Enhanced mechanical properties in oxide-dispersion-strengthened alloys achieved *via* interface segregation of cation dopants

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ABSTRACT With significantly enhanced irradiation resistance, high-temperature strength, and creep resistance, oxide-dispersion-strengthened tungsten (ODS-W) alloys present tremendous potential for high-temperature applications. However, the oxide particles tend to segregate at W grain boundary and grow up (even to micron), greatly suppressing their strengthening effect. It is always a great challenge to effectively refine and disperse the oxide particles at W grain boundary. Here, we successfully developed a new type of cation-doped W-Y₂O₃ alloy *via* a wet chemical method and subsequent low-temperature sintering. It was found that proper cation doping could not only significantly refine the intergranular Y₂O₃ second phase particles but also dramatically improve the sinterability of W matrix. These doping effects, as a result, simultaneously enhance the strength and ductility of the W-Y₂O₃ alloy. It was confirmed that the segregation of cation dopants at the W/Y₂O₃ interface is the origin of these doping effects. Furthermore, X-ray photoemission spectra (XPS) analyses confirmed that cation dopant segregation also obviously affects the chemical bonding (i.e., W–O bond) along the W/Y₂O₃ interface. As a result, the rate-limiting mechanism for W grain growth is influenced remarkably, explaining well the difference of W grain size in various cation-doped W-Y₂O₃ alloys. For the refinement of intergranular Y₂O₃ particles, it can be understood well from both thermodynamic and kinetic views. Detailedly, W/Y₂O₃ interfacial energy and atom mobility for Y₂O₃ coarsening are all limited by cation dopant segregation. More importantly, this cation-doping approach can also be applicable to other ODS alloys for enhancing their comprehensive mechanical properties.

Keywords: oxide-dispersion-strengthened alloys, cation doping, interfacial segregation, strengthening-toughening

INTRODUCTION

Oxide-dispersion-strengthened (ODS) alloys exhibit remarkably enhanced high-temperature strength and creep resistance compared with their base materials, making them very attractive for applications in various fields such as aerospace [1,2], nuclear [3] and military industry [4]. Especially, for fusion application, the demanding work environment, including high-energy particle irradiation, high temperature field, high stress field and hydrogen retention, put forward a higher quality requirement for material selection [5]. Recently, ODS tungsten (ODS-W) alloys are considered as the most promising candidate for plasma facing materials (PFMs) due to their outstanding microstructural and mechanical stability, especially at high temperatures [3,6]. Generally, the intergranular oxide second phase particles can effectively pin grain boundary of W matrix, which is beneficial to the high-temperature microstructural stability of ODS-W alloys and then raises their recrystallization temperature [7]. The intragranular oxide particles, on the other hand, can inhibit the movement of dislocation through dispersion/dislocation interaction, contributing to the promotion of work hardening capacity of W matrix [8–10]. What is more notable is the abundant phase interface introduced by second phase particle in ODS-W alloys. Radiation defects can be absorbed and dispersed by these phase interface, which inhibits the presence of H/He bubbles in W alloys and then improves their radiation resistance [11,12]. In addition, the structural materials in future fission and fusion reactors are also challenges because of their high level of neutron displacement damage and high operating temperatures (500–1000°C) [13]. Fortunately, the high-temperature creep and tolerance to radiation damage of steels can be improved greatly by dispersing

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ultrafine oxide particles [14]. Due to these characteristics of ODS steels, they have been widely used as the candidate materials in fission and fusion applications.

Recently, the composite powder precursors for sintering ODS alloys were generally prepared by mechanical alloying or the wet chemical method [15–18]. For ODS steels, mechanical alloying is the most successful technology [19,20]. Combining mechanical alloying with hot isostatic pressing (HIP), commercial ODS steels on the 1000 kg scale with remarkably enhanced creep strength has been fabricated. In order to further improve the high-temperature performance of ODS steels, some important parameters such as impurity contents, microstructural refinement of matrix and homogeneous distribution of oxide particles should be controlled carefully. For the preparation of refractory metal alloys such as ODS-W and ODS-Mo, mechanical alloying and the wet chemical method are usually adopted. By sintering the powder precursor produced by mechanical alloying, Xie *et al.* [21] prepared a W-1% Y_2O_3 alloy. After ensuing rolling, refined equiaxed subgrains are full in elongated mother grains. This special microstructure not only weakens the anisotropy of the rolled plate but also is conducive to the simultaneous enhancement of ductility and strength. However, most of Y_2O_3 second phase particles with a size from 500 to 1000 nm are distributed at the grain boundary, and some are even larger than 1 μm [21]. For the wet chemical method, the uniform distribution of oxide second phase particles in composite powder can be controlled easily [22,23]. The refined alloy matrix particles possess tremendous driving force for rapid densification at lower sintering temperatures [24,25]. Nevertheless, after sintering of a Mo- La_2O_3 composite powder produced by liquid-liquid doping method, large-sized La_2O_3 particles (300–900 nm) still exist at Mo grain boundaries although the volume fraction of intragranular La_2O_3 particles is increased significantly [9]. Owing to deformation incompatibility, especially for the case of the larger intergranular oxide particles, severe stress concentration could be introduced at these particles easily, resulting in interfacial decohesion or particle cracking and eventual crack initiation along the grain boundary [9,10,26,27]. Consequently, the improvement effect of oxide second phase particle addition on the mechanical properties of alloy matrix is depressed greatly. Nowadays, it is urgent and still a great challenge to efficiently refine and disperse the oxide second phase particles within alloy matrix for achieving ODS alloys with excellent mechanical properties.

