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Progress in Application of First Principles in Oxide Metallurgy

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Abstract

Oxide metallurgy technology has become a core strategy for optimizing the microstructure and properties of the heat-affected zone (HAZ) in welding by precisely controlling the micro-characteristics of oxide inclusions in steel. This paper systematically reviews the research progress in revealing the adsorption behavior of inclusions, bulk phase stability, cluster evolution, interfacial interaction, and corrosion mechanism at the atomic scale based on first-principles calculations using density functional theory (DFT). Studies have shown that this method can accurately analyze the heterogeneous nucleation mechanism of complex inclusions and optimize the size and distribution of inclusions through parameters such as interfacial energy and adhesion work, thereby significantly improving the mechanical properties of HAZ by pinning austenite grain boundaries and inducing intragranular ferrite nucleation. In addition, the corrosion sensitivity of inclusions can be predicted through work function calculations. Current challenges are focused on the unified model of intragranular nucleation kinetics and multi-scale coupling simulation of dynamic metallurgical processes. In the future, the combination of artificial intelligence, high-throughput computing, and experimental verification will promote the development of this technology towards precision and intelligence, accelerating the industrial application of high-performance steel.

Keywords: Density functional theory, First-principles, Oxide metallurgy, Optimization of material properties

1. Introduction

Since experts began to study oxide metallurgy technology in 1970s, it has gone through three development courses, from basic theoretical research and preliminary application, to process optimization and industrialization promotion, and then to technology integration and innovation promotion. At present, technical research is still in the stage of exploration and maturation. Now HTUFF (Super High HAZ Toughness with Fine Microstructures Impacted by Fine Particles) technology [1].The successful development has changed the traditional view of nonmetallic inclusions (such as oxides). HTUFF technology uses fine inclusions as heterogeneous precipitation points, which never changes the structure and grain size of steel, not only improves the toughness of steel, but also enhances its strength and weldability. However, there is still a lack of a more comprehensive and detailed understanding of it, and the research on oxide metallurgy technology is still in the stage of exploration and maturity.

By optimizing the microstructure of welding Heat Affected Zone (HAZ), "oxide metallurgy" technology provides a new research path for the development of welding steel with high input energy [2]. First-principles calculation method is a calculation method based on quantum mechanics and nuclear motion, which does not depend on any empirical parameters, effectively predicts the microstructure state and characteristics, and can accurately determine the physical and chemical characteristics of various phase states. Its research focuses on key parameters such as surface energy, atomic binding energy, adsorption energy and

interface energy. It provides a new way for material researchers to optimize materials according to the physical and chemical properties of these phases. In this paper, oxide metallurgy technology and first principles based on density functional theory are introduced in turn. The application status of first principles in different aspects of oxide metallurgy is expounded in order to provide more scientific theoretical basis for future industrial production.

2. Organization of the Text

The technical idea of "oxide metallurgy" was put forward in Japan in 1990 [3-5]. This technology holds that there are fine dispersed high melting point oxide inclusions in steel, which pin austenite grains and contribute to the nucleation of Intragranular Acicular Ferrite (IAF) [6-7]. In addition, multiple IAF phenomena are induced in a single oxide inclusion at the same time, thus effectively improving the phenomena of coarse grains, decreased toughness and strength in the welding HAZ and improving the welding performance. The morphology of IAF induced by typical inclusions is shown in Fig. 1.

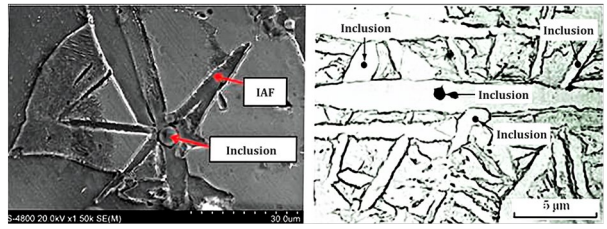

Fig. 1. Typical acicular ferrite morphology

After Japanese scholars put forward oxide metallurgy technology, it attracted the attention of metallurgical researchers all over the world, and everyone worked together to conduct in-depth research. Japanese steel mills, such as Nippon Steel, JFE, Sumitomo Metals and Kobe Steel, were the first companies to introduce oxide metallurgy technology in steelmaking [8-9]. On the basis of preliminary research, metallurgical oxide technology has entered a stage of rapid development, and the first, second and third generation metallurgical oxide technologies have been put forward one after another, as shown in Table 1.

Table 1.
Summary of technology iterations

Intergeneration	Core particle	Stability	Particle size range	Typical application
The first generation	TiN	centre	＜100 nm	Regular board steel
The second generation	TiO_2, Ti_2O_3	tall	50~300 nm	High-strength Marine engineering steel
The third generation	$MgO{\cdot}Al_2O_3$	superelevation	＜50 nm	Polar ship steel, ultra-large line energy welding material

The first generation of oxide metallurgy technology: put forward by Nippon Steel Company in 1970 and applied to practical production [10]. The principle is to use the TiN particles in the steel that are not dissolved at high welding temperature and have a fine size to nail the austenite grain boundaries to inhibit the roughness of the γ microstructure, so as to improve the toughness of the welding HAZ. Its limitation is that with the increase of welding line energy, when the highest welding temperature exceeds 1400℃, the roughness of TiN increases, melts and loses its pinning effect [11]. And with the decrease of temperature in the later period, TiN particles will not precipitate in large quantities.

The second generation of oxide metallurgy technology: In 1990, experts and scholars proposed that Ti_xO_y particles, which are still stable at high temperature, can promote the nucleation of IAF, thus achieving the effect of grain refinement and increasing the toughness of HAZ welding. However, in the actual industrial production process, Ti oxides are easy to aggregate and grow, and are easy to be removed during molten steel treatment, so it is difficult to obtain fine and dispersed Ti_xO_y particles [12]. Because it is difficult to control the characteristics of high temperature aggregation and growth, the second generation oxide metallurgy technology with Ti oxide as fine inclusion is limited.

