Hf Doping of an Aluminide Bond Coat for Single Crystal Jet Engine Turbine Blades

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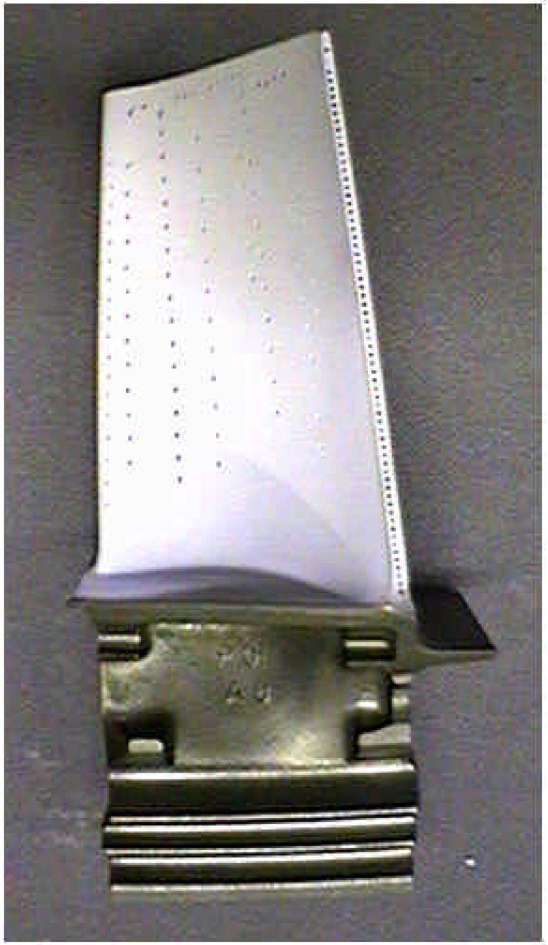
Summary of Efforts

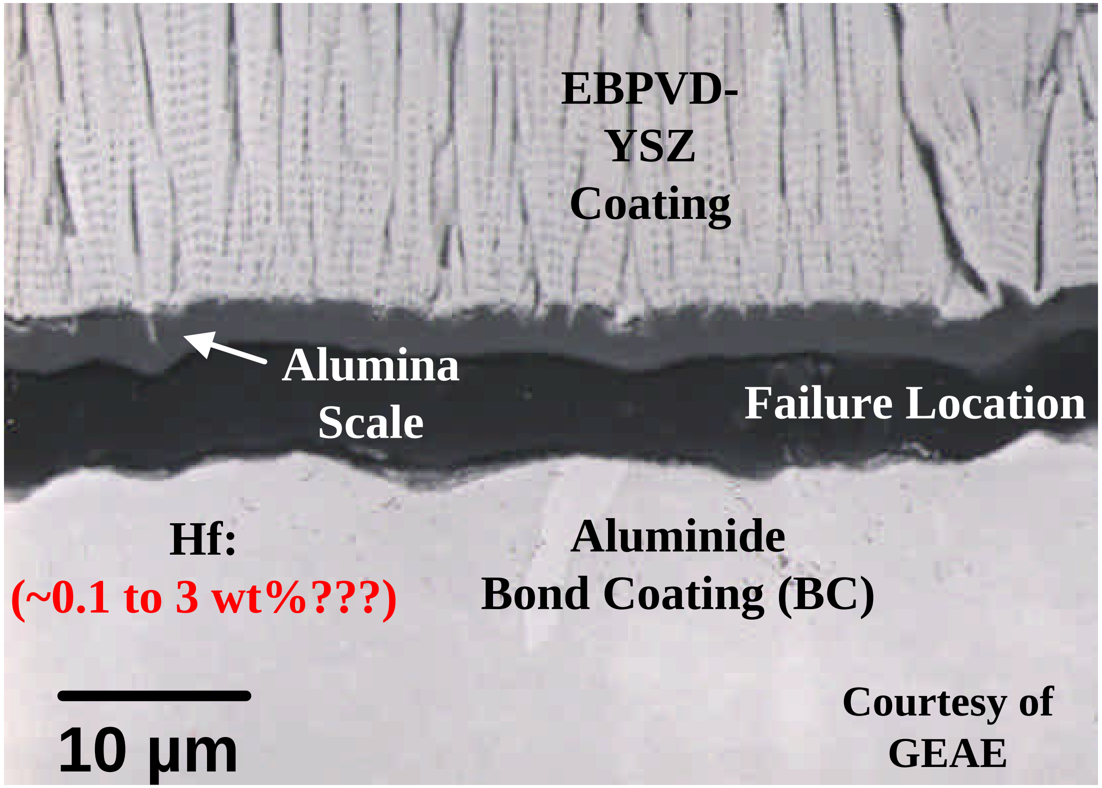
Thermal barrier coatings (TBCs) are currently used, in conjunction with air cooling, to prolong the life of metallic "hot-section" Ni-based superalloy components used in aircraft engines and power generation turbines with an annual market size of ~$1.5 billion. The advent of next-generation TBCs requires superior oxidation characteristics over those of current metallic bond coatings. One potent way of improving oxidation resistance is to dope Ni-based alloys with a small amount of a reactive element such as Y, Hf, or Zr. We have performed Hf doping experiments while the surface of a single crystal Ni alloy was being aluminized to form an aluminide (β-NiAl) coating matrix by chemical vapor deposition for improved oxidation resistance of the NiAl coating.

A continuous doping procedure, in which $HfCl_4$ and $AlCl_3$ were simultaneously introduced with H_2, required a high $HfCl_4/AlCl_3$ ratio (>~0.6) to cause the precipitation of Hf-rich particles (~0.1 μm) at grain boundaries of the coating layer with the overall Hf concentration of ~0.05 to 0.25 wt%. Below this ratio, Hf did not incorporate as a dopant from the gas phase as the coating matrix appeared to be “saturated” with other refractory elements partitioned from the alloy substrate. We have also studied a sequential doping procedure that consists of pretreating the alloy surface with $HfCl_4$ and H_2 followed by aluminizing. The Ni alloy surface reacted significantly with $HfCl_4$ and H_2, even for a short exposure of 30 seconds, to form an Hf-rich layer containing Hf_8Ni_{21}, Hf_3Ni_7, and $HfNi_3$ precipitates. This Hf-rich layer apparently worked as a diffusion barrier to mitigate the columnar growth of β-NiAl grains. Our results suggest that the most promising avenue for controlling Hf concentration and distribution is to periodically nucleate very small Hf particles in the coating matrix via time-resolved switching between $AlCl_3$ and $HfCl_4$ precursors.

