



Article First-Principles Calculations of Y-Si-O Nanoclusters and Effect of Si on Microstructure and Mechanical Properties of 12Cr ODS Steel in Vacuum Sintering System

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Abstract: High density of thermally stable Y-Si-O nanoparticles dispersed in the Fe matrix play a primary role in oxide dispersion strengthened (ODS) steel. In this study, the binding energies of solutes Y, O and Si with vacancies have been calculated in the framework of first-principles density functional theory. According to the calculations, any two solutes of Y, O and Si bound with each other strongly in the second nearest neighboring (NN) sites while not in 1NN. A vacancy (*v*) bounds strongly with Y and O in 1NN site. The binding sequence of solutes with *v* followed O-*v* \rightarrow Y-*v* \rightarrow Si-*v*, and the affinity of Y, Si and *v* with O followed O-Y \rightarrow O-*v* \rightarrow O-Si. The nucleation mechanism of Y-O-Si nanoclusters was determined, which gave the feasibility of adding Si to ODS steels. The core (consisting of Si and O)-shell (enriched Fe and Cr) structure of the microparticles was found in ODS steels containing Si, fabricated by mechanical alloying (MA) and vacuum sintering. Moreover the nanoparticles of monoclinic cubic Y₂O₃, Y₂SiO₅ and Y₂Si₂O₇ with sizes of 5~12 nm were observed in ODS steel. Si reduced the sintering temperature by maximizing densities and mechanical properties at a lower sintering temperature. The steel with 3 wt% Si was sintered at 1280 °C, exhibiting the best comprehensive mechanical properties. The tensile strength, hardness and relative density were 1025 MPa, 442.44 HV and 95.3%, respectively.

Keywords: ODS steel; density functional theory; core-shell structure; tensile strength

1. Introduction

Oxide dispersion strengthened (ODS) steel exhibits the advantages of high thermal conductivity, low thermal expansion coefficient, low radiation swelling rate and great resistance of high-temperature creep properties [1], so it is being planned to be used in the nuclear industry (Gen. IV concept and ITER concept) [2].

Ti (or Zr/Hf/Al)-Y-O enriched nanoclusters with a fine structural size (≤ 10 nm), high distribution density ($\geq 10^{23}$ m⁻³) and thermal stability are homogeneously dispersed in ODS steels [3–5]. These clusters are deemed to be the reason for the excellent high-temperature properties of ODS steels since it can effectively retard grain growth and dislocation movement [6–9]. Many scholars have found clusters of different composition. Y-Ti-O nanoclusters are the most common, including non-stoichiometric Y-Ti-O nanoparticles and Y-Ti-O oxides, such as Y₂Ti₂O₇ and Y₂TiO₅ [10–12]. Other fine nanoparticles, such as Y₂Hf₂O₇, Y₄Zr₃O₁₂ and non-stoichiometric Y-Al-O nanoparticles are also obtained by introducing new elements into the steel [4,5].

Si as an active element can effectively promote the sintering process by forming a eutectic liquid phase, and the addition of Si is conducive to reduce the sintering temperature of alloyed powders [13,14]. Song et al. found $Y_2Si_2O_7$ and Y_2SiO_5 nanoparticles (both with



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). monoclinic cubic crystal structure) in Si-containing 9Cr-ODS ferrite steel, and they confirmed that the addition of Si can improve the corrosion resistance according to the test of 1000 h exposure to liquid lead-bismuth eutectic [15]. Simultaneously, Wahida R. Ilaham et al. observed Cr_2TiO_4 and SiO_2 along with $Y_2Ti_2O_7$ particles in Si-containing ODS steel fabricated by mechanical alloying (MA) and spark plasma (SPS) sintering [16]. However, there is little theoretical support for Si addition in ODS steel. In order to comprehensively understand the structure and stability of nanoclusters in bcc Fe matrix, Murali et al. studied the effect of Ti and Zr on the stability of nanoclusters with the introduced vacancy through first-principles calculations [17,18], and they found that the binding energies of Y-O-vacancy clusters increase when Ti is replaced with Zr, which means higher stability of Y-Zr-O nanoclusters. Sruthi Mohan et al. compared the binding energies of different stages of Y-Zr-O-vacancy and Y-Al-O-vacancy nanoclusters in bcc Fe matrix and determined that Y-Zr-O clusters were more stable and preferred to nucleate than Y-Al-O clusters [19].

