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<https://orcid.org/0000-0001-6132-1228>, Guo, J and Yang, Q **Insights into effect of CeO₂ on microstructures and wear resistance of hypereutectic high chromium cast iron as well as interface properties of CeO₂/M₇C₃☆.**

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Insights into effect of CeO₂ on microstructures and wear resistance of hypereutectic

high chromium cast iron as well as interface properties of CeO₂/M₇C₃

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Abstract: Rare earth oxide CeO_2 was introduced into the hypereutectic high chromium cast iron (HHCCI), in order to refine the pre-precipitated M_7C_3 carbides and improve their wear resistance in this paper. The evolution of microstructure was comprehensively analyzed through advanced microscopy techniques, including optical microscopy (OM) and scanning electron microscopy (SEM). Their friction coefficient and wear morphology were measured and the frictional morphology was observed using a white light confocal microscope. The interfacial compatibility between CeO_2 and M_7C_3 was investigated through lattice mismatch calculations and first-principles simulations. Experimental results demonstrate that 2.0 wt.% CeO_2 addition effectively reduces the average diameter of primary M_7C_3 carbides to $6.8\text{ }\mu\text{m}$, accompanied by an increased steady-state friction coefficient (from 0.58 to 0.63) and a 38.7% reduction in wear rate (from 4.675×10^{-6} to $2.865 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m}^{-1})$). Theoretical calculations reveal a lattice mismatch of 9.23% at the CeO_2 (111)/ M_7C_3 (0001) interface, which reveals that CeO_2 can function as the non-spontaneous core of M_7C_3 . Three distinct interface models (Ce- M_7C_3 , O1- M_7C_3 and O2- M_7C_3) were constructed, with the O2- M_7C_3 configuration exhibiting optimal interfacial stability through maximum adhesion work (16.29 J/m^2) and minimum interface energy (-9.49 J/m^2). Therefore, CeO_2 can serve as the non-spontaneous core of M_7C_3 to refine the pre-precipitated M_7C_3 carbide and enhance the wear resistance of the HHCCI.

1. Introduction

With excellent wear-resistance, the hypereutectic high chromium cast iron (HHCCI) is usually coated on the surface of the alloys, which have been interestingly applied in additive manufacturing fields to print different shape workpieces [1,2]. There are many pre-precipitated M_7C_3 carbide in HHCCI, which have high hardness and wear-resistance phase [3-5]. Higher carbon content levels lead to an enlargement of the pre-precipitated M_7C_3 carbides in the HHCCI, and with decrease of temperature they grow rapidly from the liquid metal [6]. When it reaches the eutectic temperature, they stop growing and keep very large size and polygon shape [7,8]. However, such large sized pre-precipitated M_7C_3 carbide will be desquamated very easily during the serving process of the workpieces, which decreases their wear-resistance [9-11]. Therefore, it is a key issue to refine the pre-precipitated M_7C_3 carbides in the HHCCI.

Recently, it is found that by adding some carbide forming elements such as Ti, Nb into the HHCCI, the size of the pre-precipitated M_7C_3 carbide can be decreased. Wu et al. [12] studied the pre-precipitated M_7C_3 carbides containing element Ti in the HHCCI, and found that the solute Ti atom can react with C atom to form TiC particles under certain conditions to act as the matrix of non-spontaneous nucleation of M_7C_3 carbides, so M_7C_3 carbides can be refined. Zhang et al. [13] introduced the elements Nb and Ti in the pre-precipitated M_7C_3 carbides synchronously, and found that (Nb, Ti)C can refine the pre-precipitated M_7C_3 carbides well. Meanwhile, RE oxides have also been found to refine the pre-precipitated M_7C_3 carbide. Yang et al. [14] considered that La_2O_3 additives were added into the HHCCI, and it discovers that the size of the pre-precipitated M_7C_3 carbides diminishes with the increase of La_2O_3 additives. Similarly, Yun [15] and Liu et al. [16] introduced Y_2O_3 into the HHCCI and it is found that the pre-precipitated M_7C_3 carbides are gradually refined by Y_2O_3 .

Rare earth elements (REEs), encompassing the lanthanide series supplemented by scandium (Sc) and yttrium (Y), exhibit distinctive chemical properties characterized by high chemical reactivity and pronounced affinity for oxygen and sulfur [17-19]. These unique characteristics underpin their widespread application in metallurgical processes, where REEs serve as purifying agents to eliminate impurities, refine grain structures, and enhance mechanical properties of engineered materials [20-22].

In RE oxides, with excellent properties and large reserves in nature, CeO_2 was added to the alloy as an additive to enhance the alloy mechanical properties [23-26]. Research by Gou et al. [27] on Fe-Cr-C-B hardfacing alloys incorporated with nano- CeO_2 demonstrated that cerium oxide nanoparticles facilitate heterogeneous nucleation of carbides through Ce-O-S compound formation, effectively enhancing wear resistance. Jiao et al. [28] researched on interface characteristics and nucleation pathways of $\gamma\text{-Fe/CeO}_2$ non-spontaneous nucleation interface. It concluded that CeO_2

serves as an effective substrate for non-spontaneous nucleation of $\gamma\text{-Fe}$, thereby refining austenite grain structures. However, the refinement role of CeO_2 on pre-precipitated M_7C_3 carbide has not been reported yet. Moreover, the interfacial properties between CeO_2 and the pre-precipitated M_7C_3 carbide are crucial for the refinement effect, while it is hard to investigate it by experimental.

The first principles calculation has been extensively used to reveal the surfacial and interfacial properties, such as the bonding configurations between atoms through electronic structure analysis [29-32]. Zou et al. [33] researched the influence of Cu doping on the of Al (100)/ Mg_2Si (111) interface with first principles method. It is found that the tensile strength of Al (100)/ Mg_2Si (111) interface is higher than that of undoped interface. Li et al. [34] studied the change of the adhesion work, electronic characteristics and tensile strength of WC/diamond interface with Ti doping by first principles methods. Therefore, the interface structure and binding strength between CeO_2 and M_7C_3 carbides can be calculated from the atomic scale by using the first principles method, and the mechanism of refine crystal strengthening of CeO_2 on the pre-precipitated M_7C_3 carbides can be explained.

In this paper, CeO_2 were added into the HHCCI, and its microstructure was investigated using optical microscope and scanning electron microscope. The friction coefficient and wear morphology of the HHCCI were measured by CSM friction wear testing machine and white light confocal microscope. The interfacial lattice misfit between CeO_2 and M_7C_3 phases was quantitatively determined through computational analysis. First-principles methods were employed to systematically investigate the structural and electronic properties of the $\text{CeO}_2/\text{M}_7\text{C}_3$ interface. The efficacy of CeO_2 as the non-spontaneous core of the pre-precipitated M_7C_3 carbide in HHCCI was evaluated and the wear resistance improvement mechanism of the HHCCI was revealed.

2. Experimental method and computational details

2.1 Experimental materials and method

The hypereutectic high chromium cast iron (Fe-25 wt.%Cr-4 wt.%C) was taken in this paper. Four specimens with different CeO_2 additions (0.0 wt.%, 1.0 wt.%, 2.0 wt.% and 4 wt.%) were prepared. The friction coefficient features of the samples were analyzed using an optical microscope (OM) of the Axiovert 200 MAT model and a Hitachi S4800 field emission scanning electron microscope (FESEM). Elemental composition was characterized using an energy dispersive spectrometer (EDS).

The hardness of the HHCCI were ascertained by the FM-ARS 9000 micro-Vickers sclerometer. The wear resistance of the HHCCI was measured by using CSM friction wear testing machine. The high hardness and wear resistance tungsten steel balls with a diameter of 3mm were applied as the friction pair. The load of 10 N was applied in the vertical direction for reciprocating friction wear with the frequency set to 3 Hz, amplitude set to 4mm, total travel distance set to 200m, and the acquisition frequency set to 30 Hz. Conscan white light confocal microscope was used to scan the width, depth and three-dimensional morphology of the surface abrasion marks on the surface of the alloy specimens after the friction wear experiments. The sampling range was a square area with a size of 1mm×1mm on both sides of the wear marks. The scanning results was processed by the Image Pro Plus software, the width and depth of the wear marks was measured, and the three-dimensional morphology was obtained.

2.2 Computational details

Density functional theory (DFT) based first-principles simulations were performed utilizing the Vienna Ab Initio Simulation Package (VASP) [35] to investigate the interfacial properties of the $\text{CeO}_2/\text{M}_7\text{C}_3$ interface. The exchange-correlation interactions were modeled with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional [36], while the projector augmented-wave (PAW) method [37] was adopted to represent ion-electron interactions. Convergence criteria for the plane-wave basis set cutoff energy (E_{cut}) and Brillouin zone k-point sampling density were rigorously validated prior to computational analysis. Therefore, E_{cut} was set as 450 eV, and k-point was set as $11 \times 11 \times 11$ in the optimization of the bulk structure of M_7C_3 . When the CeO_2 bulk structure was optimized, the E_{cut} was 500 eV and the k-point was $9 \times 9 \times 9$. When the surface properties of M_7C_3 and CeO_2 were calculated, E_{cut} were selected as 450 eV and 500 eV, k-point were $11 \times 11 \times 1$ and $9 \times 9 \times 1$.

