Aluminide Coatings for Power Generation Applications

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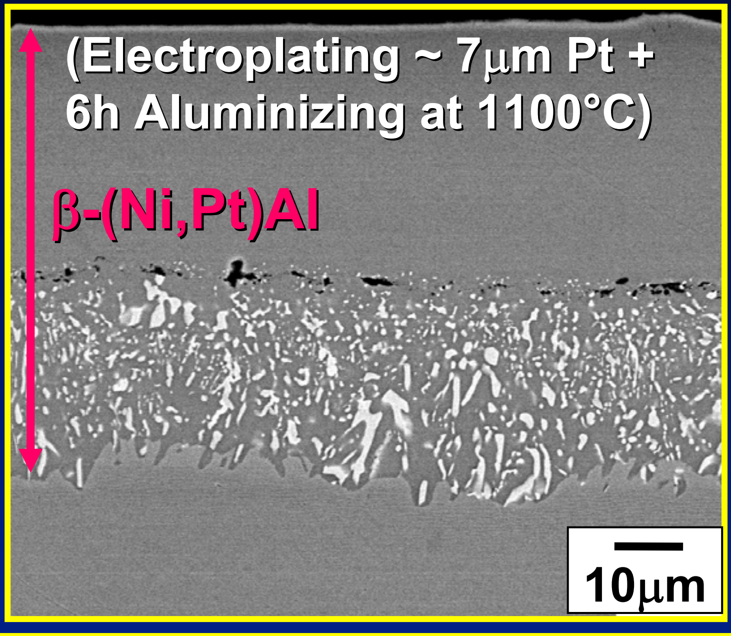
Two Main Research Components

- Investigate critical issues associated with aluminide coatings on Fe-base alloys & Ni-based superalloys to develop a comprehensive coating lifetime evaluation approach and to improve long-term coating durability

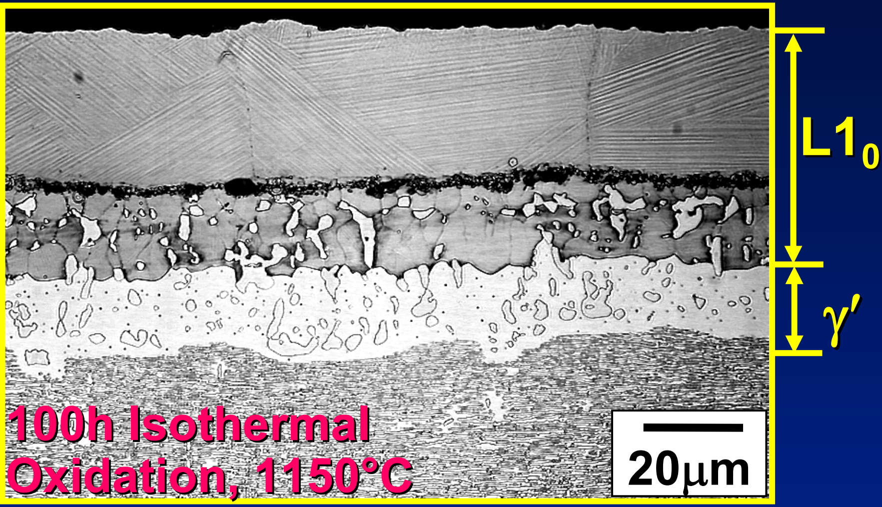
  - Task I: Assess long-term performance of aluminide coatings on Fe-base alloys to explore potential benefits of iron aluminide coatings in terms of lifetime and applicable environments

