Experimental validation of density functional theory calculations on the Zr/Al oxide nanocluster formation in bcc Fe

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Abstract

Ab initio simulations carried out in different atomic cluster configurations in bcc Fe matrix containing Zr and Al suggest energetic favorability of Y-Zr-O phase nucleation, preferably with trigonal Y₄Zr₃O₁₂ structure. Subsequently, the HRTEM investigation of the as-prepared Fe - 14 Cr-0.3 Y₂O₃ - 0.6 Zr - 4Al oxide dispersion strengthened (ODS) alloy shows 78% of precipitates with Y₄Zr₃O₁₂ structure, thereby confirming the predictive power of ab initio simulations on the secondary formation in multi-component alloys.
With significant improvement in high temperature creep resistance and radiation damage resistance by the virtue of thermally stable, homogeneous distribution of nano-sized oxide precipitates in the matrix, the oxide dispersion strengthened (ODS) ferrite/martensite alloys have gained considerable attention as a major candidate material for future fission and fusion reactor applications. The morphology, spacial density, chemistry and interface structure of the dispersed precipitates of varying compositions in alloys synthesized by extended hours of ball milling and high temperature consolidation (HIP or hot extrusion) have been explored in depth using atom probe tomography (APT), transmission electron microscopy (TEM) and small angle neutron scattering (SANS) spectroscopy. Density functional theory based calculations of formation energies and binding energies of solute clusters in a matrix have been suggested as a method to predict the possibility of nanocluster formation, especially Y-Ti-O, Y-Al-O and Y-Zr-O, in ODS steels by various authors [1–4]. However, the extendability of these 0K, equilibrium calculations to explain the non-equilibrium ball milling process and hot consolidation is always debatable and hence experimental validation of such predictions are essential. In the present study, the ab initio simulations are used to forecast the structure and chemistry of the dispersoids in alloy containing Zr and Al [5, 6]. Further using HRTEM investigations in as-prepared ferritic ODS alloy containing Zr and Al, the suitability of ab initio simulations as a predictive tool to understand the nucleation of secondary phases in multi-component alloys is discussed.

The Density Functional Theory (DFT) simulations in this study are carried out using the VASP package with PAW pseudopotentials and PBE-GGA exchange-correlation functional [7–9]. The details of calculations along with equations to find formation energies and binding energies of atomic clusters are reported elsewhere [5]. As the first step, the minimum formation energies of individual solute atoms, Zr, Y, Al and O in the bcc Fe matrix are found to be +0.26 eV, +1.82 eV, -0.74 eV, +1.33 eV respectively, with Zr, Al and Y in the substitutional site and O occupying the octahedral interstitial site. The formation energy trend implies that Al has a higher solubility than other elements studied, which means its interaction with a vacancy (□) in the matrix will be minimum. Further calculations showed that Y-□ binding is the strongest (-1.20 eV) followed by Zr-□ binding (-0.73) and Al-□ binding (-0.30). In short, the larger the atom, the more it relaxes towards a vacancy. Likewise, the solute-oxygen binding energy is in accordance with the formation energy trend: Y-O binding energy is -0.87 eV, Zr-O binding is -0.74 eV and Al-O binding energy is -0.22 eV. The increased binding energy values of Zr with O and vacancy, compared to Al, reflects in □-Al-O and □-Zr-O cluster formation as increased □-Zr-O cluster binding energy (2.55 eV) than the □-Al-O binding energy (2.01 eV). As we increase the number of atoms in the cluster, the number of probable structural configurations also increase [5]. After invoking those configurations, Y-Zr-O-□ is found to have a larger binding energy (4.16 eV) than Y-Al-O-□ configuration (3.03 eV).

The results of ab initio simulations are summarized in Figure 1 (a), and it is evident that in all the stages of formation of Y-Zr-O-□ and Y-Al-O-□ clusters, Zr containing clusters have higher binding energy compared to Al containing clusters, which imply that when both Zr and Al are present in a ferrite matrix with yttrium and oxygen, the formation of Y-Zr-O-vacancy clusters are energetically favored as compared to that of Y-Al-O-vacancy clusters.

