

High-Temperature Diffusion Barriers for Protective Coatings

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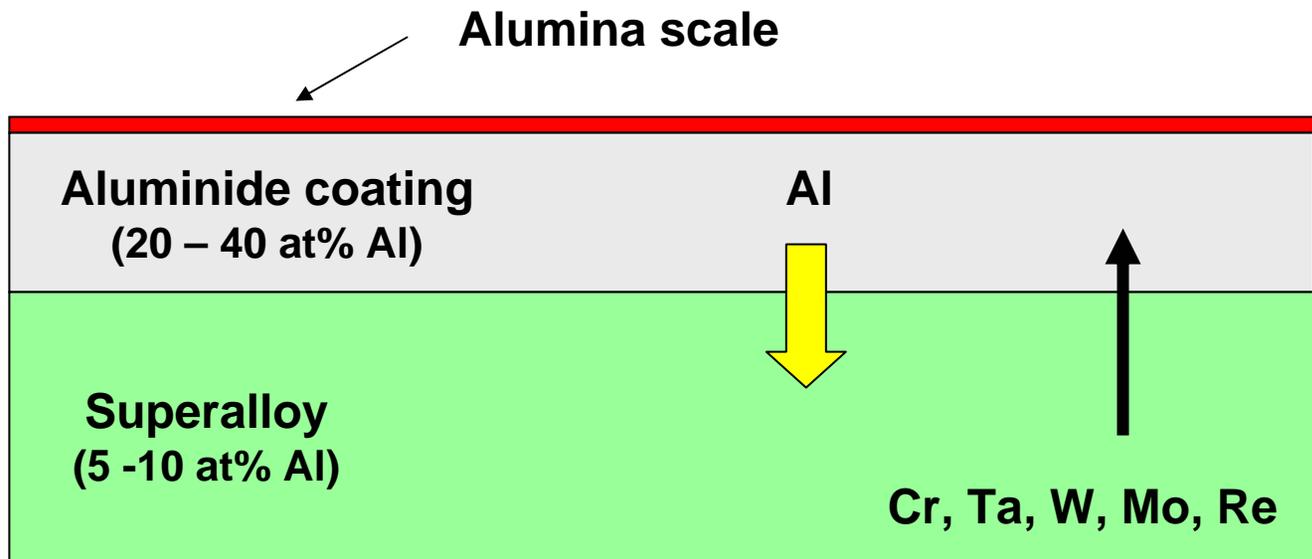
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Abstract

An effective diffusion barrier between a superalloy and aluminide coating would reduce coating degradation by lowering the rate of Al loss to the substrate by interdiffusion, and by inhibiting diffusion of substrate elements (such as Cr, Re, Ta, W) into the coating, both of which reduce corrosion and oxidation resistance. In this preliminary study, Hf-Ni and Hf-Pt were evaluated as potential high-temperature diffusion barrier layers. These materials were sputter deposited onto single-crystal superalloys, followed by various heat treatments. Coatings were subsequently aluminized to form NiAl or NiPtAl coatings for characterization and testing in cyclic oxidation at 1150°C.