This research was divided into two parts. Primarily, a first-principles calculation was carried out. The binding energies of Y-Si-O nanoclusters with different structures were calculated to find optimal cluster configuration, which would provide theoretical support for the addition of Si in ODS steels. Then, Fe-12Cr-3W-0.3Y₂O₃-*x*Si ODS steels with four components, x = (0, 1, 2 and 3) were synthesized via MA and the vacuum sintering process to study the influence of different Si content on the microstructure and mechanical properties of 12Cr-ODS steels.

2. Calculation and Experiment Methods

2.1. Calculation Method

We have accomplished first-principles density functional theory (DFT) [20] calculations using Cambridge Sequential Total Energy Package (CASTEP) module in Materials Studio with plane-wave pseudopotential method. The electron–core interaction was described by the OTFG ultra-soft pseudopotential and the Perdew–Burke–Ernzerhof (PBE) version in the generalized gradient approximation (GGA) was used as the exchange correlation functional [21]; the electron configurations assumed for the atomic species in structure were: Fe $1s^22s^22p^43s^23p^43d^64s^2$, O $1s^22s^22p^4$, Y $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^15s^2$, Si $1s^22s^22p^63s^23p^2$. A plane-wave cutoff energy of 500 eV and a uniform $2 \times 2 \times 2$ k-point set were used for the $4 \times 4 \times 4$ supercell of bcc Fe containing 128 atoms, which could adequately achieve a reasonable total energy convergence of $<1 \times 10^{-5}$ eV/atom for the bcc-Fe supercell. All the calculations were spin polarized. Structural relaxations were implemented until all force components converged below 0.03 eV/Å.

The solute atoms Si, Y and O were dissolved in a $4 \times 4 \times 4$ supercell of bcc Fe matrix. A vacancy (v) was added into the supercell to calculate the binding energy of v-(O or Y or Si), O-(Y or Si) atom and non-stoichiometry Y-O-Si-v nanoclusters, respectively. Then, the optimal structure of nanocluster was determined.

Formation energy of one single solute atom (Y, O or Si) dissolved in 128-atom bcc-Fe supercell is:

$$E_{\text{form}}(X) = E(X) - n_{\text{Fe}}\mu_{\text{Fe}} - \mu_x \tag{1}$$

where E(X) is the energy of a 4 × 4 × 4 bcc Fe supercell with one single solute atom (Y, O or Si) dissolved at a substitutional or interstitial locations; n_{Fe} is the number of Fe atoms in the supercell; μ_i (i = Fe or X) is the chemical potential of Fe or solute atoms at its pure solid standard state. The chemical potentials of Si, Y were calculated relative to the equilibrium hcp phases. A positive formation energy represents the endothermic reaction and the negative one denotes exothermic reaction. Low positive formation energy of elements signifies its high solubility in Fe matrix and vice versa.

Binding energy of two defects is [17]:

$$E_{\rm b}(X_1, X_2) = E(X_1 + X_2) + E({\rm Fe}) - E(X_1) - E(X_2)$$
(2)

Binding energy of *N* defects is:

$$E_{\mathbf{b}}(X_1, X_2, \dots, X_n) = E(X_1 + X_2 + \dots, X_n) + (n-1)E(\mathbf{Fe}) - [E(X_1) + E(X_2) + \dots, E(X_n)]$$
(3)

where E(Fe) is the energy of perfect Fe supercell (consisting of 128 Fe atoms) without defect; $E(X_i)$ is the energy of Fe supercell with X_i defect; $E(X_1 + X_2)$ is the energy of Fe supercell with both X_1 and X_2 defects.

