Effects of Grain Size and CeO_2 Addition on the Corrosion Behaviour of Cr_2O_3 based Ceramics in High Temperature Supercritical Water Environment

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Summary

In this investigation, Cr_2O_3 ceramics with different grain sizes were prepared and tested in supercritical water (SCW) environment at 650°C /25 MPa for 200 hours. The results show that the stability of Cr_2O_3 in SCW was affected by its grain size. In addition, various amounts of CeO_2 were added to Cr_2O_3 to examine the effect of CeO_2 on the corrosion behaviour of the Cr_2O_3 based ceramic under SCW condition. These Cr_2O_3-based ceramics were exposed to an SCW environment at 650°C/ 25 MPa for up to 600 hours. The results showed that adding a proper amount ($\leq$ 5 wt. %) of CeO_2 increased the corrosion resistance of Cr_2O_3-based ceramics in SCW.

1. Introduction

Cooled by the water above its thermodynamic critical point (374°C, 22.1MPa), Supercritical Water-cooled Reactor (SCWR) shows its superiority in higher thermal efficiency and greater configuration simplicity comparing to the current light water reactor (LWR). However, the severely corrosive environment related to the high-temperature and high pressure situation also brings great challenges to the selection of proper candidate materials used for SCWR.

Cr_2O_3 ceramic offers the advantages of high chemical stability, high wear resistance and low thermal conductivity, thus it has been applied as coating materials to prevent corrosion in various harsh environments [1-3]. Furthermore, a protective Cr_2O_3 layer is commonly formed on the surface of Cr-containing steels and alloys when exposed to oxidative environment, and the corrosion resistance of the steels or alloys will be closely related to the stability of the Cr_2O_3 formed. Therefore, studying the corrosion behaviour of Cr_2O_3 based ceramics under SCW condition can not only examine the feasibility of applying Cr_2O_3 protective coatings in SCWR, but also generate valuable knowledge benefiting the selection of proper Cr-containing steels and alloys applied in SCW environment.

It has been found that the corrosion of Cr_2O_3 ceramic in oxidative SCW environment occurs mainly through the corrosion reaction between Cr_2O_3 with H_2O and O_2, which forms soluble Cr^{6+} species in SCW [4]. In this study, the effects of Cr_2O_3 grain sizes and CeO_2 addition on the SCW stability of Cr_2O_3 ceramics were investigated.

2. Effects of grain size on the SCW stability of Cr_2O_3 ceramics.

Three Cr_2O_3 powders with various particle sizes were compressed in a cylindrical mold and sintered at 1200°C for 15hrs. Figure 1 shows the surface morphologies of the three groups of samples. The grain sizes of three groups sample were estimated based on the SEM images and are listed in Table 1.

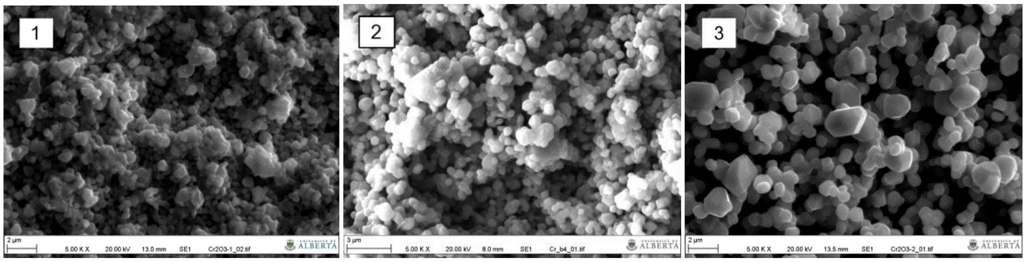


Figure 1 The surface morphologies of Cr_2O_3 ceramics with various grain sizes.

Table 1 estimated average grain sizes of Cr_2O_3 ceramics.

Sample group	1	2	3
Average grain size(nm)	372.6±24	453.5±18	719.9±21

SCW tests were conducted using a static reactor made of Inconel 625 alloy. Controlled amount of deionized water with an oxygen concentration of about 8 ppm was used and sealed into the reactor. All SCW tests were conducted at 650°C /25MPa. The weight changes of samples after 200hrs SCW exposure are shown in Figure 2.