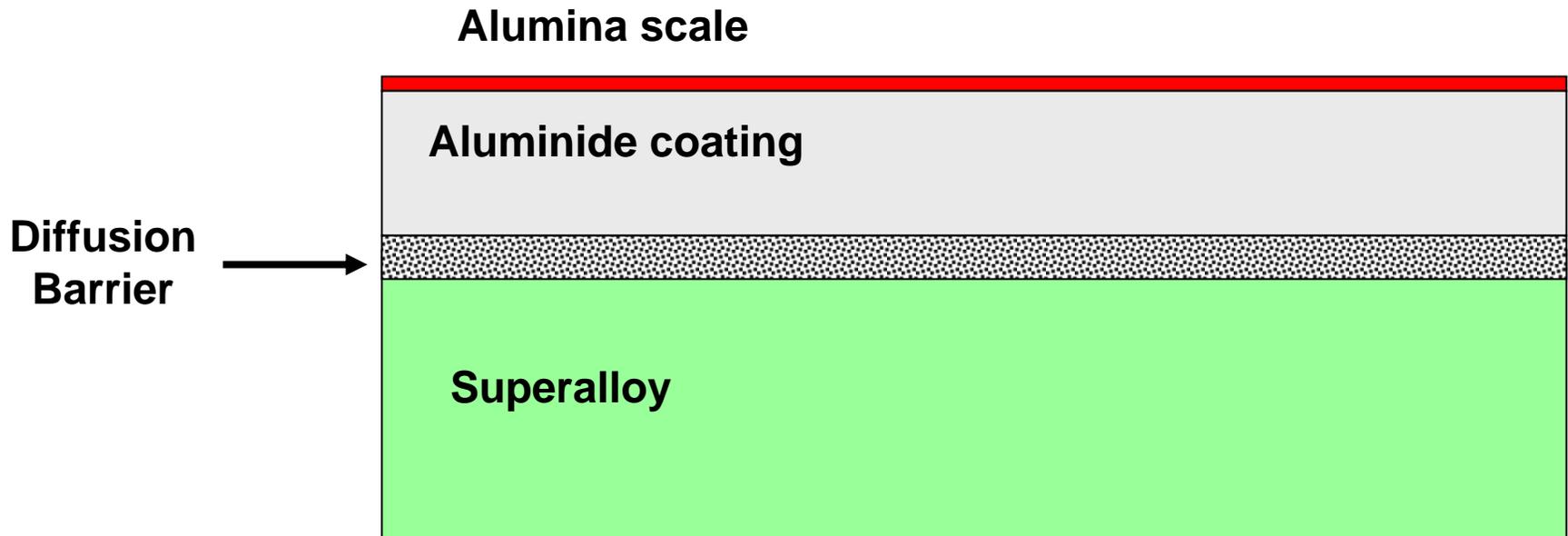
Introduction

- The oxidation resistance of protective aluminide coatings on high temperature superalloy components is degraded by:
 - Loss of Al to the substrate by interdiffusion
 - Diffusion of refractory elements from the superalloy into the coating



Diffusion Barrier Concept

An effective diffusion barrier between the coating and superalloy would slow the loss of Al to the substrate and limit or delay diffusion of refractory elements into the coating.



Diffusion Barrier Challenges

- Development of materials for application as diffusion barriers presents a significant challenge.
 - Must retard diffusion of Al
 - Ideally should retard diffusion of refractory elements
 - Must be thermo-mechanically compatible with coating and superalloy
 - Must be able to be deposited as a coating
 - Must remain relatively stable at high temperatures
 - Must not contain elements that degrade the oxidation and/or corrosion resistance of aluminide coatings

Candidate Diffusion Barrier Materials

- Ni-Hf compounds
 - Chemical vapor deposition (CVD) experiments by Lee and co-workers at Stevens Institute (unpublished results) suggested retardation of Al diffusion when Ni-Hf compounds were present at the surface of a coating.

Candidate Diffusion Barrier Materials

- Engle-Brewer compounds [1, 2]
 - Family of: $ZrIr_3$, $HfIr_3$, $HfPt_3$
 - High melting point
 - Unusual phase stability
 - Properties suggest potential for diffusion barrier characteristics.
- Another advantage of Engle-Brewer compounds is the positive influence of both precious metals (Ir, Pt) and reactive elements (Hf, Zr) on the oxidation resistance of aluminide coatings.

1. L. Brewer and P.R. Wengert, *Met. Trans.* 4, 83 (1973).
2. L. Brewer, *Acta. Met.*, 15, 553 (1967).

Objective

- Examine the diffusion barrier potential of Ni-Hf and Pt-Hf layers sputtered on a superalloy surface and subsequently CVD aluminized.
 - Primary focus of this preliminary study was Ni-Hf coatings.

Experimental

- **Substrate Material**
 - Rene N5 single-crystal superalloy discs
 - 1.65 cm diameter x 0.16 cm thick
- **Fabrication of Sputter Coatings**
 - Magnetron sputter coatings deposited on one surface of superalloy
 - Phase 1: Hf thin films
 - 1, 4 & 7 μm thick
 - Phase 2: Hf + Pt thin films
 - 1 μm Hf/3 μm Pt; 1 μm Hf/5 μm Pt; 3 μm Hf/9 μm Pt;
- **Fabrication of Aluminide Coatings**
 - Heat treat sputter coatings
 - CVD aluminize (lab-scale reactor at ORNL)

Table 1: Examples of Mass Changes during CVD Aluminizing

CVD Batch	Specimen	Hf Thickness (μm)	Heat-treat prior to CVD	CVD Time (hr)	CVD Mass Change (mg)
1	N5-1 ⁺	0	No	6	21
2	H7-1 [*]	7	No	6	7.6
4	H1-3 [*]	1	700C, 30 min	6	20.4
4	H7-2 [*]	7	700C, 30 min	6	4.9
6	H1-4 [*]	1	800C, 10 min	6	15.1
7	H7-5 [*]	7	700C, 10 min	2	-6.1
7	H1-5 [*]	1	700C, 10 min	2	9.5
8	N5-2 ⁺	0	700C, 10 min	6	20.9
9	H4-5 [*]	4	800C, 10 min	6	19.9
9	H1-6 [*]	1	800C, 10 min	6	8.6
11	H4-6 [*]	4	800°C, 20 min	6	10.6

⁺ No sputter coating was applied to these specimens.