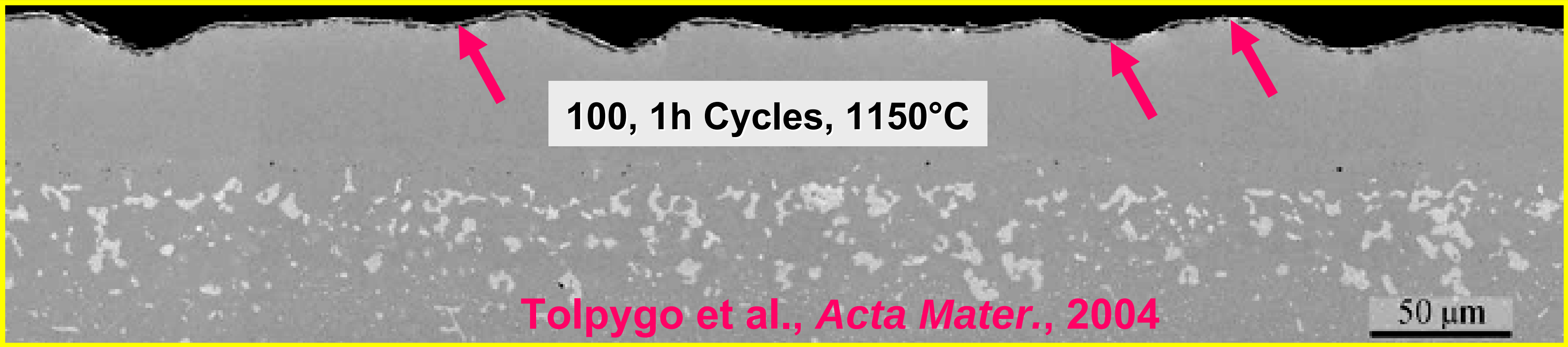
  - Task II: Develop a type of Pt-enriched $\gamma+\gamma'$ two-phase bond coat on Ni-based superalloys and evaluate its performance for land-base turbine applications

Issues Related to Current β-(Ni,Pt)Al Bond Coat



Zhang et al., *Surf. Coat. Technol.*, 2003





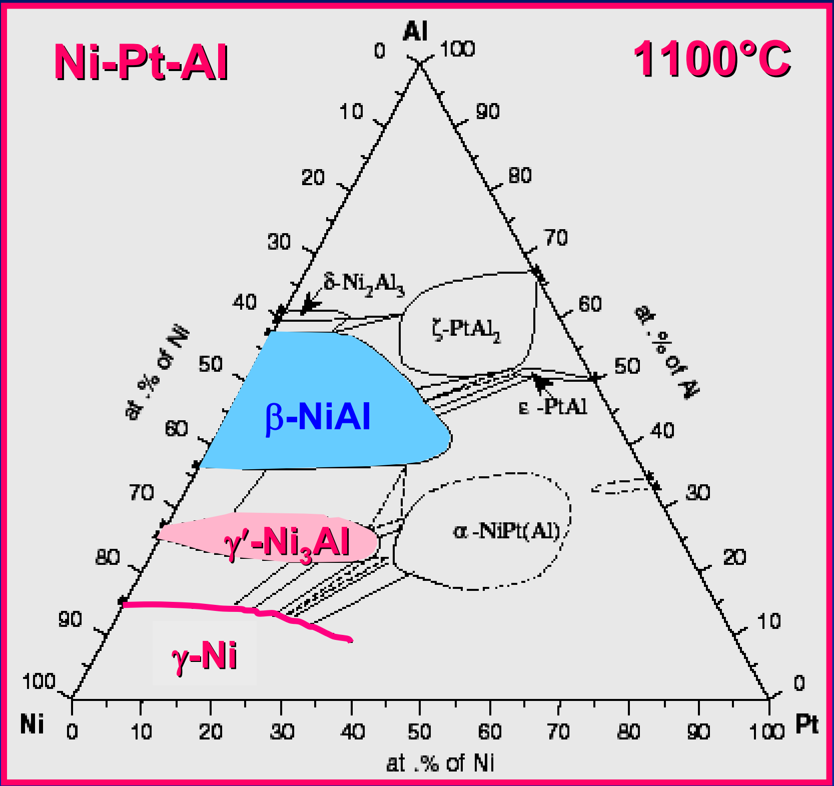
- Phase transformations & rumpling affect the ability of bond coat to accommodate TGO, leading to TBC spallation

Why Pt-Enriched $\gamma+\gamma'$ Two-Phase Bond Coat?