Third-generation oxide metallurgy technology: Based on the first-generation and second-generation oxide metallurgy technologies, in order to meet the increasing demand of large-line energy welding, Nippon Steel Company of Japan developed HTUFF technology in 2003, which uses strong deoxidizers (oxide particles and sulfide particles of Ca/Mg) which are not easily dissolved at high temperature and can still be dispersed in molten steel, and uses nano-scale strong deoxidizers to pin austenite grain boundaries to prevent grain growth during heating and welding at high temperature; In the process of cooling and solidification, micron-sized strong deoxidizer is used as the nucleation particle of IAF to refine the grains. The toughness of welding HAZ is improved, and the steel has good mechanical properties.

3. First principles based on density functional theory

3.1. Schrodinger equation

Based on the first-principles calculation method, the Schrodinger equation is solved by accurate numerical method, and the research on the microstructure of materials at atomic level is focused. By simulating the electronic state of the material, the key parameters such as interface energy and adsorption energy are obtained, and then the optical properties, geometric structure, surface properties and magnetism of the material are determined

by self-consistent calculation, and the relationship between the structure and properties of the material is explained theoretically. The calculation model is independent of any empirical parameters and adopts "non-empirical" simulation, which provides a strong theoretical basis for experimental research.

Since the advent of Schrodinger equation, in order to improve its calculation feasibility, many approximate methods have been put forward in academic circles. At first, Born-Oppenheimer approximation simplified the multi-body dynamics problem into a multi-electron problem, but due to the complexity of the calculation process, the practical application faced challenges. Subsequently, Hartree-Fock approximation was put forward, which realized a major breakthrough in transforming multi-electron problems into single-electron problems through adiabatic approximation. This greatly promotes the development and application of the first-principles calculation method, but does not consider the influence of relativistic effect and electron correlation interaction, and there will be a great error between the calculation of atomic excitation process and the search process of transition state [13]. With the increasing storage capacity and computing space of computer, the computing speed of computer is getting faster and faster, and the calculation accuracy is also improving. In order to make up for the deficiency of simplified Hartree-Fock approximation, a density functional theory with higher calculation accuracy, simplified calculation difficulty and better calculation results is proposed.

3.2. Schrodinger equation

Density Functional Theory (DFT) is a method to study the electronic structure of multi-particle systems The quantum mechanics method, in 1927, scientists Thomas L H and Fermi E K [14]. When solving the expression of electron gas density, until 1964, Hohenberg and Kohn put forward the basic principle of density functional theory, namely Hohenberg-Kohn theorem. Its core idea is to transform the complex wave function description of multi-particle system into the description of electron density.

3.2.1 Hohenberg-Kohn theorem

Hohenberg-Kohn theorem consists of the following two basic theorems [15-16]□

Theorem 1: The ground state energy of the system is the only functional of electron density, that is, for any multi-particle system, its ground state energy can be expressed as the functional of electron density.

Theorem 2: When the number of particles in the system remains constant, the energy functional takes the minimum value of the correct particle number density function, which is consistent with the ground state energy.

The system can always be expressed as:

$$E_{total}[p] = T[p] + U[p] + E_{XC}[p] \tag{1}$$

In formula:

$T[p]$ —Electronic kinetic energy;

$U[p]$ —Coulomb action potential energy;

$E_{XC}[p]$ —The exchange correlation energy contributed by all multi-particle groups.

3.2.2 Kohn-Sham equation

Subsequently, Kohn and Sham put forward Kohn-Sham equation in 1965, which made density functional theory widely popularized in practical application.

At present, the first-principles calculation method plays an increasingly important role in materials science, physics, chemistry and other fields, especially after combining artificial intelligence technology, it shows great potential in studying new materials and solving complex scientific problems.

4. Application of First Principles in Oxide Metallurgy

As an advanced material preparation technology, oxide metallurgy has significantly improved the grain structure and mechanical properties of HAZ by optimizing the type, size and distribution of oxide inclusions in steel, and has become an important means to solve the problem of toughness decline in welding heat affected zone. However, traditional experimental methods have many limitations in revealing the microscopic mechanism of oxide metallurgy, especially in complex systems, and it is difficult to accurately describe the microscopic process of interaction between oxide inclusions and matrix. Compared with traditional experimental methods, first-principles calculation can accurately simulate the electronic structure and physical and chemical properties of materials at the atomic level through quantum mechanics and DFT, without relying on empirical parameters. By calculating the total energy, electronic structure and interatomic interaction of the system, this method provides a new perspective for the study of micro-mechanism in oxide metallurgy, accurately describes the micro-process in complex systems, reveals the interaction mechanism between oxide inclusions and steel matrix, and predicts the changing trend of material properties. At the same time, it reveals the mechanism of oxide nucleation, interface bonding and element interaction, accurately predicts thermodynamic/kinetic parameters (such as formation energy and diffusion barrier), guides multi-component design and interface optimization, and provides key input data for cross-scale simulation. Especially in extreme conditions or complex systems (such as rare earth doping and composite precipitation), its irreplaceable microscopic analytical ability can greatly reduce the trial and error cost of experiments and promote the rational design of high-performance steel materials.

At present, first-principles calculation has been widely used in the study of adsorption behavior, bulk phase properties, cluster stability, interface characteristics of inclusions and corrosion mechanism in oxide metallurgy, which provides important theoretical support for optimizing metallurgical process and designing new high-performance steel materials.

4.1. Application of first principles in oxide metallurgical adsorption

Adsorption is one of the key microscopic processes in oxide metallurgy. In the process of metal or alloy melting, some elements or compounds in gas, liquid or solid will be enriched on the surface of solid oxide to form an adsorption layer, which affects the nucleation, growth and distribution of oxide particles and their interface bonding with steel matrix. Adsorption behavior optimizes the size and stability of oxide particles, enhances their ability as nucleation sites, promotes the formation of IAF, and inhibits the growth of austenite grains, thus refining the microstructure of steel. In addition, the adsorption behavior can also improve the purity of steel, which provides important support for the precise control and efficient application of oxide metallurgy technology.