^{*} Sputter-coated on one surface with Hf.

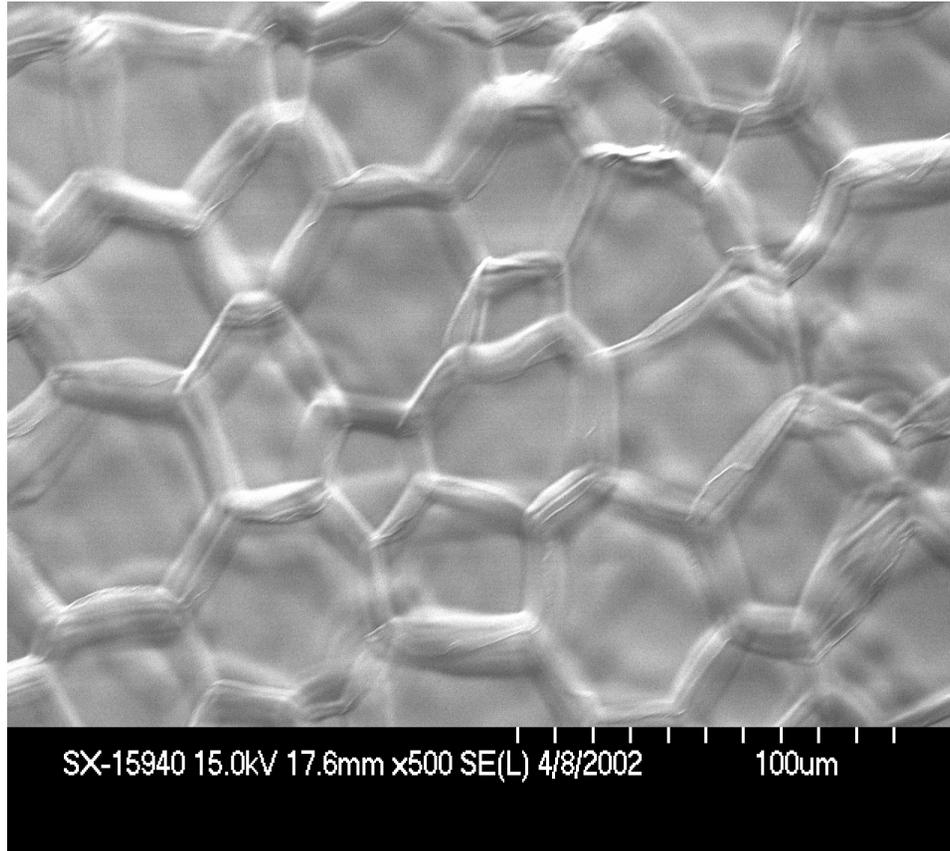
Preliminary Aluminizing Results Were Misleading

- Mass gains in Table 1 indicate inward diffusion of Al into the specimen during aluminizing.
- Preliminary experiments appeared to confirm that the presence of a Hf-Ni layer retarded inward diffusion of Al, since mass gains were significantly reduced in Batch 2 (Hf) vs. Batch 1 (no Hf).
- Batch 4 seemed to further confirm the effect, since the thicker Hf coating resulted in significant reductions in Al uptake during aluminizing.