Superior Adhesion Needed for Next Generation TBCs



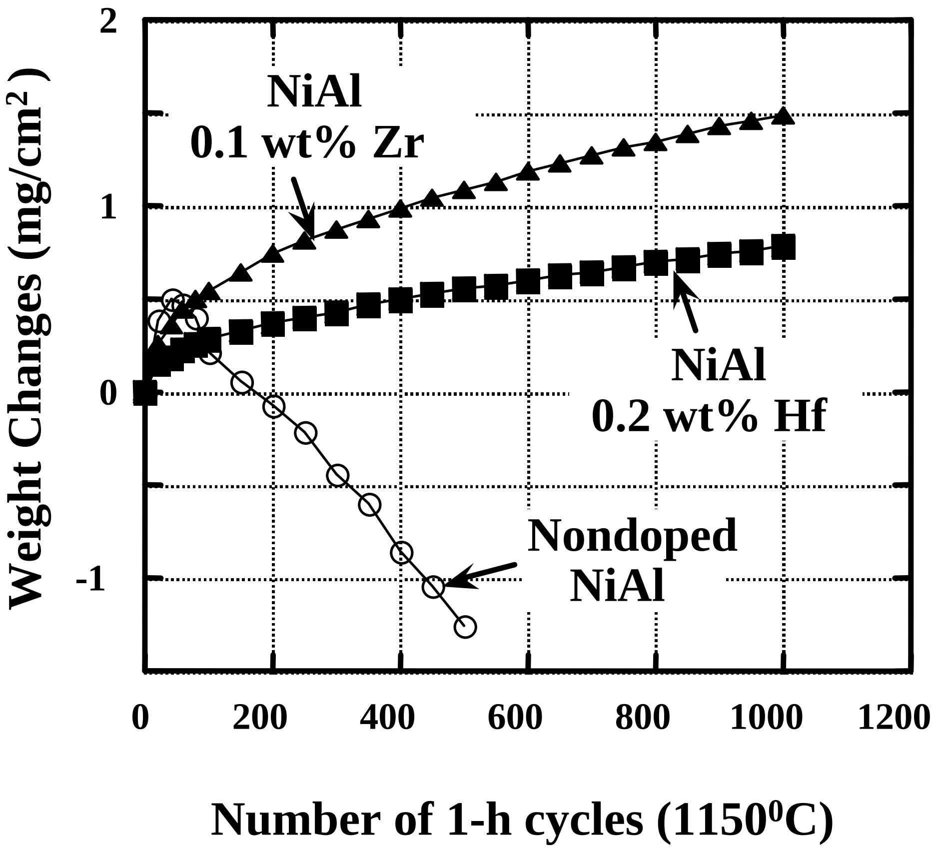
Single crystal Ni super alloy with TBC



Problems observed in industry

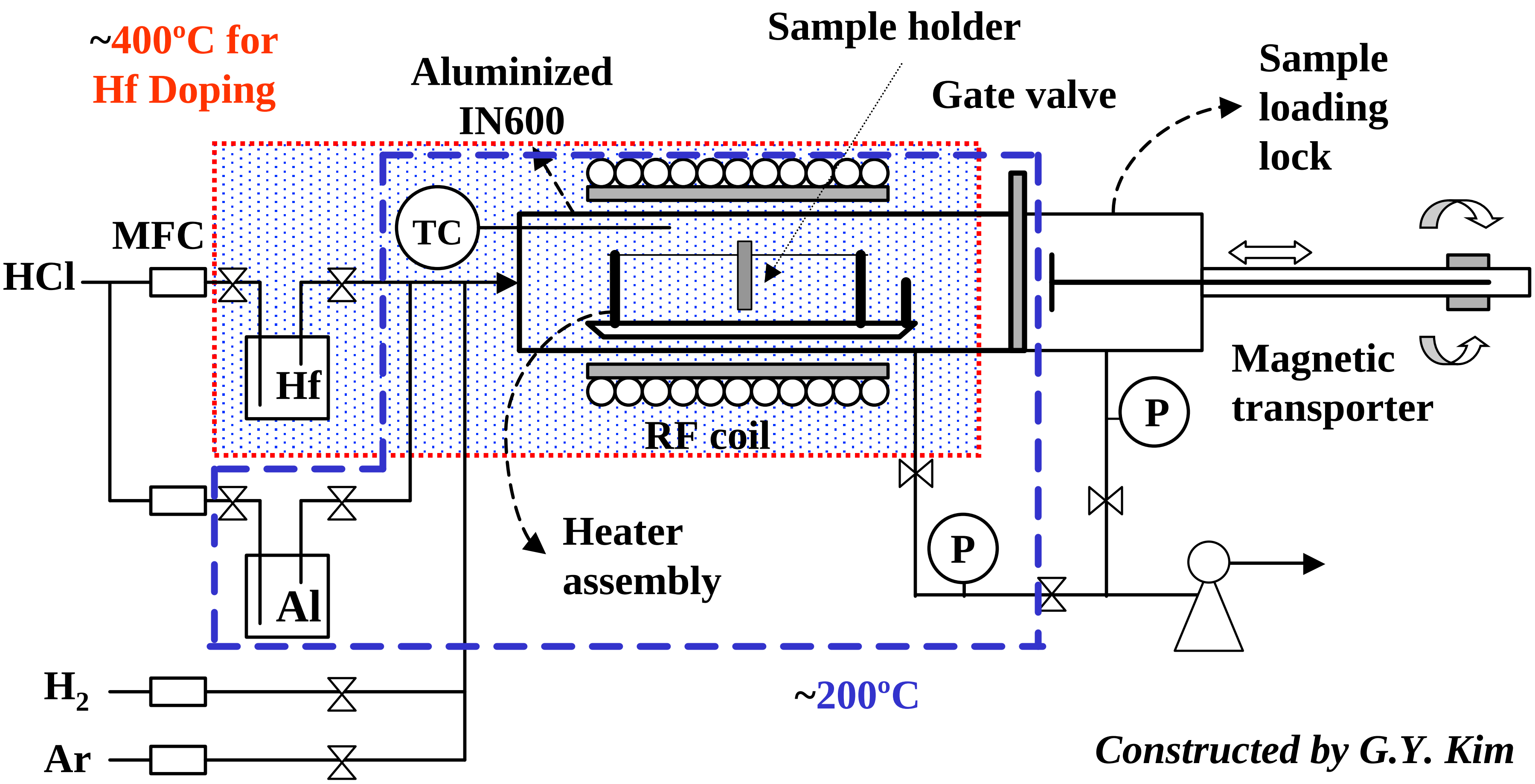
- Lack of process reproducibility
- Inconsistent composition/performance relationships

