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Effect of atmosphere on the vaporization behavior of CsFeSiO₄

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Effects of atmospheres on the vaporization behavior of Cs chemisorbed compound CsFeSiO₄ was experimentally investigated. A pure CsFeSiO₄ sample was synthesized by a powder metallurgical route and was subjected to the thermogravimetric analysis. Weight loss of CsFeSiO₄ was larger in the order of those under Ar-5 %H₂ and Ar-5 %H₂O-5 %H₂, Ar-5 %H₂O, Ar and air. This would correspond to the varied vapor pressures of CsFeSiO₄ by different oxygen potentials in the atmospheres. On the other hand, larger weight losses under H₂ containing atmospheres were observed regardless of the oxygen potential. An X-ray diffraction analysis and a chemical equilibrium calculation have indicated the possible decomposition of CsFeSiO₄ by the interaction with H₂ in the vapor phase.

Keywords: cesium; chemisorption; CsFeSiO₄; revaporization; atmosphere; thermogravimetry

1. Introduction

The Cs chemisorption phenomena under an LWR severe accident (SA) is of crucial importance especially for the determination of debris removal strategy from Fukushima Daiichi Nuclear Power Station (1F), since chemisorbed Cs can become a major long-term radiation source. We have therefore conducted an experimental test series CREST (Chemical REaction with stainless Steel) for the investigation of the Cs chemisorption with a focus on the chemical behavior of Cs chemisorbed compounds [1,2]. A test for the investigation of atmospheric effects on the Cs chemisorption (CREST-ATM) has shown the atmospheric dependence of revaporization for the main Cs chemisorbed compound on the stainless steel (SS) surface, CsFeSiO₄ [3]. Namely, only Cs was revaporized from the Cs chemisorbed compound CsFeSiO₄ on the SS surface after a heating at 1073 K under a Cs-absent reductive atmosphere (Ar-5 %H₂), while Si remained on the SS surface. It was inferred that possible decomposition of CsFeSiO₄ at 1073 K has taken place by the interaction with H₂ in the vapor phase. This revaporization phenomena should be accurately known for the evaluation of the Cs chemisorption.

In this study, effects of atmosphere on the revaporization of CsFeSiO₄ was experimentally investigated. A pure CsFeSiO₄ sample was synthesized for the thermogravimetric analysis (TGA) in order to know the vaporization behavior. Characterization of the samples after the TGA together with a chemical equilibrium calculation was carried out for the

discussion of the chemical reaction occurred in relation with the revaporization.

2. Experimental and calculation

Table 1 shows the experimental conditions for the sample synthesis, TGA and characterization after the TGA. Details are described below.

Table 1. Experimental conditions for the Cs revaporization and characterization tests.

Synthesis of CsFeSiO ₄	
Starting materials	Cs ₂ CO ₃ , Fe ₂ O ₃ and SiO ₂ , Cs : Fe : Si = 1.4 : 1.0 : 1.0
Heat treatment	1073 to 1273 K, 9 h
Thermogravimetric analysis (TGA)	
Temperature	1573 K (holding time: 1 min., heating rate: 20 K/min.)
Atmosphere	Air, Ar, Ar-5 %H ₂ O, Ar-5 %H ₂ O-5 %H ₂ , Ar-5 %H ₂
Characterization	
Heat treatment condition for samples simulated the post TGA	CsFeSiO ₄ , heated at 1073 K, under Ar-5 %H ₂ O-5 %H ₂ or Ar-5 %H ₂
X-Ray diffractometry	CuK α , 40 kV, 15 mA
Chemical equilibrium calculation	Corresponding elemental moles to CsFeSiO ₄ , using SGTE database, under Ar-5 %H ₂ O-5 %H ₂ , Ar-5 %H ₂

A pure CsFeSiO₄ sample was synthesized by a heat treatment of a mixed powder of each starting material. The starting materials of Cs₂CO₃, Fe₂O₃ and SiO₂ compounds with a molar ratio of Cs : Fe : Si = 1.4 : 1.0 : 1.0 were intimately mixed in an agate mortar with a

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pestle. The mixed powder was compacted into a columnar shaped pellet for the heat treatment. The heat treatment was carried out in a static air repeatedly at 1073K for 5 h, at 1173 K for 2 h and 1273 K at 2 h. The heat-treated mixed powders were then characterized by an X-ray diffractometer (XRD).

