

Microstructural Evolution of Electrodeposited Cr Barrier Layers and Carbide Induced Interface Degradation of HT9 Cladding during Long Term Thermal Aging at 650 °C

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1. Introduction

Metallic fuels are promising candidates for Sodium Fast Reactor (SFR) systems owing to their high thermal conductivity and efficient fuel utilization. However, fuel swelling with increasing burnup eventually brings the fuel into contact with the cladding and promotes Fuel Cladding Chemical Interaction (FCCI), in which interdiffusion among fuel constituents, lanthanide fission products, and cladding elements forms lower melting point intermetallic compounds that degrade the safety and performance of the fuel system. A chromium (Cr) barrier placed between the fuel and the cladding effectively suppresses this interaction [1], and electrodeposited Cr coatings are attractive because they form continuous, well adhered layers while adding only a limited thermal resistance.

The cladding considered here is HT9, a 12Cr ferritic martensitic steel (FMS), whose elevated temperature strength relies on a fine dispersion of $M_{23}C_6$ carbides, so that the substrate is a reservoir of carbon located immediately adjacent to the barrier. Carbon transport in such steels is governed by the gradient of carbon activity rather than of concentration, and a sufficiently large activity difference readily produces Cr rich carbides at an interface [2]. Previous studies of Cr barriers have nevertheless focused almost exclusively on the fuel cladding interface [3], whereas the long term evolution of the Cr/cladding interface itself remains insufficiently understood. The stability of this interface determines the service life of the coating as a whole, since interfacial reaction layers, voids, and phase changes degrade adhesion and can locally detach the coating; in a coated cladding, such a loss of integrity would expose the cladding directly to the fuel and negate the barrier function. In this study, Cr layers were electrodeposited on HT9 by direct current (DC) and pulse reverse (PR) plating, the two waveforms being used to obtain coatings with distinctly different initial grain structures and defect populations. The specimens were aged at 650 °C, the maximum operating temperature anticipated for SFR cladding, for up to 3000 h, and the evolution of the Cr layer was correlated with the formation of interfacial reaction products in

order to clarify how the interface changes during long term thermal exposure.

2. Experimental Methods

HT9 ingot containing 0.18 wt.% carbon was machined into disk shaped specimens, ground with SiC papers, and polished with a 1 μm diamond suspension for electroplating. Cr layers were deposited from a bath of 250 g L⁻¹ chromic acid (CrO_3) and 2.5 g L⁻¹ sulfuric acid (H_2SO_4) at 55 °C under agitation at 150 rpm. After surface activation and the formation of an initial Cr layer, the main coatings were deposited by DC or PR plating methods as shown in Fig. 1: the DC coating at a constant 0.58 A cm⁻² for 30 min, and the PR coating by alternating a forward 0.58 A cm⁻² with a reverse 0.16 A cm⁻² for the same total time. Both as deposited coatings were approximately 20 μm thick. The specimens were sealed in quartz tubes under vacuum, aged at 650 °C for 0, 1000, 2000, and 3000 h, and air cooled in order to examine the carbon diffusion state at the interface as a function of aging time. Cross sections prepared by mechanical polishing and ion milling were characterized by SEM-EDS and EBSD, and the interfacial reaction products were examined by TEM/STEM, SAED, and EELS using site specific specimens prepared by focused ion beam (FIB) milling.

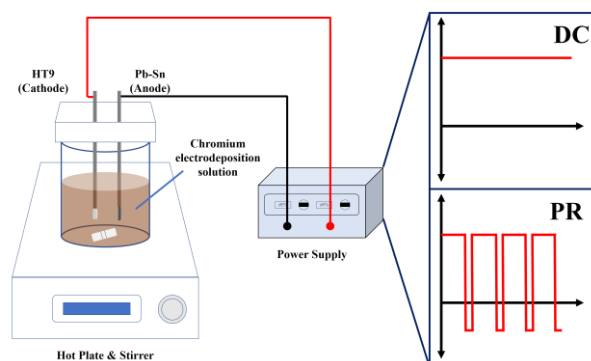


Fig. 1. Experimental setup for Cr electrodeposition and the applied current waveforms.