As a powerful tool, first-principles calculation has made a breakthrough in the study of oxide metallurgical adsorption. Through the accurate description of oxide surface structure and adsorption characteristics, the first-principles method reveals the microscopic mechanism in the adsorption process, which provides a theoretical basis for optimizing metallurgical process and designing new alloy materials. Zhou Linsen et al. calculated the adsorption behavior of hydrogen atoms in PuGa alloy by first principles [17]. Li Junwei et al. calculated the adsorption and dissociation behavior of oxygen on the surface of uranium-molybdenum system by first principles [18].

Adsorption Energy (Eads) indicates the bonding strength between adsorbents (such as atoms and molecules) and substrates (such as oxide surfaces), and is usually used to quantify the stability of adsorption process. Positive value (endothermic): the adsorption process requires external energy input and the system is unstable; Negative value (exotherm): the adsorption process is spontaneous and the system is more stable. Based on the first-principles DFT microscopic calculation, the adsorption energy at the atomic scale can be expressed by DFT model calculation:

$$E_{ads} = \frac{E_{slab+adsorbate} - E_{slab} - E_{adsorbate}}{N_{adsorbate}} \quad (2)$$

In formula:

$E_{slab+adsorbate}$ —Total energy after adsorbent adsorption on the base surface;

E_{slab} —Base surface energy;

$E_{adsorbate}$ —Energy in the isolated state of the adsorbent substance;

$N_{adsorbate}$ —Number of adsorbed particles (usually 1).

Among them, Wang Q's research team focused on oxide metallurgy technology, and systematically explored the mechanism of intragranular ferrite nucleation induced by Mg-Ti oxide /MnS composite inclusions by first-principles calculation method [19]. The study focuses on revealing the adsorption and growth characteristics of MnS on Ti oxide surface in composite inclusions, and finds that the adsorption and growth ability of MnS on $MgTiO_3$ surface is significantly better than that of Ti_2O_3. Specifically, on the O-Mg-Mg surface of $MgTi_2O_3$ (adsorption energy -16.33 eV), MnS shows vertical orientation growth characteristics, while on the Ti-Ti-O surface of Ti_2O_3 (adsorption energy -4.00 eV), it shows plane expansion mode. The calculation of adsorption energy shows that the adsorption capacity of MnS on $MgTiO_3$ surface is stronger, and MnS has the following characteristics when it grows on its surface. Higher structural stability. According to the migration mechanism of Mn atoms, it is found that Mn atoms absorbed by oxide phase in composite inclusions mainly come from Mn atoms in the surrounding steel matrix (dissociation energy -3.03 eV), not MnS (dissociation energy +19.18 eV). Among them, $MgTiO_3$ is easier to form Mg vacancies (vacancy formation energy is 0.30 eV), and both $MgTiO_3$ and Ti_2O_3 containing cationic vacancies can spontaneously absorb and stably store Mn atoms in steel matrix.

As for the diffusion behavior of Mn atoms in oxides, it is found that the addition of Mg element significantly changes its diffusion path, which further reveals the dual mechanism of Mg-Ti oxides inducing the nucleation of IAF through manganese depletion region, as shown in Fig. 2. It is shown that on the one hand, the heterogeneous nucleation of MnS on different oxide surfaces (cluster growth on the surface of $MgTiO_3$, planar growth on the surface of Ti_2O_3) is regulated, and on the other hand, the local micro-area composition is changed through different absorption and diffusion paths of Mn atoms.

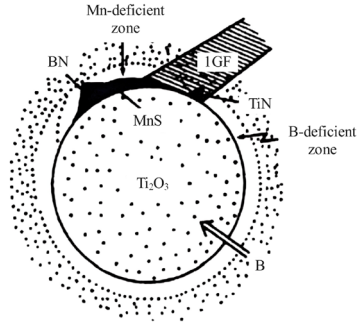

Fig. 2. Mn and B poor regions formed around Ti_2O_3 inclusions

First-principles calculation provides atomic-scale theoretical guidance for solute adsorption behavior in oxide metallurgy. Through accurate calculation of adsorption energy and interface characteristics, its regulation mechanism on nano-oxide precipitation is revealed. This microscopic cognition realizes the accurate control of the size and distribution of precipitated phases, significantly improves the weldability and mechanical properties of steel, which is of great research significance for preparing high-strength low-alloy steel, reduces the research and development cost, and contributes to the development of high-performance steel.

4.2. Application of first principles in the study of oxide metallurgy bulk phase

The evolution of microstructure or phase structure of austenite, ferrite and martensite in steel matrix will directly affect the properties of steel, especially in microstructure control and performance optimization of welding HAZ. However, by adding fine oxide particles, oxide metallurgy technology can pin austenite grain boundaries at high temperature, inhibit grain growth, and promote the nucleation of IAF during cooling, so as to refine the bulk structure and optimize the toughness of welding heat affected zone, and meet the requirements of high-input energy welding and high-strength steel.

In the field of oxide metallurgy, first-principles calculation based on DFT has been widely used to study the bulk properties of nonmetallic inclusions in steel, so as to reveal the effects of their thermodynamic stability, electronic structure and mechanical properties on the properties of materials. Related research is shown in Table 2.

