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# Hydrothermal corrosion behavior of iron aluminide under SCWO conditions

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**Abstract** $Fe_3Al$ based iron aluminide was tested under supercritical water oxidation (SCWO) conditions to explore its possible use as a reactor material for hydrothermal processes. Degradation resistance of the material were evaluated in distilled water at 450 °C and 300 atm in a closed reactor. The results of the kinetics studies, metallographic observations as well as phase and chemical analysis of the corrosion products indicated limited applicability of iron aluminide in SCWO conditions.

## Introduction

Development of $Fe_3Al$ based iron aluminides was initiated with an objective to utilize these materials for high-temperature applications due to their excellent oxidation resistance and high-strength to weight ratio [1–3]. These alloys show limited ductility unless there is an alloying element addition or/and processed by advanced process roots [4]. Despite this fact, these materials are continued to gain considerable interest for structural materials. In recent years, due to its low fabrication cost, research activities have taken one more root to explore this material for room temperature applications. This resulted, considerable amount of works on the aqueous corrosion behavior of iron aluminides in various media [5–7]. A survey on these reports highlights that these materials have reasonable corrosion resistance, though it is not comparable with stainless steels [8]. Moreover, there are reports claiming that the corrosion resistance of iron aluminide can be further enhanced by formation of alumina layer on the surface through high-temperature oxidation process [9, 10]. All these facts together make iron aluminide attractive to evaluate its performance under SCWO conditions, which has not been reported so far. Materials used for SCWO environment, should have a combined properties of high-temperature oxidation and aqueous corrosion resistance apart from its required high-strength to resist the temperature and pressure of the reactor. Undoubtedly, $Fe_3Al$ based iron aluminides possess good oxidation resistance and excellent strength up to temperature of 550 °C [1], which is well above the required temperature for SCWO conditions for the production of fine ceramics such as ceria and zirconia [11].

On the other hand, though the technology basis of SCWO is well established the degradation of the reactor material is still a matter of concern [12]. Since SCWO environments have wide variation in terms of water density, viscosity, pH, dielectric constant, electrochemical potential, anion, etc. it is impossible that one single alloy can cover those. Plus the alloys, which are presently used in SCWO conditions such as duplex stainless steel, Ni based super alloys and Ti based alloys, are not cost effective. This demands development of new (cost effective) alloy for specific SCWO conditions.

Thus, in this study we explore the possible applications of iron aluminide under SCWO conditions. For

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this we will investigate the degradation resistance of iron aluminide in distilled water at 450 °C and 300 atm, similar to that of pre-heater conditions.

## Experimental

Iron aluminide fabricated for the present study were high-purity laboratory heats of Fe-16 wt.% Al. High purity alloying elements were melted in vacuum arc furnace. Specimens were prepared by cold rolling the hot rolled plates into 3 mm thick sheets. The size of the exposed coupons used was 20 mm × 10 mm × 2 mm. Specimens were prepared by polishing on SiC papers down to 2000 grade followed by 1 micron diamond finishing. Three coupons were used for each set of experiment.

A brief outline about the reactor of ceramic production plant is shown schematically in Fig. 1 [13]. In the production process, pre-heater preheats the distilled water over supercritical condition to feed the fluid in reactor where this fluid is mixed with electrolyte for further processing. The reactor employed in present study was a closed double wall vertical static autoclave made of AL-6XN grade super austenite stainless steel. Inner wall of the reactor was coated with $TiO_2$ layer. For pre-heater conditions the iron aluminide was exposed in distilled water at 450 °C and 300 atm. After a specified exposure time, the autoclave was cooled to room temperature, and the change in weight of each specimen was noted.