Aluminizing led to Mass Loss due to Hf Chlorination

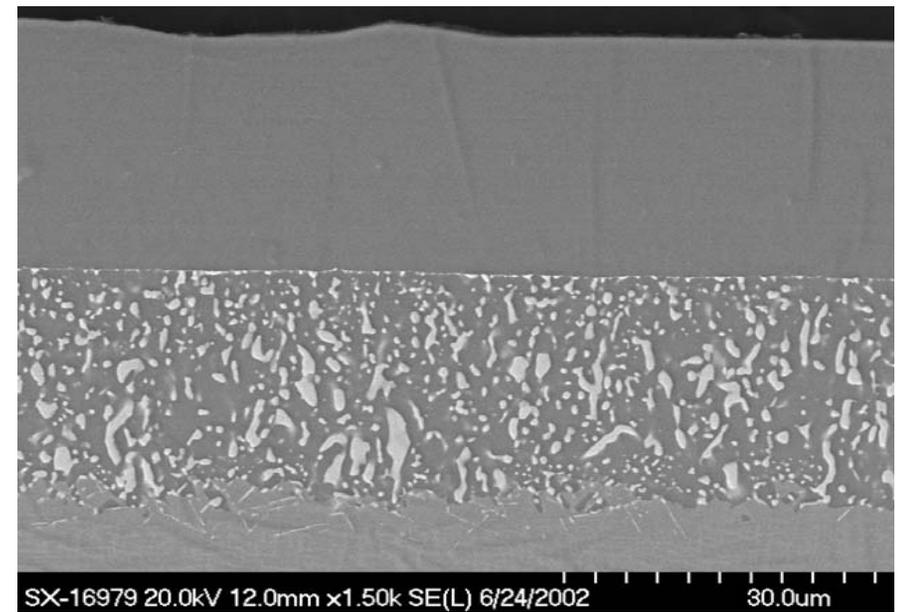
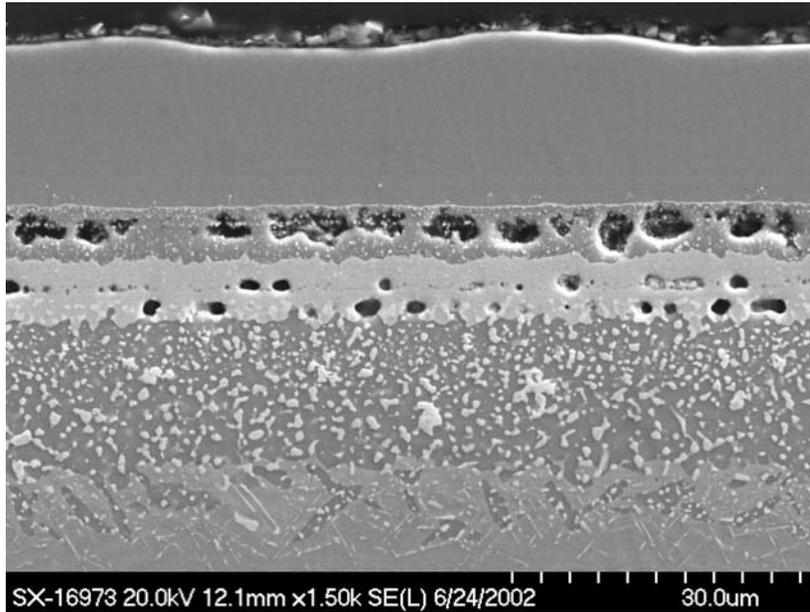
- Short-term (2 hr) aluminizing in Batch 7 (see Table 1) revealed that the differences in mass gain were actually due to Hf loss (by chlorination), not retardation of Al diffusion.
- Subsequent experiments confirmed this result.
- Specimens with thicker Hf coatings lost mass until the surface activity of Hf was lowered by interdiffusion of Ni and Al.

Surface of as-deposited CVD Aluminide with a Hf-rich underlayer



- Aluminide coating surface microstructure was not significantly influenced by the presence of a 7 μm Hf layer.