In both Equations (2) and (3), if the E_b is positive, it will indicate repellency between defects and if the E_b is negative, defects will attract. Lower value of E_b means stronger attraction ability and more stable bonding [18].

The differential charge density for a system AB is:

$$\Delta \rho = \rho_{\rm AB} - \rho_{\rm A} - \rho_{\rm B} \tag{4}$$

where ρ_{AB} is the total charge density of the Fe lattice embedded with one single solute atom after geometry optimization; ρ_A , ρ_B is that of individual systems. The value of charge density is within $-0.10 \sim +0.10$ electron/Bohr³.

2.2. Experiment Method

The iron powder had a purity of more than 99.9 wt pct, with a mean particle size of 5 μ m, while corresponding purities and granularities for Cr, W and Si and Y₂O₃ powders used were 99, 99.95, 99.00 and 99.5 wt pct, and 38 μ m, 7 μ m, 4 μ m and 60 nm, respectively.

Elemental powders of four different nominal components: Fe-12Cr-3W-0.3Y₂O₃-xSi (wt%), x = (0, 1, 2, 3) were evenly mixed and mechanically alloyed under atmosphere of argon in a high-energy planetary ball mill with components shown in Table 1.

Table 1. Four components of elemental powders.

Components (wt%)	Fe	Cr	W	Si	Y_2O_3
S0	Bal.	12	3	0	0.3
S1	Bal.	12	3	1	0.3
S2	Bal.	12	3	2	0.3
S3	Bal.	12	3	3	0.3

Alloy powders were put into stainless steel jars in descending order of density and the ball to powder ratio (BPR) was 20:1. MA was carried out at 300 rpm for 50 h in a XGB-4 planetary ball mill (Instruments Ltd., Nanjing, China). The time mode of ball milling was: forward rotation for 10 min, stop for 2 min, reverse rotation for 10 min and so on. In the first 48 h of milling, no process control agent was present, while stearic acid was added into the mechanical alloying process in the last 2 h of milling to improve the yield and formability of the powders. MA powders were compressed into the size of $45 \times 7.7 \times 4 \text{ mm}^3$ under the pressure of 600 MPa and the dwell time was 1 min. The sintering process was carried at a vacuum of 7×10^{-4} Pa in a vacuum furnace TL1600 (Boyuntong Instruments Ltd., Nanjing, China), and the sintering temperatures were 1280 °C and 1300 °C.

Microstructures were carried out by metallographic microscope (Leica Ltd., Brunswick, Germany), and the distribution of second phases were observed by electron probe micro analyzer (JEOL Inc., Tokyo, Japan) attached with INCA X-ACT scanning (EPMA + EDS). An electron microscope (JEOL Inc., Tokyo, Japan) attached with X-MAXN20 energy dispersive spectrometer (SEM + EDS) was used to observe the fracture morphology and analyze the precipitates at the fracture. Finally, field emission high-resolution transmission electron microscope (JEOL Inc., Tokyo, Japan) attached with EDAX Elite T energy spectrometer (HRTEM + EDS) was used to obtain the specific morphology, the high-resolution transmission image and the electron diffraction pattern of the nanocluster to calibrate the second phase. The testing methods of mechanical properties included electronic universal material tester Instron 5967 (Instron Inc., Boston, MA, USA) and Vickers hardness tester (WoWei technology Ltd., Beijing, China) to measure the tensile strength and hardness of ODS steels. The size of the tensile test piece is shown in Figure 1.



Figure 1. The size of the tensile test piece (unit: mm).

3. Results and Discussion

3.1. Calculation Results

3.1.1. Formation Energies of Solute Atoms

The formation energy of a vacancy in the Fe matrix was calculated to be +2.09 eV. The calculated formation energies of single Si, Y or O at substitution, octahedral interstice and tetrahedral interstice in a 128-atom bcc Fe supercell were tabulated in Table 2, which was consistent with published data in reference. It was quite clear that only the substitution of Si was zealously favored with lower formation energy (-1.23 eV) than other sites. Y(+1.93 eV) and O(+1.57) possessed the lowest formation energies in substitution and octahedral interstice, respectively, corresponding to its relatively high solubility than other sites, which means that Y prefers substitutional site and O prefers octahedral interstitial site.