"Model" TGO Behavior



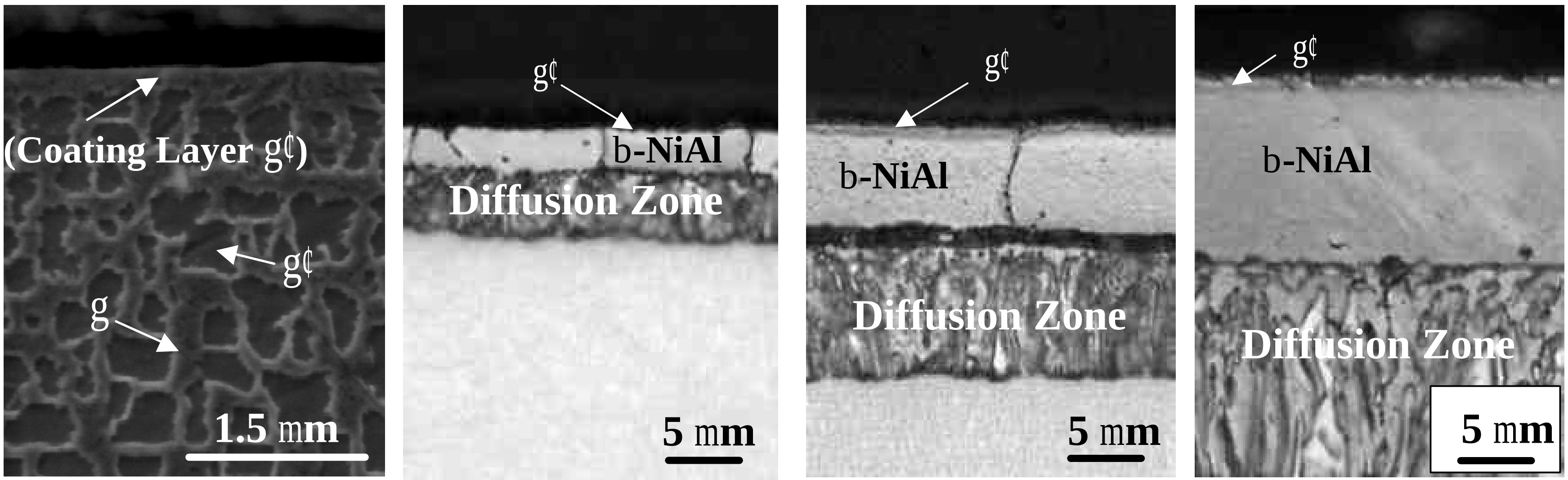
- Cast stoichiometric b-NiAl
  - Pint et al., 1998
- Beneficial effects of Hf
  - TGO growth kinetics
  - Columnar TGO
  - Immobilized sulfur impurity
  - Creep resistance of b-NiAl
- Optimum performance
  - ~0.2 wt% Hf
- Hf solubility in cast b-NiAl
  - Not precisely measured
  - Estimated ~0.1 wt% by Pint

CVD Reactor Designed for Short-time Experiments



Constructed by G.Y. Kim

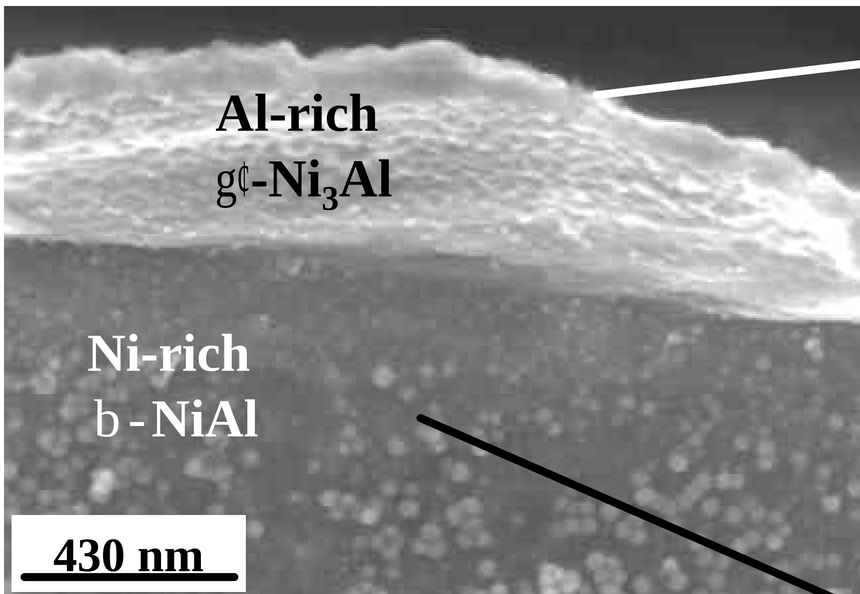
Baseline Aluminizing Behavior on René N5 (without Hf Doping)