Microstructure of as-deposited aluminide coating with Hf-rich underlayer

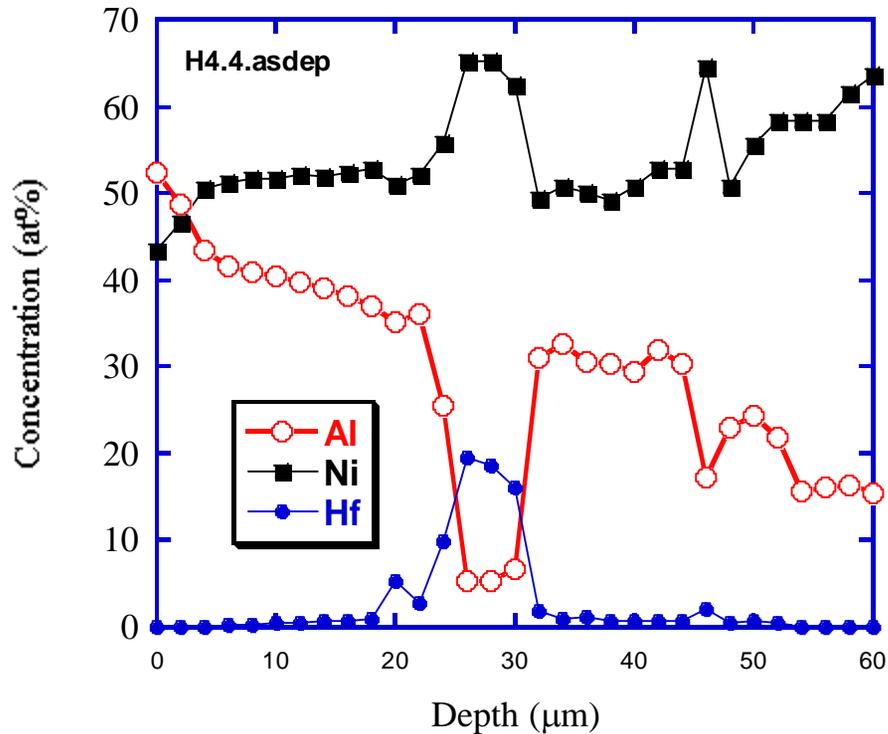


Specimen with 4 μm Hf coating (H4.4)

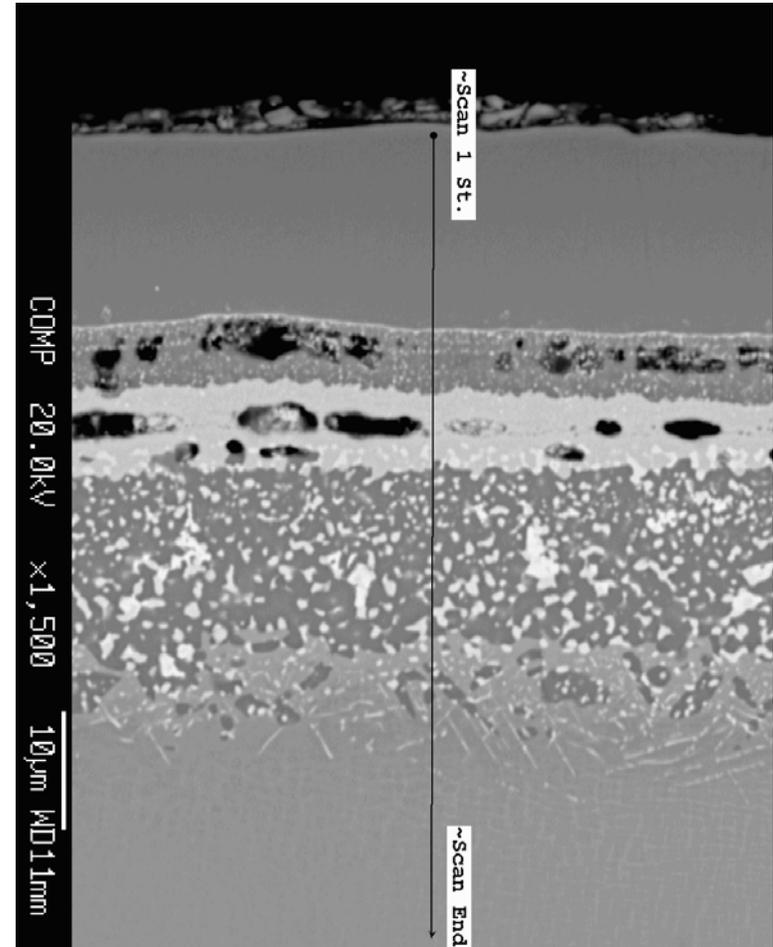
Opposite side of same specimen (no Hf)

- Microstructure of β -NiAl outer layer was not significantly impacted.
- The Hf-rich layer between coating and substrate resulted in a non-ideal microstructure, with significant porosity associated with the interfaces.