Table 2. Formation energies (eV) of Si, Y and O in different sites (substitution, octahedral interstice and tetrahedral interstice).

Elements	Si	Ŷ	0	Vacancy (v)
Substitutional	-1.23	+1.93(+2.02 ^a , +1.82 ^c)	+2.46(+2.99 ^a , +3.10 ^b)	+2.09(+2.11 ^c)
Interstitial-Octa	+2.76	+5.34(+8.99 ^a , +4.42 ^c)	+1.57(+1.41 ^a , +1.46 ^b)	-
Interstitial-Tetra	+1.58	+8.18(+8.38 ^a , +7.55 ^c)	+3.51(+3.26 ^a , +3.28 ^b)	-

^a Reference [22]. ^b Reference [21]. ^c Reference [19].

3.1.2. Interaction between Solute Atoms and Vacancies

Based on the above results, O was set in octahedral interstitial site and Si and Y were set in substitutional site for the following calculation. Binding energies of Si, Y and O pairing with the first and second nearest neighboring (NN) v were calculated, and the specific distance between different interacting partners was shown in Table 3. Binding energy of O_(octahedral)-v, Si_(substitutional)-v and Y_(substitutional)-v pairs were tabulated in Table 4. It was clear that all the binding energies of the solutes with 1NN v were always stronger than that with 2NN v [19], indicating that the vacancy has stronger catching power to the nearest solute. Among the solutes pairing with 1NN v, the binding energy of Si-v (+0.42 eV) was the weakest, followed by Y-v (-1.39 eV), and the binding energy of O-v (-1.50 eV) was the strongest.

Defect Species	1NN (Å)	2NN (Å)
O- <i>v</i>	1.43	2.03
Y- <i>v</i>	2.48	2.87
Si-v	2.48	2.87
Y-O	1.43	2.03
Si-O	1.43	2.03
Si-Y	2.48	2.87

Table 3. Nearest neighbor (NN) distances between different interacting partners.

Table 4. The binding energies between the solutes (1NN and 2NN) and vacancies.

Defect Species	Binding Energy (eV)		
	1NN	2NN	
O-v	-1.50	-0.46	
Y- <i>v</i>	-1.39	+0.12	
Si-v	+0.42	+1.13	

The charge density difference plots of $O_{(octahedral)}$ with and without 1NN v in (110) slice are compared in Figure 2. It can be seen in Figure 2a that O is surrounded by four Fe atoms (two Fe atoms in 1NN site and the other in 2NN). A mass of charge exhibiting the tough axial confinement was evident with localization in the core region of the O. This was magnetism of the Fe lattice that caused the confinement of the charge density around O [23]. With the introduction of v in Figure 2b, a large account of electrons around O delocalized into the vacancy volume to mitigate the confinement of O charge. In addition, O atom moved 0.88 Å towards the vacancy after geometry optimization, greatly enhancing the binding energy of O-v (-1.50 eV). It was distinct that a large number of vacancies generated in the bcc Fe matrix would preferentially adsorb O to form O-v pairs, which was the first and crucial step in the formation of nanoclusters.



Figure 2. (110) slice of charge density difference plots in the units of electron/Bohr³ for O atom in bcc Fe matrix: (**a**) $O_{\text{(octahedral)}}$ in free-defect bcc Fe supercell and (**b**) $O_{\text{(octahedral)}}$ with 1NN *v*.

