

Analyses on Silicide Coating for LOCA Resistant Cladding

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1. Introduction

During accident conditions at high temperatures with the presence of steam, zirconium-alloy cladding undergoes an exothermic oxidation reaction that releases hydrogen gas that may leak to the containment, accumulate and explode. In relation to the events following the tsunami at Fukushima and the loss of coolant accident (LOCA), interest in developing more accident-tolerant fuels has increased [1].

A particular focus of accident-tolerant fuel has been cladding due to the rapid high-temperature oxidation of zirconium-based cladding with the evolution of H₂ when steam is a reactant.

Some key features of the coated cladding include high-temperature resistance to oxidation, lower processing temperatures, and a high melting point of the coating [1]. Zirconium alloys exhibit a reasonably high melting temperature, so a coating for the cladding is appealing if the coating increases the high-temperature resistance to oxidation. In this case, the cladding is protected from complete oxidation.

The cladding coating involves the application of zirconium silicide onto Zr-based cladding. Zirconium silicide coating is expected to produce a glassy layer that becomes more protective at elevated temperature [1]. For this reason, silicide coatings on cladding offer the potential for improved reliability at normal operating temperatures and at the higher transient temperatures encountered during accidents.

Although ceramic coatings are brittle and may have weak points to be used as coating materials, several ceramic coatings were successful and showed adherent behavior and high resistance to oxidation [2].

In this study, the oxidation behavior of zirconium silicide and its oxidation kinetics are analyzed. The oxidation correlation, in turn, is to be used in a transient fuel performance code to study the impact of coating the Zircaloy-4 cladding on fuel performance under design basis accident conditions, particularly a loss of coolant accident (LOCA).

2. Method

2.1 Experiment

The need of the experiment rises from the limited oxidation data of zirconium silicide in the literature. For this reason, the oxidation kinetics of zirconium silicide is studied and a correlation is obtained from the literature. This correlation helps to understand the mechanism of zirconium silicide oxidation and the

expected oxidation behavior of the coating. The resulting fitted correlation can be compared with the already existing correlation for zirconium alloy cladding, so that it can be used in the transient fuel performance code FRAPTRAN.

2.2 The coating material

The analysis of thermodynamic data indicates that a ZrSi₂ or ZrSi coating offers excellent prospects to provide a more protective barrier than the native ZrO₂ films that form on alloy cladding during routine plant operations. ZrSi₂ and ZrSi also provide an exceptional protective barrier during high-temperature accident scenarios [1].

Initial choices for the silicide layer material include ZrSi₂ and ZrSi. The lower zirconium activity in the ZrSi₂ is expected to compensate in some measure for the greater stability of ZrO₂ compared to SiO₂, allowing the formation of the SiO₂ barrier layer under the water-side ZrO₂ layer. On the other hand, the monosilicide, ZrSi, is not expected to readily produce an effective silica barrier layer, producing instead the thermodynamically favored ZrO₂ outer layer, lacking the mobility and barrier properties of the silica layer.

Intermetallic silicide compounds, such as MoSi₂, are stable in air at very high temperatures. In contrast to the behavior of MoSi₂ at high temperatures, the oxidation of zirconium silicides can produce the glassy silica layer (SiO₂) along with, or after, producing ZrO₂ and ZrSiO₄ (zircon) because of the more negative free energy of the Zr-oxides.

At high temperatures, silicides form a silica layer on the surface that impedes further oxidation of the silicide. Cracks and fissures in the silicide coating can develop upon thermal cycling, as these arise from differential expansion between the coating and the substrate. However, experience shows that these potential problem areas self-heal upon reheating. As a result, silicides have widespread commercial use in high temperature applications.

A coating may be prepared similar to the schematic given in Fig. 1 [1]. The desired performance is comparable or superior to ZrO₂ on zirconium cladding alloys during normal service, and greatly superior to ZrO₂ on cladding alloys during accident and loss-of-cooling scenarios.