In this work, with the aim of refining intergranular

Y_2O_3 particles and further improving the mechanical properties of Y_2O_3 dispersion-strengthened W alloy, a new type of cation-doped W- Y_2O_3 composite powder precursor was successfully fabricated by the wet chemical method. After low-temperature sintering of this composite powder precursor, it was found that proper cation doping could not only significantly refine and disperse the intergranular Y_2O_3 second phase particles, but also dramatically improve the sinterability of W matrix. As a result, both the strength and ductility of the W- Y_2O_3 alloy are improved remarkably after cation doping, especially for La^{3+} doping. Through carefully characterizing, it was confirmed that the cation dopant segregation at the W/ Y_2O_3 interface is the origin of these doping effects. Furthermore, the effect mechanism of cation dopant segregation on the sinterability of W matrix and the refinement of intergranular Y_2O_3 particles were also discussed.

EXPERIMENTAL SECTION

Powder synthesis and reduction

W-2 vol% Y_2O_3 and the cation-doped W-2 vol% Y_2O_3 composite nanopowder precursors were synthesized through a traditional co-deposited wet chemical method. The cation dopants used here include Sc^{3+} , La^{3+} , Ti^{4+} , Zr^{4+} and Hf^{4+} . The contents of cation dopants in W- Y_2O_3 composite powder were determined by the volume fraction of corresponding ionic oxides. For example, the nominal composition of the Sc^{3+} -doped W- Y_2O_3 composite nanopowder precursors was W-2 vol% Y_2O_3 -0.4 vol% Sc_2O_3 . The volume fraction of other ionic oxides including La_2O_3 , TiO_2 , ZrO_2 and HfO_2 corresponding to cation dopants all had the same volume fraction with Sc_2O_3 .

$(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 4\text{H}_2\text{O}$ (APT, 99.95%, Aladdin) and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Aladdin) were used as raw materials, and the corresponding dopant sources were $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Aladdin), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Aladdin), TiCl_4 (99.99%, Aladdin), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (99.9%, Aladdin) and $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ (99.99%, Aldrich). Firstly, a certain amount of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and dopant sources were dissolved into distilled water where nitric acid (65%–68%) was added to suppress the hydrolysis of dopant cations. After complete dissolution, $(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 4\text{H}_2\text{O}$ was added into the solution and the codeposition reaction was initiated. About 30 min later, in order to restrain the further growth of tungsten oxide hydrate particles, anhydrous ethanol was added into the formed suspension. Then the suspension

was left to react continuously for another 3 h, followed by collecting the precipitation *via* filtration. The obtained precipitate was washed with water for three times and then kept in vacuum drying oven at 60°C for 24 h. The detailed synthesis process can be found in our previous work [28,29].

The subsequent thermal processes including calcination and reduction, were carried out in a tube furnace. In flowing argon atmosphere, the as-obtained codeposited powders were calcined at 450°C for 1 h firstly. After that, the atmosphere was changed into hydrogen and the temperature was raised to 600°C to reduce the composite oxide powders. About 3 h later, the temperature was increased to 800°C and then kept for 6 h. Finally, the reduced powders were cooled to room temperature in flowing hydrogen atmosphere and stored in argon glove box for later use.

Low-temperature sintering

The reduced powders were firstly pressed into raw compacts with a diameter of 10 mm and a height of 12 mm using cold isostatic pressing. Then these pressed compacts were sintered in a box furnace under hydrogen atmosphere. The temperature was gradually increased to 1600°C with a heating rate of 5°C min⁻¹ and the holding time at 1600°C was 4 h. The gas flow rate was maintained at around 500 mL min⁻¹ during the whole process of consolidation. Then the samples were cooled to room temperature at a rate of 10°C min⁻¹. The sintered alloys are denoted as W-Y-Sc, W-Y, W-Y-La, W-Y-Ti, W-Y-Zr and W-Y-Hf, respectively.