3. Experimental results

3.1 Effect of CeO_2 on microstructure of the HHCCI

3.1.1 Morphology of the HHCCI

When the sample without the CeO_2 , the FESEM image of the HHCCI is shown in Fig. 1. The microstructure of the HHCCI mainly contains the pre-precipitated M_7C_3 carbide, eutectic M_7C_3 carbide and eutectic $\gamma\text{-Fe}$, in which, the pre-precipitated M_7C_3 carbides are polygonal shape, while the eutectic M_7C_3 carbides are in strip one. From Fig. 1, the semi-quantitative EDS analysis on pre-precipitated carbide (Position A), eutectic carbide (Position B) and eutectic matrix (Position C) were performed, and the results are given in Table 1.

From Table 1, the pre-precipitated M_7C_3 carbide and the eutectic M_7C_3 carbide both mainly consist of Fe, Cr and C. But the Cr and C content in the pre-precipitated M_7C_3 carbide is higher than that of Fe content. The microhardness of the pre-precipitated M_7C_3 carbide was measured, with a hardness of 1536 ± 27 HV, while the eutectic M_7C_3 carbide is only half that. This declares that the pre-precipitated M_7C_3

carbide is much harder and can act as the wear-resistant phase in the HHCCI.

3.1.2 Effect of CeO₂ on pre-precipitated M₇C₃ carbide

The size of the pre-precipitated M₇C₃ carbide in the HHCCI were statistically detected, which are shown in Fig. 2. From Fig. 2, with the increase of CeO₂ addition, the average size of the pre-precipitated M₇C₃ carbide is decreased firstly. When the CeO₂ addition reaches 2%, the average size starts to increase. The smallest average size of the pre-precipitated M₇C₃ carbide is achieved in the alloy with 2.0 wt.% CeO₂ addition, where the smallest size is 6.8 μm. Moreover, the size fluctuation of the pre-precipitated M₇C₃ carbide also depends on the CeO₂ addition. The most uniform one is also the alloy with 2.0 wt.% CeO₂ addition.

The SEM images of the two alloys are shown in Fig. 3. The darker-colored areas in the picture represent the pre-precipitated M₇C₃ carbides. Fig. 3 (a) and (b) show the microstructure of HHCCI before and after the addition of CeO₂, respectively. By comparing the two figures, it can be observed that after adding CeO₂, the primary M₇C₃ carbides have been significantly refined.

It can be seen that before and after the addition of CeO₂, the sizes of most M₇C₃ carbides were below 1000 μm². Among them, the size distribution of carbides in HHCCI was more dispersed, and some carbides had sizes exceeding 1000 μm². The size distribution of M₇C₃ carbides in HHCCI with CeO₂ was relatively concentrated, with most being below 250 μm², and only a small portion being within the range of 250 to 1000 μm². Thus, it can be concluded that the addition of CeO₂ not only enables the primary carbides to be further refined but also makes the size distribution of carbides more uniform.

3.1.3 Nucleation analysis of CeO₂ as pre-precipitated M₇C₃ carbide

The FESEM image of the HHCCI, when CeO₂ addition is 2.0 wt.%, is shown in Fig. 5, accompanied by the EDS results. Fig. 5(a) is the pre-precipitated M₇C₃ carbide morphology. There exists an inclusion within the pre-precipitated M₇C₃ carbide, which is marked by the circle. Its composition was detected by EDS, and the result is displayed in Fig. 5(b). From Fig. 5(b), the inclusion mainly consists of elements Ce and O. Because the carbide grows upon CeO₂ in Fig. 5(a), it indicates that CeO₂ maybe the non-spontaneous core of the pre-precipitated M₇C₃ carbide.

3.2 Effect of CeO₂ on friction performance of the HHCCI

3.2.1 Hardness of the HHCCI

The micro-Vickers hardness of M₇C₃ carbide and macro-Rockwell hardness of the specimens in the HHCCI and that with CeO₂ are shown in Fig. 6.

It is evident that the Vickers hardness of M₇C₃ carbide in the HHCCI is about HV 1450, and the Rockwell hardness of the HHCCI is HRC 60. The Vickers hardness of M₇C₃ carbide in the HHCCI with CeO₂ has no obvious change, but the Rockwell

hardness of the alloy is increased to about HRC 62. It is revealed that the addition of CeO₂ in the HHCCI refined and evenly distributed the M₇C₃ carbide, and improves the overall hardness of the HHCCI.

3.2.2 Friction coefficient of the HHCCI

The friction coefficient curves of the HHCCI and that with CeO₂ are shown in Fig. 7. From Fig. 7, it can be seen that the friction coefficient changes greatly in the early wear stage, which is the wear running-in stage. As the wear process progresses, it enters the stage of stable wear. The friction coefficient of the HHCCI is approximately 0.58. During the stable wear stage, wear occurs primarily via abrasive mechanisms due to spalling of large M₇C₃ carbides, leading to three-body wear. The friction coefficient of the HHCCI with CeO₂ is about 0.63, which is higher than that of the HHCCI. It is because M₇C₃ carbide is refined and less peeling, which can play a wear-resistant skeleton and play a greater wear-resistant role. Enhanced wear resistance in the alloy correlates directly with microstructural refinement of the primary M₇C₃ carbide phase, as evidenced by the experimental results.

3.2.3 Three-dimensional morphology of the HHCCI

The white confocal microscan of the wear marks of the HHCCI and that with CeO₂ is shown in Fig. 8. Fig. 8(a) – 8(b) are the three-dimensional morphology of wear marks, and different colors express different wear depths. It can be seen from the cross section that the wear depth of the HHCCI is very large and there is a deep furrow, which is due to the weakening of the wear resistance of large bulk pre-precipitated M₇C₃ carbide during the wear process, and the aggravation of wear caused by abrasive wear and the formation of furrow. The HHCCI with CeO₂ has the smallest wear depth and almost no furrow. It indicates that the pre-precipitated M₇C₃ carbide in the HHCCI is refined to enhance its wear resistance. Fig. 8(a') – 8(b') are the top view of the wear marks. It is clear that the wear marks width of the HHCCI with CeO₂ is small. 3 lines were taken randomly on the top view of the wear marks of the two HHCCI, and the depth and width of the wear marks at corresponding positions were measured, as shown in Fig. 8(a'') – 8(b''). The average depth and width of the wear marks of the HHCCI are 6.97 μm and 406 μm respectively. After adding CeO₂, the width and depth of the wear marks on the HHCCI with CeO₂ are decreased. The average depth is 4.01 μm, and the average width is 301 μm.

3.2.4 Wear rate of the HHCCI

Based on this, the wear rates of the HHCCI were calculated. The calculation formula is as follows:

$$K = V/F \cdot S \quad (1)$$

where V represents the total volume of the HHCCI lost after friction and wear (mm³); F enotes the applied normal contact pressure (N) during sliding; S corresponds to the total sliding distance (m) measured over the wear duration.

The cross-sectional area of the wear marks was obtained by Image-Pro plus software. The length of the wear marks is 8 mm, the positive pressure applied is 10 N, and the total distance is 200 m. As shown in Fig. 9, the wear rate of the HHCCI is $4.675 \times 10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m}^{-1})$, and that with CeO₂ is $2.865 \times 10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m}^{-1})$.

4. Computational results

4.1 Lattice mismatch degree of CeO₂/M₇C₃ interface

The two-dimensional lattice mismatch formula is as follow [38]:

$$\delta_{(hkl)_n}^{(hkl)_s} = \sum_{i=1}^3 [(|d_{[uvw]_s}^i \cos \theta - d_{[uvw]_n}^i| / d_{[uvw]_n}^i) / 3] \times 100\% \quad (2)$$

where $(hkl)_s$ is a primary crystallographic plane in the matrix material; $[uvw]_s$ is a principal direction within $(hkl)_s$; $d_{[uvw]_s}$ is the interatomic distances along the $[uvw]_s$; $(hkl)_n$ is a dominant lattice plane in the nucleating phase; $[uvw]_n$ is a major crystallographic orientation within $(hkl)_n$; $d_{[uvw]_n}$ is the interatomic distances along the $[uvw]_n$; θ is the angular deviation between $[uvw]_s$ and $[uvw]_n$; i is the evaluation parameters across three orthogonal low-index crystal.

When the lattice mismatch between the matrix and crystalline phase is smaller than 12%, crystalline phase can act as the non-spontaneous nucleation core of matrix. The various interfaces between the matrix and crystalline phase, which were established based on their planes and their lattice mismatch, are listed in Table 2. The mismatch degree of M₇C₃ (0001)//CeO₂ (111) interface is 9.23%. It is obvious that CeO₂ as non-spontaneous nucleation core of M₇C₃ is medium effective. Therefore, the interface model constructed by M₇C₃ (0001) plane and CeO₂ (111) plane was applied in the following.

4.2. Interface properties of CeO₂/M₇C₃

4.2.1 Crystal structure and bulk phase properties of CeO₂ and M₇C₃

Fig. 10 is the crystal structures of CeO₂ and M₇C₃, respectively. CeO₂ is Fm-3m space group of face centered cubic structure. The lattice constants were optimized, which are $a = b = c = 0.545$ nm. It is agreement with the previous research 0.541 nm [39]. M₇C₃ is P63mc space group of hexagonal structure. The lattice constants after optimizing are $a = b = 0.702$ nm, $c = 0.424$ nm. By comparing the optimization results with data [39-42] from reference as shown in Table 3, it is evident that the results are very close and can be used for subsequent calculations.