2
Further, from various reports, it is obvious that the precipitate phases in ODS steels with Ti are the most stable Y-Ti-O oxides in \( \text{Y}_2\text{O}_3-\text{TiO}_2 \) system: \( \text{Y}_2\text{Ti}_2\text{O}_7 \) and \( \text{YTiO}_5 \). Therefore, being found the Y-Zr-O phase is probable than Y-Al-O phase in bcc Fe, finding the most probable oxides in the \( \text{Y}_2\text{O}_3-\text{ZrO}_2 \) system will provide an insight into the possible precipitate structure. The fluorite related structures, pyrochlore, \( \delta \)-phase and disordered fluorite are considered \[6\], disordered fluorite being modelled using a previously reported special quasi-random structure (SQS) \[10\]. The formation energy trend (shown in Figure 1(b)) indicate the formation energy/atom of \( \text{Y}_4\text{Zr}_3\text{O}_{12} \) (\( \delta \)-phase) is lower than other structures. Therefore, Y-Zr-O precipitates in Zr and Al containing ODS steels are likely to possess \( \text{Y}_4\text{Zr}_3\text{O}_{12} \), \( \delta \)-phase structure.

As a note, the role of vacancies in the precipitation mechanism is often debatable. One argument is that the vacancies produced during high energy milling plays a crucial role in bringing the solute atoms together during precipitation \[1, 3\]. The contradicting argument says that the binding with O itself is enough to bypass the repulsion between solute elements to form complex oxide precipitate \[4, 11\]. Since the alloys made of ball milling is found to be containing high dislocation densities and excess vacancies, present authors have chosen the atomic clusters with vacancies. However, the formation energy trend remains the same with or without vacancies.

![Figure 1: Ab initio simulation results of atomic cluster formation in bcc Fe in the presence of Zr and Al (a) The solute-O, solute-Vac, solute-O-vac and Y-solute-O-vac binding energies in bcc Fe, solute being Zr and Al. (b) The trend of formation energy (eV)/Atom of different compound in Y-Zr-O system. \( \text{Y}_2\text{Zr}_2\text{O}_7 \) can have two variants: 1-with Zr at origin and 2-with Y at origin.](image)

Now, to synthesize Fe-14Cr-0.6Zr-0.3\( \text{Y}_2\text{O}_3 \)-4Al alloy (named Al-ODS), ultra high pure (99.9% pure) metallic powders along with bcc \( \text{Y}_2\text{O}_3 \) powder is milled in a high energy horizontal ball mill (Simoloyer CM08 mill) for 6h under argon atmosphere using stainless steel vial and hardened steel balls (diameter=5mm) with a ball to powder ratio of 10:1. Thereafter, the milled powder is filled in mild steel cans, degassed at 450 °C, forged at 1050 °C and subsequently hot extruded at 1150 °C to get rods of diameter 16 mm, which are further homogenized at 900 °C for 1h and then water quenched. The carbon extraction replica specimens for TEM are made.
by coating the etched surface of the radial disc sliced from the road with a thin carbon film and then separating the film by further etching. This method ensures maximum spatial frequencies from the precipitate without ferromagnetic interference from the matrix. The micrographs obtained using LIBRA 200FE (Carl Zeiss) HRTEM are thoroughly analyzed using software Digital Micrograph [12], ProcessDiffraction [13–15] and JEMS [16].

The bright field and dark field micrographs acquired from the replica (Figure 2) shows nanoparticles of diameter range 2 nm to 43 nm with a mean diameter of 8 nm. The polycrystalline rings in the SAED pattern (Figure 2(c)) are in exact agreement with trigonal Y$_4$Zr$_3$O$_{12}$ with lattice parameters a=9.738 and c=9.115 (ICDD: 01-077-0743, [17]), which indicates that Y$_4$Zr$_3$O$_{12}$ is indeed the predominant precipitate phase.

![Figure 2](image-url)

**Figure 2:** (a) Bright Field image with particle size distribution and (b) Dark Field image of oxide particles in the carbon extraction replica of Al-ODS. (c) The SAED pattern of the extraction replica, which can be indexed for trigonal Y$_4$Zr$_3$O$_{12}$ (ICDD: 01-077-0743)

The SAED analysis was followed by a detailed HRTEM investigation to determine the crystal structure of the precipitates, by comparing the power spectra with simulated diffraction patterns of several possible oxide phases and intermetallics containing Fe, Y, Al, Zr and Cr. Due to the low symmetry of trigonal structure, the same diffraction pattern can be indexed for more than one directions, and multislice simulations are essential to determine the accurate zone axis. Nearly 74% of the precipitates in the replica possess phase contrast of Figure 3(a) and power spectrum similar to Figure 3(b), which can be indexed for <120> or <210> directions of Y$_4$Zr$_3$O$_{12}$ shown in Figure 3(d). Earlier multislice simulations indicated that the <120>$_\delta$ produces ‘spot-like’ contrast in HRTEM images and <210>$_\delta$ is characterized by a ‘line like’ contrast [18]. The contrast observed in the current study is exactly similar to the contrast of <120>$_\delta$, as superimposed in the Bragg filtered image Figure 3(d).