Characterization

The microstructure of sintered alloys was examined by scanning electron microscopy (SEM, Hitachi Model No. S 4800) and transmission electron microscopy (TEM, JEM-2100) equipped with energy-dispersive X-ray spectroscopy (EDX) detectors, respectively. High-resolution X-ray photoelectron spectroscopy (XPS) analyses were carried out using a Thermo VG Scientific ESCALAB 250XI spectrometer with an Al K α source. Data were acquired and analyzed using Advantage software (v5.967). All the binding energies were calibrated by setting the C 1s peak to 284.8 eV of the surface adventitious carbon. The hot compression tests of La³⁺-doped, Hf⁴⁺-doped and undoped W-Y₂O₃ alloys were conducted on a Gleeble-3500 thermo-simulation machine. The specimens used for the hot compression tests were 6 mm in diameter and 8 mm in height, and machined from the sintered alloys. The temperature for hot compression was 700°C and the strain

rate was 0.01 s⁻¹, and three tests were performed on each single-component sample.

RESULTS

The effect of cation doping on the microstructure, sinterability and mechanical property of W-Y₂O₃ alloy

Fig. S1 shows the X-ray diffraction (XRD) patterns of the composite powder precursors prepared by the wet chemical method. The absence of other impurity peaks in Fig. S1 indicates that these composite powders have been reduced completely. Using the Scherrer's equation, the average grain sizes of W are calculated to be 57.9, 61.1, 61.2, 58.3, 62.0 and 59.7 nm for Sc³⁺-doped, undoped, La³⁺-doped, Ti⁴⁺-doped, Zr⁴⁺-doped and Hf⁴⁺-doped W-Y₂O₃ composite powders, respectively. Therefore, it can be found that cation doping has no significant effect on the W grain size of composite powder precursors, which may originate from their uniform distribution in composite powders. Fig. 1a-f present the etched surfaces of undoped W-Y₂O₃ and cation-doped W-Y₂O₃ alloys after sintering at 1600°C. The average sizes of second phase particles were calculated statistically based on about 500 intergranular oxide particles, and the calculated values are summarized in Table S1. In undoped W-Y₂O₃ alloy, the oxide second phase particles possess an average size of 448 nm. After Sc³⁺ doping, the average size of oxide particles increases to 478 nm, as shown in Fig. 1a. For another trivalent cation La³⁺, in contrast, its doping significantly suppresses the average size of oxide particles to only 96 nm (Fig. 1c and Table S1) under the same sintering condition. Similarly, the doping effect of tetravalent cations on the size of oxide particles also depends on the cation dopant species. The Ti⁴⁺-doped W-Y₂O₃ alloy exhibits a larger size of Y₂O₃ particles (460 nm, Table S1) than the undoped W-Y₂O₃ alloy. However, the doping with Zr⁴⁺ has a slightly inhibitory effect on the coarsening of Y₂O₃ second phase particles, and the Y₂O₃ particles in Zr⁴⁺-doped W-Y₂O₃ alloy have an average size of 314 nm. Among all the tetravalent cations employed in our work, Hf⁴⁺ is the most effective dopant to limit Y₂O₃ growth, and an average size of 123 nm is obtained after sintering at 1600°C. Fig. S2 shows the distribution of oxide particle sizes in each alloy. Clearly, for the Sc³⁺ and Ti⁴⁺ dopants, the changes of size distributions are not obvious compared with the undoped alloy, although the oxides in corresponding cation-doped alloys are coarsened. In contrast, La³⁺, Hf⁴⁺ and Zr⁴⁺ dopants could not only significantly refine the oxide sizes but also shrink their size distributions. That is, the oxide particles in

Figure 1 (a–f) Etched surfaces and (g–l) fracture surfaces of undoped W-Y₂O₃ and cation-doped W-Y₂O₃ alloys sintered at 1600°C, including (a, g) Sc³⁺-doped W-Y₂O₃ alloy, (b, h) undoped W-Y₂O₃ alloy, (c, i) La³⁺-doped W-Y₂O₃ alloy, (d, j) Ti⁴⁺-doped W-Y₂O₃ alloy, (e, k) Zr⁴⁺-doped W-Y₂O₃ alloy and (f, l) Hf⁴⁺-doped W-Y₂O₃ alloy. The W matrix in (a–f) is denoted by the blue contrast and intergranular second phase particles are denoted by the red contrast.

these cation-doped alloys have more uniform sizes. In order to exclude the influence of dopant concentration on the refinement of oxide particles, especially for the Sc³⁺ and Ti⁴⁺ doping, Sc³⁺ or Ti⁴⁺ dopants with different concentrations from 0.4 to 2 vol% were added in the W-Y₂O₃ composite nanopowder precursor, and the results are presented in Figs S3 and S4, respectively. It can be found that, whether Sc³⁺ doping or Ti⁴⁺ doping, the average sizes of intergranular Y₂O₃ particles all increase with the increasing cation dopant concentration. Besides, the fraction of large-sized Y₂O₃ particles also has a positive correlation with the cation dopant concentration, which indicates, different from La³⁺, Zr⁴⁺ and Hf⁴⁺ doping, Sc³⁺ and Ti⁴⁺ doping cannot refine the intergranular Y₂O₃ particles, independent with their dopant concentration.

