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ARTICLE

Preparation of Li_4SiO_4 Ceramics Tritium Breeder and Its Interface Corrosion Behavior with 14Cr-ODS Steel

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Abstract: The chemical compatibility between Li_4SiO_4 pebbles and ODS steel is important for the safe operation of the fusion reactor. In the present paper, the transformation of microstructure and component for contact interface between ODS steel and pebbles after 300 h heat preservation in an argon atmosphere at 500, 600, and 700 °C was investigated. The results show that serious element interdiffusion and reaction can be observed at the interface between Li_4SiO_4 pebbles and ODS steel at temperatures of 600~700 °C. For the surface of Li_4SiO_4 pebbles, a thin reaction layer appears due to the diffusion of Fe and Cr from ODS steel, which also causes the increase of density and decrease of crush load from 51 N (500 °C) to 32 N (700 °C). XRD patterns show that the new phase of $LiCrO_2$ and $LiFeO_2$ appears on the surface of ODS steel, which suggests that the Li and O atoms in Li_4SiO_4 pebbles can diffuse into ODS, and react with Fe and Cr elements to form corrosion layers at high temperature. The corrosion layers can be divided into two oxide sub-layers at 700 °C. The outermost layer is a mixture of $LiFeO_2$ and $LiCrO_2$, and the next layer is mainly $LiFeO_2$. For the surface of ODS steel, the oxygen diffusion coefficient is 2.2×10^{-14} cm^2/s at 700 °C for 300 h. It suggests that the ODS steel as a blanket structure material steel needs a resisted corrosion coating in the design of a blanket in the future.

Key words: ODS steel; Li_4SiO_4 pebbles; tritium breeder blanket; compatibility; corrosion

Deuterium-tritium (D-T) thermonuclear fusion has been considered to be one of the most promising alternative energy sources in the future on account of its advantages such as safety, cleanness, and abundance[1-3]. Contrary to the abundant reserves of deuterium in nature, tritium is rare. Hence, a tritium breeder blanket has been designed for obtaining tritium artificially. The design of the tritium breeder blanket is crucial to the fusion reactor, and it has become the core technology of competition in the world for fusion energy research and development[4-6]. For the selection of tritium breeders in the blanket, an important consideration is whether the tritium breeder has good chemical compatibility with the structural materials. So far, many types of research have focused on the corrosion behavior of fusion structure materials and liquid lithium lead. A large number of experiments (such as heat convection and forced convection experimental loops) have been conducted to evaluate and verify the compatibility of structural materials and liquid lithium lead[7-9]. In recent years, a solid-state lithium base breeder has been regarded as an important part of the D-T fusion reactor due to its higher chemical stability, higher safety, and better non-MHD effects[10,11]. Therefore, in different design schemes[12], different ceramic oxides have been used as candidate materials for tritium breeders, while Li_4SiO_4 pebbles have been considered to be one of the most promising candidates for tritium breeding due to its high lithium concentration and good tritium release behavior[13,14]. In the fusion reactor, the temperature of the solid breeder blanket has been controlled between 300 °C and 800 °C[15]. Besides, once the Li_4SiO_4 pebble is loaded into the cladding, it needs to serve for 2~3 years in the environment of high temperature, high electromagnetic field, and high energy neutron irradiation, which will influence the blanket structure materials. The chemical compatibility between Li_4SiO_4 pebbles and EUROFER97 steel at 550 °C has been studied[16]. Nowadays, ODS steel (nano oxide dispersion strengthened) with excellent

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anti irradiation performance, high-temperature mechanical properties, and corrosion potential, has been selected as the structural materials for a new generation[17]. But the chemical compatibility between Li_4SiO_4 pebbles and ODS steel in high temperature and inert atmosphere remains to be studied. In fusion reactors, tritium contents are very scarce and ceramic breeder pebbles in contact with structural material of the blanket at a high temperature are packed in a blanket to produce tritium by nuclear transmutation. Considering fuel cycle efficiency and radiation safety, tritium permeation through structural materials is a significant issue for fusion demonstration reactor blankets. Therefore, it is very important to study the compatibility between ceramic pebbles and structural materials.

In this study, Li_4SiO_4 pebbles were fabricated by an indirect wet process, the chemical compatibility between Li_4SiO_4 pebbles and ODS steel was investigated in an argon atmosphere at 500, 600 and 700 ° C, and the composition and microstructure of the interface were analyzed. The relative density and crush load of Li_4SiO_4 pebbles were also investigated.