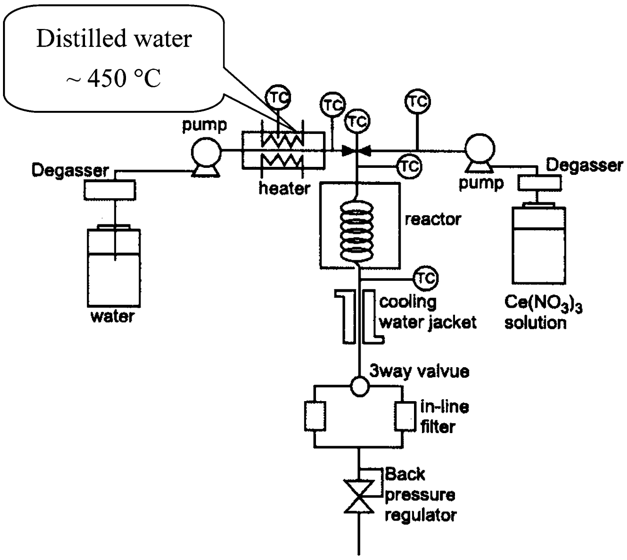

**Fig. 1** Schematic representation for the flow apparatus using in the ceria synthesis under SCWO condition [13]

Surface morphologies of the exposed specimens were studied with scanning electron microscope (SEM). Energy disperssive X-ray (EDX) analysis attached to SEM was used to identify the elements present in the oxide scale. The formation of oxide phases after exposure to SCWO was analyzed with X-ray diffractometer (XRD) using Cu target having $K_\infty$ = 1.5418 Å. All the analysis measurements were conducted on samples at ambient temperature. Quantification of dissolved metal ions from the alloy into reactor solution was done by a Hewlett-Packard (Model 4500) induction coupled plasma atomic mass spectroscopy (ICP-MS). The instrument was calibrated by external calibration method with multielement standards.

## Results

The time dependence of the degree of corrosion of iron aluminide in distilled water under SCWO condition is shown in Fig. 2. It was found difficult to measure the actual weight change in the alloy as the surface was covered with some loose oxides. Therefore, the graph has been plotted for the minimum and the maximum values. The minimum value corresponds to the weight-change just after removing the specimen from the electrolyte and air dried in open atmosphere. The maximum value corresponds to the weight of the alloy after complete removal of the oxide products with ultrasonic cleaning in distilled water and under air pressure. The timing for these processes varies sample-to-sample ≈ 5 to 15 min, depending upon the oxide layers and its adhesion to surface. The error bar covers

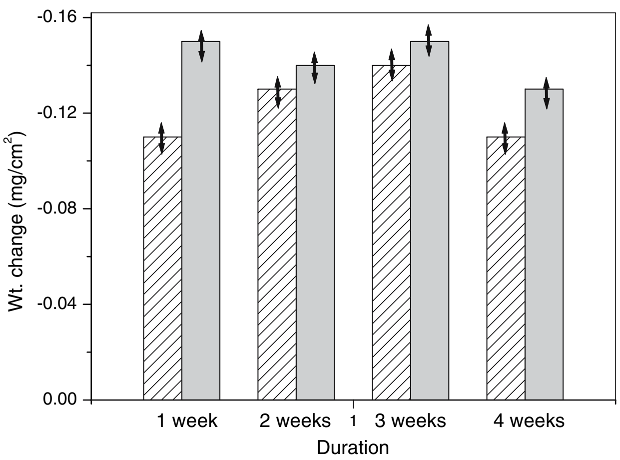

**Fig. 2** Weight changes in the iron aluminide after exposure into the distilled water at 450 °C and 300 atm for different exposure time

for maximum and minimum values in the multiple numbers of specimens. As seen in Fig. 2, there is loss in weight of the alloy irrespective of the exposure time. During initial period there is an apparent increase in corrosion rate with time, and with increase of exposure time weight loss of the alloy is decreased. This might be due to the decrease in dissolution tendency of the electrolyte due to saturation with corrosion product or/and oxide products remained on the surface of the alloy, as the experiments were conducted in a closed reactor.

SEM micrograph in Fig. 3a, b, c show the surface morphology of iron aluminide after exposure in distilled water at 450 °C for different periods of time. The corroded surface and the surface covered with oxide product could be seen from these figures. An increase in the nature of attack with increase of time is evident. The presence of crack Fig. 3c disappears after complete removal of the oxide layer from the surface. EDX analysis was performed at two different locations, 1 and 2 as shown in Fig. 3a, are listed in Table 1. The analysis reveals that the oxide scale in location 1 is mainly due to iron oxide, whereas the location 2 corresponds to the $Fe_3Al$ substrate. XRD analysis of these surfaces reveals the presence of iron oxide on the surface is in the form of $Fe_2O_3$. For illustration, one such spectra of the iron aluminide after exposure into the SCWO condition for 2 weeks is shown in Fig. 4, where the corresponding peaks for $Fe_2O_3$ are indexed based on JSPS file number PDF # 33-0664.