Fig. 1g–l show the fracture surfaces of undoped and

cation-doped W-Y₂O₃ alloys. The sinterability of W skeleton in undoped and cation-doped W-Y₂O₃ alloys can be reflected to a large extent by the average W grain size calculated from these micrographs (about 500 randomly selected W grains). Noteworthily, the trivalent cation-doped W-Y₂O₃ alloys and tetravalent cation-doped W-Y₂O₃ alloys present completely opposite grain growth trend. Typically, for the trivalent cation doping, the W grain growth is gradually suppressed as the oxide particles are refined from Sc³⁺ to La³⁺ doping, as summarized in Table S1. Conversely, for the tetravalent cation doping, W grain growth is promoted with the refinement of oxide particles from Ti⁴⁺, Zr⁴⁺ to Hf⁴⁺ doping.

Given a system containing finely dispersed oxide second phase particles, the grain microstructure state of metal matrix could be attributed to the pinning force exerted by the intergranular oxide particles. If the oxide

particles are considered as immovable, the limiting grain size of metal matrix should be proportional to the particle radius and inversely proportional to the volume fraction of intergranular particles under a certain sintering condition according to the Zener relation [30,31]. For the same volume fraction of oxide, smaller particle size is more effective at pinning grain boundary migration [32]. Therefore, compared with undoped W-Y₂O₃ alloy, it is understandable that Sc³⁺-doped and Ti⁴⁺-doped W-Y₂O₃ alloys both have larger W grain sizes (1160 and 1200 nm, respectively) because of the coarsening of Y₂O₃ second phase particles. And it is also reasonable that La³⁺-doped W-Y₂O₃ alloy exhibits a smaller W grain size (770 nm) than undoped W-Y₂O₃ alloy due to the refinement of Y₂O₃ particles. But it is abnormal that Zr⁴⁺ and Hf⁴⁺ doping increase the W grain size compared with undoped W-Y₂O₃ alloy, considering that they also refine the oxide particles remarkably, as shown in Table S1. Based on previous studies, W grain growth and W matrix densification are ascribed to grain boundary diffusion or surface diffusion [33,34], and the present results indicate that cation doping probably play a key role in altering the diffusivity of W, which exactly is the origin of this doping effect [35,36]. For example, the diffusivity of W is supposed to be accelerated by Hf⁴⁺ doping, thus improving the sinterability of W matrix. However, for the case of La³⁺ doping, the diffusivity of W might be suppressed, which leads to the retardation of W grain growth. This speculation will be discussed detailedly in the later section.

In consideration of the significant microstructural change caused by cation doping, including the size of intergranular Y₂O₃ particles and the grain size of W matrix, the mechanical properties of cation-doped W-Y₂O₃ alloys should be affected dramatically. Taking La³⁺-doped and Hf⁴⁺-doped W-Y₂O₃ alloys with the most obvious microstructural change for examples, Fig. 2 presents the true stress-strain curves of these two alloys tested at 700°C. The curve of undoped W-Y₂O₃ alloy is also provided for comparison. The compressive properties measured from Fig. 2 are summarized and listed in Table S2. It can be seen that the undoped W-Y₂O₃ alloy has an ultimate strength of 744.8 MPa, together with a strain-to-failure of 30.5% and a uniform shrinkage of 17.9%. After La³⁺ doping, the alloy exhibits both enhanced strength (800.7 MPa) and improved ductility (37.8%). Meanwhile, the uniform shrinkage of La³⁺-doped W-Y₂O₃ alloy is 30.7% (increasing from 17.9% to 23.4%) higher than the undoped W-Y₂O₃ alloy. However, Hf⁴⁺-doping leads to a remarkable decrease in ultimate

Figure 2 Compressive true stress-strain curves of undoped, La³⁺- and Hf⁴⁺-doped W-Y₂O₃ alloys at 700°C.

strength (638.2 MPa), although its strain-to-failure increases evidently to 38.9%. These results explicitly confirm that the mechanical properties of W-Y₂O₃ alloys can be effectively improved by proper cation doping *via* tailoring their microstructures. To the best of our knowledge, cation doping, especially La³⁺ doping, is firstly reported to be capable of simultaneously enhancing the strength and ductility of W-Y₂O₃ alloy.

