ADVANCED COATING FOR NUCLEAR FUEL CLADDING

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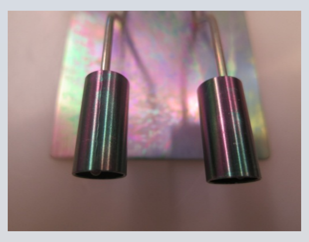
Abstract

Zirconium based alloys are used in almost all types of nuclear reactors as cladding of nuclear fuel, separating fuel from cooling water. During LOCA accidents (when the temperature of coating exceed 800 °C) intense heat and pressure triggers a reaction between zirconium cladding and the surrounding water / steam. The high temperature oxidation of zirconium is accompanied by hydrogen and heat production and can lead up to the degradation of coating and than to the contamination of the primary circuit by fission products. A solution to the problem is to cover the surface with a thin film of a protective substance.

Coatings

PCD



- Substrate: Zirlo and Zircaloy-2
- Plasma Enhanced Microwave Chemical Vapor Deposition
- Seeding was used to create diamond structure
- PCD – mixture sp^3 (diamond) and sp^2 (graphite) phase.
- Coating thickness is 200 – 500 nm (700 nm).
- Only outer surface fully coated.

CrAlSiN

- Commercially available coating
- Substrate: Zircaloy-2
- Composition: 37 % Al, 5 % Si, 58 % Cr
- Coating prepared by PVD method
- Primary designed for improving properties of cutting devices (drills etc.)
- 2 – 4,5 µm thickness
- Only outer diameter coated
- Roughness Ra 0,15 – 0,20 µm

Coating Testing

Long term exposure of PCD coated in operation (p, T) conditions - PCD coated samples **has lower weight gains** (see Fig. 1.) compared to uncoated samples in autoclave conditions simulating nuclear reactor environment.

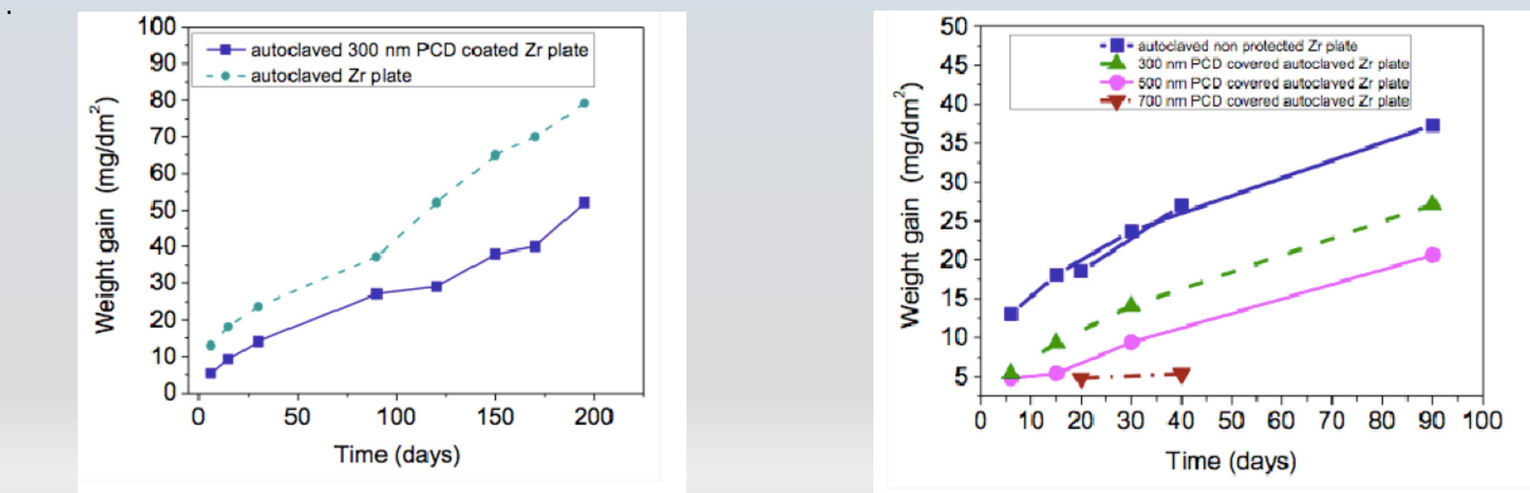
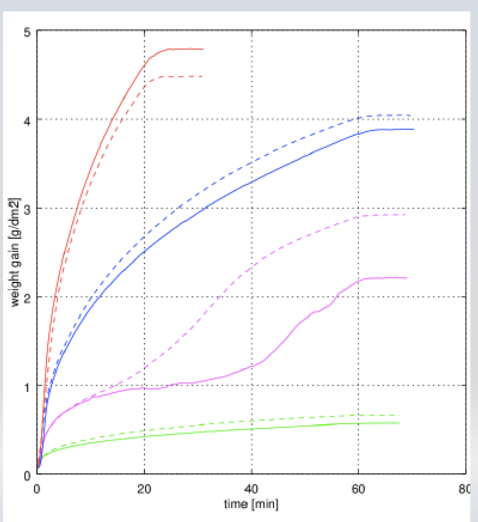