The computational bulk performances [43] of CeO₂ are presented in Fig. 11. Fig. 11(a) is the electronic band structure of CeO₂, with a large band gap between conduction and valence bands that suppresses electron excitation across the gap. Fig. 11(b) is the density of states of CeO₂ shows there is almost no electron at the Fermi level (marked by dashed lines), confirming the absence of metallic characteristics in this oxide

material. As energies ranging from -5 eV to nearly Fermi level, both the Ce-d and O-p orbitals display the density of states, while the O-p orbitals completely contain the Ce-d orbitals. The peak shapes and strength of Ce-d orbital are similar to those of O-p orbital at -5 –10 eV, which reveals that a strong orbital hybridization and then a covalent bond forms between the two atoms.

The bulk properties of M₇C₃ are shown in Fig. 12. Fig. 12(a) is the band structure of M₇C₃, which is composed of bands that traverse the Fermi level. The observed electronic transitions between valence and conduction bands implying the metallic properties of M₇C₃. Fig. 12(b) is the density of states of M₇C₃ carbide. At the Fermi level, the electrons are present in harmony with the band structure, mirroring the metallic characteristics of M₇C₃. It indicates the presence of metallic bonds within it. Within the energy range of -7.5 to -4.3 eV, significant contributions to the density of states arise from the d-orbitals of Fe and Cr, along with the p-orbital of C. Their peak morphologies and strength are similar, which evidences that the orbitals of Cr, Fe and C are entangled, and then a covalent bond is formed. Moreover, the gravity centers of Fe-d orbit, Cr-d orbit and C-p orbit are different, which suggests the ionic bond.

4.2.2 Surface convergence

It is known that when the interface mismatch degree is minuscule, the stability of the interface structure can be established [44]. The surface models were constructed with CeO₂ (111) and M₇C₃ (0001) plane, which are depicted in Fig. 13. As CeO₂ (111) is polar plane, the upper and lower planes of the model are terminated with the same atomic type to maintain symmetry. To eliminate the interactions between periodic images, a 15 Å vacuum spacer was incorporated into the computational model following rigorous convergence verification. For the atomic type in CeO₂ (111) plane, three surface models can be constructed. Fig. 13(a) – (c) demonstrate Ce, O1, and O2 as the terminations, while Fig. 13(d) displays the M₇C₃ (0001) surface model.

Ensuring the interior characteristics of surface model are identical to those of the bulk, the surface energy dependence on atomic layers should be computed. CeO₂ (111) and M₇C₃ (0001) are all polar surfaces, Botteger formula [45] is used to calculate their surface energy, which are as follows:

$$\sigma_{\text{CeO}_2(111)} = \frac{1}{2A} (E_{\text{slab}} - N_{\text{Ce}}\mu_{\text{Ce}}^{\text{slab}} - N_{\text{O}}\mu_{\text{O}}^{\text{slab}}) \quad (3)$$

$$\sigma_{\text{M}_7\text{C}_3(0001)} = \frac{1}{2A} (E_{\text{slab}} - N_{\text{Fe}}\mu_{\text{Fe}}^{\text{slab}} - N_{\text{Cr}}\mu_{\text{Cr}}^{\text{slab}} - N_{\text{C}}\mu_{\text{C}}^{\text{slab}}) \quad (4)$$

where E_{slab} is the computed energy of each atomic layer; N_{Ce} , N_{O} , N_{Fe} , N_{Cr} and N_{C} are the quantity of element Ce, O, Fe, Cr and C, respectively; $\mu_{\text{Ce}}^{\text{slab}}$, $\mu_{\text{O}}^{\text{slab}}$, $\mu_{\text{Fe}}^{\text{slab}}$, $\mu_{\text{Cr}}^{\text{slab}}$ and $\mu_{\text{C}}^{\text{slab}}$ are the chemical potential for the element Ce, O, Fe, Cr and C; A is the surface area.

After full relaxation, the atoms in the surface model are distributed stably and

reach equilibrium with the volume phase. The chemical potential of the surface model is thought to be equivalent to that of the bulk, thus leading to the following formulas being used to calculate it:

$$\mu_{\text{CeO}_2}^{\text{slab}} = \mu_{\text{CeO}_2}^{\text{bulk}} = \mu_{\text{Ce}}^{\text{slab}} + 2\mu_{\text{O}}^{\text{slab}} \quad (5)$$

$$\mu_{\text{M}_7\text{C}_3}^{\text{slab}} = \mu_{\text{M}_7\text{C}_3}^{\text{bulk}} = 3\mu_{\text{Fe}}^{\text{slab}} + 4\mu_{\text{Cr}}^{\text{slab}} + 3\mu_{\text{C}}^{\text{slab}} \quad (6)$$

where $\mu_{\text{CeO}_2}^{\text{bulk}}$ and $\mu_{\text{M}_7\text{C}_3}^{\text{bulk}}$ are the bulk phase structure energy of CeO_2 and M_7C_3 , respectively.

The stoichiometric relationship $N_{\text{Fe}} = N_{\text{C}}$ arises from the crystallographic configuration of M_7C_3 . Combined with formula (3) - (6), the surface energy formula can be expressed as:

$$\sigma_{\text{CeO}_2(111)} = \frac{1}{2A} (E_{\text{slab}} - N_{\text{Ce}}\mu_{\text{CeO}_2}^{\text{bulk}} + (2N_{\text{Ce}} - N_{\text{O}})\mu_{\text{O}}^{\text{slab}}) \quad (7)$$

$$\sigma_{\text{M}_7\text{C}_3(0001)} = \frac{1}{2A} (E_{\text{slab}} - \frac{N_{\text{Fe}}}{3}\mu_{\text{M}_7\text{C}_3}^{\text{bulk}} + (\frac{4}{3}N_{\text{Fe}} - N_{\text{Cr}})\mu_{\text{Cr}}^{\text{slab}}) \quad (8)$$

It can be approximated that $\mu_{\text{O}}^{\text{slab}} \approx \mu_{\text{O}}^{\text{bulk}}$, $\mu_{\text{Cr}}^{\text{slab}} \approx \mu_{\text{Cr}}^{\text{bulk}}$, and the surface energy of each terminating configurations can be calculated by bringing them into equations (7) and (8). The surface energies of three terminations about $\text{CeO}_2(111)$ surface models are given in [Table 4-6](#).

As is evident from Table 4, for Ce-termination model, surface energy converges to a stable value of 5.299 J/m², with negligible fluctuations observed upon reaching a 10-layer atomic configuration. From Table 5, surface energy converges to a stable value of 0.564 J/m² with 6 atomic layers for O1-terminated model. Table 6 reveals that the surface energy converges to a stable value of 3.768 J/m² in O2-termination surface models with 8 atomic layers.

The surface energies of M₇C₃ (0001) are listed in Table 7. The surface energy converges to a stable value of 3.031 J/m² with 17 atomic layers.

Therefore, the Ce-terminated CeO₂ (111) model containing 10 layers, O1-terminated one containing 6 layers, and O2-terminated one containing 8 layers, and the M₇C₃ (0001) model containing 17 layers are used to construct the interface model. By substituting each value into formula (7) and (8), the equations are simplified as follows:

$$\sigma_{\text{Ce-terminated-CeO}_2} = \frac{1}{2A} (E_{\text{slab}} - 16\mu_{\text{CeO}_2}^{\text{bulk}} + 8\mu_{\text{O}}^{\text{slab}}) \quad (9)$$

$$\sigma_{\text{O1-terminated-CeO}_2} = \frac{1}{2A} (E_{\text{slab}} - 8\mu_{\text{CeO}_2}^{\text{bulk}}) \quad (10)$$

$$\sigma_{\text{O2-terminated-CeO}_2} = \frac{1}{2A} (E_{\text{slab}} - 8\mu_{\text{CeO}_2}^{\text{bulk}} - 8\mu_{\text{O}}^{\text{slab}}) \quad (11)$$

$$\sigma_{\text{M}_7\text{C}_3(0001)} = \frac{1}{2A} (E_{\text{slab}} - 4\mu_{\text{M}_7\text{C}_3}^{\text{bulk}} - 3\mu_{\text{Cr}}) \quad (12)$$

It is well known that, the bulk phase exhibit marginally higher chemical potential of atoms compared to that in the surface model. Therefore, the following equations can be obtained:

$$\Delta\mu_{\text{O}} = \mu_{\text{O}}^{\text{slab}} - \mu_{\text{O}}^{\text{bulk}} \leq 0 \quad (13)$$

$$\Delta\mu_{\text{Cr}} = \mu_{\text{Cr}}^{\text{slab}} - \mu_{\text{Cr}}^{\text{bulk}} \leq 0 \quad (14)$$