1 Experiment

Li_4SiO_4 pebbles were prepared using Li_2SiO_3 and Li_2CO_3 as raw materials with a wet method[18]. The detailed process is as follows. Firstly, the Li_2CO_3 and the SiO_2 were blended with a molar ratio of 1:1 using deionized water as a milling medium. The Li_2SiO_3 powder was synthesized at 750 °C by the solid-state reaction method. Secondly, the Li_2CO_3 and the Li_2SiO_3 were blended with a molar ratio of 1:1 using deionized water as a milling medium. Finally, the homogeneous slurry mixed with 3wt% PVA (polyvinyl alcohol) was added into the heating tank (80 °C). Then, the slurry was dropped dropwise into the silicone oil through multiple nozzles, where green pebbles were generated due to the gravity and surface tension. The green pebbles were dried at room temperature for 72 h. The Li_4SiO_4 ceramic pebbles were obtained by sintering the green pebbles in a muffle furnace at 950 °C for 2 h. Fig.1 displays the equipment drawing for preparing Li_4SiO_4 green pebbles. The diameter was about 1 mm, sphericity was 1.03, relative density was 86.7% and crush load was 51 N. The composition of 14Cr-ODS steel is shown in Table 1.

The samples were packed (Fig.2) and placed in the atmosphere furnace. After the furnace was closed, the atmosphere furnace was evacuated (10^{-2} Pa) and the chamber was cleaned 3 times with high purity argon (Ar content≥99.999%, N_2 content≤5.0 μL/L, O_2 content≤2.0 μL/L, H_2 content≤1.0 μL/L, CH_4 content≤3.0 μL/L, H_2O content≤3.0 μL/L). Then, the argon was injected at a speed of 150 mL/min. Thereafter, the sample was heated at 500, 600 and 700 °C for 300 h. After the heat preservation was finished, the argon was closed and the samples were removed when the furnace was cooled down to room temperature.

Sintered Li_4SiO_4 pebbles and ODS's crystal structures were investigated by X-ray diffractometer (D/max-RB Rigaku, Japan). Microstructures were observed by scanning electron microscope (SEM, S-250MK3 JEOL, Japan). The composition was analyzed by the EDS spectrometer attached to the scanning electron microscope. The relative density of Li_4SiO_4 pebbles was tested by the Archimedes principle. Crush load of Li_4SiO_4 pebbles was measured by ceramic strength measuring machine (CDW-5 Changchun Aowei Inc., China).

2 Results and Discussion

2.1 Morphology and crystal structure of Li_4SiO_4 pebbles

The morphology and crystal structure of Li_4SiO_4 (PDF-37-1472) pebbles fabricated by an indirect wet process are shown in Fig.3. It can be seen from Fig.3a that the surface of Li_4SiO_4 pebbles is clean and bright, the average diameter of pebbles is about 1 mm, and the degree of sphericity is 1.03. XRD result shows that all diffraction peaks can be indexed according to Li_4SiO_4, and no other phases can be observed (Fig.3b). It suggests that Li_4SiO_4 pebbles fabricated by the indirect wet method may meet the requirement of chemical compatibility experiments.

2.2 Microstructure evolution of Li_4SiO_4 pebbles

The morphology and microstructure of Li_4SiO_4 pebbles contacted with ODS steel after heating at different tempera-

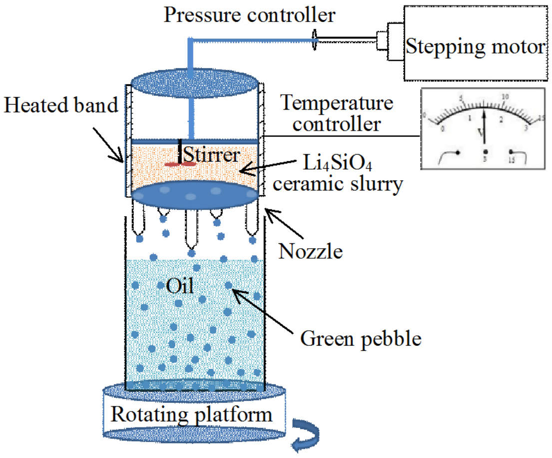

Fig.1 Equipment drawing for preparing Li_4SiO_4 pebbles

Table 1 Component content of 14Cr-ODS steel (at%)