Table 2.
Examples of first-principles applications in somatophase studies

Author and year	Subject investigated	Research contents	The main discovery	Key parameters / methods	Document
Pan Yangxuan, et al□ 2024)	$Cs_2Ag_{1-x}Cu_xBiBr_6$	Structural, elastic, electrical properties	Cu^+ doping significantly improves the stability of $Cs_2AgBiBr_6$ (the doping formation energy is negative)	DFT, Difference factor, octahedral factor	[20]
Ju J, et al □ 2020□	$Fe_3Al_2C_2$ Compound	Stability, the electronic structure	$Fe_3Al_2C_2$ thermodynamic stability; C element improves the compound stability, the bond is covalent-metal mixed bond	Formation energy, elastic modulus calculation	[21]
Liu Pei □ 2019□	Ti_2AlN bulk phase	Lattice constant, the elastic constant	The calculated values match the experimental values, Ti_2AlN has a high elastic modulus, and the surface properties calculations provide the basis for subsequent studies	Structure optimization parameters, GGA-PBE functional	[22]
Zheng Y, et al □ 2017□	FeAl intermetallic compound	Structure, elasticity, electronic properties	Al atoms are easily replaced by alloy elements (Cr, Ti, Co) to enhance the stability of Fe-Al; the bonding characteristic is a covalent-metal mixing bond	Formation energy, density of state analysis	[23]
Liu Y H, et al. (2017)	Fe-Al binary compound	Elastic properties, the electronic structure	The Fe-Al compound has a negative binding energy and is thermodynamically stable; Fe3Al has the maximum volume modulus (233.2 GPa)	Analysis of the density of states and electron density distribution	[24]

Through first-principles calculation, researchers can also optimize the crystal structure and calculate the formation energy to verify the thermodynamic stability of the bulk phase. The calculation of $MgAl_2O_4$ spinel structure by Huo Jinxia shows that its formation energy is -21.350 eV, and its lattice constant (a = 8.169) is highly consistent with the experimental value (8.093), which proves its good thermodynamic stability [25]. Similarly, the formation energy and binding energy of Fe-Al intermetallic compounds (such as Fe_3Al and $FeAl_2$) are negative, which further supports their existence as stable phases. As shown in Fig. 3 and Fig. 4, the analysis of energy band structure and Density Of States (DOS) reveals the conductivity and chemical bond type of the material. $MgAl_2O_4$ is determined as a direct band gap semiconductor (band gap value is 5.128 eV), and its valence band is mainly contributed by O-2p orbital and Al-3s/p orbital, and its conduction band is dominated by s/p orbital of Mg and Al. Mulliken atomic layout analysis shows that O atoms in $MgAl_2O_4$ form strong ionic bonds by trapping electrons, while Al-O bonds have covalent bond characteristics. Similarly, the electronic structure analysis of $Fe_3Al_2C_2$ shows that its bonding is covalent-metal mixed bond, and the addition of C element significantly improves the structural stability. The mechanical properties of materials can be evaluated by calculating elastic constants (such as bulk modulus and shear modulus). It is found that the bulk modulus of Fe_3Al is as high as 233.2 GPa, which indicates that Fe_3Al has excellent compression resistance. Doping research (such as Cr and Ni doping Fe_3Al) shows that Cr tends to occupy Fe i site and Ni occupies Fe ii site, and the plasticity of the material is enhanced by charge redistribution.

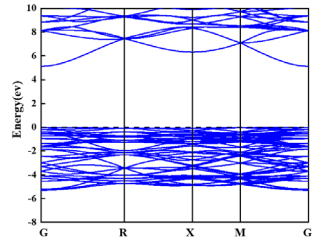

Fig. 3. Energy band structure diagram of $MgAl_2O_4$ [25]

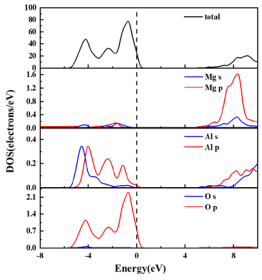

Fig. 4. State density diagram of $MgAl_2O_4$ [25]

First-principles directly reveal the intrinsic characteristics of bulk materials in oxide metallurgy by means of quantum mechanics based on DFT, accurately analyze key atomic scale processes such as solute-oxygen interaction, point defect formation and diffusion behavior, and provide theoretical support for predicting the macroscopic performance of materials at the micro level. This method not only explains the structure-activity relationship between bulk electronic structure and macro-properties, but also provides a quantitative theoretical basis for optimizing the thermodynamics/kinetics of oxide precipitation, realizes the cross-scale design from atomic interaction to material properties, and significantly improves the science and predictability of oxide metallurgy technology.

4.3. Application of first principles in the calculation of oxide metallurgical clusters

Cluster is one of the basic building blocks in the nano-world. It is an aggregate (particle size ≤ 1nm) composed of several to several hundred atoms, which is in a state between atoms, molecules and bulk materials. Cluster calculation reveals the nucleation mechanism, stability and interface interaction between oxide particles and steel matrix by simulating the structure, energy and dynamic behavior of small-scale atomic clusters (such as oxide particles and inclusions) in oxide metallurgy technology. It can optimize the addition strategy of deoxidizer and alloying elements, promote the formation of fine and dispersed oxide particles, enhance its pinning effect on austenite grain boundaries, inhibit grain growth, predict the formation and evolution of inclusions and improve the purity of steel.

First-principles calculation provides key parameters such as cluster formation energy, interface binding energy and electronic structure, and optimizes deoxidation. The strategy of adding additives and alloying elements is suitable for large-scale calculation of complex systems, thus revealing the micro-mechanism of electronic structure, stability and reactivity of clusters, , as shown in Table 3. Xu H explored the geometric and electronic structures of Al-S clusters and their interaction with graphene substrates by first-principles calculation, and revealed the potential stability and interaction mechanism of these clusters as electrode materials for Al-S batteries [26].