3.1.3. Interactions between Solute Atoms

O-*v* pairs in the bcc Fe matrix would further promote the abundant solution of other atoms. Calculated binding energies of Y-O, Si-O and Si-Y in the 1NN and 2NN sites were respectively summarized in Table 5. The binding of solute atoms in the 2NN site was always stronger than that in 1NN site because of the repulsive effect between too close atoms. Appropriately increasing the distance between the atoms would enhance the attraction between the atoms [19]. Y-O binding energy (-1.55 eV) > Si-Y binding energy (-0.81 eV) > Si-O binding energy (-0.67 eV), indicating that the formed O-*v* pairs would preferentially adsorb Y atoms till its saturation; then, Si atoms would preferentially bond with Y-O-*v* pairs to form Si-Y-O-*v* nanoclusters with the lowest energy.

Defect Species –	Binding Energy/eV		
	1NN	2NN	
Y-O	-0.72	-1.55	
Si-O	-0.24	-0.67	
Si-Y	-0.62	-0.81	

Table 5. The binding energies between solutes Y, O and Si (1NN and 2NN).

3.1.4. Binding Energies of Si-Y-O-v Nanoclusters

The first nearest neighboring $O_{(octahedral)}$ -v pair possessed the strongest binding energy according to the above results, which means it has maximum stability. Therefore, all the nanoclusters were designed in such a mode that Y and Si were introduced around 1NN $O_{(octahedral)}$ -v pair.

According to all the possible positions of Si and Y in a cube centered on v, 10 designed structures were tabulated in Table 6. One with maximum binding energy of -2.60 eV (g) possessed the most stability. In the bcc Fe matrix, the most stable nanoclusters would be preferentially precipitated, which could effectively increase the nucleation rate and dispersion of the nanoclusters.

Table 6. Binding energies of 10 non-stoichiometric Y-Si-O nanoclusters $(\mathbf{a}-\mathbf{j})$ in bcc Fe (White atoms are Fe atoms, red is O, yellow is Si, blue is the Y and the purple cube is the vacancy (v)).



According to the first-principles simulation analysis, the forming process of Y-Si-O nanoclusters in the bcc Fe matrix determined that a large number of vacancies generated

during the mechanical alloying process preferentially combined with $O_{(octahedral)}$ atoms to form stable $O_{(octahedral)}$ -v pairs. When O solid solution reached saturation, the surrounding Y and Si solutes would be attracted to form the Y-O-Si nanocluster with the lowest energy and the strongest relative stability. The above simulation results have given the feasibility of adding Si to ODS steels. The magnitude and stability of the nanoclusters would be greatly improved because of Si, thereby enhancing the mechanical properties and high-temperature stability of the ODS steels. The specific effects of different Si contents on the microstructure and mechanical properties of ODS steels would be discussed below.

3.2. Experimental Results

To facilitate the description of the experimental results, we named S0, S1, S2 and S3 ODS steels sintered at 1280 °C and 1300 °C as 1280-S0, 1280-S1, 1280-S2, 1280-S3, 1300-S0, 1300-S1, 1300-S2 and 1300-S3, respectively.

3.2.1. The Influence of Different Si Content on the Density of ODS Steels

The density distribution of ODS steels at 1280 °C and 1300 °C sintering temperature is shown in Figure 3. The addition of 1%wt Si caused a reduction of density. With the continuous addition of Si, the density curve presented an upward trend. In Figure 4, it is obvious that many anomalous pores appeared in 1280-S1 ODS steel, which explained its lowest density (84.11%). The densest steel was 1280-S3 ODS steel (density = 95.30%). However, as the sintering temperature rose to 1300 °C, the density reduced to 92.89%. Comparing different sintering temperatures, it could be found that higher sintering temperatures lead to denser ODS steels within 0~1 wt% Si, while the Si content of 2% and 3% played a dominant role on the densities rather than the sintering temperature, which showed that a moderately increased Si content could obtain sintered alloys with higher density at a lower sintering temperature. In other words, Si reduced the sintering temperature.



Figure 3. Density of ODS steels with 0, 1%, 2% and 3% wt Si at 1280 °C and 1300 °C sintering temperature.

