MECHANISMS OF STEAM OXIDATION IN Cr-COATED Zr ALLOY

INTRODUCTION

The study of corrosion phenomena and the development of corrosion-resistant materials and coatings are necessary tasks in many industrial processes. For example, materials used in the nuclear industry have to withstand harsh conditions such as high temperature, intense irradiation and/or steam and water exposure and as a result they develop corrosion issues.

As an illustration, the development of protective coatings against corrosion (such as Cr based) for zirconium alloy is needed to ensure the safety of nuclear reactors in case of incidents such as loss of coolant accident.
During this type of event, the material is subjected to temperatures higher than 1000°C and a high-level relative humidity (RH). It causes fast oxidation of Zr, leading to structural failure and hydrogen release.

THEMYS TGA instrument can be used to simulate this extreme environment and study the behavior of materials used in this application. An example is provided here with the study of phenomenology and the comparison of oxidation kinetics between Cr coated and uncoated zirconium alloy.

EXPERIMENT

- Sample: Zr-Nb alloy
- Geometry: 10mm high, Ø 9.5mm and 0.57mm thickness tube
- Coating: Cr-based, only on the outside of the tube
- Instrument/Technique: THEMYS TGA, measurement of weight variations
- Protocol: fast heating to 1200°C (50°C/min), followed by an isotherm at 1200°C under steam (80% RH, 50ml/min) during 3h

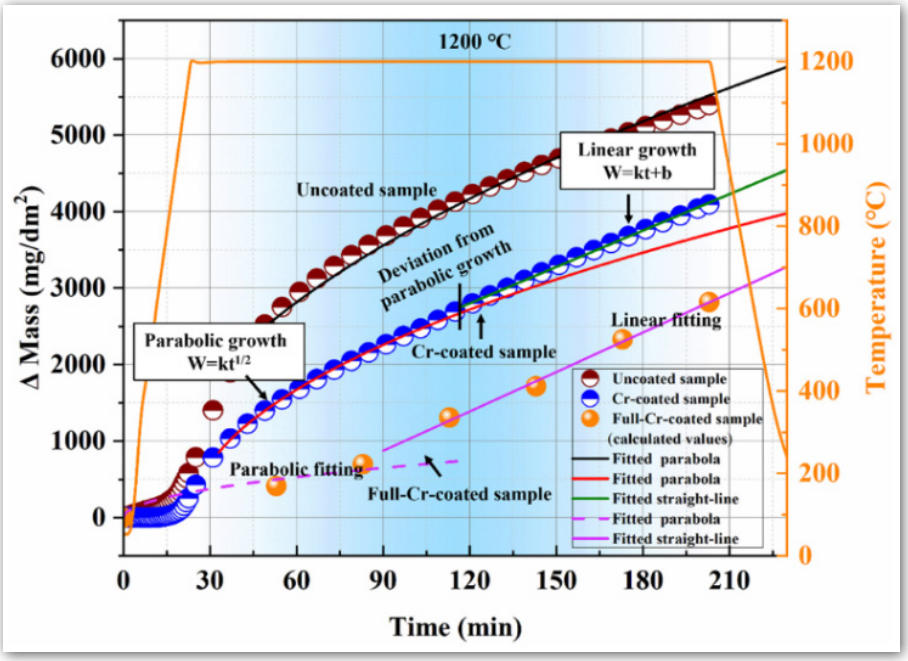

Figure 1 : Mass variation of uncoated and coated samples measured by TGA

RESULTS AND CONCLUSION

Figure 1 shows the weight variation of samples divided by their surface. For both single coated and uncoated sample, a weight increase is measured during the heating and isotherm.

Results show that oxidation kinetics do not follow the same trend between uncoated and coated samples. The weight increase is faster for the uncoated sample and fits a parabolic law, which is attributed to the fast oxidation of Zr.

In the case of the coated sample, the growth follows a "paralinear" trend, meaning that it shifts from the initial parabolic curve to a linear one. The slower oxidation kinetics for the coated sample demonstrate the protection provided by the coating.

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RESULTS AND CONCLUSION

From these results, the expected weight gain for a fully coated sample is calculated.

In addition to TGA, other characterization techniques can provide explanations about the evolution of the microstructure at the sample surface.

During the initial parabolic stage, oxidation of Cr in Cr_2O_3 is observed. During the second stage, several phenomena gradually occur, such as redox reactions between Cr_2O_3 and Zr, leading to the formation of ZrO_2 and the loss of the coating protective properties.

INSTRUMENT

THEMYS TGA

HIGH ACCURACY & VERSATILITY
Hang-down symmetrical beam balance, specifically designed for TGA applications

ULTRA-HIGH TEMPERATURE CAPABILITY
to *2400°C* with a single furnace.

MODULAR ADAPTIONS ALLOWING
TGA only, DTA only, TG-DTA, andTMA up to 2400°C, DSC only and TG-DSC up to 1600°C all in one instrument

EXTERNAL COUPLING CAPABILITY
designed for evolved gas analyzers (FTIR, MS, GCMS, MSFTIR, or FTIR-GCMS)

Jianxi Deng, Donghui Geng, Qiaoyan Sun, Zhongxiao Song, Jun Sun, "Steam oxidation of Cr-coated zirconium alloy claddings at 1200 °C: Kinetics transition and failure mechanism of Cr coatings", Journal of Nuclear Materials, Volume 586, 2023, 154684, ISSN 0022-3115, https://doi.org/10.1016/j.jnucmat.2023.154684.