Table 3.
Basic cluster types, typical representatives, bonding characteristics and average binding energy

Type	Typical representative	Bond characteristics	Average binding energy
The Van der Waals cluster	Ar_n, CO_2 clusters	Instantaneous dipolar action, which is weak and short-range	≤ 0.3eV
Molecular clusters	$(I_2)_n$, $(NH_3)_n$	Dipolar action, and the directionality	0.3-1.0eV
Hydrogen bond clusters	$(HF)_n$, $(H_2O)_n$	Hydrogen bonds, and the electron-transfer characteristics	0.3-0.5eV
Covalent bond clusters	C_{60} Si_n	Strong covalent bonds, directionality / saturation	1.0-4.0eV
Ion bond clusters	$(NaCl)_n$, $(MgO)_n$ clusters	Electrostatic gravity, with no directionality	2.0-4.0eV
Metal bond clusters	Au_n, Ag_n	Decococalized electrons with cation, high conductivity	0.5-3.0eV

It is widely used in cluster calculation, Jiang Xin constructed and screened the global optimal configuration of $(Y_2O_3)_n$ (n=1~15) cluster by combining Artificial Bee Colony algorithm (ABC) with DFT [27]. This method breaks through the limitation of traditional experimental methods and successfully predicts the novel structure of medium and large clusters (n=6~15). The average binding energy E_b, second-order energy difference Δ^2E and HOMO-LUMO energy gap of yttrium oxide clusters are calculated by first principles, and the structural stability of the clusters is analyzed. The results show that the stability of binary mixed yttrium oxide clusters is higher than that of pure yttrium clusters, which is mainly due to the difference in electron filling between 2p orbitals with incomplete oxygen atoms and 5s orbitals with full yttrium atoms. When n=2, 4, 7 and 9, the clusters show stronger relative stability because of their higher Δ^2E and HOMO-LUMO energy gaps. Finally, the wave function analysis program Multiwfn is used to pair,the molecular orbital components of $(Y_2O_3)_n$ (n=1~15) clusters were analyzed. The results show that oxygen atoms and yttrium atoms have different contributions to the molecular orbital of clusters in different energy ranges, such as around -20eV, and the molecular orbital of clusters is mainly contributed by the S orbital of oxygen atoms. In order to study the thermodynamic properties of yttrium oxide clusters, with the help of Gaussian 09 software package and thermodynamic analysis software Shermo, the vibration frequency of yttrium oxide clusters is calculated by first principles, and the thermodynamic data of clusters with different sizes at 0-2000K are obtained. The calculation shows that the heat capacity C_p, enthalpy H and entropy S of yttrium oxide clusters all increase with the increase of temperature and cluster size, and the vibration free energy G_v

decreases with the increase of temperature, and the cluster stability changes in the temperature range of 300-500 K.

In this study, the structural evolution law, thermodynamic size effect and nucleation mechanism of yttrium oxide nanoclusters are systematically expounded by first-principles method,as shown in Fig. 5, which further enriches the nano-thermodynamic database of rare earth oxides and provides theoretical support for the regulation of inclusion size in oxide metallurgy.

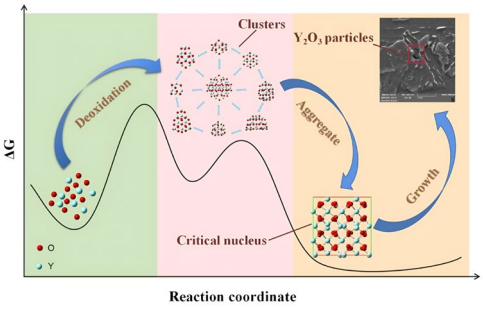

Fig. 5. Schematic diagram of nucleation and growth mechanism of yttrium oxide inclusion particles [27]

First-principles calculation and cluster simulation are both powerful means to explore the properties of matter, and they complement each other. First-principles calculation is mainly aimed at periodic systems, while cluster simulation focuses on small aperiodic systems, describing the local structure and properties of clusters in detail. This method not only clarifies the quantum mechanical nature of the interaction between cluster size effect and interface, but also establishes a quantitative correlation between cluster evolution dynamics and macro-precipitation behavior, which provides a theoretical basis for regulating the nucleation and distribution of oxide nanoclusters and significantly improves the accuracy and efficiency of microstructure and properties design in oxide metallurgy.

4.4. Application of First Principles in Interface Properties of Oxide Metallurgical Inclusions

Inclusions often refer to heterogeneous phases in metals or alloys, such as small particles, bubbles and other discontinuous phases. Oxide metallurgy technology The technique can adjust the interface characteristics between inclusions and steel matrix (including interface energy, binding energy and electronic structure, etc.) to improve its efficiency as nucleation point, and then refine the microstructure of steel.

In the past, the discussion of inclusions mostly relied on experimental observation and empirical rules. Although these methods can provide some information, they lack an accurate grasp of microstructure and interface properties, which limits the prediction and control of material properties. However, the first-principles method, based on the principle of quantum mechanics and the basic physical laws, can not only accurately analyze the interface structure between inclusions and substrate, provide quantitative data of interface energy, but also grasp the distribution and transmission characteristics of electrons at the interface and reveal the mechanical properties of the interface of inclusions.

Zhang Jing et al. can reveal and predict the mechanism of inclusion formation from the microscopic level by using first-principles calculation technology, and clarify the relationship between its structure and properties [28]. This method has been gradually applied to the study of steel inclusion properties. Zhang Jing and others reviewed the application of first-principles calculation in the study of inclusion control in steel, covering the corrosion caused by inclusions, heterogeneous nucleation and mechanical properties, and calculated the properties of inclusions in steel, which provided a theoretical basis for inclusion control.