- The constant demand for increased operating temperatures in gas turbine engines has been the driving force for development of more reliable thermal barrier coating (TBC) systems

- Pt-enriched $\gamma+\gamma'$ two-phase coatings may offer several advantages over the β-(Ni,Pt)Al bond coat
  - better compatibility
  - improved metallurgical stability
  - higher creep strength
  - reduced manufacturing cost

Hayashi et al., *Acta Mater.*, 2005



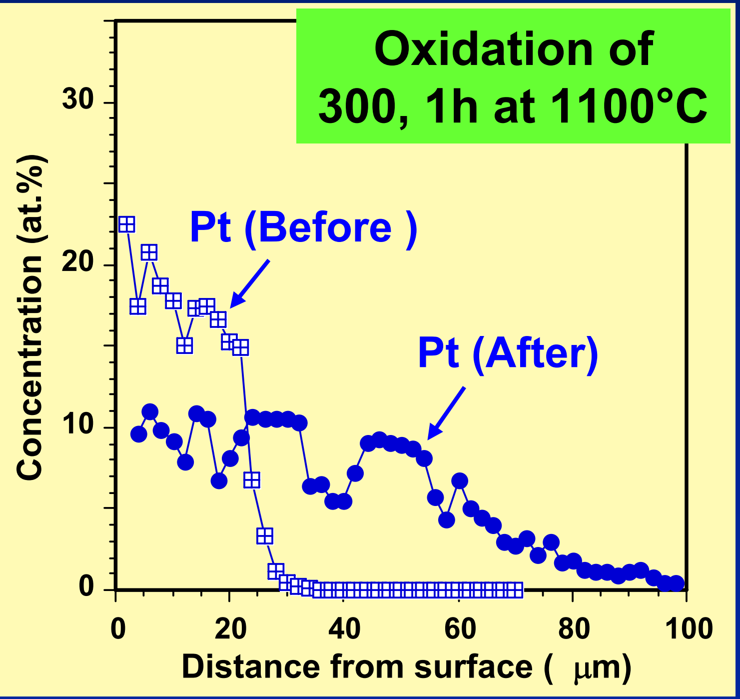
Potential Concerns about Pt-Enriched γ+γ′ Coatings

- **Oxidation performance is sensitive to substrate composition. They may not be suitable for certain superalloys.**

  (Tawancy et al., *J. Mater. Sci.*, 2003; Haynes et al., *Surf. Coat. Technol.*, 2007; Pint et al., submitted to *Superalloys 2008*)

- **Pt back-diffusion upon thermal exposure for thin-walled components or land-based turbine applications**
  - **Significant Pt diffusion occurred from γ+γ′ coating into substrate after 300, 1h cycles at 1100°C**
  - **Pt diffused into the substrate from ~30 to ~100 μm**

  (Zhang et al., *Surf. Coat. Technol.*, 2005)



Research Focus

- Interdiffusion between Pt-diffused $\gamma+\gamma'$ coatings & superalloy substrates
  - SX Y-free René N5 and DS René 142 (~14 at.% Al)
  - Interdiffusion experiments: 900-1050°C
  - Preliminary diffusion modeling
    - Pt concentration profiles & Pt penetration depth
- Cyclic Oxidation Performance
  - Different types of $\gamma+\gamma'$ coatings: 1h cycles at 1100°C

Alloys	Al	Cr	Co	Ta	W	Re	Mo	Hf	S
N5 (at.%)	13.5	8.1	7.5	2.1	1.7	1.0	0.9	0.07	1.0
(wt.%)	(6.1)	(7.0)	(7.5)	(6.3)	(5.2)	(3.1)	(1.4)	(0.2)	(0.5)
R142 (at.%)	13.4	7.7	11.9	2.1	1.6	0.9	0.9	0.45	38ppma
(wt.%)	(6.0)	(6.6)	(11.7)	(6.3)	(4.7)	(2.8)	(1.5)	(1.32)	(20)