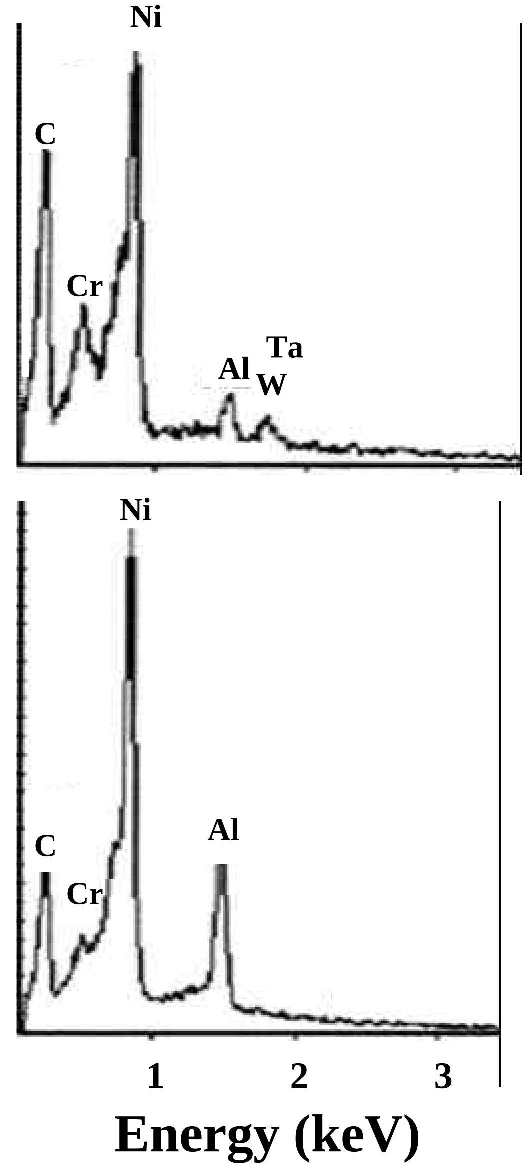
5 min 20 min 45 min 180 min

Kim et al., Metall. Trans. A. (in press)

g¢ Presence at Coating Surface Caused by W and Ta Segregation

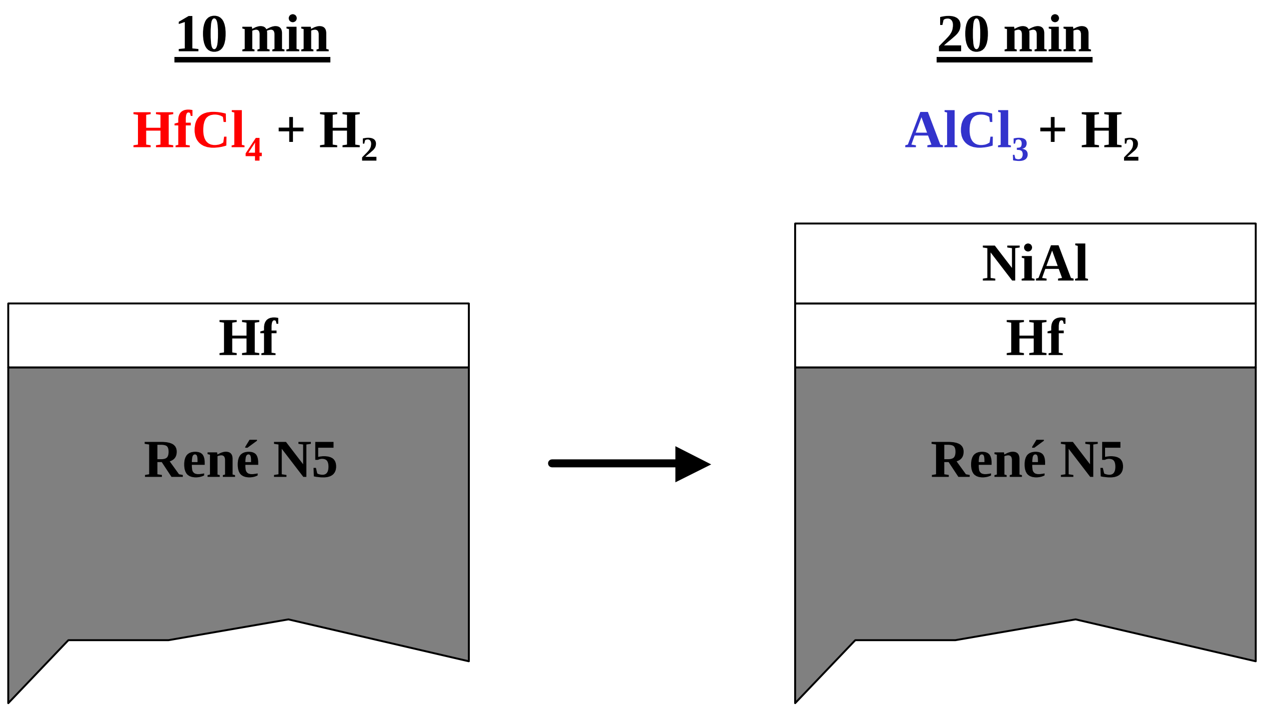


After 180 min of aluminizing



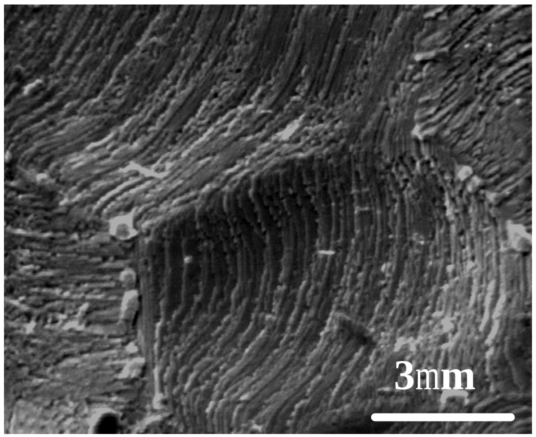
Kim et al., Metall. Trans. A., 2001

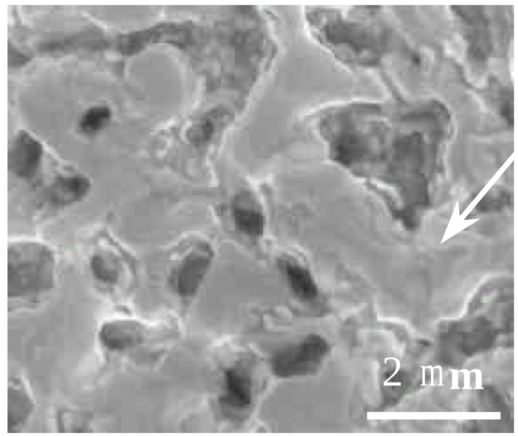
First Approach: Sequential Doping Procedure