It has been pointed out in the introduction that the corrosion resistance of iron aluminide may be improved by formation of alumina layer on the surface. Generally, protective alumina on iron aluminide is formed above 700 °C in gaseous atmosphere. Therefore, with such an objective some additional experiments were performed. Iron aluminide was oxidized at 800 °C for 24 h in presence of oxygen atmosphere. The formation of $Al_2O_3$ layer on iron aluminide was confirmed by XRD analysis. This alloy was then exposed in the SCWO conditions as described above for 1 week. The change in weights of the alloys without and with alumina layer formation after exposure in SCWO condition is compared in Fig. 5. It is evident that there is not much advantage on the corrosion resistance of the alloy with pre-alumina layer formation on the surface in SCWO conditions.

Quantification of the dissolved cations from iron aluminide in the solution after exposing in reactor for 2 weeks under SCWO condition, obtained from ICP-mass spectroscopy, is shown in Table 2. The result shows higher concentration of Al than Fe, in electrolyte. The relative sensitive distribution (RSD) of Al is very good while in case of iron it is very high. This could be inhomogeneous distribution of Fe in the solution. However, despite this fact the concentration of Al is higher than that of the Fe, while considering the alloy compositions (Fe-16wt.%Al). This finding supports the dissolution of alumina layer from the surface of iron aluminide under SCWO conditions.

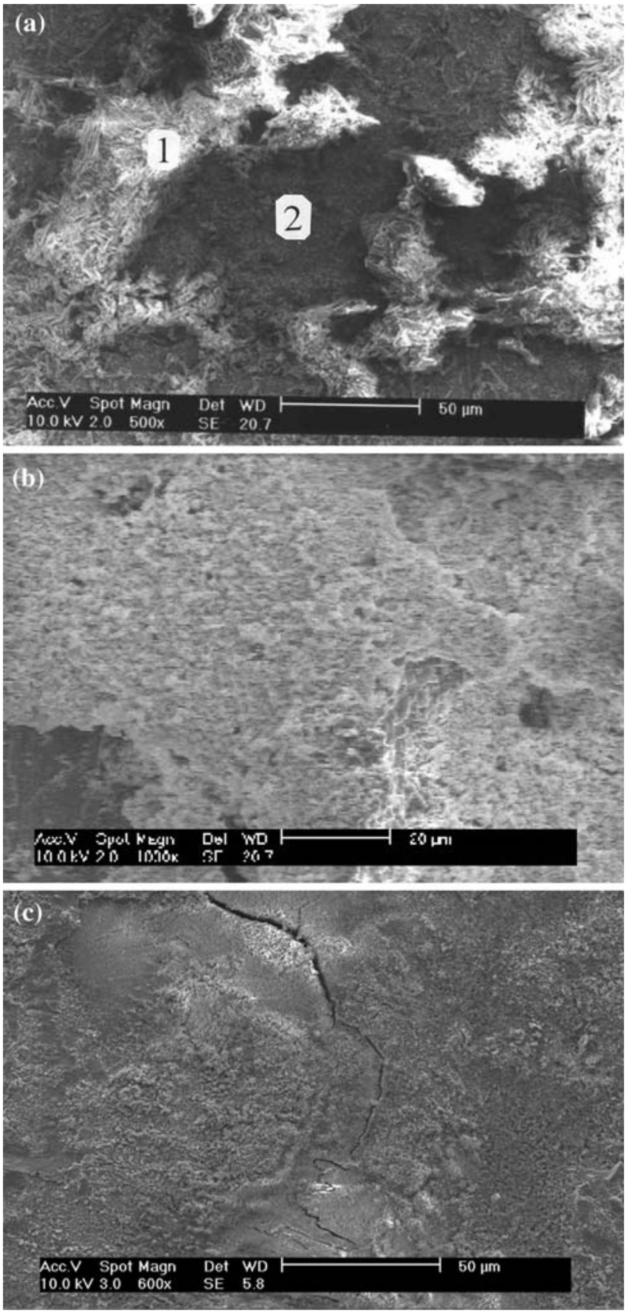

**Fig. 3** SEM micrographs of the iron aluminide after different exposure of time in distilled water at 450 °C and 300 atm: (**a**) after 1 week, (**b**) after 2 weeks and (**c**) after 3 weeks