C	Si	Ti	Cr	W	Y
0.06	0.24	0.41	14.2	1.8	0.15

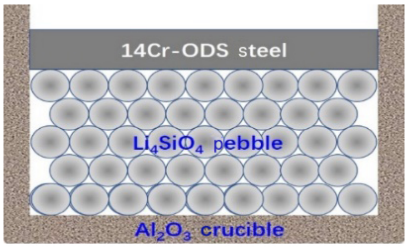

Fig.2 Schematic diagram of loading samples

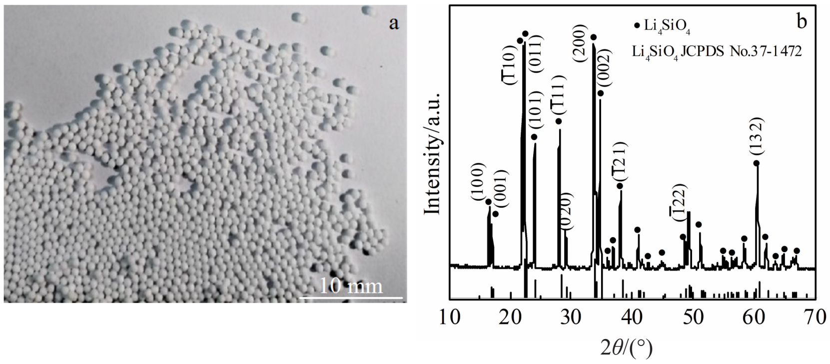

Fig.3 Morphology (a) and XRD patterns (b) of Li_4SiO_4 pebbles

tures for 300 h are shown in Fig.4. As the heating temperature is 500 °C (Fig.4a and 4d), there is no obvious corrosion layer on the surface of the microsphere, and the grain shape remains intact. However, surface of the microsphere becomes markedly roughened, the pores grow up, and a thin reaction layer appears as the heating temperature is 600 °C (Fig.4b and 4e). With further increasing the temperature to 700 °C, the reaction at the interface of Li_4SiO_4 pebble contacted with ODS steel becomes severe (Fig. 4c and 4f), and the reaction layer comes off the pebble, which can be also seen from the EDS element mapping of the pebble surface that there are a lot of Fe and Cr on the surface of microspheres. Furthermore, the Fe element is concentrated at the contact point where the microsphere and ODS steel contact directly. For Cr element, in