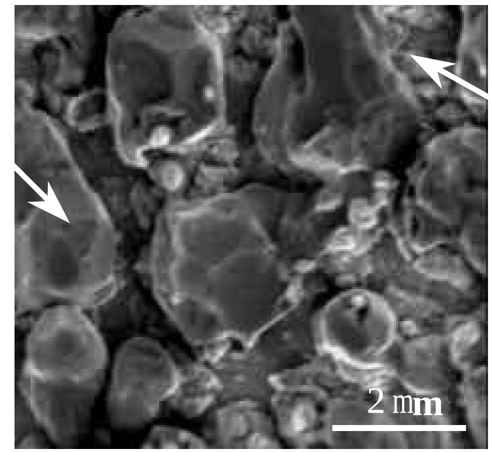
Hf-rich Precipitates Act as Ni Outward Diffusion Barrier and Retard b-NiAl Formation

20 min aluminizing | **0.5 min Hf predeposition** | **10 min Hf predeposition**





b



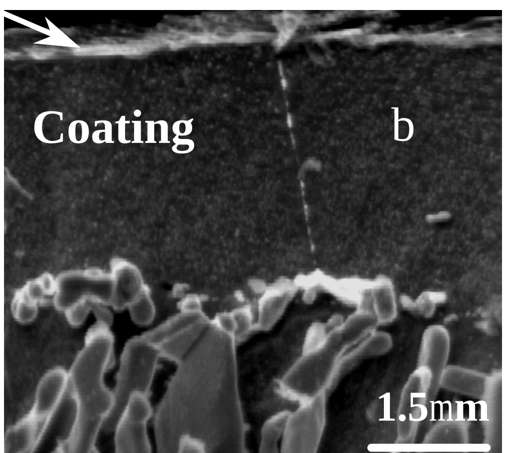
Hf ppts

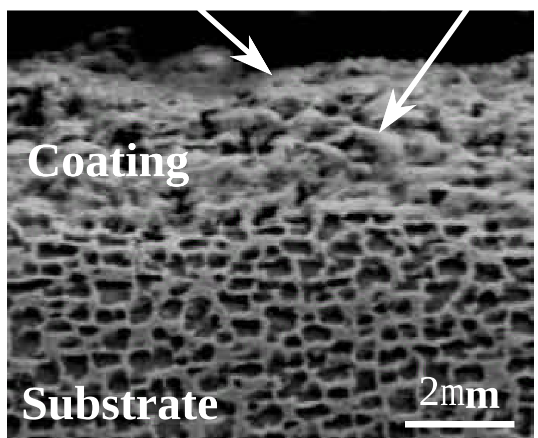
g¢

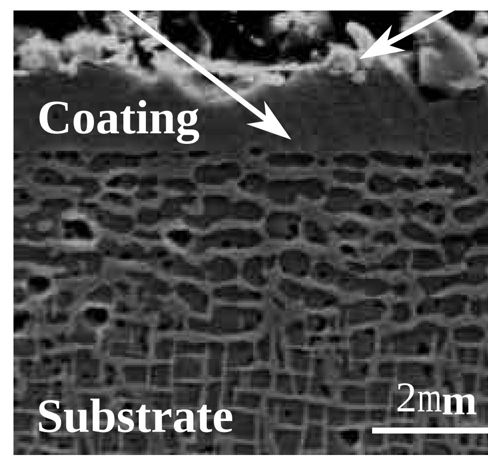