3.2.2. The Influence of Different Si Content on the Second Phases in ODS Steels

The second phases in the alloy played a vital role in the mechanical properties of ODS steels. The electron probe maps for 1280-S0, 1280-S1, 1280-S2 and 1280-S3 ODS steels are shown in Figure 5. The black particles were the second phases dispersed in the matrix. It was obvious that with the addition of Si content, the density of the second phase gradually increased and the distribution was more uniform, contributing to more significant dispersion strengthening. In the distribution diagram of each element in the 1280-S3 ODS steels (Figure 6), it could be found that the Si, O and Y elements were mainly distributed in the positions corresponding to the black particles, which was mainly represented by more vivid colors of the Si, O and Y. These enriched Si-O-Y particles interacted with grain boundaries and dislocations to improve the strength of ODS steels by pinning the dislocations. According to the analysis, the unstable ultra-microstructures, such as Si-O and

Y-O pairs which were formed during the mechanical alloying process, gradually combined to form stable and fine Si-Y-O nanostructures under the high-temperature environment provided by vacuum sintering.







Figure 5. Electron probe maps of (a) 1280-S1, (b) 1280-S2 and (c) 1280-S3 ODS steels.



Figure 6. Distribution of (a) Si, (b) Y and (c) O elements in 1280-S3 ODS steels.

3.2.3. The Structure of Microparticles and Stoichiometric Nanoparticles in ODS Steels

A high-angle annular dark field image (HAADF) of 1280-S3 ODS steels is shown in Figure 7. The matrix contained many dispersed second phases, including microparticles and nanoparticles (105 nm to 1.91 μ m), all of which tended to be spherical. A line scan component analysis of a microparticle marked by the blue line in Figure 7 showed that the

content of Fe element decreased sharply from the edge to the center of the microparticle. The content of Cr element presented a slightly decreasing trend, but it was not nearly as clear as for Fe. O and Si were basically absent at the edge, mainly concentrated in the center. For the furthest edge (distance > 2500 nm), the Cr curve almost coincided with Si and O. The microparticle in the matrix seemed to be a core-shell structure with Si, O in the core and enriched Fe, slight Cr in the shell, which was consistent with the typical core-shell structure with Y, Si and O in the core and Cr in the shell that many scholars found [24].



Figure 7. (a) High-angle circular dark field (HAADF) image of 1280-S3 ODS steels. (b) Line scan component analysis of 1280-S3 ODS steels.

EDS analysis on the red mark in Figure 7 is shown in Figure 8; the core of the microparticle was mainly composed of Si and O with the atomic ratios of 25.69% and 16.92%, respectively. The formation of these SiO_X and some Si-O-Y clusters was a result of the high oxygen affinity of Si and Y. The solutes Si and Y combined with O atoms during the sintering process to precipitate the microparticle, which confirmed the strong binding energies between Si, Y and O solutes in the above calculation results.



Figure 8. EDS analysis at the center of the microparticle in the 1280-S3 ODS steels (red point in Figure 7).

In order to figure out the stoichiometric Y-Si-O nanoparticles, HRTEM analysis on 1280-S3 ODS steels at 20 °C was performed. Digital micrograph was used to fast Fourier transform (FFT) the HRTEM images to obtain electron diffraction patterns. Figure 9 was