Yuan X et al. studied the interface behavior of ferrite nucleation induced by TiN inclusions in steel by using the first-principles calculation technique, focusing on the atomic scale structure, adhesion work, interface energy and electronic properties of the interface between bcc-Fe and TiN [29]. DFT combined with two-dimensional mismatch theory is used to reveal the key role of low mismatch interface in heterogeneous nucleation, which provides a theoretical basis for optimizing the design of TiN inclusions. By constructing six stacking models (TS, CS, HS) of Fe(100)/TiN(100) and Fe(110)/TiN(110), it is found that HS stacking will spontaneously transform into CS stacking after geometric optimization, which shows that CS configuration has higher stability. The Fe(110)/TiN(110)-CS interface shows the strongest interfacial bonding due to the maximum adhesion work (3.003 J/m^2), while the Fe(100)/TiN(100)-CS interface becomes the most stable structure due to the lowest interfacial energy (2.404 J/m^2). The analysis of charge density and charge density difference shows that the interface bonding is mainly Fe-N covalent bond, accompanied by Fe-Ti metal bond. For example, in the Fe(110)/TiN(110)-CS interface, the Fe atom transfers significantly to the N atom, forming a strong covalent interaction, while the Fe-Ti bond contributes to the metal properties. This mixed bonding mode explains the source of high adhesion work at the interface. Through the dynamic simulation of the layer-by-layer growth of Fe atoms on the surface of TiN, it is found that Fe preferentially aggregates on the surface of TiN(100) and epitaxially grows along the direction of Fe(100), forming a stable interface with low mismatch (4.61%). This process is consistent with the layered growth theory, and the parallel orientation relationship of (001) crystal plane is verified by TEM experiments.

The two-dimensional mismatch is calculated by the formula proposed by Bramfitt:

$$\delta_d^{bbl} = \sum_{i=1}^{3}\left[\left(d^i_{[uvw]Fe}\cos\theta - d^i_{[uvw]TiN}\right)/d^i_{[uvw]Fe}\right]/3\times 100\% \qquad (3)$$

In formula: $d^i_{[uvw]Fe}$ and $d^i_{[uvw]TiN}$ are the atomic spacing of Fe and TiN along a specific crystal direction; θ is the included angle between two crystal orientations. The mismatch data are shown in Table 4.

Table 4.
Mismatch data summary table

Fe crystal face	TiN crystal face	Two-dimensional mismatch δ degree (%)	Matching direction		
Fe(100)	TiN(100)	4.61	[001]Fe	[011]TiN, [011]Fe	[020]TiN
Fe(110)	TiN(110)	4.61	[001]Fe	[−110]TiN, [−111]Fe	[−112]TiN
Fe(100)	TiN(110)	16.18	[010]Fe	[01–1]TiN, [012]Fe	[–112]TiN
Fe(110)	TiN(100)	18.5	[001]Fe	[011]TiN, [–111]Fe	[020]TiN
Fe(111)	TiN(100)	14.1	[–110]Fe	[001]TiN, [–202]Fe	[021]TiN
Fe(111)	TiN(111)	26.0	[10–1]Fe	[10–1]TiN, [–211]Fe	[–211]TiN

By accurately describing the structure and properties of the interface with inclusions, the microscopic mechanism of the interface is analyzed by first principles, which provides a theoretical basis for improving material properties and developing new alloys. The application of this method not only deepens our understanding of the interface characteristics of materials, but also brings new perspectives and tools for material design and engineering application, enabling us to predict and control the properties of materials more accurately, and then play an increasingly critical role in aviation, automobile, energy conversion and other industries.

4.5. Application of first principles in oxide metallurgical corrosion

In the in-depth study of materials science, the degradation of materials, especially the corrosion problem, has always been a complex and challenging topic. The environmental adaptability and long-term performance stability of steel will affect the corrosion resistance of materials. By regulating the distribution and characteristics of oxide particles in steel, oxide metallurgy technology not only optimizes the mechanical properties of steel, but also reduces grain boundaries and defects in steel, thus reducing the starting point and propagation path of corrosion. In addition, the stable inclusions formed by oxide particles in steel can improve the surface characteristics of steel and enhance its corrosion resistance. Therefore, oxide metallurgy technology not only improves the strength and toughness of steel, but also enhances the durability of steel in corrosive environment through the optimization of microstructure, making it have a wider application potential in harsh environments such as marine engineering and chemical equipment.

First principles can accurately simulate the electronic structure and chemical reaction of materials at the atomic level, which provides a new way to deeply understand the nature of corrosion, not only to gain insight into the microscopic process of corrosion, but also to predict the corrosion resistance of materials in specific environments, providing theoretical support for designing corrosion-resistant materials and formulating protection strategies. Li Y et al studied the electrochemical corrosion of Fe(111) surface, and found that Bi atoms had a great influence on the electrode potential, while Al and Si atoms significantly slowed down the anodic corrosion [30].

Cao Yuxin calculated the rare earth inclusions in steel with the help of first principles, (such as TiN, MnS, $Cao \cdot 2Al_2O_3$, Ce_2O_2S, $CeAlO_3$) and steel matrix are calculated by first principles, and the location of pitting initiation is judged by comparing the work functions [31]. As the germination site of pitting corrosion, the part with lower work function is dissolved first. If the work function of inclusions is lower than that of steel matrix, pitting corrosion occurs in inclusions themselves. On the contrary, it occurs in the steel matrix around the inclusion. It is found that MnS has a smaller work function than Ce_2O_2S, and it can be used as an induction source to induce pitting in the early stage. Combined with the continuous immersion experiment, it is found that at the initial stage of pitting corrosion, the inclusions form a micro-galvanic couple with the surrounding steel matrix. Due to the difference of work function, sulfide inclusions (such as MnS and Ce_2O_2S) dissolve preferentially as anodes, and the corrosion products produced by their dissolution will reduce the pH value of the solution, accelerate the corrosion rate and lead to partial dissolution of the steel matrix. When the sulfide is dissolved, the steel matrix continues to dissolve as the anode, and the pitting pit begins to expand. At the same time, the hydrolysis of metal cations makes the solution more acidic, and the inclusions with higher work function gradually dissolve. The corrosive Cl- influx accelerates the pitting expansion and finally forms stable pitting. Through first-principles calculation, it is found that rare earth inclusions (such as $CeAlO_3$ and Ce_2O_2S) are better than their counterparts. Other inclusions (such as MnS and $Cao \cdot 2Al_2O_3$) have higher work function, which indicates that they have better pitting corrosion resistance.

The common work functions (electronic work functions, EWF) of inclusions based on first-principles calculation and experimental research and their roles in corrosion are shown in Table 5.