The characterization of cation dopant segregation

In order to explore the role of dopant cations, the distribution of different cation dopants in corresponding alloys should be investigated firstly. Fig. 3a, c show the high angle annular dark-field-scanning TEM (HAADF-STEM) images from TEM of an intergranular oxide particle in La³⁺-doped and Hf⁴⁺-doped W-Y₂O₃ alloys, respectively. Interestingly, it can be observed that some areas with brighter contrast than the matrix of Y₂O₃ particles appear at the W/Y₂O₃ interface in both alloys. The brighter contrast is due to the higher atomic number or Z contrast of element, which preliminarily indicates some components in cation-doped alloys tend to segregate in the vicinity of W/Y₂O₃ interface. The orange lines in these images are the routes of EDX line scan for analyzing the elemental distribution and the corresponding results are present in Fig. 3b, d, respectively. The La-M and Hf-M signals demonstrate that La³⁺ and Hf⁴⁺ dopants could segregate from Y₂O₃ matrix to W/Y₂O₃ interface during the process of sintering. EDX line scan of the Y₂O₃ particle in the Zr⁴⁺-doped W-Y₂O₃ alloy (Fig. S5) also reveals the segregation of Zr⁴⁺ dopant at the W/Y₂O₃ interface, as observed for La³⁺ and Hf⁴⁺ dopants. However, what calls for special attention is that the segregation

Figure 3 HAADF images from TEM of an oxide particle at W grain boundary in (a) La³⁺- and (c) Hf⁴⁺-doped W-Y₂O₃ alloys, where the orange lines are the routes of EDX line scan, and the results are presented in (b, d), respectively.

region in Zr⁴⁺-doped W-Y₂O₃ alloy is recognized easily only in the nanosized Y₂O₃ particles. For most oxide particles with submicron size in spite of finer than that in undoped W-Y₂O₃ alloy, the Zr⁴⁺ dopant is detected homogeneously in the Y₂O₃ matrix, which suggests the segregation of Zr⁴⁺ dopant in the W-Y₂O₃ system is less compared with La³⁺ and Hf⁴⁺ dopants. Accordingly, it can be found that the refinement of oxide particles is closely associated with the segregation tendency of cation dopants (Table S1). This conclusion is also supported by the elemental mapping for the Y₂O₃ particles in Sc³⁺- and Ti⁴⁺-doped W-Y₂O₃ alloys, as shown in Figs S6 and S7, respectively. The average sizes of oxide particles in these alloys are all larger than that in the undoped W-Y₂O₃ alloy. From the EDS maps for special elements, it can be found that Sc³⁺ and Ti⁴⁺ dopants distribute homogeneously within the Y₂O₃ matrix without any evidence of segregation (Figs S6 and S7). This result suggests that Sc³⁺ and Ti⁴⁺ dopants seem to react with Y₂O₃ and form thermodynamically stable ternary oxides such as Sc-Y-O

and Ti-Y-O, losing their ability to refine Y₂O₃ particles.

Fig. 4a shows a TEM image of an oxide particle in La³⁺-doped W-Y₂O₃ alloy. It can be clearly seen that segregated areas with gray contrast appear at the W/Y₂O₃ interface and their corresponding high-resolution TEM (HRTEM) images are exhibited in Fig. 4b, c. Lattice fringes for three areas including W matrix, segregated area and Y₂O₃ particle can be observed clearly in these HRTEM images. Therefore, the segregation area of La³⁺ dopant exists in the form of crystal. Fig. 4d-f present the fast Fourier transform (FFT) of these three areas (denoted as 1, 2, 3, respectively) in Fig. 4c. The identical diffraction spots in Fig. 4d, e indicate the crystallographic orientation of Y₂O₃ is not altered by the segregation of La³⁺ dopant, suggesting the fully coherent interface relationship between the segregation area and Y₂O₃ matrix. In this regard, it is suggested that the segregation of dopant cation is a process of replacing the site of host cation Y. Therefore, the interface relationship of tungsten and segregation area still retains the initial interface relationship of tungsten

Figure 4 (a) Low-magnification TEM image of an oxide particle in La^{3+} -doped $\text{W-Y}_2\text{O}_3$ alloy. (b, c) HRTEM images of $\text{W/Y}_2\text{O}_3$ interface in (a). (d–f) FFT of three areas (denoted as 1, 2, 3, respectively) in (c). (g, h) Low-magnification TEM images of oxide particles in Hf^{4+} -doped $\text{W-Y}_2\text{O}_3$ alloy. (i, j) HRTEM images of $\text{W/Y}_2\text{O}_3$ interface in (h). (k, l) FFT of these two areas (denoted as 1, 2, respectively) in (j).

and Y_2O_3 before segregation. Furthermore, Fig. 4f shows that there is a defined orientational relationship between the Y_2O_3 particles and W matrix, i.e., $\text{W}(110)//\text{Y}_2\text{O}_3(200)$. Fig. 4g, h show the TEM images of oxide particles in the Hf^{4+} -doped $\text{W-Y}_2\text{O}_3$ alloy. As observed in Fig. 4g, segregation areas with gray contrast also appear at the $\text{W/Y}_2\text{O}_3$ interfaces. Distinct lattice fringes can also be found in the HRTEM image of segregated areas (Fig. 4i, j), indicating the segregation of Hf^{4+} dopant also exists in the form of crystal. Fig. 4k, l are the FFT of the Hf^{4+} segregation area at the $\text{W/Y}_2\text{O}_3$ interface and inner Y_2O_3 matrix, respectively, and verify again the fully coherent interface be-

tween them. These observations directly reveal the segregation of La^{3+} and Hf^{4+} dopants at the $\text{W/Y}_2\text{O}_3$ interfaces, which is fully consistent with the EDX line scan (Fig. 3).