g¢+Hf ppts

b+Hf ppts

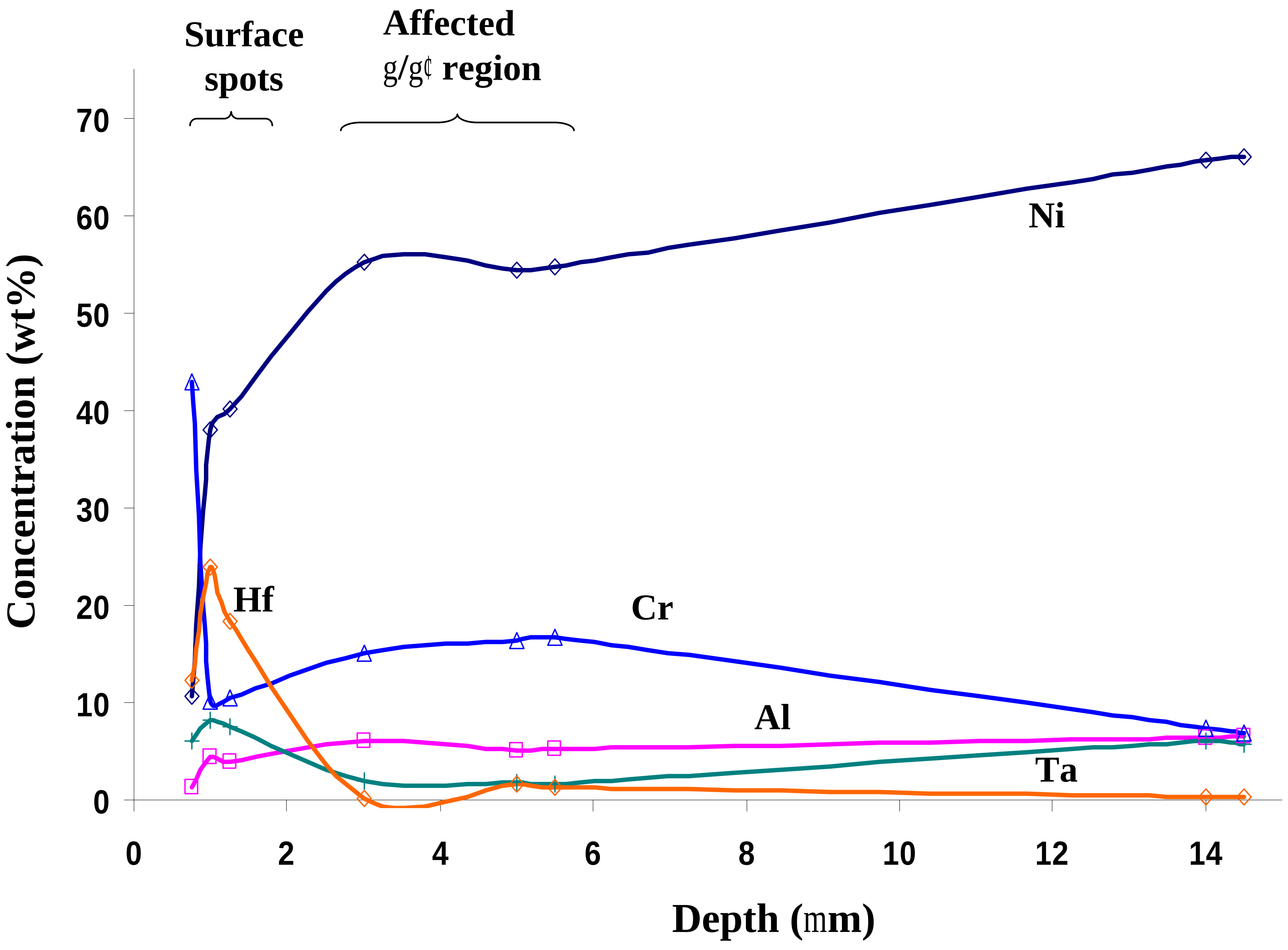
g¢+Hf ppts





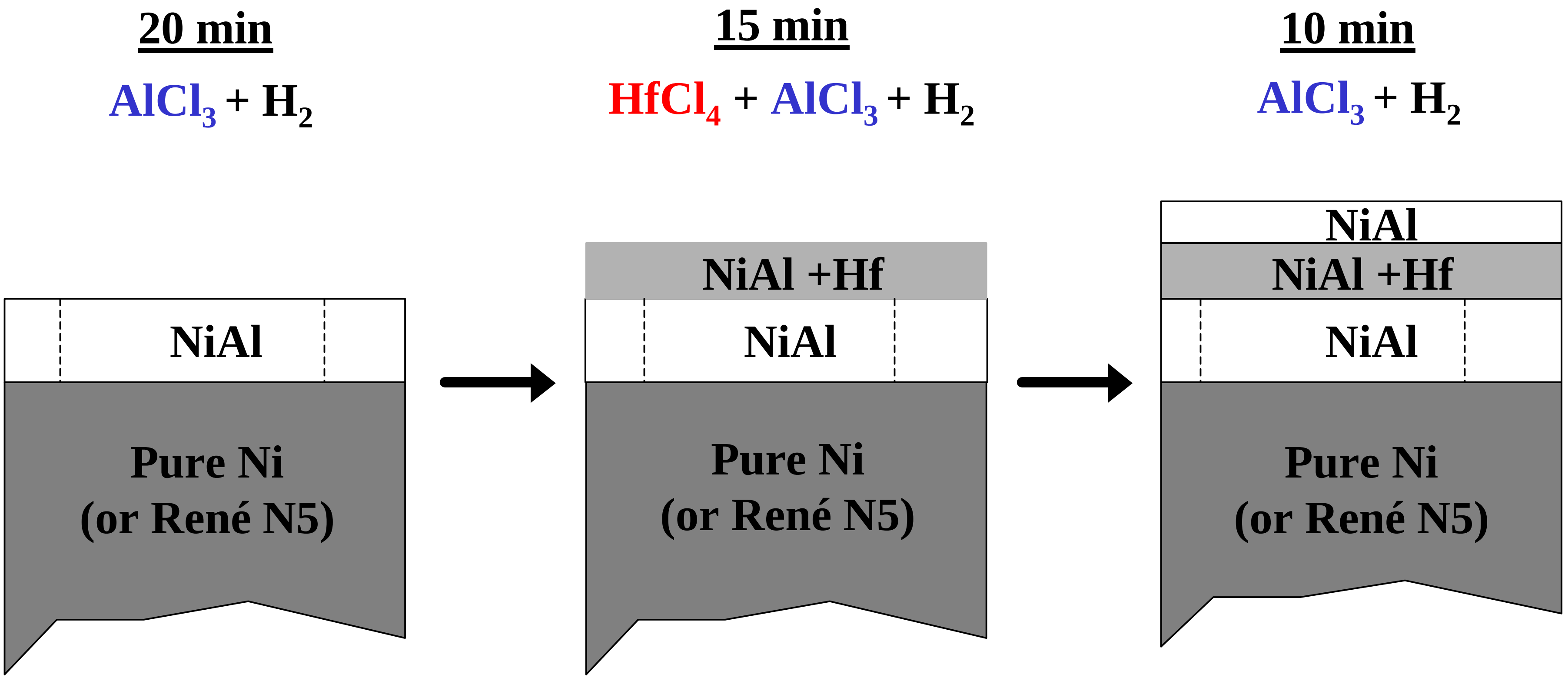


Significant Hf Incorporation by Sequential Doping



10 min Hf predeposition

Second Approach: Continuous Doping Procedure



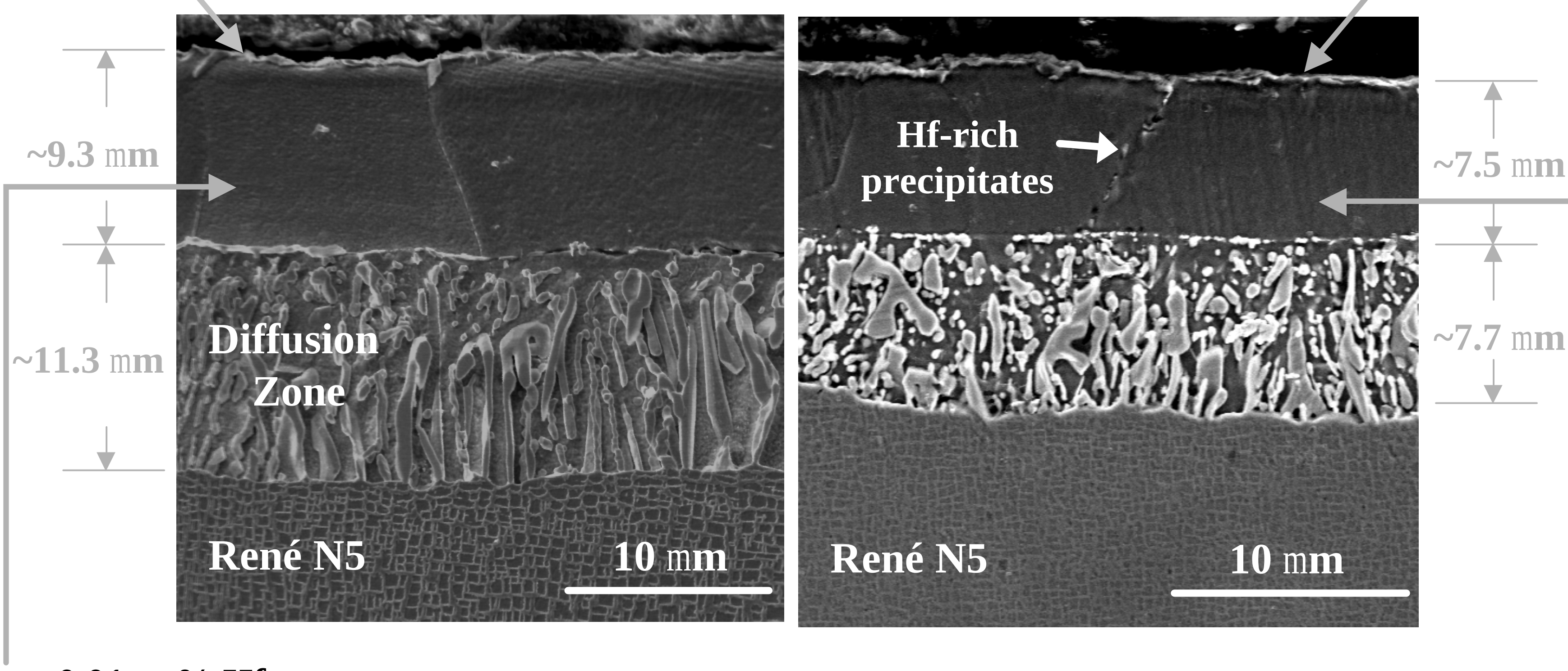
$$\left(\frac{HfCl_4}{AlCl_3} = 0.02 \sim 1.88\right)$$