After oxidation, the as-fabricated coating involves the zirconium alloy substrate, an inner ZrO₂ layer, the silicide layer (ZrSi₂), and an outermost layer of SiO₂/ZrO₂ (or zircon, ZrSiO₄), which is exposed to the reactor coolant. The inner layer of ZrO₂ is present

either as the native film or as an anodized layer. It is believed that the existence of the ZrO₂ inner layer improves the performance of the coating that follows from the expected self-limiting degradation that develops through thermal excursions, either prior to or after reactor insertion.

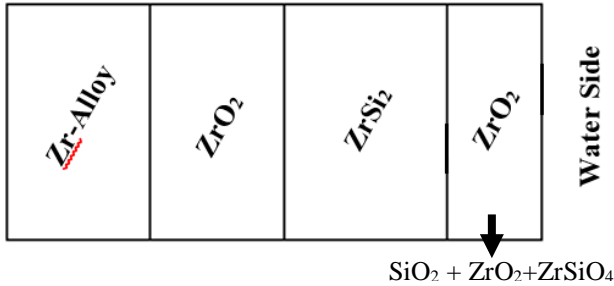


Fig.1: As-fabricated ZrSi₂ coating schematic, not to scale [1].

2.3 Coating technique

Coatings may be applied following one or more methods described in the literature. Two particularly interesting coating methods described in ref. 1 are fused-slurry and silane (SiH₄) decomposition on heated substrates [1]. Short thermal exposures should be performed to develop the coatings to help avoid the change in microstructure as much as possible. Another coating method of ceramics on zirconium alloys is done at room temperature by pulsed laser deposition (PLD) [2].

According to ref. 3, the Radio Frequency (RF) sputtering method was used to coat SiC on Zircaloy-4. Although the coating method is typically done at room temperature, the coating in ref. 3's experiment experienced peel-off, indicating that this type of coating is not protective. For that reason, other coating methods that are chemically based become more attractive to coat ceramics on zirconium alloys.

Pack cementation coating is another attractive coating method and is essentially an in-situ chemical vapor deposition process (CVD) and a thermal diffusion process [4]. This process has been widely and chronically used to treat components of various dimensions and geometries. However, it is seriously limited by requiring thermal activation to boost chemical reaction and interdiffusion kinetics.

Pack cementation is widely used to confer oxidation resistance on ferrous alloys. Pack cementation processes include aluminizing, chromizing, and siliconizing. Components are packed in metal powders in sealed heat-resistant retorts and heated inside a furnace to precisely controlled temperature-time profiles. The coating forms at temperatures ranging from 700 to 1100°C over a period of several hours.

The coating method used is pack cementation. Small Zircaloy-4 tube specimens (less than 1 cm

length) are coated using pack cementation at a temperature range of 1000-1200 °C using tube furnace.

3. The oxidation behavior of zirconium disilicide (ZrSi₂)

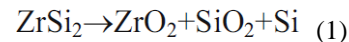
The oxidation of disilicides is a complex multistage process associated with the formation of silicide phases with a lower silicon content, metal oxides, silicon oxides SiO₂ and SiO, and silicate phases of MeSiO₄ and Me₂SiO₂ types [6].

Zirconium silicides have good oxidation resistances at elevated temperatures [7], thus making them an attractive choice for use as coating material.

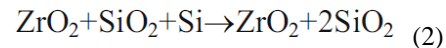
The first stage of the oxidation leads to the formation of elemental silicon as an intermediate reaction product. Upon further temperature increase, the newly-formed silicon is oxidized. Completely oxidized ZrSi₂ consists of ZrSiO₄, amorphous and crystalline SiO₂, as well as some residual ZrO₂.

At temperatures below 800 °C, the reaction rate is very low and increases considerably only at 900 °C. Further temperature increase does not accelerate the process.