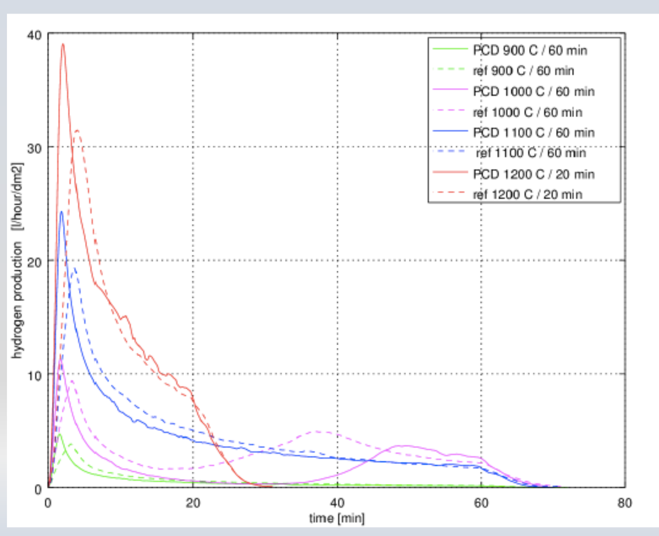
Fig.1. Weight gain of PCD coated samples after long term exposure [1]

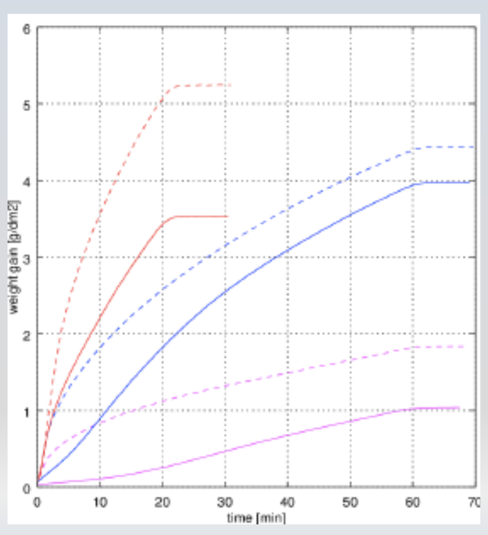
High temperature steam oxidation simulating accidental conditions. Weight gain (weight change to surface area) and composition of outgoing gas was measured for PCD and CrAlSiN coated samples. Only outer surface was coated.



PCD coatings

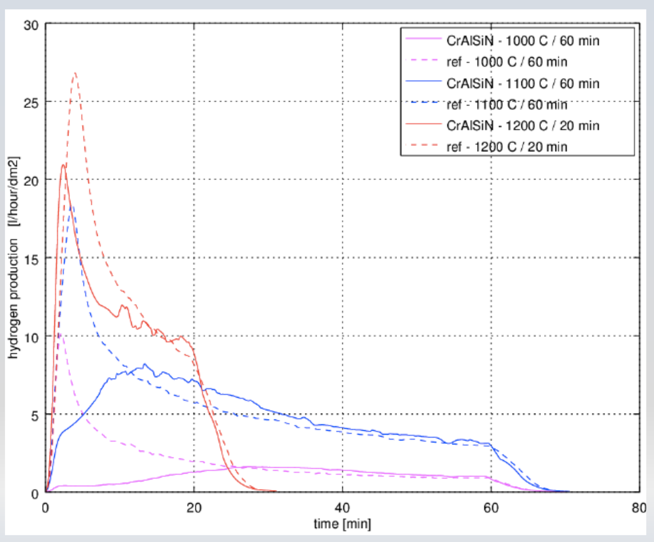
- ❑ Lower weight gain till 1100 °C than reference samples (dashed)
- ❑ Lower overall hydrogen production
- ❑ Initial hydrogen peak is higher.
- ❑ Delay in breakaway oxidation (20 minutes) at 1000 °C.