The formulas of the volume phase formation energy are:

$$\mu_{\text{CeO}_2}^{\text{bulk}} = \mu_{\text{Ce}}^{\text{bulk}} + 2\mu_{\text{O}}^{\text{bulk}} + \Delta H_{\text{CeO}_2} \quad (15)$$

$$\mu_{\text{M}_7\text{C}_3}^{\text{bulk}} = 3\mu_{\text{Fe}}^{\text{bulk}} + 4\mu_{\text{Cr}}^{\text{bulk}} + 3\mu_{\text{C}}^{\text{bulk}} + \Delta H_{\text{M}_7\text{C}_3} \quad (16)$$

Combining equations (9) - (16), the equations can be given as follows:

$$\frac{1}{2}\Delta H_{\text{CeO}_2} \leq \mu_{\text{O}}^{\text{slab}} - \mu_{\text{O}}^{\text{bulk}} \leq 0 \quad (17)$$

$$\frac{1}{4}\Delta H_{\text{M}_7\text{C}_3} \leq \mu_{\text{Cr}}^{\text{slab}} - \mu_{\text{Cr}}^{\text{bulk}} \leq 0 \quad (18)$$

From above calculated results, the fluctuation curve of surface energies about CeO_2 (111) and M_7C_3 (0001) plane can be obtained, which is illustrated in Fig. 14. Fig. 14(a) is the correlation about surface energy and chemical potential ($\mu_{\text{O}}^{\text{slab}} - \mu_{\text{O}}^{\text{bulk}}$) of the Ce-termination with 10 layers, the O1-termination with 6 layers, and the O2-termination with 8 layers. It can be found that in the interval of $\mu_{\text{O}}^{\text{slab}} - \mu_{\text{O}}^{\text{bulk}}$, the surface energy curves of the three terminations on CeO_2 (111) plane are crossed, and three surface cases should be considered when building the interface. Fig. 14(b) is the interaction between surface energy and the chemical potential ($\mu_{\text{Cr}}^{\text{slab}} - \mu_{\text{Cr}}^{\text{bulk}}$) of the M_7C_3 (0001) plane. Since there is only one surface model for M_7C_3 (0001) plane, it is necessary to construct three different interface structures for CeO_2 and M_7C_3 planes.

4.3 Interface structure and stability

The three interface structures are illustrated in Fig. 15, which are the Ce-M₇C₃, O1-M₇C₃ and O2-M₇C₃ interface models, respectively, as seen in Fig. 15(a) – (C). And Fig. 15(a') – (c') are them vertical views.

The adhesion work of an ideal interface is defined as the reversible work required to separate an interface into two free surfaces. When the interface adhesion work is high, the likelihood of forming the interface is also high. The equation is given as follow [46]:

$$W_{ad} = \frac{1}{A}(E_{CeO_2} + E_{M_7C_3} - E_{CeO_2/M_7C_3}) \quad (19)$$

where E_{CeO_2} and $E_{M_7C_3}$ are the total surface energy of the CeO₂(111) and M₇C₃(0001) planes, respectively; E_{CeO_2/M_7C_3} is the total interface energy of the model; A is the interface area.

Based on formula (19), the ideal interface adhesion work of three interfaces are listed in Table 8. The result for W_{ad} is as follows: $W_{ad}^{O2-M_7C_3} > W_{ad}^{Ce-M_7C_3} > W_{ad}^{O1-M_7C_3}$, in which, $W_{ad}^{O2-M_7C_3}$ is the largest (16.29 J/m²).

The interface energy is evaluated the stability of a structure, which is a critical factor. Reduced interfacial energy corresponds to greater thermodynamic stability and enhanced propensity for interface formation. The equation is as follows [47]:

$$\gamma = \sigma_{CeO_2} + \sigma_{M_7C_3} - W_{ad} \quad (20)$$

where σ_{CeO_2} and $\sigma_{\text{M}_7\text{C}_3}$ are the surface energy of CeO_2 (100) and M_7C_3 (111) planes, respectively; W_{ad} is the adhesion work of CeO_2 (111)/ M_7C_3 (0001) interface.

From formula (20), the interface energies of three interfaces are listed in Table 9. It is evident that the interface energy of the three interfaces is very small, and the relationship for γ is as follows: $\gamma_{\text{O2-M}_7\text{C}_3} < \gamma_{\text{O1-M}_7\text{C}_3} < \gamma_{\text{Ce-M}_7\text{C}_3}$, in which, $\gamma_{\text{O2-M}_7\text{C}_3}$ is the smallest (-9.49 J/m²). Among them, the interface energies of O1-M₇C₃ and O2-M₇C₃ interface models are less than zero, which illustrates that the resistance can be formed spontaneously when the interface is formed.

Based on the calculated results both the adhesion work and interface energy, the adhesion work of O2-M₇C₃ interface model is the least and its interface energy is the greatest, which reveals that its structure is the most secure thermodynamically. It also shows that CeO_2 can be utilized as the nucleation core of M_7C_3 and the nucleation interface preferentially forms the interface structure of O2-M₇C₃.

4.4 Interfacial electronic structure and bonding properties

The electronic structures of the above three interface models were calculated too, and the charge transfer at the interfaces was examined. This representation of atom bonding at the interfaces of the three models was further examined, with the interface differential charge density (DCD), electron localization function (ELF) and density of states (DOS) being simultaneously studied.

The differential charge density $\Delta\rho$ is given as follow [48]:

$$\Delta\rho = \rho_{\text{Total}} - \rho_{\text{CeO}_2} - \rho_{\text{M}_7\text{C}_3} \quad (21)$$

where ρ_{Total} is the total charge density of the interface; ρ_{CeO_2} and $\rho_{\text{M}_7\text{C}_3}$ are the charge densities of isolate CeO₂ (111) and M₇C₃ (0001) planes, respectively.

The DCD of CeO₂ (111)/M₇C₃ (0001) interface model is illustrated in Fig. 16. The dotted line has been used to designate the interfaces. In order to form an interface, the atoms nearby will move. It results in atoms misarrangement and charges redistribution.

Fig. 16(a) is the DCD map of the Ce-M₇C₃ interface. Comparative charge density analysis reveals enhanced electron accumulation at Ce-C interfacial regions compared to Ce-Fe atomic pairs. At the same time, the O atoms of CeO₂ moves towards the interface and obtains some electrons, while the electric charge around Cr atoms is decreased, which reveals that ionic bond is formed of O-Cr. Fig. 16(b) is the DCD map of the O1-M₇C₃ interface. At the interface, O atoms exhibit significant charge accumulation, contrasting sharply with charge depletion observed near Fe and Cr atoms, suggesting electron transfer from Fe and Cr atoms to O atoms. Fig. 16(c) is the DCD map of the O2-M₇C₃ interface. At the interface, Cr and Fe atomic sites exhibit localized charge depletion, with greater electron deficiency observed at Cr positions compared to Fe. Concurrently, O atoms demonstrate significant electron density enrichment, indicating charge transfer from Fe and Cr atoms to O atoms.

The interface electronic structure has been analyzed by calculating the ELF, and the interface bonding properties analyzed by combining the DOS. The ELF range lies between 0 and 1; when it is set to 1, it signifies an ideal electronic localization state and when ELF is 0, it implies a completely localized state. When ELF is set to 0.5, it denotes a homogeneous electron gas state. The equation of ELF is as follows [49]:

$$\text{ELF} = 1 / [1 + (\frac{D_{(r)}}{D_{h(r)}})^2] \quad (22)$$

where $D_{(r)}$ is the real electron gas density; $D_{h(r)}$ is the homogeneous electron gas density.

The ELF between CeO₂ (111)/M₇C₃ (0001) interface is shown in Fig. 17. Fig. 17(a) is the ELF between the Ce-M₇C₃ interface. The ELF value between O and Cr atoms at the interface is 0 – 0.3, while the value between Ce and Fe atoms at the interface is 0.5 – 0.8. Therefore, the interface bond type of Ce-M₇C₃ interface is a hybrid bonds containing ionic bonds between O and Cr atoms, covalent bonds and metallic bonds between Ce and Fe atoms. Fig. 17(b) is the ELF of the O1-M₇C₃ interface. The ELF values between O, Fe, and Cr atoms at the interface span from 0 to 0.3, suggesting that the bonding between atoms is mainly ionic. Fig. 17(c) is the ELF of the O2-M₇C₃ interface. The ELF values between C and Cr atoms at the interface ranged from 0 to 0.2, and between O and Fe atoms from 0.2 to 0.5, suggesting the ionic bond and covalent bond.

The DOS of the three interface models are shown in Fig. 18. It is clear to see that the DOS at the Fermi level are larger than zero, which reveals the metallicity of CeO₂

(111)/M₇C₃ (0001) interface. In the same energy range, the DOS waveforms of different atomic are similar, which indicates that the electron orbitals are hybridized. Fig. 18(a) is the DOS of the Ce-M₇C₃ interface. It is obvious that the waveforms of the O atoms, Fe and Cr atoms are similar at -7 eV – -1 eV, while the waveforms have a large difference in the gravity center, which evidences the existence of ionic bonds. Fig. 18(b) is the DOS of the O1-M₇C₃ interface. The waveforms of O atoms, Fe and Cr atoms are similar to each other, while the waveforms gravity center is different at -7 eV– -1 eV. Therefore, it is considered that the bonding type of O1-M₇C₃ interface is mainly ionic bonds. Fig. 18(c) is the DOS of the O2-M₇C₃ interface. It is similar to O1-M₇C₃ interface. The waveforms of O atoms, Fe and Cr atoms are similar, while the gravity center of the waveforms is different at -7 eV– -1 eV. Therefore, it is considered that the bonding type of O2-M₇C₃ interface is mainly ionic bonds.