When analyzing the oxidation behavior and its kinetics, oxidation starts at a temperature of approximately 500°C, and the sample mass increases continuously up to 900°C [7]. This first part of the oxidation process has a mass gain of approximately 45% and is represented in the following equation:



With increasing temperature, a second oxidation process with a mass change of approximately 14% and a much lower mass gain rate compared to the first step can be observed and can be represented in the following equation:



4. Zirconium silicide chemical instability

Kinetic measurements show that SiO₂ formation on silicides is much larger during steam oxidation than during oxidation in dry oxygen [5].

In terms of chemical stability, ZrSi₂ has been compared with several silicides to show if it is chemically stable during oxidation. Oxidation was carried out between 750 and 1100 °C, through which steam or dry oxygen flowed at atmospheric pressure [5]. Pure SiO₂ layers could be grown on all the silicides except ZrSi₂, in which case a mixed SiO₂-zirconium oxide layer formed.

In the case of ZrSi₂ oxidation, it can be seen that metal oxidation has taken place with incorporation of the metal in the growing SiO₂ layer. More specifically, the percentage chemical stability test of ZrSi₂ during

steam oxidation for 20 minutes at different temperatures reveals that $ZrSi_2$ is chemically very unstable, leading to a completely mixed layer of SiO_2 and zirconium oxide [5].

5. Analysis and results

Zirconium disilicide is compared with FeCrAl, an already suggested accident tolerant fuel material, to show the oxidation resistance of $ZrSi_2$.

Due to the limited availability of $ZrSi_2$ oxidation data, air oxidation at temperature of $1200^\circ C$ is used and reviewed from the literature. In the case of FeCrAl, surface oxidation data in flowing air are available in the literature [8], and for $ZrSi_2$, powder oxidation is the only available data in the literature and has been normalized for the preliminary comparison. Fig. 2 shows the weight gain data of FeCrAl and $ZrSi_2$ available in the literature.

From the results shown, $ZrSi_2$ shows strong oxidation resistance at high temperatures, which gives an indication about the potential of using $ZrSi_2$ as coating material for the existing zirconium-based nuclear fuel cladding.

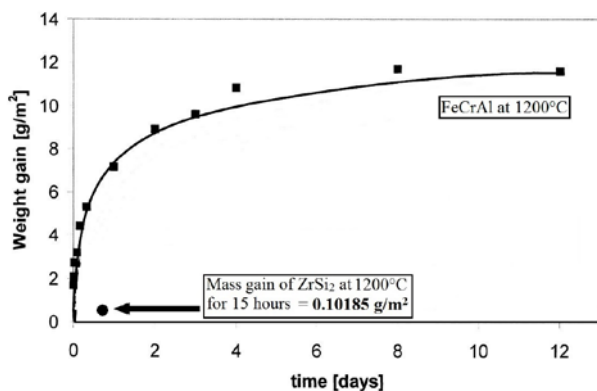


Fig.2: Mass gain of $ZrSi_2$ and FeCrAl in air and temperature of $1200^\circ C$.

Oxidation tests are necessary to obtain data about the oxidation behavior of $ZrSi_2$ in high temperature steam environments, and to do comparative studies with the already proposed accident tolerant fuels, claddings and coatings.

6. Conclusions

Zirconium silicide is a new suggested material to be used as coatings on existing Zr-based cladding alloys, the aim of this study is to evaluate if zirconium silicide is applicable to be used, so they can be more rapidly developed using existing cladding technology with some modifications. These silicide coatings are an attractive alternative to the use of coatings on zirconium claddings or to the lengthy development of monolithic ceramic or ceramic composite claddings and coatings.

The chemical instability of zirconium silicide is a limiting factor for the use as cladding material, some modifications have to be done to enhance the stability of the coating during oxidation by adding other elements to minimize the formation of the completely mixed layer of SiO_2 and zirconium oxide.

Further experiments are needed to study the oxidation behavior of $ZrSi_2$ in steam environment at high temperature, and to be used in normal operation and transient fuel performance codes as well as doing comparative studies with the existing accident resistant claddings and coatings such as FeCrAl and SiC.

Acknowledgements

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