CrAlSiN coatings

- ❑ Lower weight than reference samples (dashed)
- ❑ Lower overall hydrogen production
- ❑ No hydrogen peak till 1200 °C
- ❑ Significant changes in oxidation curves



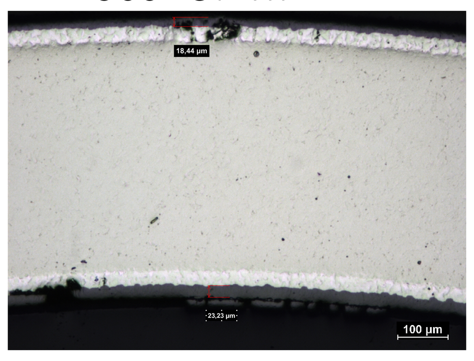
Thermogravimetry experiments were performed at **NETZSCH thermo-balance**, using **argon** as a cover gas. Simple alumina holder was used as sample support. All steam expositions were **isothermal** without any changes in steam or cover gas flow-rate. All oxidations were realized with argon flow-rate of 3 l per hour and with steam flow-rate of 3 g per hour. Measured TG data were smoothed using moving average filter, in order to eliminate oscillations of thermo-balance mechanism.

- ❑ Oxidation kinetics of PCD coated samples is similar to kinetics of uncoated samples at almost all temperatures, but with lower hydrogen production and lower weight gains. Most important difference is in later beginning of breakaway oxidation at 1000 °C, when breakaway oxidation starts on PCD coated sample 20 minutes later.
- ❑ Lower hydrogen production and lower mass gain of CrAlSiN coated sample are visible at temperature 1000 °C. Even at temperature 1100 °C is no hydrogen peak present at the beginning of steam exposure and also weight gain denotes lower reaction kinetics. Exposure at 1200 °C also shows lower oxidation kinetics but hydrogen peak during beginning of oxidations phase is present.

Results

- ❑ From optical microscopy is clear that PCD coating serves as **partial barrier** against oxygen diffusion and protective function is based on changes at PCD/Zr interface.

900 °C / 1h



1000 °C / 1h

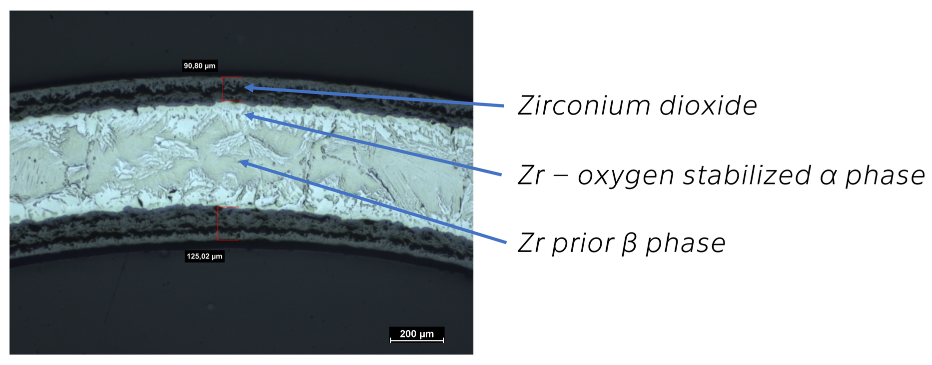


Fig.1.PCDcoated samples – cross section optical microscopy [5]

- ❑ From optical microscopy is clear that CrAlSiN coating serves as **full barrier** against oxygen diffusion, until mechanical failure of the coating. But when the CrAlSiN coatings mechanically failed the oxidation process is even faster than in the case of unprotected samples.