Very Low Hf Conc. Even at High $HfCl_4$ Conc.

Without Doping	**With Doping**
($P_{HfCl_4}/P_{AlCl_3} = 0$)	**($P_{HfCl_4}/P_{AlCl_3} = 0.6$)**

g¢-Ni_3Al

More g¢-Ni_3Al

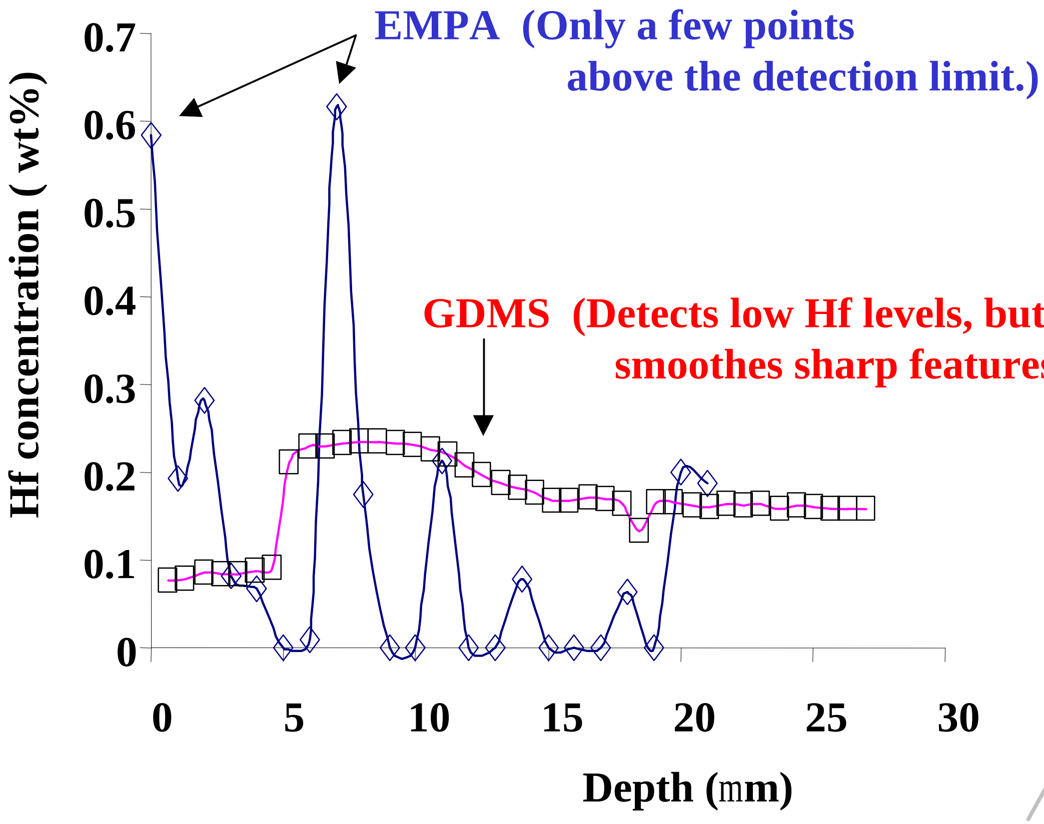


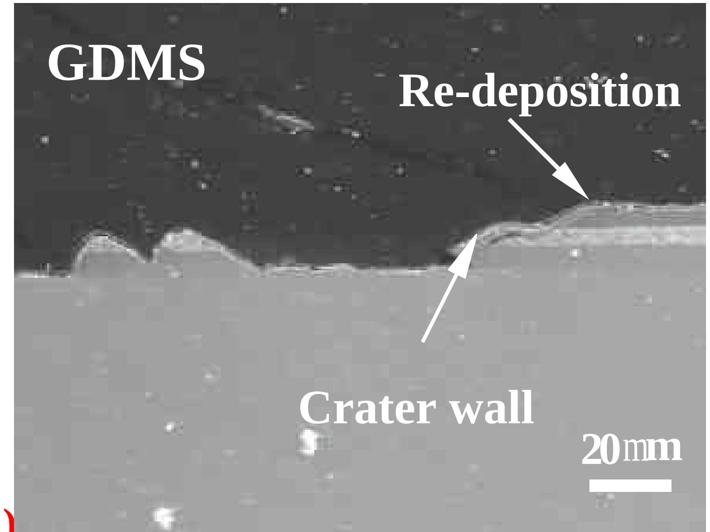
~0.01 wt% Hf (from René N5)