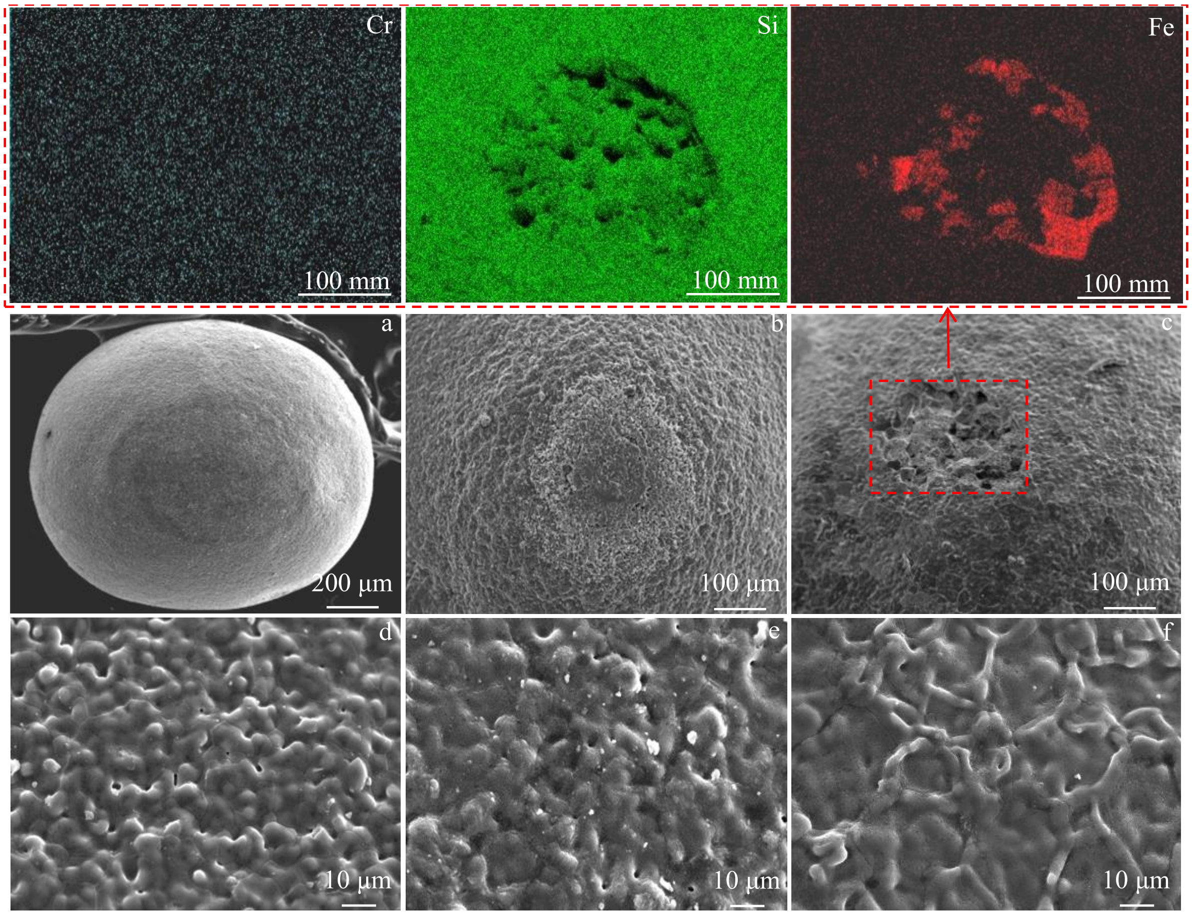

Fig.4 Surface morphologies (a~f) and corresponding EDS mapping of area marked in Fig.4c for Li_4SiO_4 pebbles contacted with ODS steel at different temperatures for 300 h: (a, d) 500 °C, (b, e) 600 °C, and (c, f) 700 °C

addition to the distribution at the direct contact point, it is also distributed uniformly in the whole contact area. The Fe and Cr on the pebble surface mainly come from the diffusion of ODS steel. Those phenomena suggest that a diffusion-reaction layer forms on the surface of Li_4SiO_4 pebble, and the Fe and Cr elements in ODS steel will diffuse into the surface of Li_4SiO_4 pebble as the heating temperature is above 600 °C.

2.3 Phase analysis of ODS steel

Fig.5 shows the XRD patterns of the ODS steel before and after the compatibility experiment. The phase of the blank sample in Fig.5 is 14Cr-ODS (Fe-Cr alloy, PDF-54-0331), and the space group is Im-3m (229). The two new phases with weak diffraction peaks form when ODS steel and Li_4SiO_4 pebbles are heated at 500 °C for 300 h. One is $LiFeO_2$ (PDF-17-0938), whose space group is Fm-3m (225), and the other is $LiCrO_2$ (PDF-24-0600) with a space group of Fd-3m (227). With the increase of temperature, the intensity of diffraction peaks of these two phases increases gradually. It is well known that in the process of high-temperature heating for a long time, the fastest diffusion atom in 14Cr-ODS is the Fe atoms, followed by the Cr atoms. They spread to the grain boundaries and surfaces and react with Li and O atoms from Li_4SiO_4 pebbles. There may be two reasons for the emergence of Li and O atoms. One is that the thermal vibration of Li and O atoms is enhanced by the high temperature. The atoms surmount the energy barriers and diffuse. The other is the volatilization of lithium compounds (Li (g), LiO (g), and Li_2O (g)) in Li_4SiO_4 at high temperature. They are deposited on the surface of ODS steel and react with Fe and Cr to form $LiFeO_2$ and $LiCrO_2$ corrosion layers, and the reaction process can be described as the following equations:

$$Li+2O+Fe \rightarrow LiFeO_2 \quad (1)$$

$$Li+2O+Cr \rightarrow LiCrO_2 \quad (2)$$

2.4 Microstructure evolution of ODS steel

The surface morphologies and EDS spectra of ODS steel contacted with Li_4SiO_4 pebbles heated at 600 ℃ for 300 h are shown in Fig. 6. It can be seen that the contact region (light gray color) and non-contact region (dark gray color, Fig.6a) of ODS steel with Li_4SiO_4 pebbles show different morphologies. A lot of white flaky materials are generated in the contact region (Fig. 6b and 6e), while in the non-contact region (Fig.6c), only a small amount of the white flake phase can be found and they are mainly composed of flat and tiny grains (2~3 μm). Besides, a large number of cracks are found in the non-contact region, and the average width of the cracks is about 0.05 μm. From EDS spectra of Fig.6f and Fig.6g, it can be found that the content of Fe in the non-contact region (40.85at%) is much higher than that in the contact region (10.63at%), but the content of Cr in the non-contact region (1.14at%) is far lower than that in the contact region (21.10at%). Therefore, combined with XRD analysis, the non-contact region forms the corrosion layer of $LiFeO_2$, while the contact region forms the corrosion layer of $LiCrO_2$ and $LiFeO_2$.

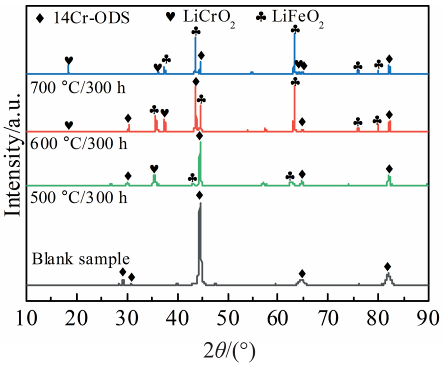

Fig.5 XRD patterns of ODS steel at different heating temperatures

The mechanism of forming oxide corrosion layer may be as follows. In the early stage of oxidation, due to the higher concentration of Cr in ODS, the faster diffusion of Cr in contact region and the lower Gibbs free energy of chemical reaction of Cr, Li and O, the Cr atoms diffuse rapidly to the grain boundaries of the contact region and react with the Li atoms and O atoms to form white flaky $LiCrO_2$ on the surface of the sample[19,20]. With the oxidation reaction going on, the non-contact region of the 14Cr-ODS steel surface reacts with the Li atoms and O atoms which are volatilized or diffused from the Li_4SiO_4 pebbles and form the $LiFeO_2$. This leads to the change of the volume of the substrate surface and the stress is generated between the matrix and the corrosion layer. Meanwhile, $LiCrO_2$ and $LiFeO_2$ in the contact region also cause local stress on the surface due to their different volumes and result in cracks in the non-contact region. Besides, the circular corrosion trace (Fig.6d) is found in the contact region. From the energy spectrum of Fig.6g, it is found that there are 29.22at% Fe, 1.57at% Cr, 64.49at% O, 4.42at% C, and 0.03at% W. Therefore, in combination with the macroscopic morphology analysis of the ODS sample, the circular corrosion trace may be the hemispherical corrosion pits left after the removal of the pebbles.

Fig.7 shows the SEM images and EDS analysis areas of the surface of ODS steel heated with Li_4SiO_4 pebbles at 700 °C for 300 h. We found a large number of cracks in some regions (Fig.7c and 7f). It can be seen that the degree of corrosion at 700 °C is more serious than that at 600 °C, and there are two kinds of shedding modes. Fig.7a and 7b show a dent produced by taking the pebble away from the ODS steel, and the enlarged image of this dent shows that it consists of different grain shapes (Fig. 7c, 7e, 7f). Fig. 7d and 7g show that the contact part of the pebbles falls off and forms a bulge on the surface of ODS steel when Li_4SiO_4 pebbles are removed. The surface of the bulge is composed of coherent dendritic small grains, which can be concluded that the protuberance is Li_4SiO_4. In addition, some cracks are also found in the non-contact region (Fig. 7h and 7i), and the average width of the cracks is larger than that at 600 °C (about 0.2 μm). In the local enlarged image of pits, there are some corrosion layers on the surface.

