (in MPa) for SM85 and SM85H. $\Delta\sigma_{\text{tot}}$ (calculated) was compared with $\Delta\sigma_{\text{tot}}$ (experiment).

Temperature (°C)	SM85						SM85H					
	$\Delta\sigma_{\text{dis}}$	$\Delta\sigma_{\text{p}}$	$\Delta\sigma_{\text{gb}}$	$\Delta\sigma_{\text{m}}$	$\Delta\sigma_{\text{tot}}$ (cal)	$\Delta\sigma_{\text{tot}}$ (exp)	$\Delta\sigma_{\text{dis}}$	$\Delta\sigma_{\text{p}}$	$\Delta\sigma_{\text{gb}}$	$\Delta\sigma_{\text{m}}$	$\Delta\sigma_{\text{tot}}$ (cal)	$\Delta\sigma_{\text{tot}}$ (exp)
25	603	180	367	255	1003	1078	603	499	756	255	1626	1645
500	465	139	358	136	785	741	465	385	738	136	1342	1241
700	404	120	138	71	521	301	404	334	284	71	798	578

Table 4. List of oxides with their formation enthalpies, calculated by the DFT-based calculator provided by Materials Project [50].

Oxide	Formation enthalpies (eV/atom)	Crystal structure
YAlO ₃	-3.695	orthorhombic
Y ₄ Al ₂ O ₉	-3.821	monoclinic
Y ₃ Al ₅ O ₁₂	-3.697	cubic
Y ₂ TiO ₅	-3.876	orthorhombic
Y ₂ Ti ₂ O ₇	-3.769	cubic
TiAl ₂ O ₃	-3.458	orthorhombic

Table 5. Diffusion coefficient and diffusion length of constituents in the bcc phase at 1150 °C for 60 min.

Element	Diffusion coefficient (m ² s ⁻¹)	Diffusion length (μm)
Fe	1.7×10^{-13} [51]	50
Y	2.9×10^{-17} [27,51]	0.79
Ti	3.7×10^{-13} [27,51]	98
O	1.5×10^{-10} [27,52]	1805
Al	1.7×10^{-12} [53]	206

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Figure 3. Continued

(d)

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