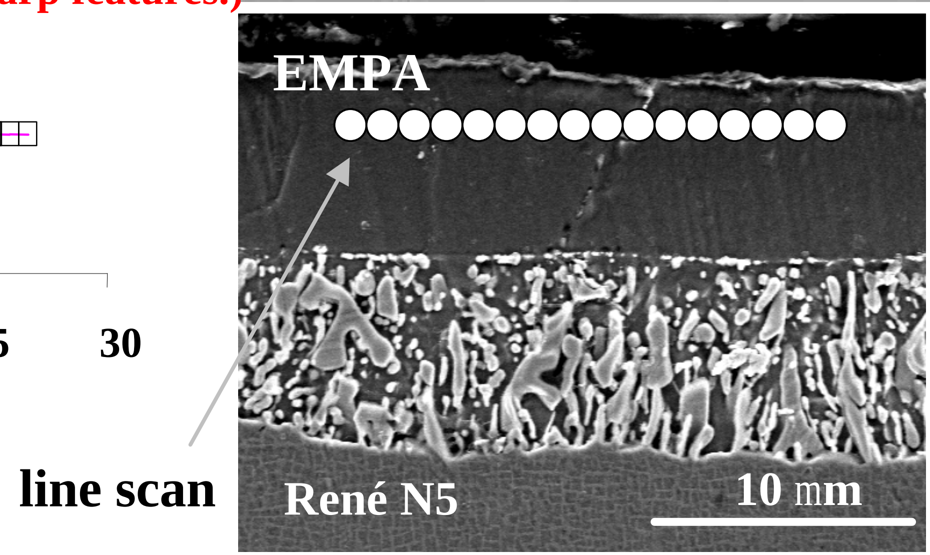
~0.1 wt% Hf due to precipitates

Kim et al., Metall. Trans. A. (submitted)

Hf Conc. And Dist. Measured by GDMS & EMPA



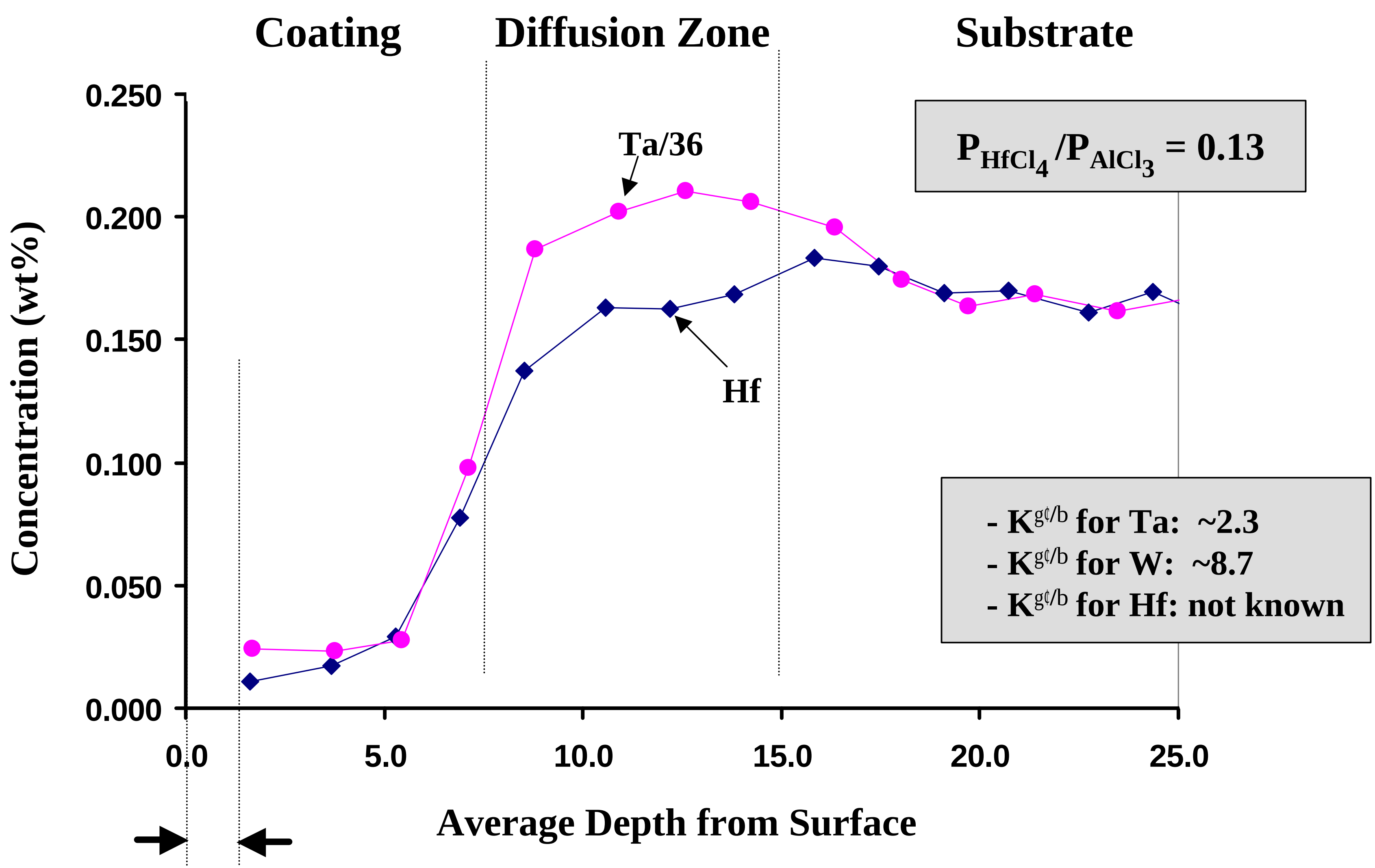




$P_{HfCl_4}/P_{AlCl_3} = 0.6$

He et al., Metall. Trans. A. (in progress)

Hf and Ta Concentration Profiles at Low $HfCl_4$



Observations During Process Development

- **Sequential Doping**
  - **Significant Hf incorporation through Hf-rich precipitates**
  - **Hf-rich Precipitates worked as diffusion barriers and altered coating microstructure**

- **Continuous Doping**
  - **Retained columnar microstructure**
  - **Hf incorporation during continuous doping appeared to limited by its solubility in b-NiAl**
  - **High $HfCl_4/AlCl_3$ ratio were needed**

- **Future Work**
  - **"Floating behavior" of g¢-Ni_3Al layer at the coating surface and its effects on aluminizing kinetics and Hf incorporation behavior**
  - **Preparation of Hf-doped coating specimens for performance evaluation ~0.01 to 3 wt% Hf**

How to Synthesize Coatings with 0.01 to 3 wt% Hf?