DISCUSSION

The effect mechanism of cation dopant segregation on the sinterability of W matrix and the refinement of intergranular Y_2O_3 particles

As mentioned above, for the isovalent dopant cations such as Sc^{3+} and La^{3+} , the sinterability of W matrix in

cation-doped $W-Y_2O_3$ alloys is suppressed with the increase of segregation degree (i.e., the segregation tendency of cation dopants), while for the aliovalent dopant cations such as Ti^{4+} , Zr^{4+} and Hf^{4+} , the segregation of cation dopants promote the sinterability of W matrix. According to previous study, the change of sinterability of W matrix is closely associated with the alteration in diffusivity of W owing to the cation doping [33]. In order to discover the reason behind this phenomenon, the mass transport mechanism of W matrix in $W-Y_2O_3$ composite powder prepared by the wet chemical method during the low-temperature sintering process should be investigated firstly. The detailed research on this topic has been reported in our previous work [37]. Briefly, the integral and differential methods deduced from the well-known grain growth power law were used to analyze the non-isothermal sintering data [34,38,39]. Consequently, it was found that, for the $W-Y_2O_3$ system, grain boundary diffusion is responsible for the mass transport mechanism during the low-temperature sintering process. Thus, according to the classical grain growth model [40], the rate-limiting mechanism for W grain growth in the $W-Y_2O_3$ system will be significantly affected by the diffusion along the W/Y_2O_3 interface. Due to the chemical bonding between W and O along the W/Y_2O_3 interface, the diffu-

sivity of W in the $W-Y_2O_3$ system decreases remarkably, thus suppressing the sinterability of W matrix [37,41].

Once cation dopants segregate to the W/Y_2O_3 interface, the chemical bonding along this interface might be affected prominently, influencing the sinterability of W matrix. To verify this speculation, narrow-scan XPS spectra of W 4f core level for undoped and cation-doped $W-Y_2O_3$ alloys were tested and the results are presented in Fig. 5. Interestingly, it is found that the fitted peak area assigned to W^{6+} state is gradually increased with the increase of segregation degree for the trivalent cation-doped $W-Y_2O_3$ alloys. However, for the tetravalent cation-doped $W-Y_2O_3$ alloys, the fitted peak area attributed to W^{6+} state decreases with the increase of segregation degree and reaches the minimum for the Hf^{4+} -doped alloy. The oxidized W observed from XPS data can be mainly attributed to the W-O bond formed along the W/Y_2O_3 interface. For comparison, the XPS results of reduced powders are also provided, as shown in Fig. S8. It can be found that the fitted peak assigned to W^{6+} state appear in all the reduced powders. The oxidized W in reduced powders mainly results from the oxidation film formed on W particle surfaces due to their high surface activity, thus the oxidation film is difficult to be reduced completely. Besides, we also find that there is no significant

Figure 5 Narrow-scan XPS spectra of W 4f core level for undoped and cation-doped $W-Y_2O_3$ alloys, including (a) Sc^{3+} -doped $W-Y_2O_3$ alloy, (b) undoped $W-Y_2O_3$ alloy, (c) La^{3+} -doped $W-Y_2O_3$ alloy, (d) Ti^{4+} -doped $W-Y_2O_3$ alloy, (e) Zr^{4+} -doped $W-Y_2O_3$ alloy and (f) Hf^{4+} -doped $W-Y_2O_3$ alloy.