In order to further explore the composition of the corrosion layer, the EDS spectra of pits are given in Table 2. Combined with previous XRD analysis, it can be inferred that the

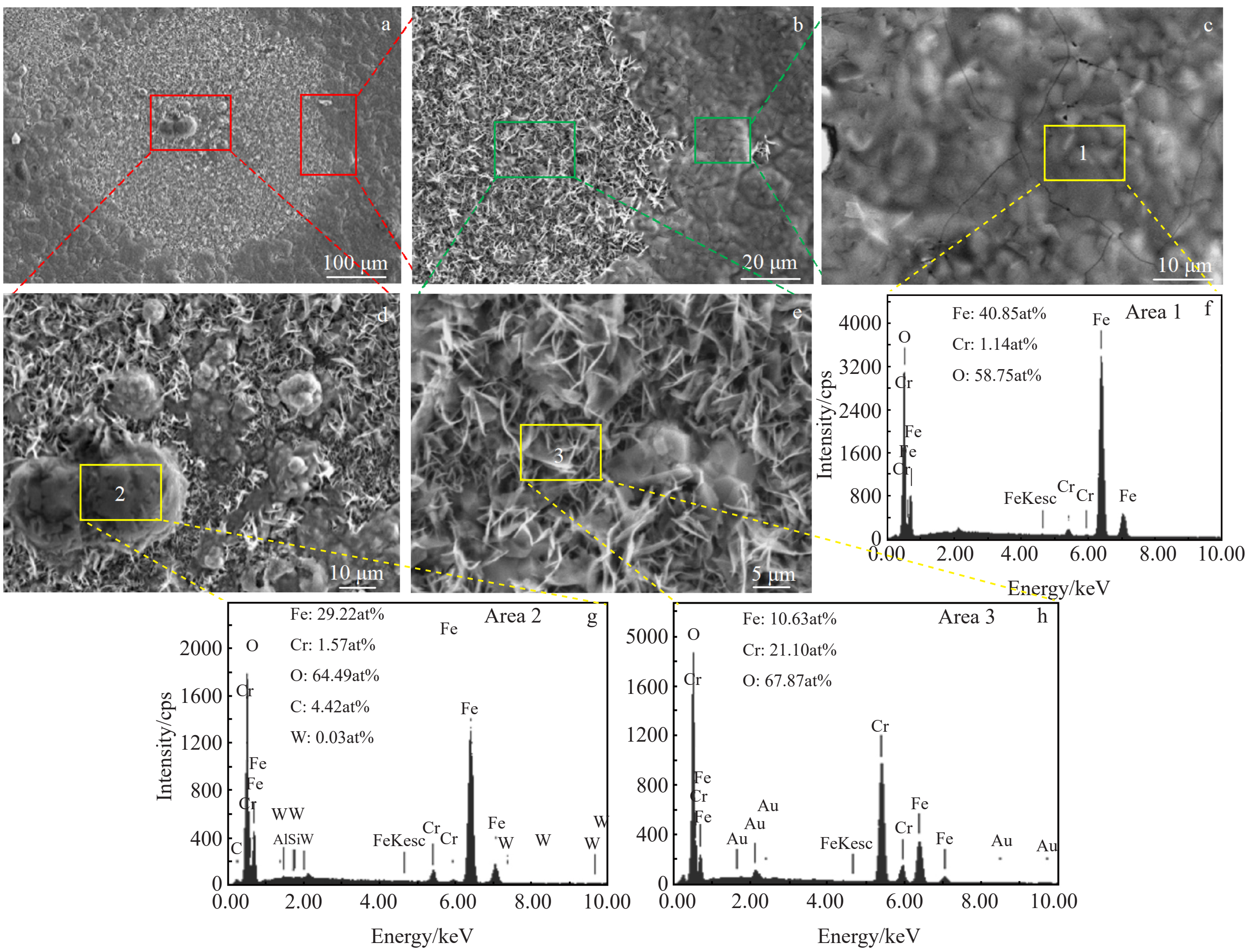

Fig.6 SEM morphologies (a~e) and EDS analysis results of area 1 (f), area 2 (g), and area 3 (h) of ODS steel contacted with Li_4SiO_4 pebbles

corrosion layer consists of two oxide sub-layers; the first layer corrosion product is a mixture of $LiFeO_2$ and $LiCrO_2$, and the middle layer is $LiFeO_2$; below that is mainly matrix ODS steel. However, Cr and Fe oxides should also be produced on the matrix surface because the content of O is much higher than that of the sample before the compatibility test.

In addition to the above study, the effective diffusivity of oxygen was estimated by measuring the thickness of the oxygen layer detected by SEM/EDS. The effective diffusion coefficient of oxygen D is given as follows[21]:

$$D=d^2/t \tag{3}$$

where d is the thickness of the oxidized layer on the 14Cr-ODS steel and t is the heating period. It is found that the oxygen diffusion coefficient is 2.2×10^{-14} cm^2/s at 700 °C for 300 h.