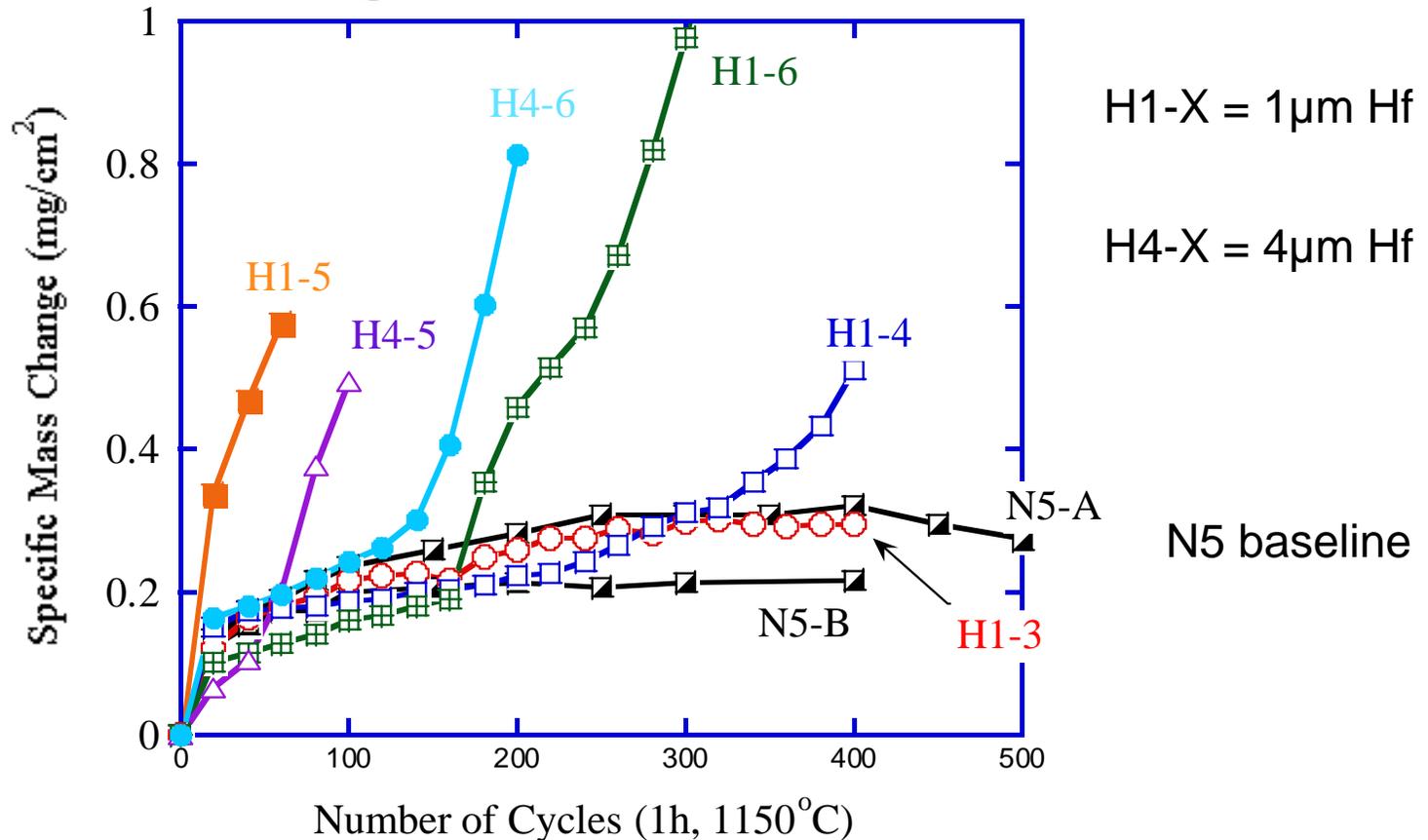
As deposited CVD Aluminide (4 μm Hf): Electron Microprobe Analysis



- The bright-contrast, Hf-rich layer had a composition similar to HfNi_3 , and contained less than 5 at% Al.
- There was no difference in the Ni or Al content in $\beta\text{-NiAl}$ as a result of the Hf layer.