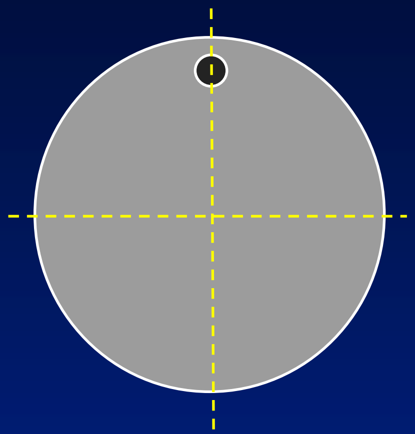
Experimental Approach

- Synthesis of Pt-diffused $\gamma+\gamma'$ coatings
  - Electroplating ~ 7μm Pt
  - Annealing in vacuum for 2h at 1175°C

    Nagaraj et al., *US Patent, 5,427,866*, 1995

    Rickerby et al., *US Patent, 5,667,663*, 1997

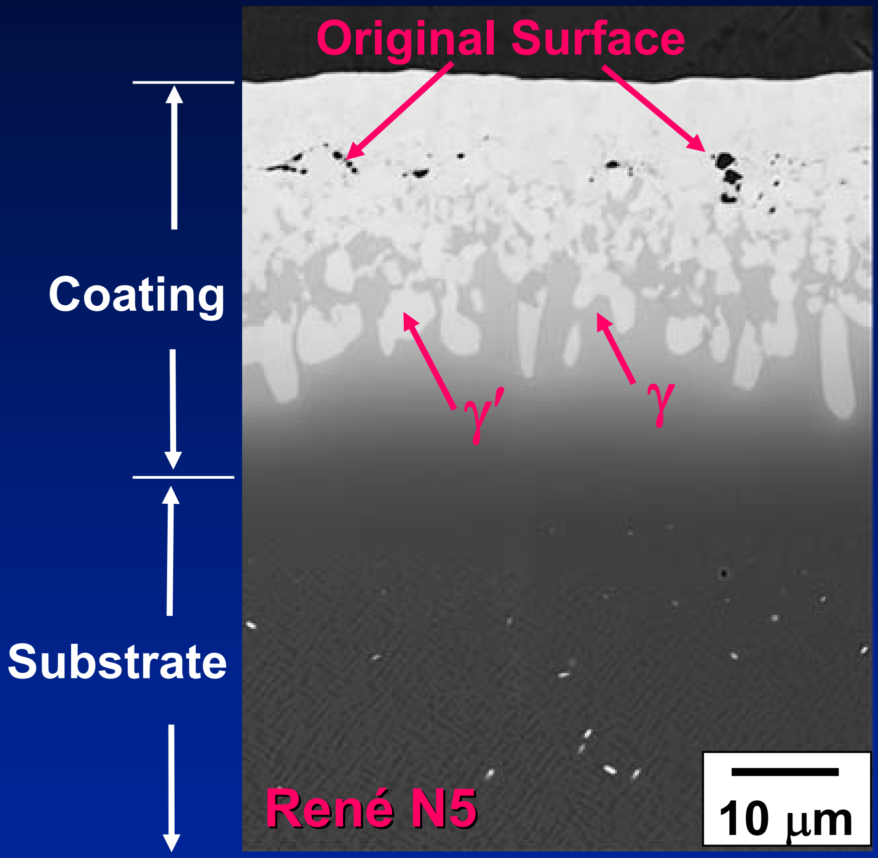
    Zhang et al., *Surf. Coat. Technol.*, 2005