As can be seen from the above results, the serious element inter-diffusion and reaction can be observed in the interface between Li_4SiO_4 pebbles and ODS steel, and a corrosion layer with two oxide sub-layers is produced by the diffusion of Li and O from Li_4SiO_4 pebbles to ODS steel. These phenomena illustrate that Li_4SiO_4 pebbles have severe corrosion on the ODS steel at temperatures of 600~700 °C in the blanket operation process.

2.5 Crush load and relative density of Li_4SiO_4 pebbles

The crush load and density of Li_4SiO_4 pebbles were further studied after contact with 14Cr-ODS steel in an argon atmosphere at different temperatures. Fig.8 shows the change of the relative density and crush load of Li_4SiO_4 pebbles in direct contact with 14Cr-ODS steel at different temperatures for 300 h. It can be seen that the relative density of the pebbles increases under the three experimental conditions of 500, 600, and 700 °C. This phenomenon is mainly because the Li_4SiO_4 pebbles undergo grain growth and sintering densification in the process of long-term heat preservation. On the contrary, the crush load is inversely proportional to the heating temperature, and the crush load of Li_4SiO_4 pebbles decreases gradually from 51 N (at 500 °C) to 32 N (at 700 °C). This phenomenon can be attributed to the surface corrosion and growth of grain. On the one hand, a severe degree of corrosion on the surface will occur in the process of Li_4SiO_4 pebbles contacting with ODS steel at 700 °C. On the other hand, the grain size of the pebbles becomes larger and the number of grain boundaries in the unit space is reduced when the pebbles are put in a high-temperature state for 300 h. As we all know,