Through atomic-level calculations, first-principles methods elucidate the electronic processes by which inclusions promote corrosion, providing a theoretical foundation for the development of corrosion-resistant steel via oxide metallurgy. Integrated with experimental investigations, the critical approach to optimizing the types and distribution of inclusions through rare earth treatment has been identified, thereby enhancing corrosion resistance and guiding the research and development of high-performance steels for marine engineering applications. Atomic-level simulations and analyses can more precisely predict material corrosion resistance, guide experimental explorations, and introduce new perspectives and technologies to materials science, thus advancing the development of efficient, environmentally friendly, and anti-corrosion technologies. Despite challenges associated with complex systems and large-scale simulations, first-principles calculations have achieved groundbreaking progress in corrosion control and industrial applications.

Table 5.
Work function (EWF) of common inclusions and its role in corrosion

Types of inclusions	Work function range (eV)	Compared with the steel matrix (α-Fe)	Corrosion sensitivity	Corrosion behavior
MnS	2.83-5.23	Most <steel matrix (4.52 eV)	tall	Preferential dissolved and induced pitting germination
$CaO·2Al_2O_3$	3.20-4.10	Part of the <steel matrix	secondary	If not covered by TiN, corrosion may be preferentially used
TiN	4.50-6.80	> Steel matrix	low	Inert, inhibiting corrosion extension
Ce_2O_2S	2.22-4.43	Most of the <steel substrate	secondary	The dissolution rate was lower than MnS, but still the pitting source
$CeAlO_3$	4.59-6.84	> Steel matrix	Very low	Almost do not participate in corrosion and inhibit pitting extension
Steel matrix (α-Fe)	~ 4.52 (121 crystal surface)	benchmark	—	Passivation of the membrane protection, but is locally susceptible to Cl^- attack
Al_2O_3	4.8-6.0	—	—	High work function, strong passivation ability, excellent corrosion resistance
SiO_2	4.3-5.1	—	—	Medium work function, with a general corrosion resistance

5. Conclusions

Oxide metallurgy technology based on first principles is one of the most effective methods to improve the toughness of welding heat affected zone, which plays an important role in the field of oxide metallurgy and can effectively predict and improve the comprehensive properties of steel. In this paper, from five aspects of adsorption, bulk phase, cluster calculation, inclusion interface and corrosion, it is concluded that first principles can not only reveal the microscopic mechanism of adsorption and predict the properties of materials, but also provide accurate information about clusters, master the mechanical properties of inclusion interfaces, and more accurately simulate the electronic structure of materials, providing theoretical support for designing corrosion-resistant materials, thus optimizing metallurgical processes and designing new alloy materials. However, according to the existing research findings, the first-principles oxide metallurgy technology is still insufficient, so the following problems need to be solved:

1) Clarify the mechanism of intragranular heterogeneous nucleation promoting the growth of acicular ferrite;
2) Unity of IGF in nucleation mechanism;
3) In DFT calculation, how to choose the appropriate basis set and energy truncation value to balance the calculation accuracy and cost;
4) Metallurgical process is often a dynamic process, and the evolution behavior and stability control methods of composite inclusions need to be studied. How to better combine theoretical calculation results with experimental data.

First principles can be combined with molecular dynamics simulation, experimental measurement, etc., and the influence of temperature, pressure and other factors can be considered in more detail, and the process of oxide metallurgy can be studied more comprehensively by cross-fusion and synergistic effect, and the theory and practice can be combined and promoted continuously.

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References

[1] Kojima, A., Kiyose, A., Uemori, R., Minagawa, M., Hoshino, M., Nakashima, T., Ishida, K. & Yasui, H. (2004). Super high HAZ toughness technology with fine microstructure imparted by fine particles. *Shinnittetsu Giho*. 90, 2-5.

[2] Takamura, J.I., Mizoguchi, S. (1990, October). Roles of oxides in steels performance. In *Proceedings of the Sixth International Iron and Steel Congress*, 21-26 October 1990 (pp. 591-597). Tokyo, Japan.

[3] Mizoguchi, S., & Takamura, J. I. (1990). Control of oxides as inoculants. In *Proceedings of the sixth international iron and steel congress*, 21-26 October 1990 (p. 598). Nagoya, Japan.

[4] Sawai, T., Wakoh, M., Ueshima, Y., Mzoguchi, S. (1990). Effect of Zr on the precipitation of MnS in low carbon steels. In Proceedings of the 6th International Iron and Steel Congress, 21-26 October 1990 (pp.605). Tokyo, Japan.

[5] Ogibayashi, S., Yamaguchi, K. & Hirai, M. (1990). The features of oxides in Ti-deoxidized steel metallurgy of oxides in steels-4. In Proceedings of Sixth International Iron

and Steel Congress, 21-26 October 1990 (pp.617). Tokyo, Japan.

[6] Zhihui Xiong. (2016). *Effect of Ti-containing oxides on the properties of pressure vessel steel*. University of Science and Technology Beijing.

[7] Oh, Y.J., Lee, S.Y., Byun, J.S., Shim, J.H. & Cho, Y.W. (2000). Non-metallic inclusions and acicular ferrite in low carbon steel. *Materials transactions, JIM.* 41(12), 1663-1669. https://doi.org/10.2320/matertrans1989.41.1663.

[8] Zhi, L.Q., Kiyoshi, F. & Nakagawa, I. (2004). High performance 550MPa high tensile steel sheet for construction - a new design standard strength thickness sheet "HBL385" to minimize steel frame cost and reduce environmental impact. *JFE Technical Report*. (5), 45-50.

[9] Kojima, A., Kiyose, A., Uemori, R., Minagawa, M., Hoshino, M., Nakashima, T., Ishida, K. & Yasui, H. (2004). Super high HAZ toughness technology with fine microstructure imparted by fine particles. *Nippon Steel Technical Report.* 90, 2-5.