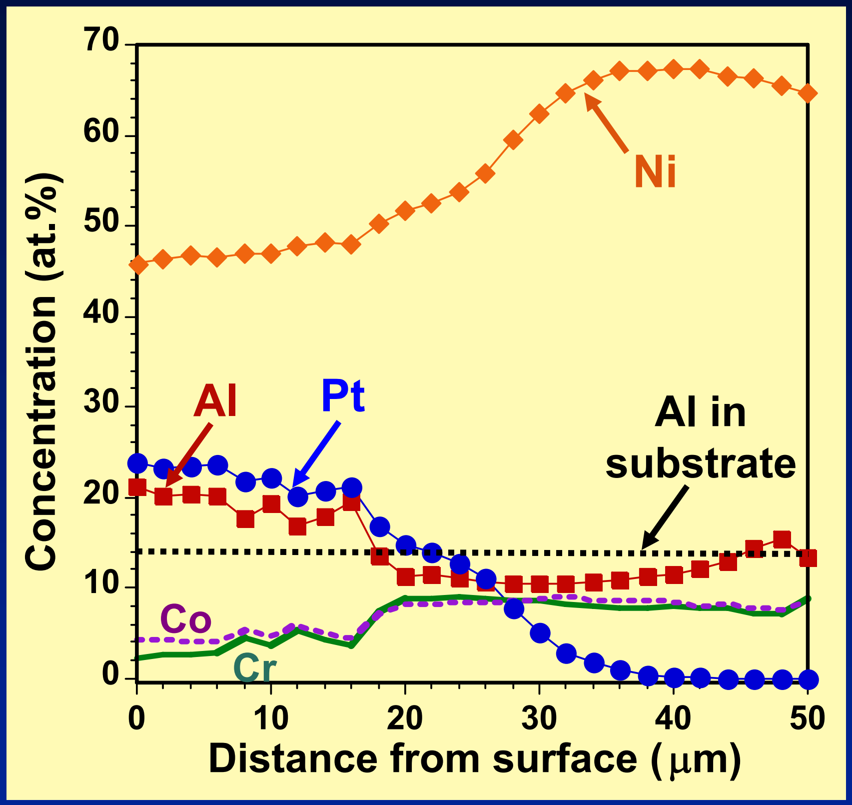


- Interdiffusion experiments
  - Encapsulated in an Ar-filled quartz capsule
  - Concentration profiles: electron probe microanalysis

Temperature (°C)	Time (h)	Substrate
900	1000	N5
1000	1000	N5 & R142
1000	2000	N5
1050	1000	N5 & R142