5. Conclusions

- (1) The size of pre-precipitated M_7C_3 carbide is the smallest, which is about 6.8 μm , when CeO_2 addition is 2.0 wt.%.
- (2) CeO_2 incorporation enhances the stable friction coefficient from 0.58 to 0.63 while reducing the wear rate by 38.7% (from 4.675×10^{-6} to $2.865 \times 10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m}^{-1})$). These improvements confirm significant optimization of wear resistance through CeO_2 modification.
- (3) The lattice mismatch degree between CeO_2 (111) and M_7C_3 (0001) plane is 9.23%. It reveals that CeO_2 can act as the non-spontaneous core of M_7C_3 carbide.
- (4) The O2- M_7C_3 interface model exhibiting maximum adhesion work (16.29 J/ m^2) and minimum interface energy (-9.49 J/ m^2). It demonstrates that the O2- M_7C_3 interface model is the most stable and can be formed spontaneously.
- (5) There are strong ionic bonds between O atoms, Fe and Cr atom at the O2- M_7C_3 interface, which illustrates the bonding effect of O2- M_7C_3 interface is obvious, and it has strong bonding property.

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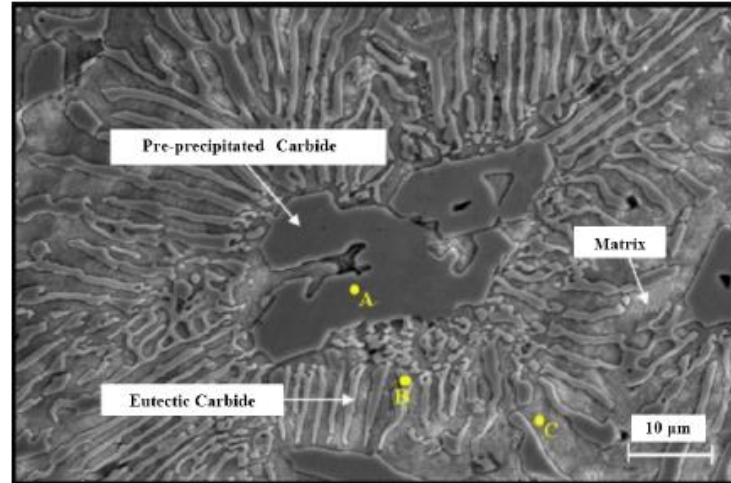


Fig. 1. FESEM image of the HHCCI.

Table 1 Micro-hardness and EDS results of micro-areas in HHCCI.

Marked position	Structure	Hardness (HV)	Chemical composition (wt.%)			
			C	Cr	Fe	Mn
A	Pre-precipitated M_7C_3 carbide	1536 ± 27	18.13	43.58	35.44	1.28
B	Eutectic M_7C_3 carbide	793 ± 20	8.684	24.45	65.52	1.72
C	Eutectic γ	799 ± 17	5.04	17.39	71.46	1.62

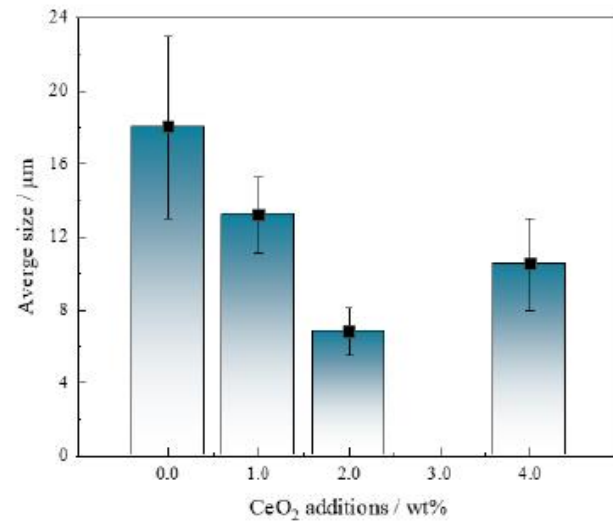


Fig. 2. Average size of the pre-precipitated M_7C_3 carbide with different CeO_2 additions.

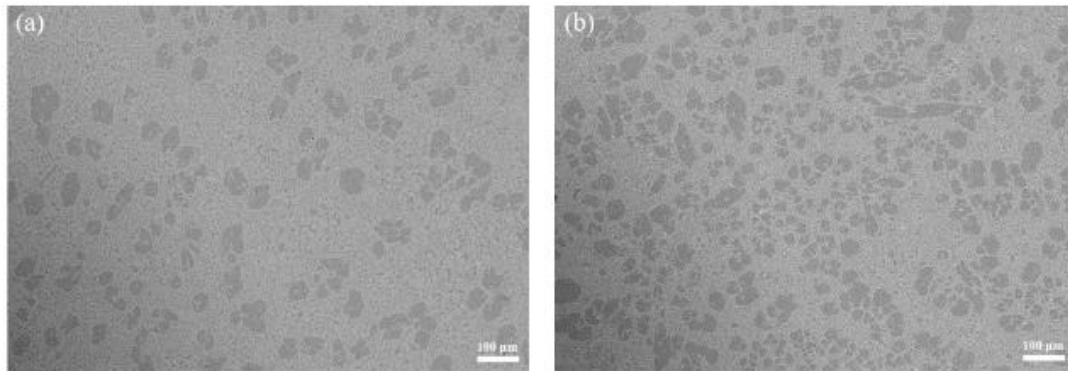


Fig. 3. SEM image of two alloys.

(a) HHCCI; (b) HHCCI with CeO_2 .

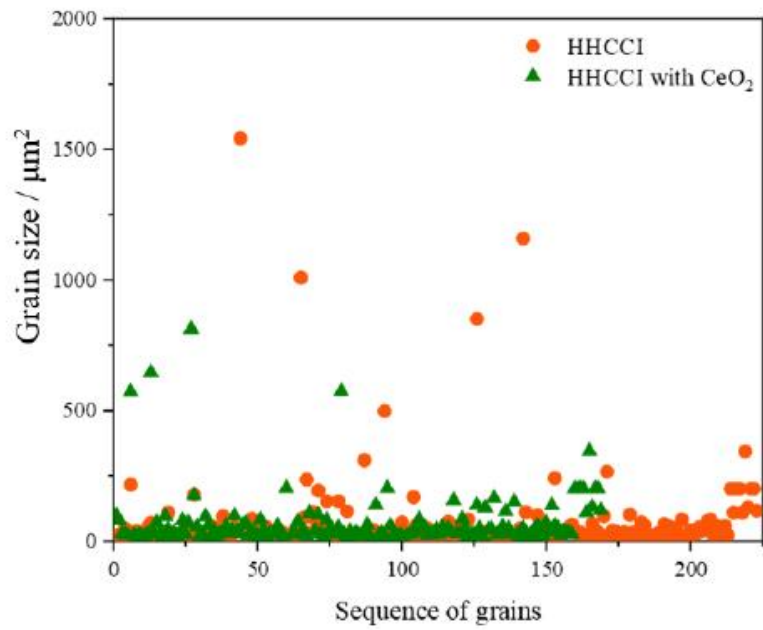


Fig. 4. Statistical results of size and distribution of M_7C_3 carbides.

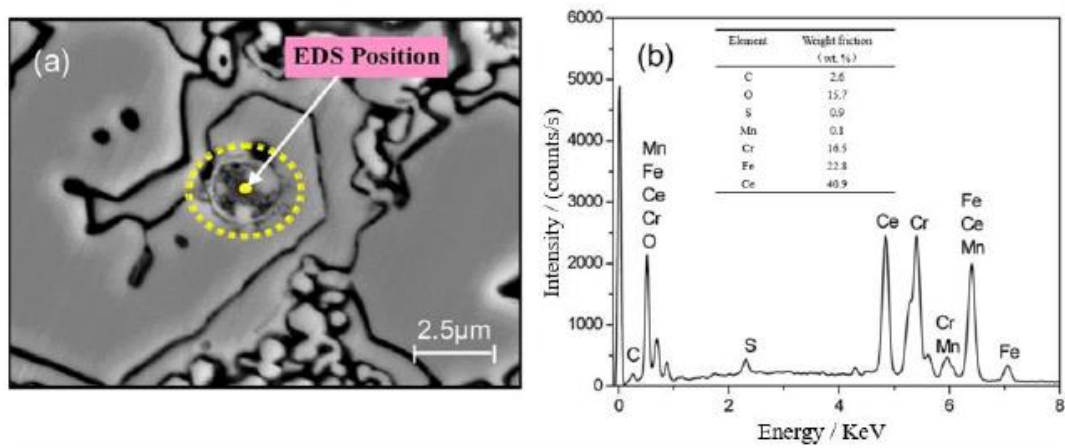


Fig. 5. FESEM image and EDS analysis of the inclusion in the HHCCI with 2.0 wt.% of CeO_2 .

(a) FESEM image; (b) EDS analysis.