The <120> is one of the closely packed direction in Y$_4$Zr$_3$O$_{12}$. According to the well-known criteria for the formation of energetically feasible interfaces, the closepacked directions of matrix and precipitates should be aligned parallel to each other [19]. Earlier <120>$_\delta$ || <111>$_\alpha$, <120>$_\delta$ || <100>$_\alpha$ and <120>$_\delta$ || <110>$_\alpha$ were found to be the directional combinations for the most probable ORs of Y$_4$Zr$_3$O$_{12}$ in bcc Fe. The abundance of <120>$_\delta$ in the replica
specimens also indicate a possible predominant energetically preferred orientation relationship in the as-prepared alloy of the current study.

Though a majority of the precipitates are identified to be \( \text{Y}_4\text{Zr}_3\text{O}_{12} \), there are signatures of tetragonal, monoclinic, and cubic \( \text{ZrO}_2 \) precipitates as analyzed and shown in Figure 4 with corresponding power spectra, simulated diffraction patterns and noise filtered images with superposed simulated HR images. The precipitate phases found in Al-ODS are tabulated in the Table 3 from which it is evident that trigonal \( \text{Y}_4\text{Zr}_3\text{O}_{12} \) is predominant. A similar observation has been done by P. Dou et al. [20] in ODS co-added with Zr, Ti and Al finding \( \sim87.4\% \) of precipitates belonged to Y-Zr-O structures, 5.7\% were Y-Ti-O, 3.5\% were Y-Al-O structures and 3.4\% were monoclinic/tetragonal/cubic \( \text{ZrO}_2 \). In alloys with lower Zr content, the fraction of Y-Ti-O and Y-Al-O phases were much larger. Thus \( \sim0.6\% \) Zr seems to be optimum for getting the desired precipitate size in Al-containing ODS steels.

Zirconia (\( \text{ZrO}_2 \)) exists as different polymorphs, depending on the temperature, pressure, and size of the atomic cluster forming the crystal. In its bulk form, \( \text{ZrO}_2 \) exhibits a monoclinic structure at ambient conditions [21] and the transition from monoclinic to tetragonal structure occurs at 1170 °C, however, the transition temperature is a function of grain size. Tetragonal to cubic structural transformation occurs at 2450 °C to 2675 °C. It is well known that even though tetragonal and cubic polymorphs of \( \text{ZrO}_2 \) cannot be quenched to room temperature, the phases can be stabilized by the addition of large cations like lanthanides and yttrium. Here, in the Al-ODS matrix, with the heat treatment at 1050 °C, the presence of yttrium and the small size of the precipitates is playing a major role in stabilizing cubic and tetragonal \( \text{ZrO}_2 \) phases at room temperature along with the monoclinic phase.

As a summary, the ab initio simulations indicate the probability of Y-Zr-O nanoclusters, preferably \( \text{Y}_4\text{Zr}_3\text{O}_{12} \) in ferritic steel with Zr and Al addition. These predictions are further substantiated by synthesizing Fe-14 Cr-0.3 \( \text{Y}_2\text{O}_3 \)-0.6 Zr - 4Al alloy and characterizing the precipitates using HRTEM and image simulations. The as-prepared alloy contains monoclinic, tetragonal and cubic \( \text{ZrO}_2 \) precipitates along with \( \text{Y}_4\text{Zr}_3\text{O}_{12} \). However, the precipitates containing Al are completely absent, which is in exact agreement with the simulation results. This also affirms the significance of DFT based first principle simulations as a device to predict the precipitation in multi-component alloys.
**Figure 3:** (a) HRTEM micrograph of a \(\text{Y}_4\text{Zr}_3\text{O}_{12}\) precipitate with zone axis [1\(\bar{2}\)0]. (b) Power spectrum of (a) (c) Simulated diffraction pattern along [1\(\bar{2}\)0] (d) Bragg filtered image of (a), the superimposed rectangle shows multi slice simulation output with defocus \(\sim 67\) nm, thickness \(\sim 10\) nm, \(C_a, C_c=1.2\) nm

**Table 1:** Inter-planar distances (d) and angles (\(\alpha\)) of the \(\text{Y}_4\text{Zr}_3\text{O}_{12}\) nanoparticle in Figure 3

| d(Å),\(\alpha\)(°) | \(d_1\) | \(d_2\) | \(d_3\) | \(\alpha_{12}\) | \(\alpha_{13}\) | \(\alpha_{23}\) |
|-----------------|--------|--------|--------|----------------|----------------|----------------|
| Measured        | 3.0    | 2.95   | 1.80   | 70             | 35             | 35             |
| Planes          | (003)  | (21\(\bar{2}\)) | (214)  | -              | -              | -              |
| ICDD: 01-077-0743 | 3.0    | 3.03   | 1.85   | 70.7           | 35.55          | 35.1           |
Figure 4: HRTEM micrographs, power spectra, simulated diffraction pattern along zone axis and bragg filtered image with superimposed multislice simulation contrast of different precipitates in Al-ODS. (a-d) [201] zone axis of tetragonal ZrO$_2$ (e-h) [100] of cubic ZrO$_2$ (i-l) [111] of monoclinic ZrO$_2$. 
Table 2: Inter-planar distances \((d)\) and angles \((\alpha)\) of the ZrO\(_2\) nanoparticles of Figure 4. Values calculated from ICDD data is included for comparison.