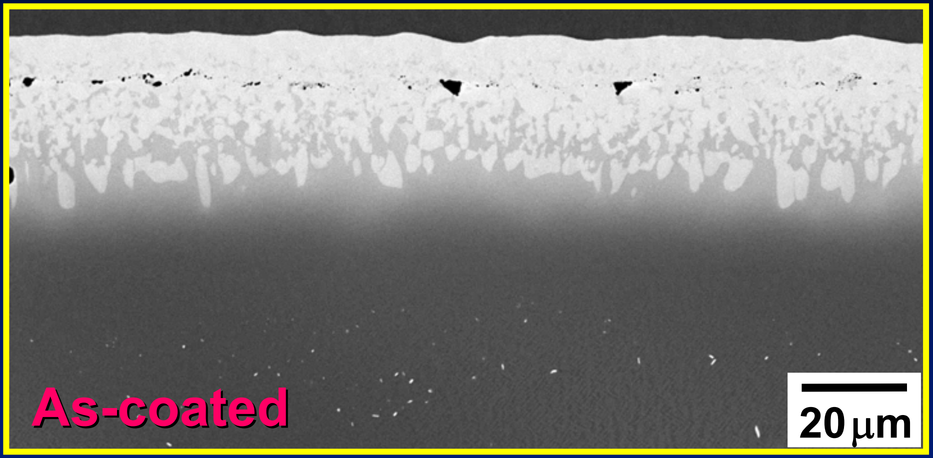
As-Fabricated Pt-Diffused γ+γ′ Coating

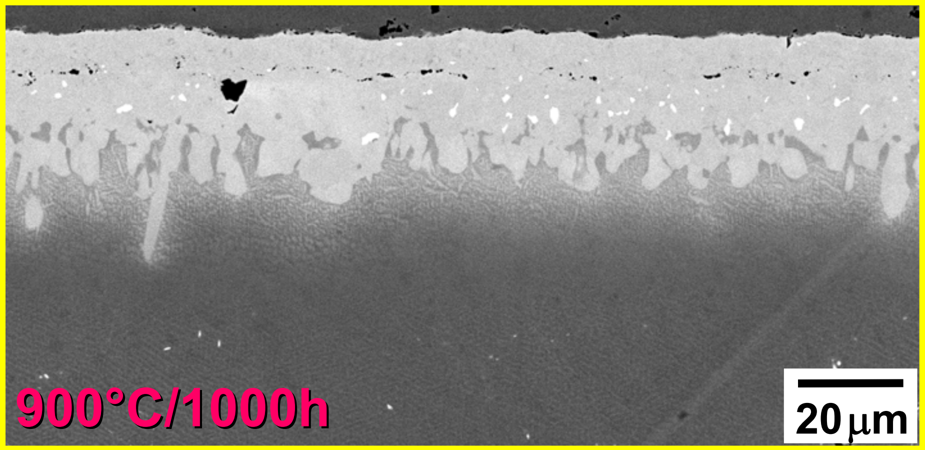


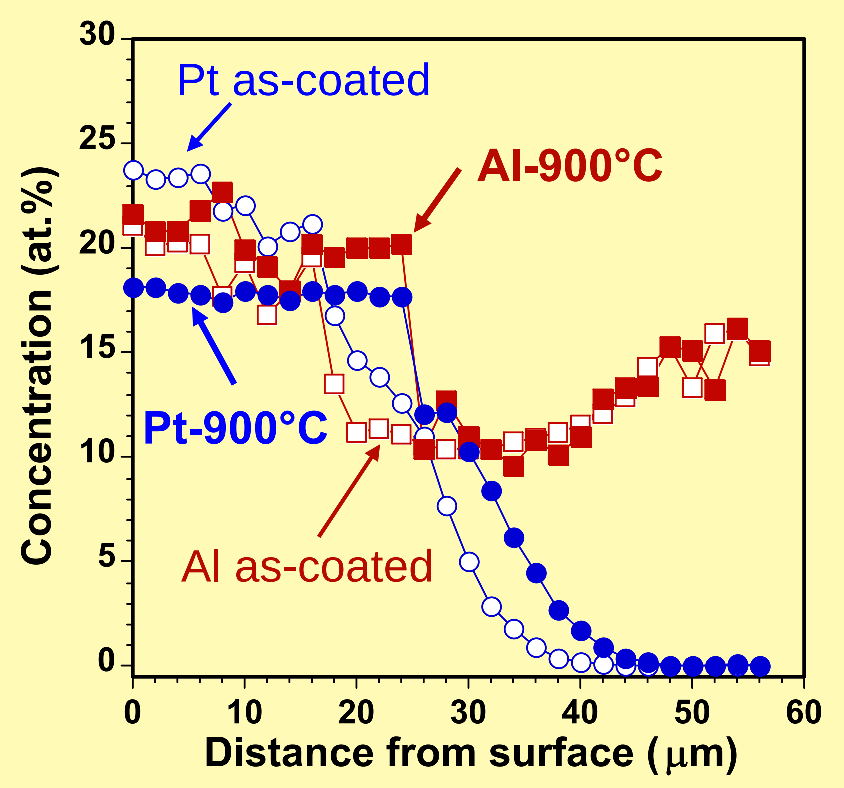


- Near coating surface: Pt = 23%, Al = 20% (Al in substrate = 14%)
- Pt penetration depth = 35~40 μm, defined as Pt < 0.5%