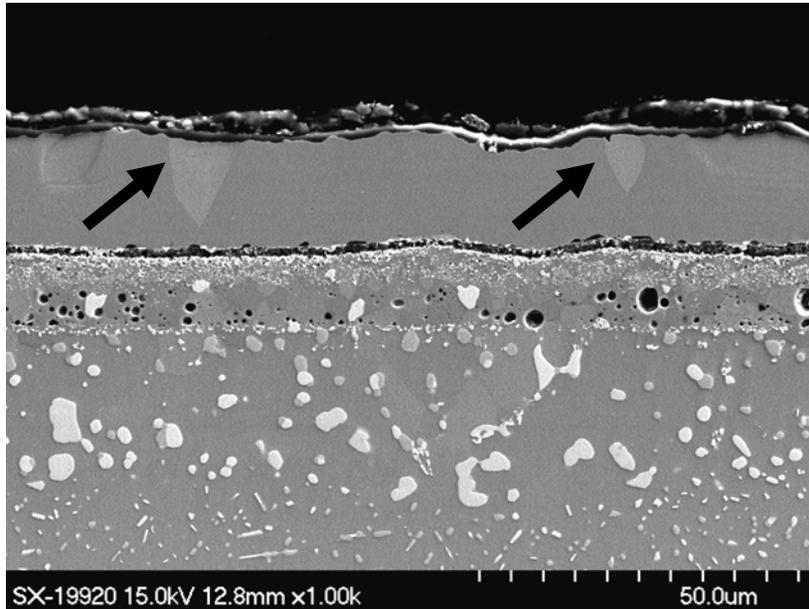
Coating Oxidation Behavior



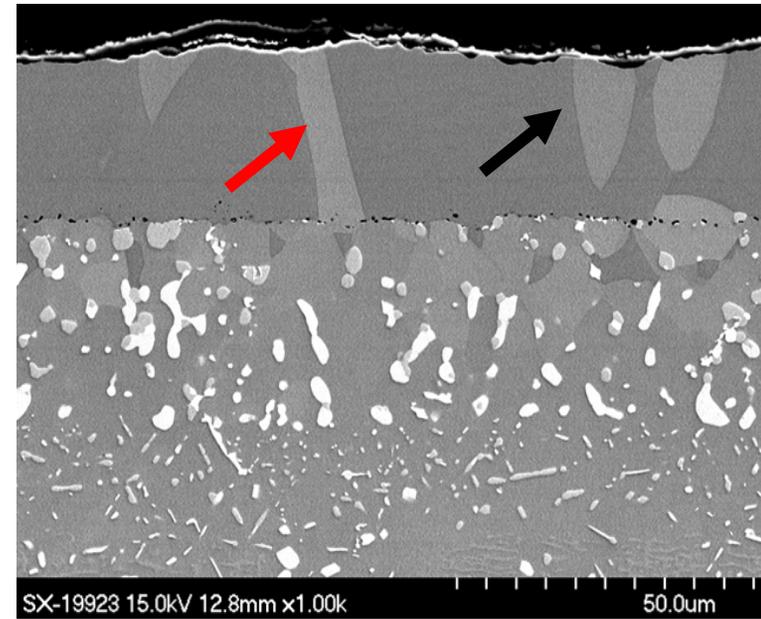
- Specimens with thicker Hf layers (H4-5 and H4-6) showed rapid mass gains, due to cracking of the β -NiAl coating.
- Specimens with thinner β -NiAl layers (H1-5 and H1-6) showed rapid mass gains due to quick depletion of Al.
- Specimens H1-4 and H1-3 (1 μ m thick Hf) showed oxidation resistance as good or better than the best CVD NiAl (N5-A and N5-B) to 400 cycles, in spite of the interface porosity.