3. Results and discussion

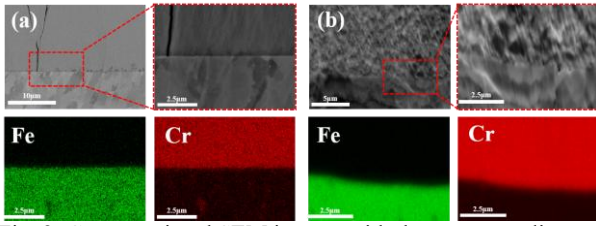


Fig. 2. Cross sectional SEM images with the corresponding EDS elemental maps of the as deposited Cr coatings on HT9: (a) DC and (b) PR plating.

Fig. 2 shows the as deposited Cr coatings on HT9 prepared by (a) DC and (b) PR electroplating. Continuous coatings were obtained in both cases, but the DC coating contained cracks propagating through its thickness, whereas the PR coating was dense and free of discernible cracks. This phenomenon was already reported in our previous publication [4], and the difference originates from the hydrogen co deposited during DC plating and the associated residual tensile stress, whereas the periodic reverse current of the PR process relieves this stress and promotes hydrogen desorption, suppressing crack formation [5]. Both interfaces were well defined before aging, with no reaction layer or elemental intermixing, so that the two coatings differ in their initial state but share an identical, chemically sharp interface as the baseline for the changes described below.

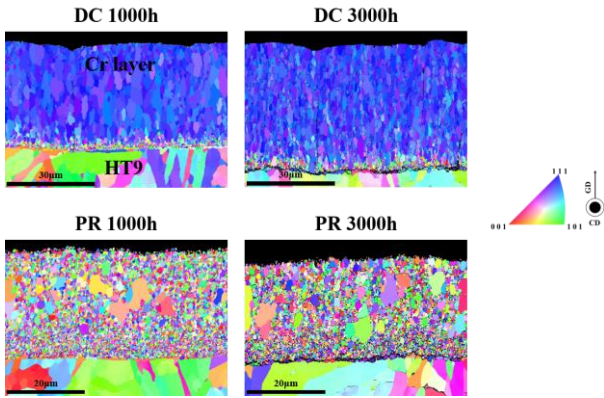


Fig. 3. Evolution of the Cr coating grain structure during aging at 650 °C for 1000 and 3000 h, shown as cross sectional EBSD IPF maps of the DC and PR coatings.

Fig. 3 presents EBSD inverse pole figure (IPF) maps of the DC and PR coated Cr layers after 1000 and 3000 h of aging at 650 °C. The as deposited DC coating could not be indexed reliably owing to its low crystallinity, an amorphous like structure being commonly reported for as coated Cr produced by the DC method. After aging, the DC coating exhibited a pronounced (111) texture, and its average grain size decreased between 1000 and 3000 h rather than coarsening. This is attributed to the high impurity content inherent to DC chromium plating: hydrogen and the decomposition products of the chromic acid bath are incorporated in a supersaturated state and are released

on heating, together with a relaxation of the residual stress and a strengthening of the fiber texture [6]. The relaxation of the distorted lattice rearranges the stored dislocations into low angle boundaries and progressively subdivides the original grains into subgrains. Because these boundaries are resolved as grain boundaries in the EBSD maps, the measured grain size decreases, reflecting subdivision rather than coarsening or nucleation. In contrast, the PR coating, which consists of fine equiaxed grains in the as deposited state and starts from a cleaner, less distorted state, underwent conventional grain growth throughout the layer between 1000 and 3000 h, on which locally enlarged grains developed in the central and near surface regions. This abnormal growth is attributed to the non uniform residual stress retained in the as deposited layer, the locally higher stored strain energy allowing a few grains to consume the surrounding matrix. The two waveforms therefore change the grain boundary density of the Cr layer in opposite directions, the DC coating generating new boundaries by subgrain formation while the PR coating eliminates them by growth, and, since grain boundaries are fast paths for carbon ingress into the coating and for the supply of Cr to the growing carbide, the two specimens present markedly different transport conditions at the interface.

Near the interface, both specimens exhibited grains differing in size and morphology from those of the bulk coating. These were clearest after 1000 h, whereas the EBSD signal from the same region became weak after 3000 h. In view of the reaction layer identified in Fig. 4, this sequence is interpreted as the nucleation and early growth of an interfacial reaction product, followed by its development into a continuous layer that could no longer be indexed as bcc Cr. The Cr surrounding these grains was also finer than the coating interior, which is attributed to local pinning of the Cr grain structure by the interfacial reaction product rather than to a pre existing fine grained region.