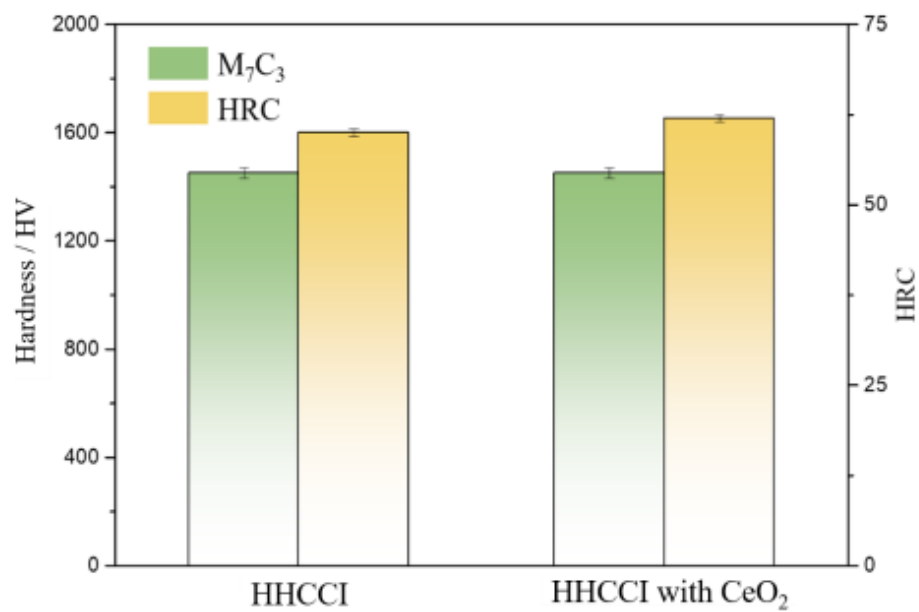


Fig. 6. Vickers hardness of M_7C_3 carbide and Rockwell hardness of specimen.

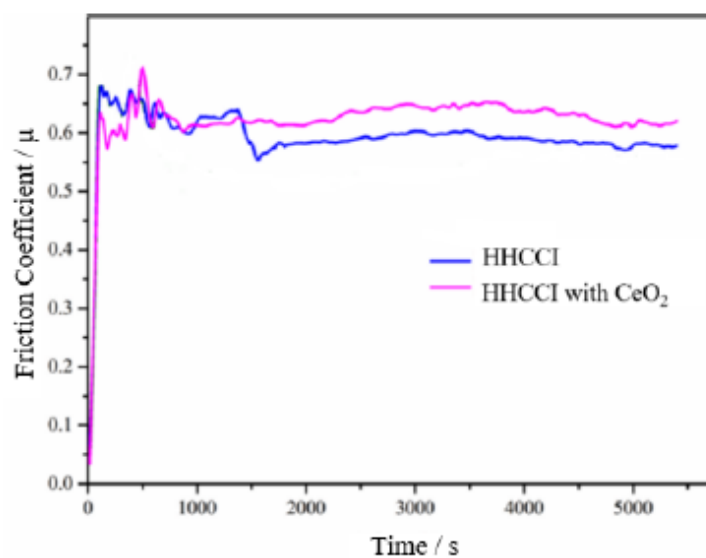


Fig. 7. Friction coefficient curves of the HHCCI.

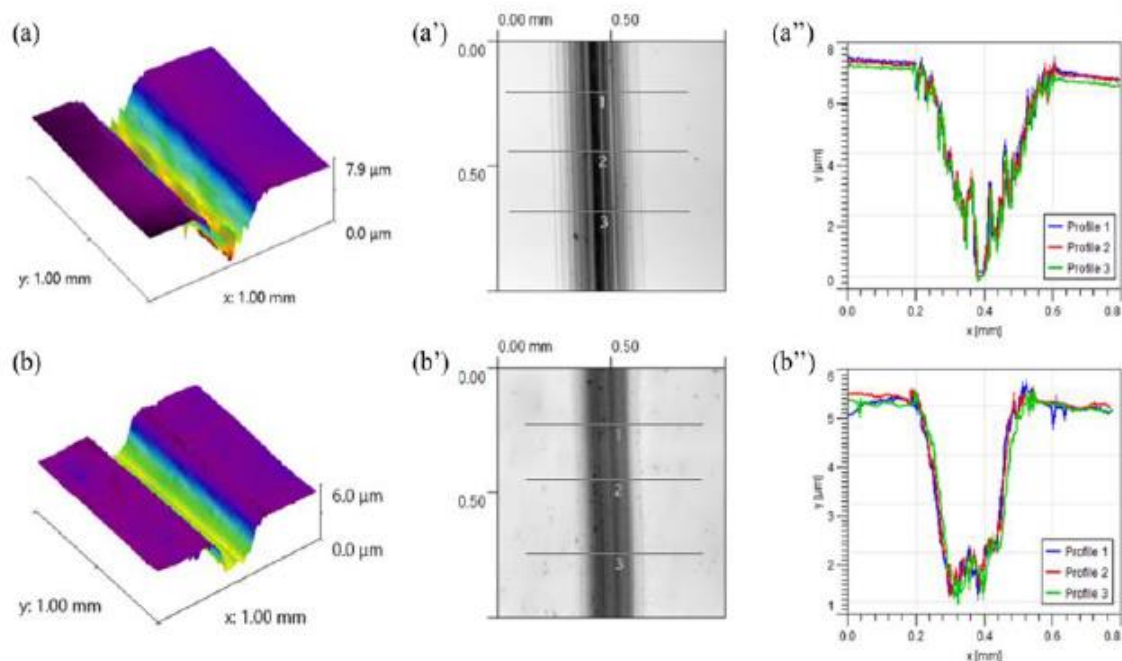


Fig. 8. White confocal microscan of the wear marks of the HHCCI.

(a)(b) Three-dimensional morphology of wear marks; (a') (b') Top view of wear marks;
(a'') (b'') Width and depth of wear marks

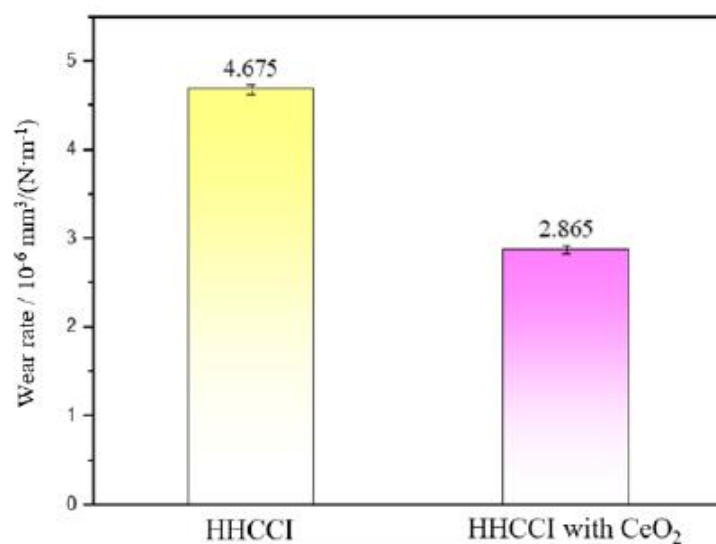


Fig. 9. Wear rate of the HHCCI.

Table 2 Calculated lattice mismatch degrees of M_7C_3/CeO_2 interface.

Matching face	M_7C_3 (0001)/ CeO_2 (111)		
M_7C_3 [uvw]	$[0\bar{1}0]$	$[210]$	$[100]$
CeO_2 [uvw]	$[1\bar{1}0]$	$[11\bar{2}]$	$[10\bar{1}]$
d M_7C_3 (Å)	7.0042	12.1316	14.0084
d CeO_2 (Å)	7.6509	13.2517	15.3018
$\delta(\%)$	9.23		

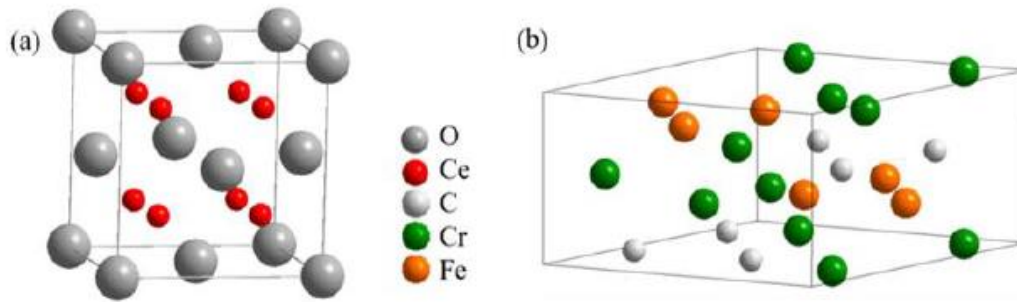


Fig. 10. Crystal structure of CeO_2 and M_7C_3 .
(a) CeO_2 ; (b) M_7C_3 .

Table 3 Calculated lattice constants of the bulk α -Fe, $\text{Fe}_3\text{Cr}_4\text{C}_3$ and $\text{Fe}_3\text{Cr}_3\text{YC}_3$ compared with other references and experimental data.