1000 °C / 1h 1100 °C / 1h 1200 °C / 20 m

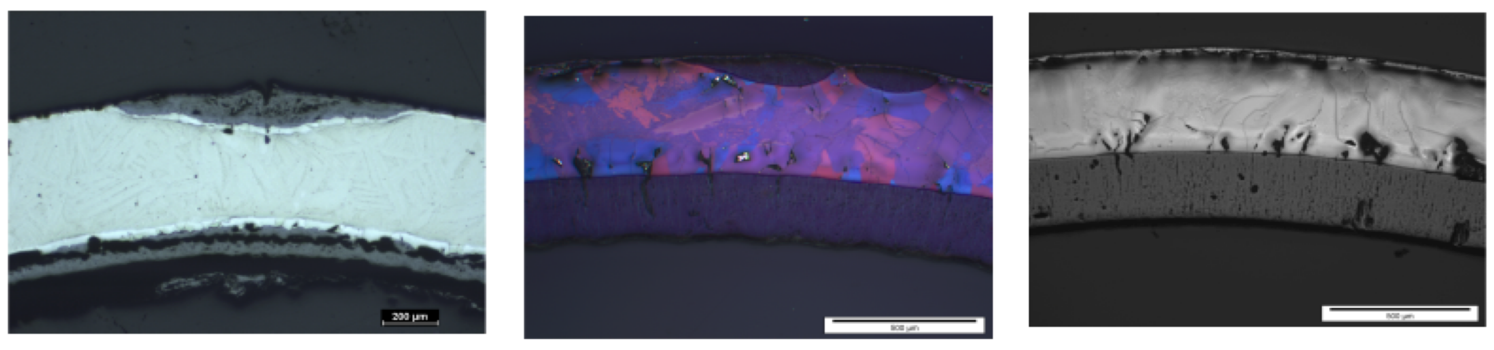


Fig.1 CrAlSiN coated samples – cross section optical microscopy

Conclusions

- ❑ Compared with Zr samples protected with 500 nm of PCD, **the hydrogen concentration in the unprotected Zr samples was found to be larger** by one order of magnitude after 1 hour at 1100 °C in autoclave.
- ❑ After 1100 °C steam oxidation of PCD coated Zr alloy samples, **zirconium atoms are incorporated into PCD layer** – first fingerprints of zirconium carbide layer were forming.
- ❑ Exposure of the PCD coated Zr alloy to hot steam (1100 °C, 30 min) caused the **infusion of oxygen and Zr substrate atoms into the protective layer.** The protective layer has a constitution of Zr carbide and underwent a phase change from diamond to sp^2 phase carbon.
- ❑ The Zr alloy under the PCD protective layer after high temperature steam oxidation differed from the original alloy material composition only very slightly (XPS), proving that the **PCD coating increases the material resistance to high temperature oxidation.**
- ❑ **Carbon released from the PCD film enters and changes the physical properties of the underlying Zr** – this effect plays significant role in PCD protective function.

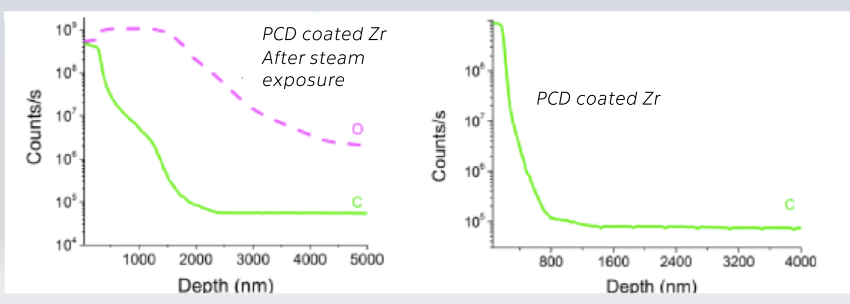


Fig.1. SIMS data showing carbon entering substrate Zr alloy [1]

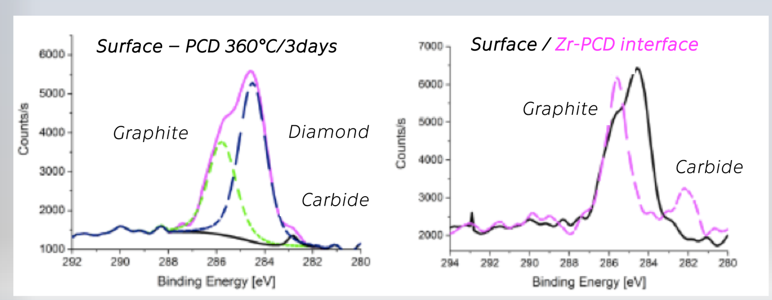


Fig.1. XPS data – carbides formed on PCD-Zr interface [1]

- ❑ CrAlSiN coating significantly eliminates initial oxidation kinetics and hydrogen production up to 1100 °C.
- ❑ CrAlSiN coating serves as **full barrier** against oxygen diffusion, until it's mechanical failure. After the coating mechanical failure (cracking), the oxidation process is even faster than in the case of unprotected samples.
- ❑ Oxidation of the primary chromium, aluminum and silicon nitrides has been detected, via XRD, leading to **creation of highly stable and high temperature resistant layers** of alumina and chromium oxide.

Publications

[1] Škarohlíd, J. et al. Nanocrystalline diamond protects Zr cladding surface against oxygen and hydrogen uptake: Nuclear fuel durability enhancement. Scientific Reports **7**, 1–14 (2017).

[2] Ashcheulov, P. et al. Thin polycrystalline diamond films protecting zirconium alloys surfaces : From technology to layer analysis and application in nuclear facilities. Applied Surface Science **359**, 621–628 (2015).

[3] Škoda, R., Škarohlíd, J., Kratochvílová, I., Taylor, A., Fendrych, F. (2015) Layer protecting the surface of zirconium alloys used in nuclear reactors. PCT WO/2015/039636, Czech patent 305059.

[4] Kratochvílová, I. et al. Nanosized polycrystalline diamond cladding for surface protection of zirconium nuclear fuel tubes. Journal of Materials Processing Technology **214**, 2600–2605 (2014).

[5] Škarohlíd, J., Škoda, R. & Kratochvílová, I. High temperature oxidation of polycrystalline diamond coated zirconium alloy. International Conference on Nuclear Engineering, Proceedings, ICONE 5, 1–4 (2016).

Acknowledgements

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