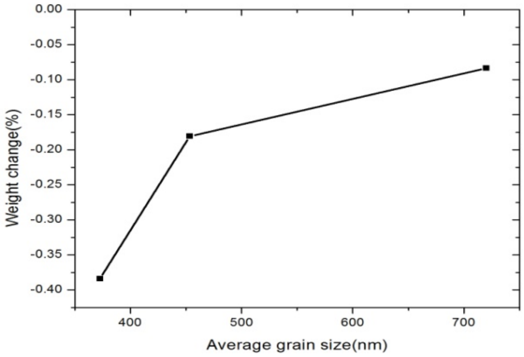


Figure 2 The weight changes of 3 groups of Cr_2O_3 ceramics under SCW exposure at 650°C and 25MPa for 200hrs

It can be seen from Figure 2 that Cr_2O_3 ceramics with smaller grain size tends to have low stability in SCW, which can be attribute to the preferential diffusion of oxygen at the grain boundaries. As average grain size became smaller, the relative fraction of grain boundaries increased which can create more paths for the oxygen diffusion and raise the rate of Cr dissolution.

3. SCW stabilities of CeO_2-added Cr_2O_3 ceramics

The micrometer-sized CeO_2 powders were added into the Cr_2O_3 powders (the powders used were from group 2 in section 2) with a mass percentage of 1%, 5% and 8%. Ball milling process was conducted at room temperature for 24hrs in order to achieve uniform powder mixture. The average particle sizes of all samples after ball milling were determined to be in the range of 200-250nm by SEM observation. The oxide powders were then compressed to form disk-shape samples and then were sintered at 1200°C for 15 hours.

3.1 Characterization of the as-fabricated ceramics

Figure 3 shows the XRD patterns of the Cr_2O_3 based ceramics with various amounts of oxide additives. For Cr_2O_3 ceramics added with 1 wt. % CeO_2, only the Cr_2O_3 peaks were identified. When the addition content increased to 5 wt. % or higher, the peaks corresponding to CeO_2 were also observed.

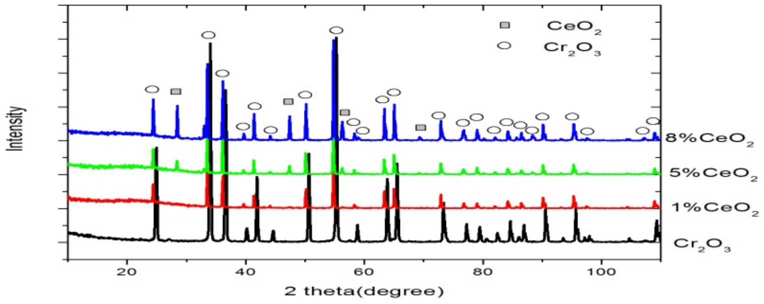


Figure 3 The XRD patterns of CeO_2-added Cr_2O_3 ceramics comparing with that of pure Cr_2O_3.

The surface morphologies of the Cr_2O_3 samples with various amounts of oxide additions are presented in Figure 4. It can be seen that the grain sizes of the ceramics were affected by the amount of additives. The average grain sizes of the samples were calculated based on the Figure 4 and are shown in Table 2. It can be seen that for CeO_2-added Cr_2O_3, grain refinement was presented when the addition amount reach 8 wt. %. The grain refinement phenomenon can be attributed to the pinning effect [5], in which the dispersed impurity particles act as obstacles to hinder the grain boundary migration during the sintering process. The pinning effects of CeO_2 additions have been reported in other studies [6].