**Table 1** EDX analysis of the surface at locations, 1 and 2 shown in Fig. 3a

| Elements | Fe K (at.%) | Al K (at.%) | O K (at.%) |
|---|---|---|---|
| Location 1 | 44.6 | 2.4 | 53.0 |
| Location 2 | 66.0 | 27.5 | 6.5 |

## Discussion

Iron aluminides have never been tested in SCWO conditions to provide any direct comparison in the present discussion. Therefore, it is logical to compare with other closely related materials to get an insight in the performance of aluminide. In the late nineties or so the Al based alloys and alumina ceramic was considered as a strong candidate for the reactor materials in SCWO conditions in replacement of the typical duplex stainless steel, Ni based superalloy and Ti based alloys. Later the development of such materials was restricted due to the dissolution of the bulk material in SCWO conditions, resulting in material loss [14, 15]. Boukis et al. [14] reported the corrosion behavior of 99.7% alumina under SCWO conditions in 1800 ppm $Cl^-$ containing aqueous solution at 465 °C and 25 Mpa. Their results show the weight loss in 99.7% alumina is less than 0.1 mg/cm$^2$ for a period of 144 h exposure, a further increase in exposure time up to 220 h did not result further increase in weight loss in material. This finding is well in agreement with the present results as there is little difference in the weight loss with time of exposure (Fig. 2). While, by comparing the weight loss data of iron aluminide with the data reported for 99.7% alumina it can be found that the corrosion behavior of iron aluminide is marginally higher than that of 99.7% alumia. The work of Schacht et al. [15] is related to the corrosion behavior of alumina ceramics in acid containing solutions at temperatures of 240 °C–500 °C. They found that the corrosion rate of alumina increases with temperature (340 °C–500 °C) in sulfuric acid containing solutions. Though, the solubility of the corrosion products was considered as crucial importance for the corrosion resistance of the aluminas, the dominant corrosion mechanisms were identified as intergranular attack and dissolution of $Al_2O_3$.

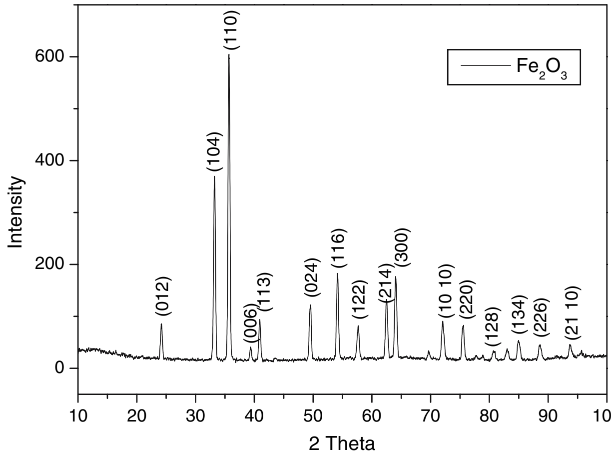

**Fig. 4** XRD spectra of the oxide surface formed on iron aluminide after exposure into distilled water at 450 °C and 300 atm

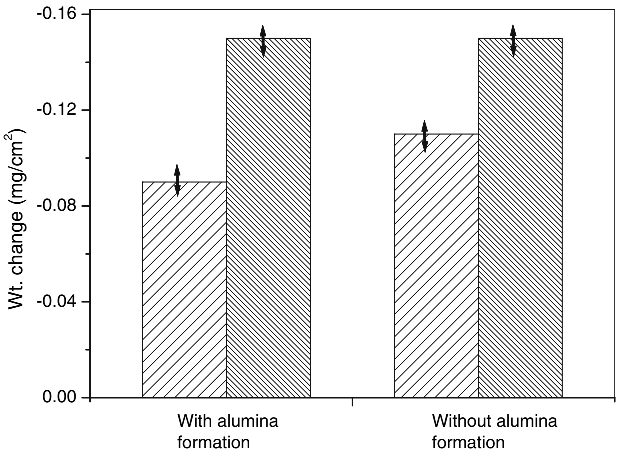

**Fig. 5** Change in weight of the alloy without and with alumina layer formation after exposure in distilled water at 450 °C and 300 atm for 1 week