| Zone axis | \(d(\text{Å}), \alpha(\degree)\) | \(d_1\) | \(d_2\) | \(d_3\) | \(\alpha_{12}\) | \(\alpha_{13}\) | \(\alpha_{23}\) |
|----------|----------------------------------|--------|--------|--------|----------|----------|----------|
| \([201]_T\) Measured | 1.85 | 2.10 | 1.81 | 30.3 | 61.2 | 30.3 |
| Planes | \((\bar{1}12)\) | \((\bar{1}02)\) | \((\bar{1}12)\) | - | - | - |
| ICDD 00-065-0729 | 1.82 | 2.10 | 1.81 | 31.6 | 60.59 | 29.6 |
| \([100]_C\) Measured | 1.76 | 2.49 | 1.76 | 45 | 90 | 45 |
| Planes | \((220)\) | \((200)\) | \((220)\) | - | - | - |
| ICDD 01-081-8080 | 1.74 | 2.46 | 1.74 | 45 | 90 | 45 |
| \([111]_M\) Measured | 3.73 | 2.19 | 3.61 | 32.4 | 29.9 | 61.7 |
| Planes | \((\bar{1}01)\) | \((211)\) | \((\bar{1}10)\) | - | - | - |
| ICDD 00-036-0420 | 3.98 | 2.21 | 3.63 | 32.40 | 30.3 | 62.4 |

Table 3: The orientations of precipitates in Al-ODS steel.

| S.No | Structure | Frequency of occurrences(%) |
|------|-----------|-----------------------------|
| 1    | \(Y_4\)Zr\(_3\)O\(_{12}\) | 78                          |
| 2    | ZrO\(_2\)-M | 2                           |
| 3    | ZrO\(_2\)-T | 18                          |
| 4    | ZrO\(_2\)-C | 2                           |

References

[1] C. L. Fu, M. Krčmar, G. S. Painter, and X.-Q. Chen, Physical Review Letters 99, 225502 (2007).

[2] Y. Jiang, J. R. Smith, and G. Odette, Physical Review B 79, 064103 (2009).

[3] D. Murali et al., Journal of Nuclear Materials 403, 113 (2010).

[4] A. Claisse and P. Olsson, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 303, 18 (2013).

[5] S. Mohan, G. Kaur, B. Panigrahi, C. David, and G. Amarendra, Journal of Alloys and Compounds 767, 122 (2018).

[6] S. Mohan, G. Kaur, C. David, B. Panigrahi, and G. Amarendra, Journal of Applied Physics 127, 235901 (2020).
[7] J. Hafner, Journal of Computational Chemistry 29, 2044 (2008).

[8] G. Kresse and J. Furthmüller, Computational Materials Science 6, 15 (1996).

[9] G. Kresse and D. Joubert, Physical Review B 59, 1758 (1999).

[10] C. Jiang, C. Stanek, K. Sickafus, and B. Uberuaga, Physical Review B 79, 104203 (2009).

[11] L. Barnard, G. Odette, I. Szlufarska, and D. Morgan, Acta Materialia 60, 935 (2012).

[12] B. Schaffer, Digital Micrograph, in Transmission Electron Microscopy, pages 167–196, Springer, 2016.

[13] J. L. Lábár, Microscopy and Microanalysis 14, 287 (2008).

[14] J. L. Lábár, Microscopy and Microanalysis 15, 20 (2009).

[15] J. L. Lábár, Ultramicroscopy 103, 237 (2005).

[16] P. Stadelmann, V4, EPFL, Lausanne, Switzerland (2012).

[17] V. Red’ko and L. Lopato, Inorganic Materials 27, 1609 (1991).

[18] S. Mohan, A. George, R. Vijay, C. David, and G. Amarendra, arXiv preprint arXiv:2105.02530 (2021).

[19] M.-X. Zhang and P. Kelly, Acta Materialia 53, 1073 (2005).

[20] P. Dou et al., Journal of Nuclear Materials 485, 189 (2017).

[21] C. Howard, R. Hill, and B. Reichert, Acta Crystallographica Section B: Structural Science 44, 116 (1988).