Interdiffusion was insignificant after 1000h at 900°C

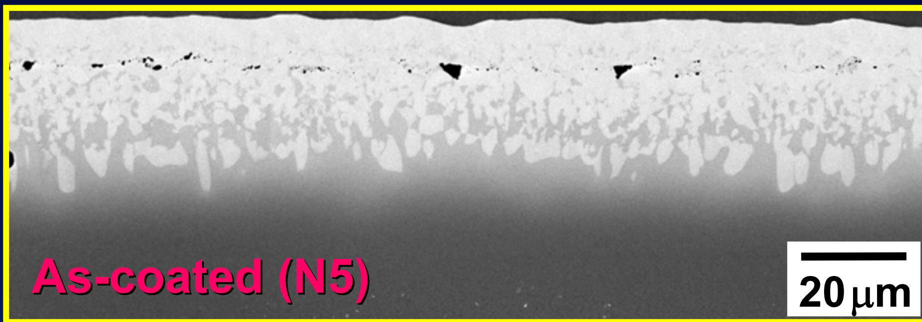


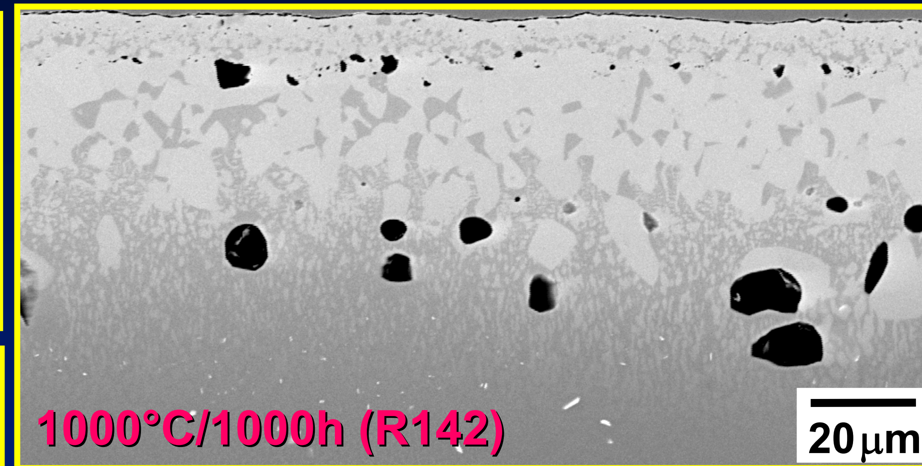


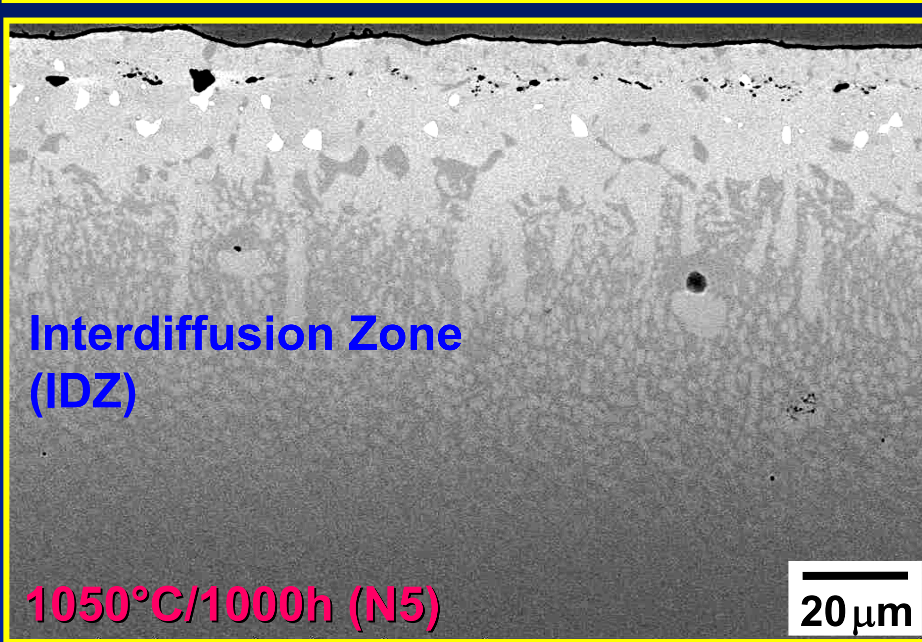


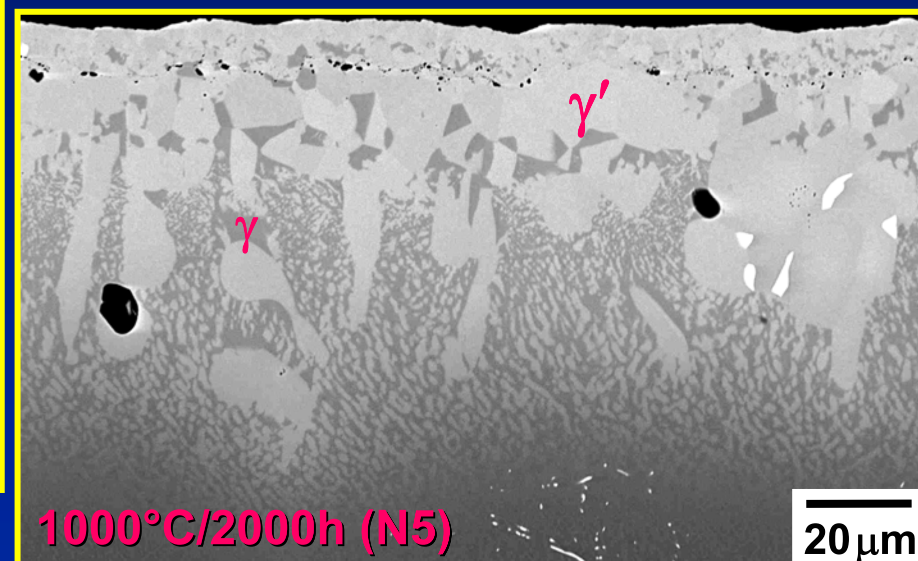