The TGA of the synthesized CsFeSiO_4 sample was carried out by using a RIGAKU model Thermo-plus EVO2 and Al_2O_3 crucibles. TGA were carried out at a heating rate of 20 K/min. up to 1573K, temperature held for 1 min. before decreasing the temperature. Five kinds of atmosphere were applied for the TGA, specifically Air, Ar, Ar-5 % H_2O , Ar-5 % H_2O -5 % H_2 and Ar-5 % H_2 . The last two atmospheres were the same as in the CREST-ATM test in which the revaporization of CsFeSiO_4 were observed.

The XRD was done on the CsFeSiO_4 samples after the heat treatment at 1073 K for 1 h in another heating furnace in the corresponding atmosphere to the TGA. As shown later, since a notable gravimetric difference during TGA and preferable Cs loss under Ar-5 % H_2 in the CREST-ATM were observed at this temperature of 1073 K, this heat treatment was carried out for the detailed investigation on what kind of chemical reaction has taken place. A chemical equilibrium calculation as the corresponding condition to this experimental observation at 1073 K was also carried out for the discussion of the chemical reactions taken place. In the calculation, each elemental fraction was set so as to correspond to the 1 mol of CsFeSiO_4 under atmospheres of Ar-5 % H_2O -5 % H_2 or Ar-5 % H_2 .

3. Results and discussion

Figure 1 and Table 2 show XRD pattern and determined lattice parameters of the synthesized sample, respectively. Since almost all the peaks match the reference peaks and the lattice parameters agree with the reference ones with experimental errors, a pure CsFeSiO_4 sample is considered to be successfully obtained.

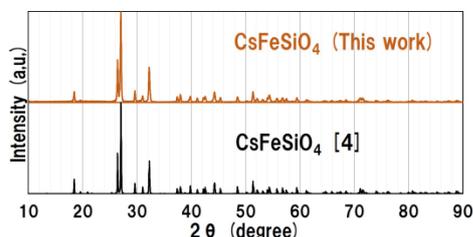


Figure 1. X-ray diffraction patterns of synthesized CsFeSiO_4 sample and reference [4].

Table 2. Determined lattice parameters of synthesized CsFeSiO_4 sample

	Lattice parameter [m]	
	Henry [4]	This work
a / Å	9.5858 (4)	9.5833 (42)
b / Å	5.5538 (3)	5.5552 (26)
c / Å	9.0476 (4)	9.0501 (35)

Figure 2 shows the TGA results for CsFeSiO_4 under the five different atmospheres. The common feature for all atmospheres was observed above around 1373 K; namely acceleration of weight loss compared to that under 1373 K. This feature could correspond to a phase transition or decomposition of CsFeSiO_4 , or some chemical reactions at around this temperature, although presently no information is available for the phase states at such high temperature for CsFeSiO_4 .

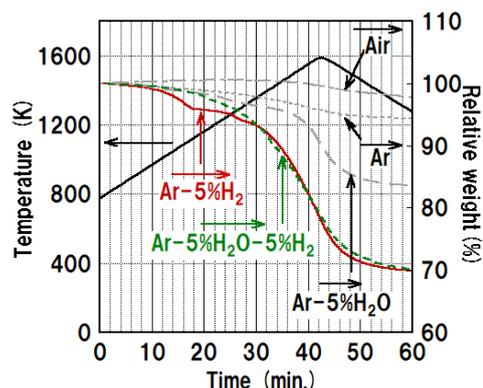


Figure 2. TGA of CsFeSiO_4 under the different atmospheres.

Weight losses at the end of the TGA (60 min.) are larger in the order of those under Ar-5 % H_2 and Ar-5 % H_2O -5 % H_2 , Ar-5 % H_2O , Ar and air. One possible reason for this would be caused by increase of vapor pressures with decrease of the oxygen potential in the atmosphere.

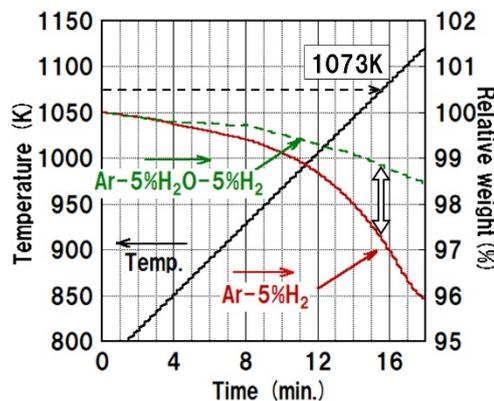


Figure 3. TGA of CsFeSiO_4 under Ar-5 % H_2O -5 % H_2 and Ar-5 % H_2 ; enlargement of the TGA graph shown in Figure 2 up to 1123 K.