Microstructural Evidence for Diffusion Barrier Effects

Comparing both sides of the same specimen after 200 cycles at 1150°C



Al content
in both
 β -NiAl
coatings
was
~18 at%



4 μ m Hf coating: porous interlayer

No Hf coating: thicker β -NiAl

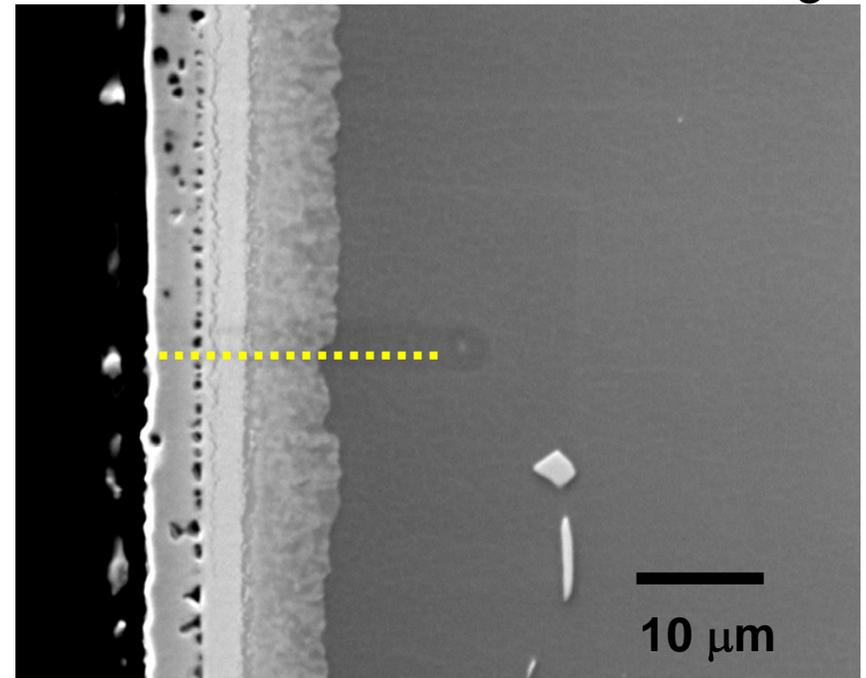
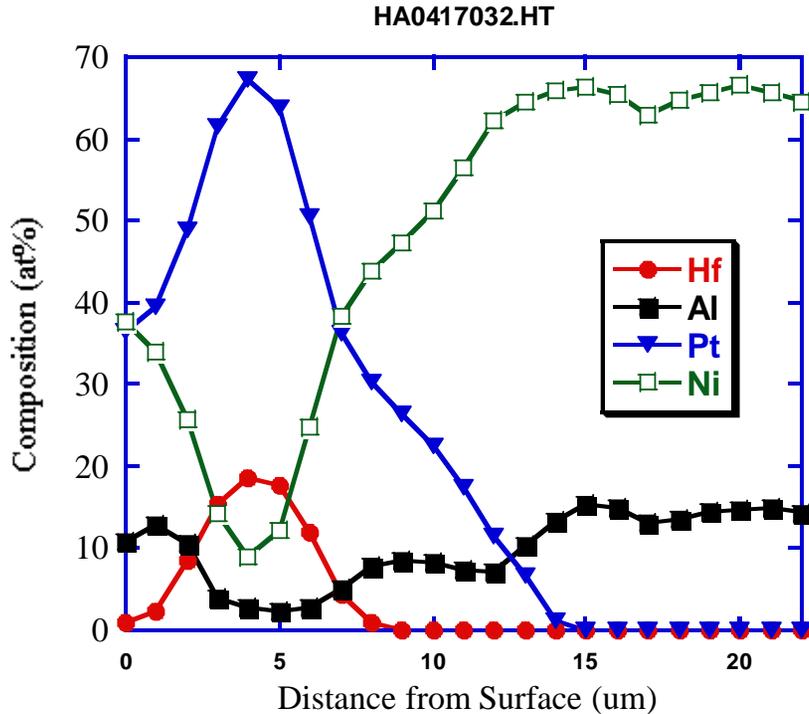
- There was more through-thickness depletion (red arrow) of Al in the thicker β -NiAl of the coating without the Hf underlayer.
- Slower Al depletion in Hf-containing coating could be the result of porosity, improved scale adherence, or a barrier effect.
- After 200 cycles, the Hf-rich layer was no longer evident – suggesting the Ni-Hf compound was not stable at 1150°C.

Pt-Hf Coatings

- The preliminary goal for Pt-Hf coatings was to achieve the HfPt_3 compound.
- Pt-Hf was deposited and heat treated in an attempt to form HfPt_3 via interdiffusion.
- The heat treated specimens were then aluminized at 1100°C .

Heat-Treated Pt-Hf Coatings

Goal = HfPt_3



- Heat treatment (500°C and 900°C in Ar) of a specimen sputtered with 1 μm Hf + 5 μm Pt resulted in a Pt-Hf surface layer with 67 at% Pt and 19 at% Hf (ratio 3.5 : 1); close to HfPt_3

Summary

- **Aluminizing of Hf-coated specimens resulted in mass loss due to Hf chlorination.**
- **Hf-containing coatings formed a HfNi₃ type layer during aluminizing and showed reduced Al depletion in the β -NiAl after extended oxidation testing. However, this layer had limited stability at 1150°C.**
- **Thicker Hf films disrupted the coating microstructure and reduced performance.**
- **Thinner Hf films (1 μ m) resulted in β -NiAl coatings with very good oxidation resistance.**
- **Heat treatment of Hf-Pt coatings at 900°C formed a layer with a composition slightly more Pt-rich than HfPt₃. This layer subsequently dissolved during aluminizing at 1100°C.**