difference in the corresponding fitted peak area among these reduced powders, which might be attributed to the homogeneous distribution of dopant cations in reduced powders rather than the segregation state after subsequent sintering. Thus, it can be concluded that the amount of W–O bonds is increased by La^{3+} dopant segregation, while it is reduced by Hf^{4+} dopant segregation. This result can be further supported by the density functional theory (DFT)-calculated average magnetization of W atoms. Specially, the average magnetizations of W atoms with and without La^{3+} dopant segregating to interface are very close (1.9 and 2.0 μ_{B} , respectively), which results from their almost identical chemical states. Nevertheless, with Hf^{4+} dopant segregating to W/ Y_2O_3 interface, the average magnetization of W atoms drops to 1.3 μ_{B} , suggesting the oxidized W, i.e., W–O bond decreases significantly. The reason behind might be associated with the oxygen affinity of different cations. For example, the oxygen affinity of Hf^{4+} ($-808.4 \text{ kJ mol}^{-1}$, corresponding oxide formation energy, per mol cation) is much higher than that of Y^{3+} ($-681.3 \text{ kJ mol}^{-1}$), resulting in partially oxidized W along the W/ Y_2O_3 interface being reduced by the segregated Hf^{4+} dopant. As a consequence, the activation energy for the W diffusion along the W/ Y_2O_3 interface declines greatly by the unleashed W atoms due to the cleavage of W–O bonds, which promotes the sinterability of W matrix. Thus, the resulting grain microstructure in the Hf^{4+} -doped alloy is coarsened, as observed in Fig. 1l. For the La^{3+} cation-doped W- Y_2O_3 alloy, however, the oxygen affinity of La^{3+} ($-626.7 \text{ kJ mol}^{-1}$) is lower than that of Y^{3+} , which is beneficial to the oxidation of W atoms along the interface after segregation. Coupled with the increased W/oxide interface area caused by the refined oxide particles, the dramatically increased W–O bonds will constrain the diffusion of W atoms along the W/ Y_2O_3 interface, suppressing the sinterability of W matrix. As a result, the grain size of W in the La^{3+} -doped W- Y_2O_3 alloy is refined (Fig. 1i).

Next, the effect mechanism of cation dopant segregation on the refinement of intergranular Y_2O_3 particles is studied. According to our previous study, from the view of thermodynamics, coarsening of the intergranular Y_2O_3 second phase particle is driven by the reduction in W/ Y_2O_3 interfacial energy [37]. From the view of kinetics, Ostwald ripening is the mechanism acting to determine the diffusion path of Y_2O_3 [42]. Specially, in order to drive a W/ Y_2O_3 interface to move (i.e., coarsening of Y_2O_3 particle), the atoms in a Y_2O_3 particle have to diffuse through the W/W grain boundary and then reprecipitate into another larger Y_2O_3 particle [37].

In order to explain the refinement of Y_2O_3 particle in the cation-doped W- Y_2O_3 alloy, the dual effect of cation dopant segregation on the W/ Y_2O_3 interfacial energy and Y_2O_3 diffusion should be considered. Here, DFT calculation was performed for atomic configuration optimization and interfacial energy calculations (see Fig. S9). The detailed calculation process is described in Supplementary information, and the corresponding interface formation energy results with and without cation doping are demonstrated in Fig. 6. It can be found that with La^{3+} or Hf^{4+} doping, the interface formation energy is lower than the undoped case. To be more specific, at 1600°C , the W/ Y_2O_3 interfacial energy is calculated as 0.59 J m^{-2} for the undoped case, and 0.15 and 0.35 J m^{-2} for the La^{3+} - and Hf^{4+} -doped cases, respectively. Therefore, thermodynamically, the driving force for Y_2O_3 grain growth declines. Kinetically, the cation dopant segregating to W/ Y_2O_3 interface is expected to block the diffusion of Y_2O_3 from the Y_2O_3 matrix to the W grain boundary (i.e., the coarsening of Y_2O_3), slowing or inhibiting the growth of Y_2O_3 .

The origin of enhanced mechanical properties in cation-doped W- Y_2O_3 alloy

Next, the origin of enhanced strength and ductility of cation-doped W- Y_2O_3 alloys was analyzed. As mentioned above, these improved properties affirmatively benefit from the microstructure actually formed through cation doping. In terms of La^{3+} -doped W- Y_2O_3 alloy, the intergranular oxide particles have an average size of only 96 nm, which could produce a more frequent interaction between the W grain boundary and oxide particles than undoped W- Y_2O_3 alloy, leading to the ultrafine W grain

Figure 6 Interface formation energy as a function of temperature for undoped W(110)/ Y_2O_3 (200) interface, La^{3+} - and Hf^{4+} -doped interface.

(770 nm) and ensuing high strength. The corresponding strengthening mechanism can be understood *via* the Hall-Petch equation where the strength of materials is inversely proportional to their grain size. Therefore, the high strength of La^{3+} -doped alloy mainly originates from its refined W grains. In contrary, the coarsening of W matrix grain is induced by Hf^{4+} doping. Thus, it follows that the strength of Hf^{4+} -doped W- Y_2O_3 alloy decreases dramatically [43]. On the other hand, the refined oxide particles in both La^{3+} - and Hf^{4+} -doped W- Y_2O_3 alloys are conducive to the improvement of their ductility. Generally speaking, due to deformation incompatibility, large strain concentration can be easily introduced at oxide particles, which will give rise to the decohesion along the matrix/oxide interface and the fracture of oxide particle during load. Therefore, the intergranular oxide particles are preferential sites for crack initiation, especially for the larger (submicron or even micron) particles with lower fracture strength, deteriorating the ductility of W-based alloy [9]. Fortunately, the intergranular oxide particles in La^{3+} -doped and Hf^{4+} -doped W- Y_2O_3 alloys are all refined conspicuously, which alleviates the tendency for fracture and decohesion at these particles and then enhances the total strain before failure. Adopting the model that relates the macroscopic elongation to intergranular particles, the strain-to-failure of different cation-doped ODS-W alloys can be understood well [44,45]. From this model, it can be obviously found that given a certain amount of intergranular particles, the smaller the intergranular particle size is, the higher the ductility of W material is. Therefore, reducing the intergranular particle size is an effective method to enhance the ductility of ODS-W alloy. But, noteworthy, the total elongation of La^{3+} -doped W- Y_2O_3 alloy is slightly smaller than that of Hf^{4+} -doped W- Y_2O_3 alloy. This phenomenon might arise from the inverse strength-ductility relationship [46,47].