Of note is the almost similar weight loss profiles of Ar-5 % H_2 and of Ar-5 % H_2O -5 % H_2 regardless of difference of oxygen potential. This implies possible dominant effects of H_2 in the atmosphere, rather than the effects by the difference in the oxygen potential. Namely, some interaction of H_2 with CsFeSiO_4 could have taken place, to have made the weight losses profiles similar. However, it can be seen that the weight loss profiles are distinctly different between under these two atmosphere at around 1073K. In CREST tests, Cs revaporization from CsFeSiO_4 has occurred under reductive atmosphere

(Ar-5 %H₂) at 1073 K. As shown in the TGA profiles enlarged around this temperature (**Figure 3**), the weight loss is larger in Ar-5 %H₂ compared to that in Ar-5 %H₂O-5 %H₂. This difference implies a possible suppression of the interaction between H₂ and CsFeSiO₄ under the Ar-5 %H₂O-5 %H₂.

Figure 4 shows the XRD patterns of the simulant CsFeSiO₄ samples. As mentioned above, these samples were prepared by the heat treatment of synthesized CsFeSiO₄ at 1073 K for 1 h to simulate those experienced the TGA at that temperature.

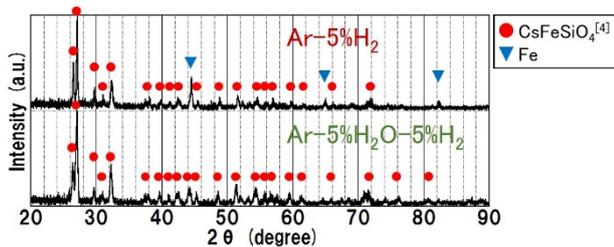
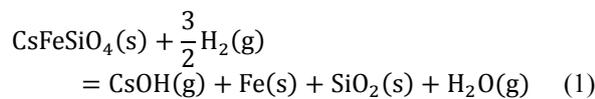
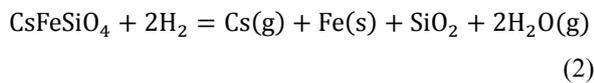


Figure 4. X-ray diffraction patterns of CsFeSiO₄ samples heat treated under Ar-5 %H₂O-5 %H₂ or Ar-5 %H₂ at 1073 K.

The bcc (body centered cubic) -Fe peaks were clearly observed in addition to those derived from CsFeSiO₄ on the sample heat treated under Ar-5 %H₂, while no bcc-Fe peaks were seen under Ar-5 %H₂O-5 %H₂. This indicates a possible decomposition of CsFeSiO₄ by the heat treatment under Ar-5 %H₂. Although only Cs loss with leaving Si was observed in the CREST-ATM, Si compounds-derived peaks, such as those from SiO₂ which has amorphous structure, were not observed in the XRD peaks. Nevertheless, the chemical equilibrium calculation results show the formation of bcc-Fe and SiO₂ under these conditions of 1073 K in Ar-5 %H₂. From the results mentioned above, it is inferred that the low temperature accelerated decomposition of CsFeSiO₄ at around 1073K under Ar-5 %H₂ can be expressed by the following equation.



or



4. Conclusion

An experimental investigation of the effects of atmosphere on the vaporization behavior of Cs chemisorbed compounds CsFeSiO₄ was performed. It was found that the weight loss was larger when the oxygen potential was lower. Of note is the greater weight loss of CsFeSiO₄ under H₂ including atmospheres regardless of H₂O inclusion. Besides, the accelerated weight loss was observed at 1073 K only under Ar-5 %H₂. It is inferred that H₂ plays an important role for the enlarged weight loss of Cs chemisorbed compound CsFeSiO₄ by the decomposition.

As the H₂ generation absolutely occurred in the LWR SA progress by the oxidation of fuel cladding and structural materials, the present result is important for the accurate estimation of Cs chemisorption in the LWR under and after SA.

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References

- [1] F.G.Di Lemma, K. Nakajima, S. Yamashita and M. Osaka, Surface analyses of cesium hydroxide chemisorbed onto type 304 stainless steel, *J. Nucl. Eng. Des.* 305 (2016), pp. 411-420.
- [2] F.G.Di Lemma, K. Nakajima, S. Yamashita and M. Osaka, Experimental investigation of the influence of Mo contained in stainless steel on Cs chemisorption behavior, *J. Nucl. Mater.* 484 (2017), pp. 174-182.
- [3] K. Nakajima, E. Suzuki and M. Osaka, Atmospheric effect on Cs chemisorption behaviors onto stainless steel, *Prog. Nucl. Sci. Technol.* 5 (2018), pp.168-170.
- [4] P.F. Henry and M.T. Weller, CsFeSiO₄ : a maximum iron content zeotype, *Chem. Commun.* 24 (1998), pp. 2723-2724.