Not to mention the excellent oxidation resistance of iron aluminide at high temperature gas environments is due to the formation of protective alumina layer [16]. Even the aqueous corrosion resistance of this alloy is mainly due to the formation of $Al_2O_3{\cdot}3H_2O$ or/and $Al(OH)_3$ based passive film on the surface [17]. In the present study, as we observed, there was no alumina layer on the surface of iron aluminide after exposure into SCWO conditions, and even the preformed alumina layer is dissolved in the SCWO conditions. This provides an explanation for the higher corrosion rate of iron aluminide than that of 99.7% alumina. In this regard, a discussion on the thermodynamic stability and solubility of the possible oxides of iron aluminide in aqueous solution at elevated temperature will be useful for understanding its corrosion behavior in SCWO condition. A direct experimental determination of the

**Table 2** ICP quantification of dissolved cations from iron aluminide during exposure in distilled water at 450 °C for 2 weeks

| Elements | Mass | Concentration | RSD (%) |
|---|---|---|---|
| Al | 27 | 0.2178 (ppm) | 2 |
| Fe | 57 | 0.1184 (ppm) | 28 |

free energy changes for the oxides in aqueous system at elevated temperature has proven difficult, principally because many electrochemical reference or indicator electrodes no longer act reversibly at elevated temperature. An alternative approach, has been used for such problems, is to integrate free energy functions over the desired temperature range using empirical relationships for the variation of heat capacity or entropy with temperature. There are such works on the pure Al and Fe describing the stability of the various oxides and hydroxide under hydrothermal conditions [18–20]. For aluminium, several hydrated oxides are reported to exist in hydrothermal systems. These include gibbsite and bayerite $Al_2O_3{\cdot}3H_2O$, boehmite and diaspore $Al_2O_3{\cdot}H_2O$ and corundum $Al_2O_3$. At room temperature to ≈155 °C $Al_2O_3{\cdot}3H_2O$ is stable, on further heating dehydrated to $Al_2O_3{\cdot}H_2O$ and finally to $Al_2O_3$ at ≈450 °C [18]. Still another study of this system shows that the film formed on Al in steam at very high temperature (>350 °C) consists of unhydrated oxide, $Al_2O_3$ [19]. Kriksunov and Macdonald [20] investigated the stability of Fe–$H_2O$ system at SCWO conditions and reported the decomposition of hydrated oxides into oxides because of the low water densities in the supercritical region at pressure of <500 bar. These authors drew the potential-pH diagram for iron in super critical water using thermodynamic data. Based on this diagram they suggested that the oxide film on iron possessed is a bilayer structure comprised of a $Fe_3O_4$ inner layer and an outer $Fe_2O_3$ layer in neutral aqueous solution. This lends credence to the present finding of iron oxide on the surface on iron aluminide. Nevertheless, it was pointed out that the formation of oxide layers on the surface of an alloy under SCWO conditions does not necessarily mean protection. These are necessary but not a sufficient condition for the protection of an alloy by surface oxides.

Macdonald and Butler [18] reported that the standard free energy changes for the reaction (1) increases with increase of temperature in a hydrothermal study of Al–$H_2O$ system.

$$2AlO_2^- + 2H^+ = Al_2O_3.H_2O \quad (1)$$

This implies that the formation of aluminate ($AlO_2^-$) ions from $Al_2O_3{\cdot}H_2O$ is favored by increasing temperature. And so the region of corrosion due to the formation of aluminate ion increases rapidly with temperature. This data provides an indirect support for the absence of alumina layer on the surface of iron aluminide and its corrosion behavior after exposure into the SCWO conditions.

## Summary

The corrosion behavior iron aluminide under SCWO conditions in pure distilled water was tried to explore. Iron aluminide was found to be corrosive in distilled water under SCWO conditions. There was no alumina layer on the surface after exposing into supercritical water, instead iron oxide in the form of $Fe_2O_3$ was found on the surface. Even the pre-formed alumina layer does not provide much protection to the aluminide from supercritical water fluid.

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