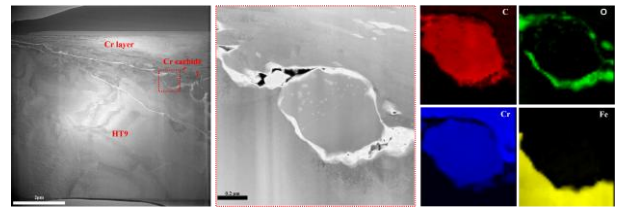


Fig. 4. Interfacial reaction layer in the PR coated specimen after 3000 h at 650 °C: cross sectional TEM overview, magnified view of the boxed region, and STEM-EELS elemental maps of C, O, Cr, and Fe.

Fig. 4 presents the interface of the PR coated specimen after 3000 h at 650 °C. A distinct reaction layer less than approximately 1 μm thick developed between the coating and the substrate, accompanied by voids that were most pronounced immediately adjacent to the layer and were also observed within the substrate. The STEM-EELS maps show pronounced enrichment of Cr and C within the layer while the Fe signal was nearly absent, identifying the reaction product as a Cr

carbide. A localized O signal was attributed to a Cr rich surface oxide formed during air exposure. These observations demonstrate that the reaction layer is a carbide formed by carbon diffusing from the HT9 into the Cr barrier. The carbon activity in the metallic Cr layer is far lower than in HT9, where carbon is bound as $M_{23}C_6$, so carbon migrates down the activity gradient and accumulates at the interface. Because the solubility of carbon in bcc Cr is extremely low at this temperature [7], it is immediately consumed by the precipitation of a Cr carbide, which thickens into the continuous layer seen after 3000 h. Consistent with this, a decarburized zone was confirmed in the HT9 adjacent to the interface. The near absence of Fe, in contrast to the $(Cr,Fe)_{23}C_6$ carbides of the substrate, indicates that carbon is essentially the only species crossing the interface and that the carbide is built from Cr supplied by the coating, so that the barrier itself is consumed as the layer grows. The DC coated specimen aged for 3000 h developed an interfacial layer of the same composition and of comparable morphology and size, despite its opposite grain boundary evolution and its higher initial impurity and crack content. The formation of the interfacial carbide is therefore governed not by transport through the Cr coating but by the supply of carbon from the substrate, which is common to both specimens, and the grain boundaries of the coating affect where the carbide nucleates rather than how much of it forms. The voids, concentrated at the reaction layer and extending into the decarburized substrate, are attributed to the volume change accompanying carbide formation and to the imbalance between the Fe and Cr fluxes, which is known to reduce the adhesion strength of electroplated Cr coatings at comparable temperatures [8]. The interface is thereby altered from a sharp, well adhered metal/metal boundary into a metal/brittle carbide/metal configuration containing voids, with a corresponding loss of structural continuity.

4. Conclusions

Electrodeposited Cr barrier layers on HT9 cladding were aged at 650 °C for up to 3000 h. The as deposited interface was a sharp metallurgical boundary in both specimens, but the Cr layer itself proved microstructurally unstable, and the two coatings evolved in opposite directions: the impurity rich DC coating developed a strong (111) texture while its grain size decreased, because impurities incorporated during DC plating were released and the accompanying lattice relaxation subdivided the original grains into subgrains, whereas the cleaner PR coating underwent conventional grain growth on which locally abnormal growth was superimposed in regions of high residual stress. The two waveforms therefore change the grain boundary density of the barrier in opposite directions, so that the two coatings offer very different transport conditions at the interface.

Irrespective of the waveform, the most pronounced changes were localized at the interface, where a reaction product nucleated after 1000 h and developed into a continuous, essentially Fe free Cr carbide layer after 3000 h. This carbide grows by consuming Cr from the coating while drawing carbon from the substrate, as confirmed by the decarburized zone in the adjacent HT9, and it replaces the original metal/metal bond by a brittle carbide interlayer accompanied by voids that degrade the continuity of the interface. Despite their opposite microstructural evolution, both coatings developed interfacial layers of comparable morphology and size, showing that the carbide is governed by the carbon supply from the substrate rather than by the coating microstructure. A Cr barrier therefore degrades from its own substrate side even without fuel contact, so that the lifetime of Cr coated HT9 cladding is governed not only by fuel side FCCI mitigation but also by carbide mediated interfacial degradation. Optimizing the deposition waveform removes the hydrogen induced cracking of the coating but does not mitigate this substrate side degradation. Quantification of the carbide growth kinetics with aging time and evaluation of the strength loss in the decarburized substrate are in progress.

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