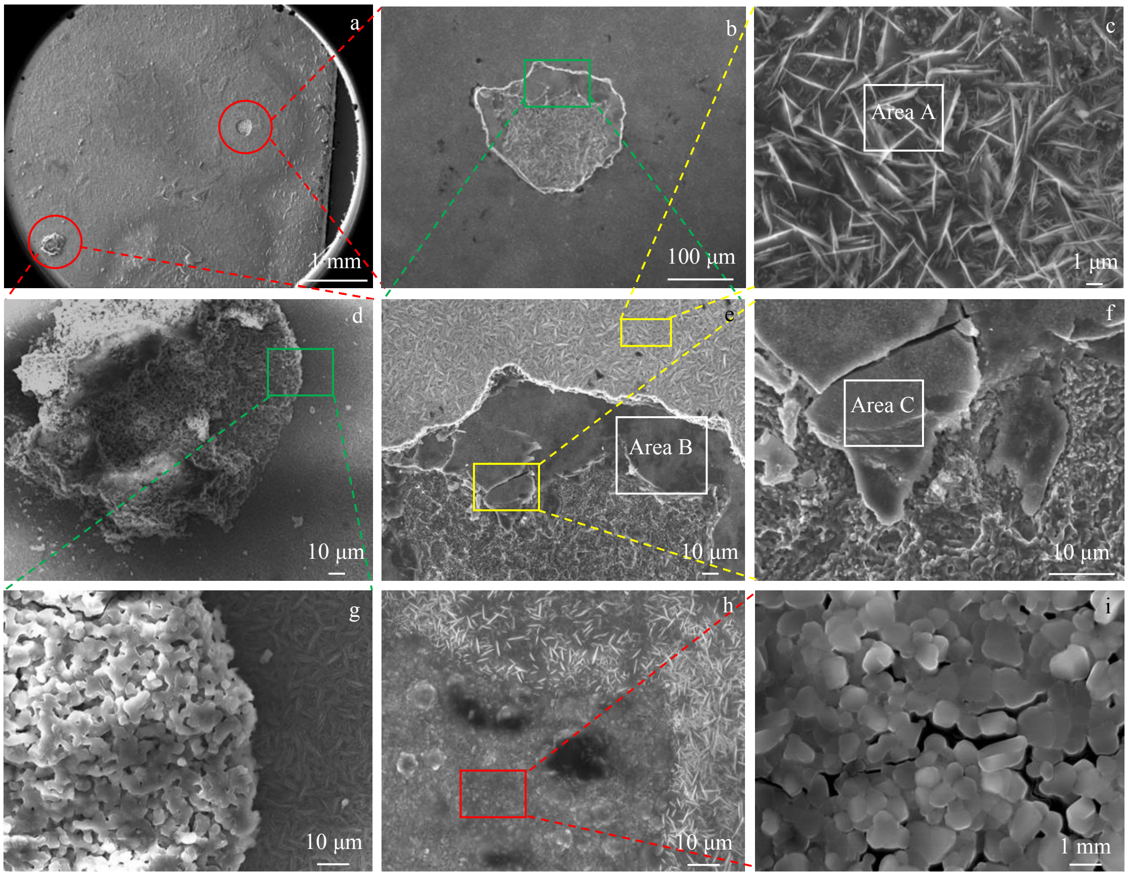

Fig.7 SEM images and EDS analysis areas of ODS steel surface heated with Li_4SiO_4 pebbles at 700 °C for 300 h

Table 2 EDS analysis results of corrosion pits (area A, B and C) heated with Li_4SiO_4 pebbles at 700 °C for 300 h in Fig.7 (at%)

Area	Fe	O	Al	C
A	34.39	45.91	16.39	2.48
B	30.27	64.22	1.83	0.69
C	72.07	12.66	4.44	5.03

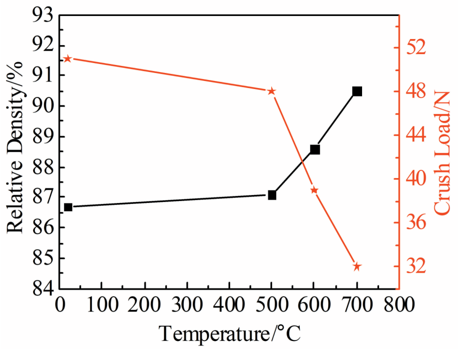

Fig.8 Change of relative density and crush load with temperature for Li_4SiO_4 pebbles

the smaller the grain size, the better the crush load[22]. Therefore, the grain growth leads to a decrease in the ability to impede the dislocation, eventually leading to a decrease in its crush load.

3 Conclusions

1) Serious element inter-diffusion and reaction can be observed at the interface between Li_4SiO_4 pebbles and ODS steel, and with the increase of temperature, the chemical compatibility becomes worse.

2) At 700 °C, a corrosion layer with two oxide sub-layers is produced by the diffusion of Li and O from Li_4SiO_4 pebbles to ODS steel. The first layer is a mixture of $LiFeO_2$ and $LiCrO_2$, and the lower layer is mainly $LiFeO_2$.

3) On the surface of ODS steel, the oxygen diffusion coefficient is 2.2×10^{-14} cm^2/s at 700 °C for 300 h. Besides, the formation of the corrosion layer induces several cracks on the surface of ODS steel, which will have an impact on the mechanical properties of ODS steel.

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Li_4SiO_4氚增殖陶瓷的制备及其与14Cr-ODS钢的腐蚀界面行为

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摘　要：Li_4SiO_4小球与ODS钢的化学相容性对聚变反应器的安全运行具有重要意义。研究了在500、600、700 ℃的氩气环境中保温300 h后ODS钢与小球接触界面组织和成分的变化。结果表明，在600~700 ℃时，Li_4SiO_4小球与ODS钢的界面发生了严重的元素互扩散和反应。在Li_4SiO_4小球表面，由于ODS钢中Fe和Cr的扩散，出现了一层薄薄的反应层，这也导致了密度的增加，破碎负荷从51 N（500 ℃）下降到32 N（700 ℃）。XRD图谱显示，ODS钢表面出现了$LiCrO_2$和$LiFeO_2$新相，说明Li_4SiO_4小球中的Li和O原子可以扩散到ODS中，与Fe、Cr元素在高温下发生反应形成腐蚀层。在700 ℃时，腐蚀层可分为2个氧化层。最外层是$LiFeO_2$和$LiCrO_2$的混合物，下一层主要是$LiFeO_2$。在ODS钢的表面，700 ℃/300 h条件下氧扩散系数为2.2×10^{-14} cm^2/s，这说明ODS钢作为一种包层结构材料，在未来的包层设计中需要一层耐腐蚀涂层。

关键词：ODS钢；Li_4SiO_4微球；氚增殖包壳；兼容性；腐蚀

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