calibrated as Y_2O_3 , the size of which was about 12 nm in Figure 9a. The structure space group of its monoclinic cubic crystal was C2/m(12) with the lattice constant: a = 13.8992 Å, b = 3.4934 Å, c = 8.6118 Å, $\alpha = 90^{\circ}$, $\beta = 100.27^{\circ}$ and $\gamma = 90^{\circ}$. The central spot in Figure 9b and the nearest three adjacent diffraction points constituted a parallelogram with an angle of 86.8°. The crystal plane indices of the three diffraction points were (511), (804) and (313), the ribbon axis index was (132) and the corresponding interplanar spacing d was 2.162 Å, 1.464 Å and 2.095 Å, respectively. Figure 9c shows the clear filtration diagram of the Y_2O_3 nanocluster. We could speculate that Y2O3 powders were dissolved in the matrix during the ball milling process; then, the Y atoms were easily combined with O atoms during the vacuum sintering process to generate Y_2O_3 nanoparticles [25]. Figure 10a was calibrated as yttrium silicate Y_2SiO_5 with the size of 8 nm, the structure of which was monoclinic cubic crystal with the space group of P21/c(14) and the lattice constant: a = 9.0139 Å, b = 6.9282 Å, c = 6.6427 Å, $\alpha = 90^\circ$, $\beta = 106.682^\circ$ and $\gamma = 90^\circ$. Figure 10b shows the crystal face index (512), $(\overline{2}13)$ and (321) which formed a parallelogram with an angle of 128.6° and the ribbon axis index (5,11,7). The corresponding interplanar spacing d was 1.6899 Å, 2.0654 Å and 1.9608 Å, respectively. Figure 11a was calibrated as the second type of yttrium silicate Y₂Si₂O₇ with the size of 5 nm, the structure of which was also a monoclinic cubic crystal with the space group of P21/a(14) and the lattice constant: a = 5.579 Å, b = 10.857 Å, c = 4.696 Å, $\alpha = 90^{\circ}$, $\beta = 95.99^{\circ}$ and $\gamma = 90^{\circ}$. The ribbon axis index in Figure 11b was (2,3,10), and the three diffraction points of (230), (221) and (051) formed a parallelogram with an angle of 121.03° with the corresponding interplanar spacing *d*: 2.201 Å, 2.102 Å and 1.965 Å, respectively.







Figure 9. (a) High-resolution transmission electron microscopy (HRTEM) image of the Y_2O_3 nanoparticle in 1280-S3 ODS steels; (b) FFT diagram micrograph by (a); (c) IFFT filtered image derived from three adjacent diffraction points in (b).





Figure 10. (a) HRTEM image of the Y_2SiO_5 nanoparticle in 1280-S3 ODS steels; (b) FFT diagram micrograph by (a); (c) IFFT filtered image derived from three adjacent diffraction points in (b).



Figure 11. (a) HRTEM image of the $Y_2Si_2O_7$ nanoparticle in 1280-S3 ODS steels; (b) FFT diagram micrograph by (a); (c) IFFT filtered image derived from three adjacent diffraction points in (b).

Many scholars have explained the dissolution–precipitation mechanism of Si-O-Y nanoparticles. Song Liangliang found nano-scale Si-O-Y precipitates in Si-containing nanocluster ferrite steels (NFAs). The Gibbs free energy (ΔG) of the two reactions $Y_2O_3 + 2Si + 4O \rightarrow Y_2Si_2O_7$ and $Y_2O_3 + Si + 2O \rightarrow Y_2SiO_5$ is negative at 1150b °C, which indicated the inevitability of two reactions from a thermodynamic view [15].

3.2.4. The Influence of Different Si Content on the Mechanical Properties of ODS Steels

The Vickers hardness distribution of ODS steels with different Si content at 1280 °C and 1300 °C is shown in Figure 12. For both sintering temperatures, the hardness of ODS steels gradually improved with Si content increasing. The 1280-S3 and 1300-S3 ODS steels were the hardest (442.33 HV, 425.33 HV).



Figure 12. Hardness of ODS steels with 0, 1%, 2% and 3% wt Si at 1280 °C and 1300 °C sintering temperature.