[10] Kanazawa, S., Nakashima, A., Okamoto, K. & Kanaya, K. (1975). Improved toughness of weld fussion zone by fine TiN particles and development of a steel for large heat input welding. *Tetsu-to-hagané.* 61(11), 2589-2603. https://doi.org/10.2355/tetsutohagane1955.61.11_2589.

[11] Tomita, Y., Saito, N., Tsuzuki, T., Tokunaga, Y. & Okamoto, K. (1994). Improvement in HAZ toughness of steel by TiN-MnS addition. *ISIJ International*. 34(10), 829-835. https://doi.org/10.2355/isijinternational.34.829.

[12] Yamamoto, K., Hasegawa, T. & Takamura, J. I. (1996). Effect of boron on intra-granular ferrite formation in Ti-oxide bearing steels. *ISIJ international*. 36(1), 80-86. https://doi.org/10.2355/isijinternational.36.80.

[13] Fock, V. (1930). Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems. *Zeitschrift für Physik*. 61, 126-148. https://doi.org/10.1007/BF01340294.

[14] Thomas, L.H. (1927). The calculation of atomic fields. *Mathematical proceedings of the Cambridge philosophical society*. 23(5), 542-548. https://doi.org/10.1017/S0305004100011683 .

[15] Hohenberg, P. & Kohn, W. (1964). Inhomogeneous electron gas. *Physical Review.* 136(3B), B864. https://doi.org/10.1103/PhysRev.136.B864.

[16] Jin, Y. & Sanxie, W. (2016). First-principles calculation of Heusler alloy. *Science Press*. 30-31.

[17] Zhou, L-S., Ji, Y-Q. & Song, J-F. (2023). First-Principle of Adsorption Behavior of H Atom in PuGa Alloy. *Journal of Nuclear and Radiochemistry*. 45(2), 153-159.

[18] Junwei, L., Weimin, J., Shasha, L., Jintao, W. & Zhengcao, L. (2023). First-Principles Study of Surface Adsorption and Dissociation Behavior of O_2 on Uranium-Molybdenum System. *Rare Metal Materials and Engineering*. 52(5), 1650-1660.

[19] Wang, Q., Zhang, B.W., Liu, E.K., Guo, Z.H., Lu, S.L., Zheng, Y.X., Wu, X.Y, Zhang, Q.J., Wang, B. & Zhu, L.G. (2024). First-principles study on atomic formation and manganese diffusion in MnS/Mg-Ti-oxide complex inclusions in steel. *Ceramics International.* 50(24), 55263-55274. https://doi.org/10.1016/j.ceramint.2024.10.381.

[20] Pan, Y., Liu, Y. & Wei, Q. (2024). First-principles simulation study on the impact of monovalent Cu ion doping on the crystal structure and electrical properties of lead-free perovskite $Cs_2AgBiBr_6$. *Nuclear Techniques*. 47(04), 040503. DOI: 10.11889/j.0253-3219.2024.hjs.47.040503.

[21] Ju, J., Kang, M., Zhou, Y., Yang, C., Wang, K., Li, J., Wang, R., Fu H. & Wang, J. (2020). First-principles investigations of the stability, electronic structures, mechanical properties and thermodynamic properties of $Fe_xAl_yC_z$ compounds in Fe-Cr-B-Al-C alloy. *Journal of Physics and Chemistry of Solids*. 143, 109366, 1-9. https://doi.org/10.1016/j.jpcs.2020.109366.

[22] Liu, P., Han, X., Sun, D. & Wang, Q. (2019). The effect of interface atomic structure on the deformation mechanisms of Ti2AlN/TiAl composite under nanoindentation using MD simulations. *Journal of Physics: Condensed Matter*. 31(12), 125002, 1-12. DOI: 10.1088/1361-648X/aafd0e.

[23] Zheng, Y., Wang, F., Ai, T. & Li, C. (2017). Structural, elastic and electronic properties of B2-type modified by ternary additions FeAl-based intermetallics: First-principles study. *Journal of Alloys and Compounds.* 710, 581-588. https://doi.org/10.1016/j.jallcom.2017.03.308.

[24] Liu, Y. H., Chong, X. Y. & Jiang, Y. H. (2017). Mechanical properties and electronic structures of Fe-Al intermetallic. *Physica B: Condensed Matter*. 506, 1-11. https://doi.org/10.1016/j.physb.2016.10.032.

[25] Huo Jinxia, D (2023). *Study on adsorption polymerization of composite inclusions in oxide metallurgy*. North China University of Science and Technology.

[26] Xu, H. (2024). Atomic-scale insights into the electrochemical mechanisms of aluminum-sulfur batteries: A first-principles study of Al-S clusters on graphene. *Chemical Physics Letters.* 851, 141492, 1-7. https://doi.org/10.1016/j.cplett.2024.141492.

[27] Jiang Xin, D (2022). *Study on thermodynamic properties and nucleation mechanism of yttrium oxide in steel based on first principles.* Jiangxi University of Science and Technology.

[28] Zhang, J., Liu, H., Zhang, S., Ren, Q. & Zhang, L. (2023). Application of first-principles calculation methods in the study of inclusions in steel. *China Metallurgy*. 33(8), 6-16. DOI: 10.13228/j.boyuan.issn1006-9356.20230164.

[29] Yuan, X., Xiao, Y., Wang, G. & Zhang, L. (2021). TiN inducing ferrite nucleation based on the bcc-Fe/TiN interfaces formation at atomic scale by first-principles calculation. *Computational Materials Science*. 197, 110570, 1-11. https://doi.org/10.1016/j.commatsci.2021.110570.

[30] Li, Y., Zhou, R., Gao, T. & Chen, C. (2023). First-principles explain the anodic dissolution corrosion of stainless steel surface. *Computational Materials Science*. 229, 112392, 1-10. https://doi.org/10.1016/j.commatsci.2023.112392.

[31] Cao Yuxin. (2021). *Effect of rare earth Ce on pitting corrosion resistance and weldability of low alloy high strength steel*. Wuhan University of Science and Technology.