Table 3 Calculated lattice constants of the bulk α -Fe, $\text{Fe}_3\text{Cr}_4\text{C}_3$ and $\text{Fe}_3\text{Cr}_3\text{YC}_3$ compared with other references and experimental data.

Structures	Method	a(nm)	b(nm)	c(nm)	Volume((nm) ³)
CeO_2	GGA-PBE ^{this work}	0.545	0.545	0.545	0.162
	GGA-PBE ^a	0.544	0.544	0.544	0.161
	Exp. ^b	0.541	0.541	0.541	0.158
M_7C_3	GGA-PBE ^{this work}	0.702	0.702	0.424	0.181
	GGA-PBE ^c	0.699	0.499	0.427	0.181
	Exp. ^d	0.700	0.700	0.427	0.181

^aRef.[39]

^bRef.[40]

^cRef.[41]

^dRef.[42]

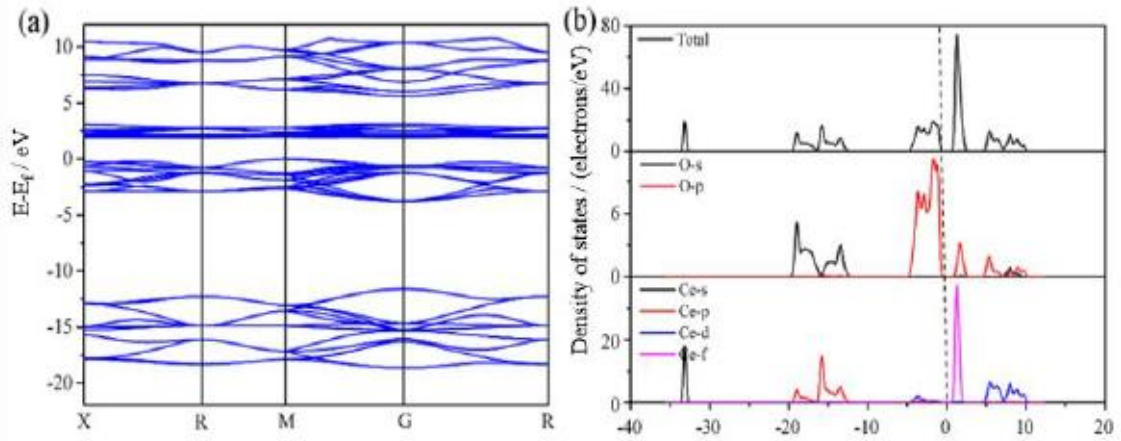


Fig.11. Band structure and density of states of CeO_2 [41].
(a) Band structure; (b) Density of states.

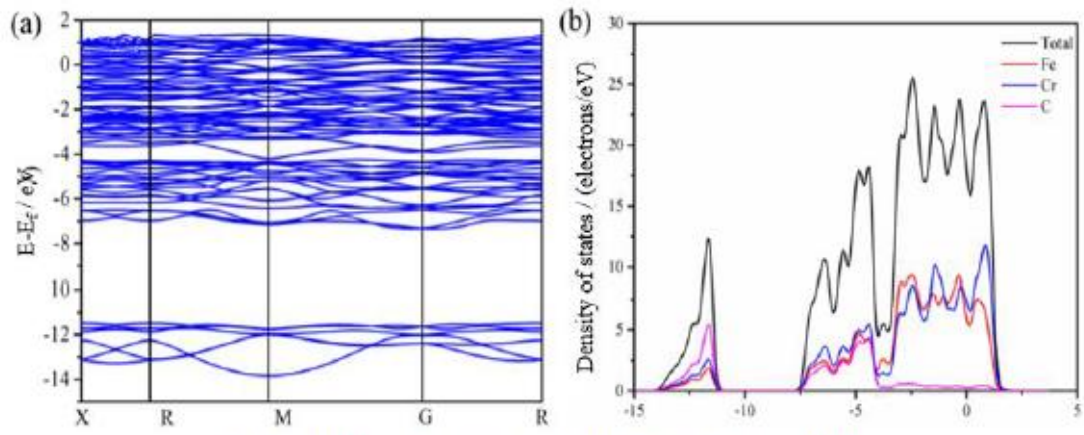


Fig.12. Band structure and density of states of M_7C_3 .
(a) Band structure; (b) Density of states.

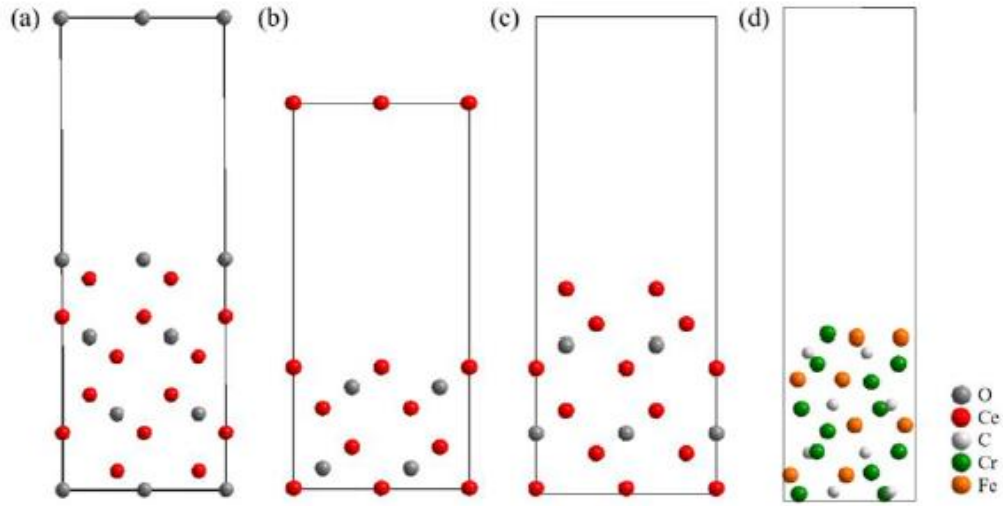


Fig. 13. Surface models of $\text{CeO}_2(111)$ and $\text{M}_7\text{C}_3(0001)$

(a) $\text{CeO}_2(111)$ Ce-termination; (b) $\text{CeO}_2(111)$ O1-termination; (c) $\text{CeO}_2(111)$ O2-termination; (d) $\text{M}_7\text{C}_3(0001)$ surface model.

Table 4 Calculated surface energy of $\text{CeO}_2(111)$ Ce-terminated models.

Layer (N)	4	7	10	13	16	19
Surface energy (J/m^2)	6.240	5.873	5.299	5.170	5.187	5.203

Table 5 Calculated surface energy of $\text{CeO}_2(111)$ O1-terminated models.

Layer (N)	3	6	9	12	15
Surface energy (J/m^2)	0.631	0.564	0.564	0.561	0.557

Table 6 Calculated surface energy of $\text{CeO}_2(111)$ O2-terminated models.

Layer (N)	5	8	11	14	17
Surface energy (J/m^2)	1.773	3.768	3.773	3.771	3.770

Table 7 Calculated surface energy of $\text{M}_7\text{C}_3(0001)$ plane.

Layer (N)	9	17	25	33
Surface energy (J/m^2)	3.174	3.031	2.997	2.958

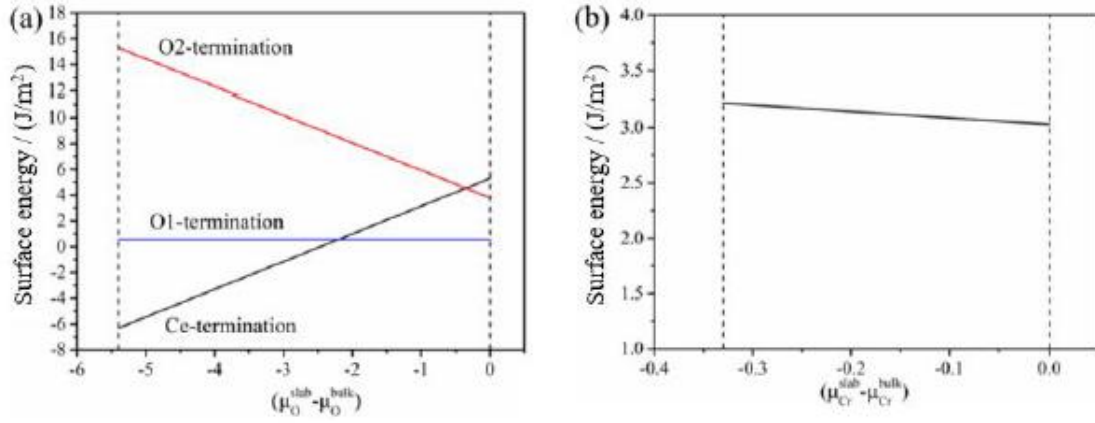


Fig. 14. Surface energy fluctuation of CeO_2 (111) and M_7C_3 (0001) planes.
(a) CeO_2 (111); (b) M_7C_3 (0001).