CONCLUSION

All long, large-sized intergranular oxide second phase particle in ODS alloys is always a bottleneck limiting their widespread applications. In this work, taking Y_2O_3 dispersion-strengthened W alloy for example, various cation-doped W- Y_2O_3 alloys have been developed successfully *via* a wet chemical method and subsequent low-temperature sintering. It was found that proper cation doping, especially La^{3+} and Hf^{4+} doping, could not only significantly refine and disperse intergranular Y_2O_3 particles, but also improve the sinterability of W matrix. As a result, the strength and ductility of W- Y_2O_3 alloy are enhanced simultaneously. After careful characterizations,

it was confirmed that cation dopant segregation at the W/ Y_2O_3 interface is the origin of these doping effects. The chemical bonding along the W/ Y_2O_3 interface can be changed by dopant segregation, influencing the rate-limiting mechanism for W grain growth, which explains well the difference of W grain size in cation-doped W- Y_2O_3 alloys. For the refinement of intergranular Y_2O_3 particles, it can be understood well from both thermodynamic and kinetic views. For the former, it is the reduction in W/ Y_2O_3 interfacial energy induced by cation dopant segregation that weakens the thermodynamic driving force for Y_2O_3 coarsening. For the latter, the diffusion path for Y_2O_3 coarsening is blocked by the segregation area at the W/ Y_2O_3 interface.

Based on the results in our work, we believe that the cation doping introduced by the wet chemical method and subsequent low-temperature sintering is an extremely promising way to fabricate high-performance ODS alloys with enhanced strength and ductility. More importantly, this approach can also be employed to improve the high-temperature stability of oxide second phase particles under extreme working environment.

Received 20 June 2020; accepted 7 August 2020;
published online 11 November 2020

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- Acknowledgements** This work was supported by the National Natural Science Foundation of China (51822404), the Science and Technology Program of Tianjin (19YFZCGX00790 and 18YFZCGX00070), the Natural Science Foundation of Tianjin (18JCYBJC17900) and the Seed Foundation of Tianjin University (2018XRX-0005).

Author contributions Dong Z designed the processing route and experiments and wrote the manuscript; Ma Z synthesized the materials and implemented the mechanical testing experiments; Yu L carried out the TEM experiments; Liu Y performed the density functional theory calculation. All authors contributed to the discussion, interpretation and presentation of the results.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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通过离子掺杂剂界面偏析来提高氧化物弥散强化合金的机械性能

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摘要 氧化物弥散强化钨合金(ODS-W)因具有显著提升的抗辐照能力、高温强度以及抗蠕变性能而展现出巨大的高温应用潜力。然而, 分散在合金中的氧化物第二相颗粒容易在钨晶界处团聚并长大(甚至到微米尺寸), 这大大抑制了它们对钨合金的强化效果。目前, 如何有效细化和分散钨晶界处的氧化物第二相颗粒一直是人们面临的巨大挑战。在本文中, 我们通过共沉积湿化学法和后续低温烧结成功制备出一种新型的离子掺杂的氧化钇弥散强化钨合金。结果发现, 合适的离子掺杂不仅可以显著细化晶界处的氧化钇颗粒, 而且可以改善钨基体的烧结特性。这些掺杂效应最终同时提高了钨合金的强度和韧性。经过分析可以确认离子掺杂剂在钨/氧化钇界面处的偏析是这些掺杂效应的起源。此外, 经X射线光电子发射光谱(XPS)表征发现, 离子掺杂剂偏析能显著改变钨/氧化钇界面的化学键合状态(即W-O键), 进而使控制W晶粒生长的表面扩散机制也受到影响, 这很好地解释了不同离子掺杂的钨合金中产生的晶粒尺寸差异。至于钨晶界处氧化钇的细化, 可以从动力学和热力学的角度来解释。在热力学方面, 钨/氧化钇界面能降低了氧化钇粒子长大的驱动力。在动力学方面, 离子掺杂剂的界面偏析降低了氧化钇分子的移动能力。更重要的是, 离子掺杂的方法也能应用于其他的氧化物弥散强化合金来提高他们的综合力学性能。