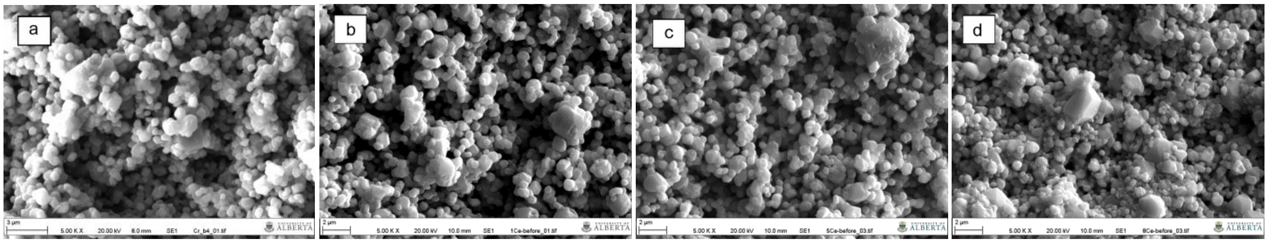


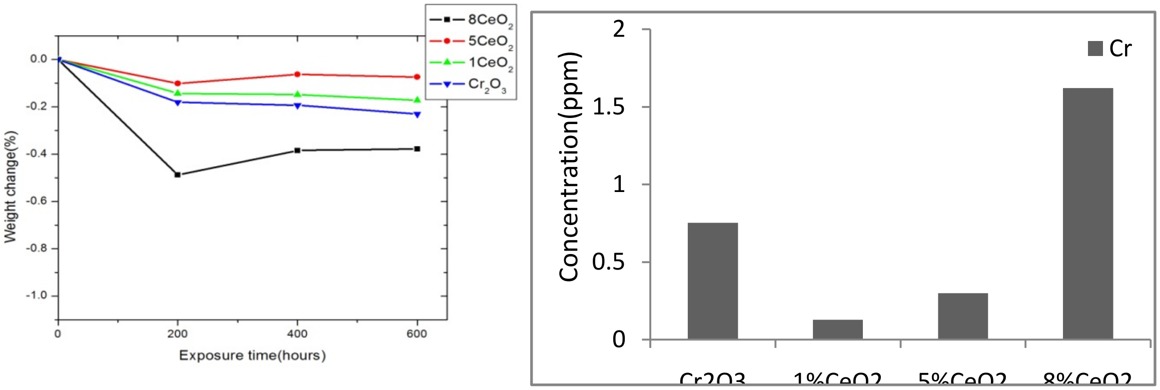
Figure 4 Surface morphologies of: (a) pure Cr_2O_3; (b) 1 wt. % CeO_2-added Cr_2O_3; (c) 5 wt. % CeO_2-added Cr_2O_3; (d) 8 wt. % CeO_2-added Cr_2O_3.

Table 2 Estimated average grain sizes of CeO_2-added Cr_2O_3 ceramics.

Sample	Cr_2O_3	1 wt. % CeO_2	5 wt. % CeO_2	8 wt. % CeO_2
Average grain size(nm)	453.5±18	451.7±19	452.5±17	411.0±24

3.2 SCW corrosion behaviour of Cr_2O_3 with oxide additions

The SCW test conditions are the same as that stated above, and the test duration hours are 200hrs, 400hrs and 600hrs, respectively. The results are shown in Figure 5 (a).



(a)

(b)

Figure 5 (a) The weight changes of CeO_2-added Cr_2O_3 ceramics under SCW exposure at 650°C and 25MPa for 200hrs, 400hrs and 600hrs; (b) The concentrations of Cr in the water remained in the tube after CeO_2-added Cr_2O_3 were exposed to SCW at 650°C and 25MPa for 400hrs.

CeO_2-added Cr_2O_3 exhibited enhanced corrosion resistance with an increase of CeO_2 up to 5 wt. %. However when the addition amount increased to 8 wt. %, decreased corrosion resistance can be observed. Figure 5(b) compares the results of mass spectrum analysis of the CeO_2-added Cr_2O_3 after test for 400hrs in SCW. It can be seen that the concentration of dissolved Cr was reduced when the addition content was below 5 wt. %. The beneficial effects can be originated from the so called "reactive element effect" [7]. When doping with CeO_2, due to its large atomic radius, Ce atoms tend to segregate at the grain boundaries where the distortion energy can be lowered. The segregation can impede the diffusion of O atoms, hence retarding the dissolution of Cr_2O_3. Nevertheless, it can be observed that the concentration of dissolved Cr increased with higher addition content and when the addition amount increased to 8 wt. %, the dissolution of Cr jumped to a very high level. The possible reason may be the grain refinement observed. As discussed above, smaller grain size resulted in higher diffusion rate of oxygen, which increased the Cr dissolution in SCW environment.

4. Conclusion

The stability of Cr_2O_3 in SCW was closely related to its grain size. As the grain size decreased, more oxygen diffusion paths were created, which led to greater oxidation rate of Cr_2O_3. Adding proper amounts (≤5 wt. %) of CeO_2 can enhance the stability of Cr_2O_3-based ceramics, which may be attributed to the presence reactive element effect of Ce. When the addition amounts increased to 8 wt. %, the higher oxygen diffusion rate, resulting from the grain refinement induced by the oxide additives, can accelerate the degradation of Cr_2O_3-based ceramics.

5. References

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