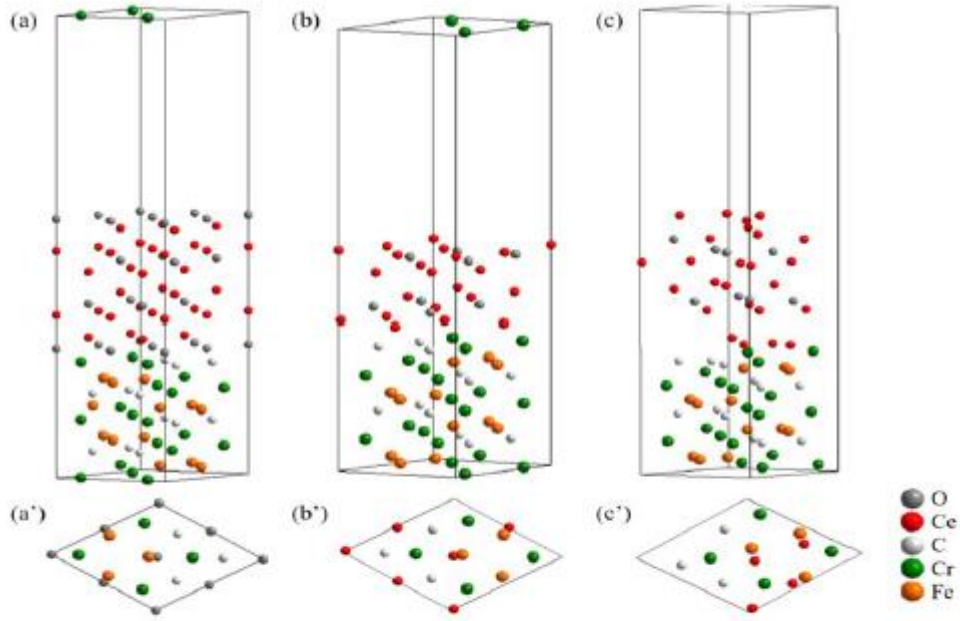


Fig. 15. Three interface models and their top views.
(a, a') $\text{Ce-M}_7\text{C}_3$ interface; (b, b') $\text{O1-M}_7\text{C}_3$ interface; (c, c') $\text{O2-M}_7\text{C}_3$ interface.

Table 8 Adhesion work of CeO_2 (111)/ M_7C_3 (0001) interface.

Interface	Ce – M_7C_3	O1 – M_7C_3	O2 – M_7C_3
Wad (J/m^2)	8.08	3.80	16.29

Table 9 Surface energy of CeO_2 (100)/ M_7C_3 (0001) interface.

Interface	Ce – M_7C_3	O1 – M_7C_3	O2 – M_7C_3
γ (J/m^2)	0.25	-0.21	-9.49

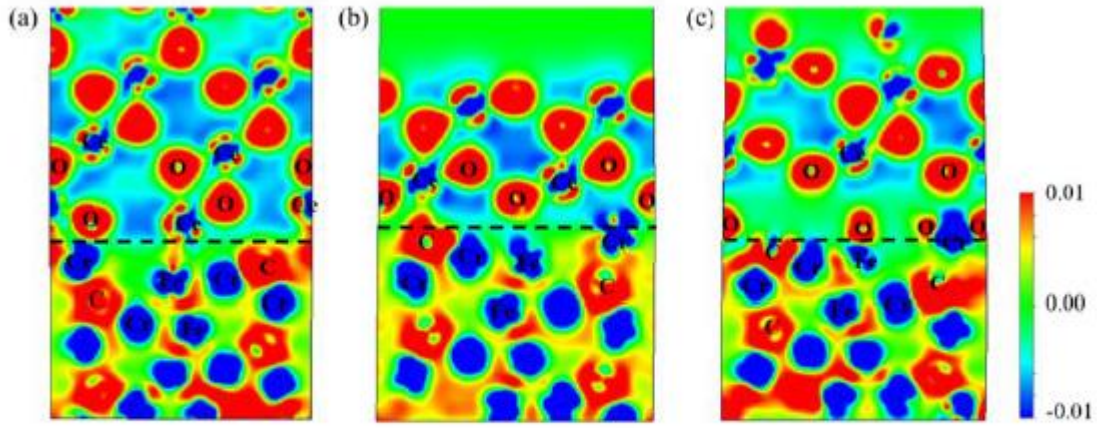


Fig. 16. DCD of CeO_2 (111)/ M_7C_3 (0001) interface.

(a) Ce – M_7C_3 ; (b) O1 – M_7C_3 ; (c) O2 – M_7C_3 .

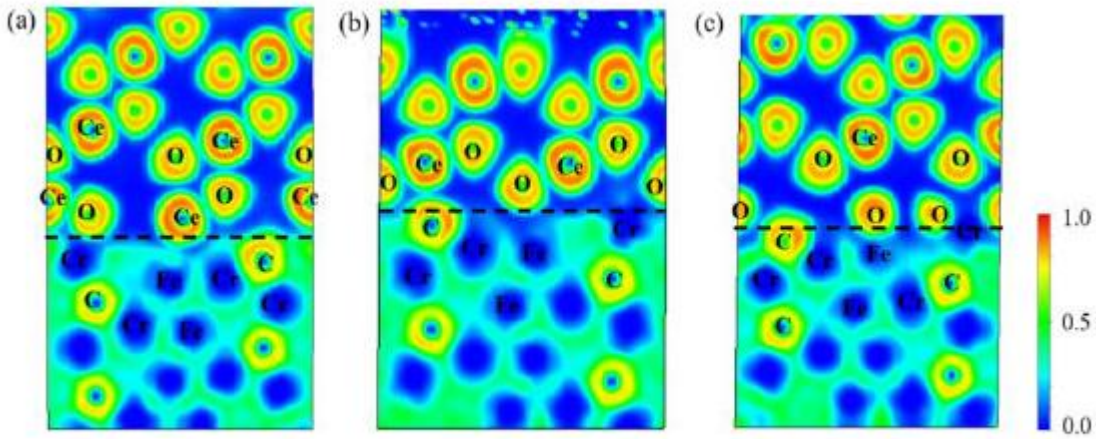


Fig. 17. ELF of CeO_2 (111)/ M_7C_3 (0001) interface.

(a) Ce – M_7C_3 ; (b) O1 – M_7C_3 ; (c) O2 – M_7C_3 .

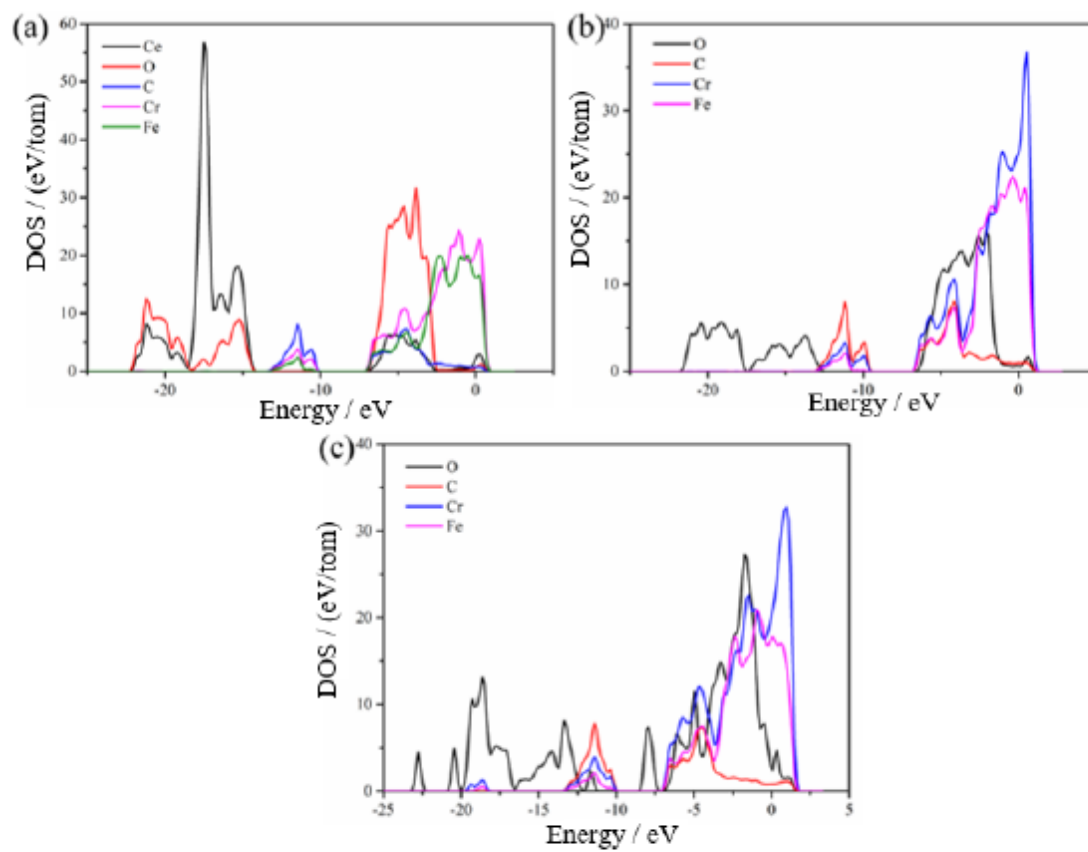


Fig. 18. DOS of CeO₂(111)/M₇C₃(0001) interface
(a) Ce-M₇C₃; (b) O1-M₇C₃; (c) O2-M₇C₃.