The variation tendency of ODS steels with different contents of Si shown in Figure 13 was consistent with the density of ODS steels in Figure 3. The tensile strength of 1280-S1 ODS steels was the lowest, only 518 MPa, the analysis of which was that the recrystallization of ODS steels could be impeded by the Si addition of $0\sim1\%$, resulting in coarse grains. The effect of grain coarsening was greater than that of dispersion strengthening, leading to the reduced tensile strength. Combined with the microstructures shown in Figure 4, 1%wt Si would cause anomalous pores with the size of $50\sim60 \,\mu\text{m}$ in ODS steel, resulting in a decrease in strength. However, the tensile strength of 1280-S2 and 1280-S3 ODS steels increased to 865 MPa and 1025 MPa, respectively, indicating that more second phases generated in ODS steels caused a more significant pinning effect on the grain boundary, which effectively

limited the growth of crystal grains. High-density dispersed second phases obstructed the dislocation movement and grain growth, which highly strengthened ODS steels. The similar rule in Figures 3, 12 and 13 showed that a higher sintering temperature lead to denser, harder and more strengthening of ODS steels within 0~1%wt Si. However, it was the Si contents of 2% and 3% that played a leading role on the densities and mechanical properties rather than the sintering temperature. Additionally, Si reduced the sintering temperature by maximizing densities and mechanical properties at a lower sintering temperature.



Figure 13. Tensile strength of ODS steels with 0, 1%, 2% and 3% wt Si at 1280 °C and 1300 °C sintering temperature.

The tensile fracture morphologies of 1280-S1 and 1280-S3 ODS steels are shown in Figure 14. The fracture modes of the two components were ductile fracture, and the second phase of different sizes were distributed in the center and around the dimples. An EDS analysis of a second phase particle in Figure 15 showed that these second phases were mainly composed of Si, Y and O elements. It was obvious from Figure 14a,b that the dimples of fracture in 1280-S3 ODS steel were shallower and denser with the finer sizes, which indicated the lower plasticity of 1280-S3 ODS steels. However, the number of the second phases in fracture of 1280-S3 ODS steels was much larger than that of the 1280-S1 ODS steels. With reference to Figure 13, we can draw a conclusion that more second phases in the Fe matrix would greatly increase the strength of ODS steels but reduce its plasticity.



Figure 14. (**a**) Tensile fracture morphology of 1280-S1 ODS steels; (**b**) Tensile fracture morphology of 1280-S3 ODS steels.



Figure 15. EDS analysis of a second phase in fracture of 1280-S3 ODS steels.

4. Conclusions

The nucleation mechanism of Y-O-Si nanoclusters in the bcc Fe matrix were expounded through first-principles calculations. Additionally, those containing Si ODS steels were synthesized through an MA and vacuum sintering process. The specific research results are summarized as followed:

- The solutes Y and Si preferred substitutional site, while O preferred octahedral interstitial site. The binding sequence of solutes with *v* followed O-*v* > Y-*v* > Si-*v*, and the affinity of Y, Si and *v* with O followed O-Y >O-*v* >O-Si. The most stable Y-O-Si nanocluster ($E_b = -2.60 \text{ eV}$) of 10 different structures were generated preferentially. The nucleation mechanism of non-stoichiometric Y-O-Si nanoclusters determined that a large number of vacancies generated during the mechanical alloying process preferentially combined with O_(octahedral) atoms to form stable O_(octahedral)-*v* pairs. When O solid solution reached saturation, the surrounding Y and Si solutes would be attracted to form the Y-O-Si nanocluster with the lowest energy and the strongest relative stability;
- The core (consisting of Si and O)-shell (enriched Fe and Cr) structure of microparticles was found in ODS steels. Additionally, three nanoparticles of Y_2O_3 , Y_2SiO_5 and $Y_2Si_2O_7$ with sizes of 5~12 nm were found in 1280-S3 ODS steels, the crystal structures of which were all monoclinic cubic crystals, indicating the inevitability of two reactions: $Y_2O_3 + 2Si + 4O \rightarrow Y_2Si_2O_7$ and $Y_2O_3 + Si + 2O \rightarrow Y_2SiO_5$ through MA and vacuum sintering process;
- ODS steels with better mechanical properties at a lower sintering temperature were fabricated when a content of 3%Si was added. In other words, Si were able to reduce the sintering temperature. The 1280-S3 ODS steels exhibited the best comprehensive mechanical properties. The tensile strength, hardness and relative density were 1025 MPa, 442.44 HV and 95.3%, respectively.

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