- Slight coarsening of γ′ in the coating
- Al remained ~20% after diffusion; Pt decreased from 23 to 18%
- Pt penetration depth: 40 to 44 μm

Interdiffusion became more profound at temperatures ≥ 1000°C



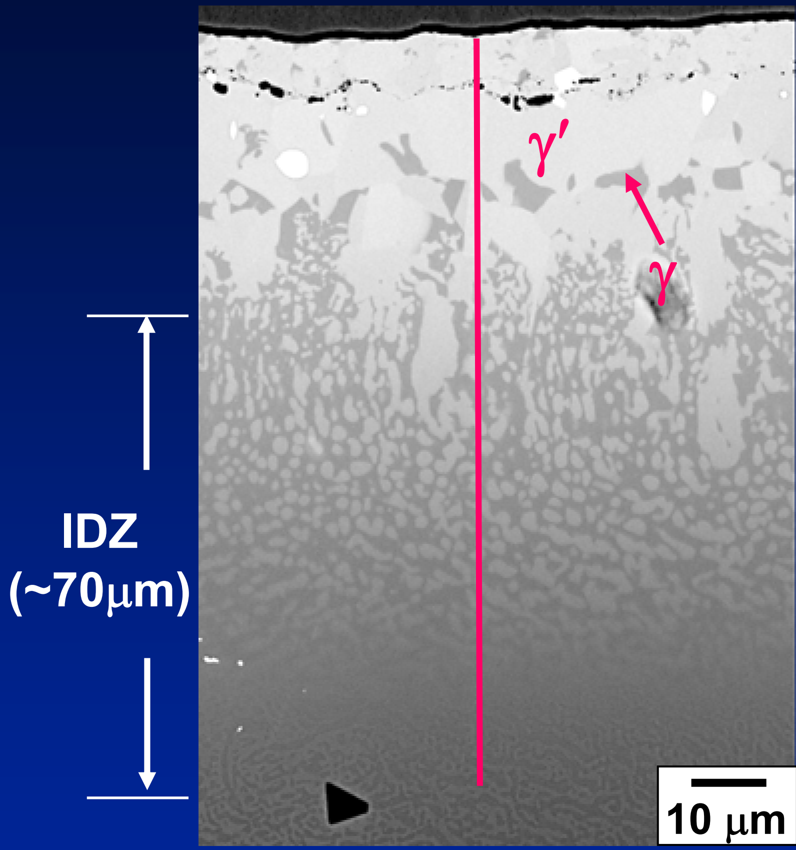


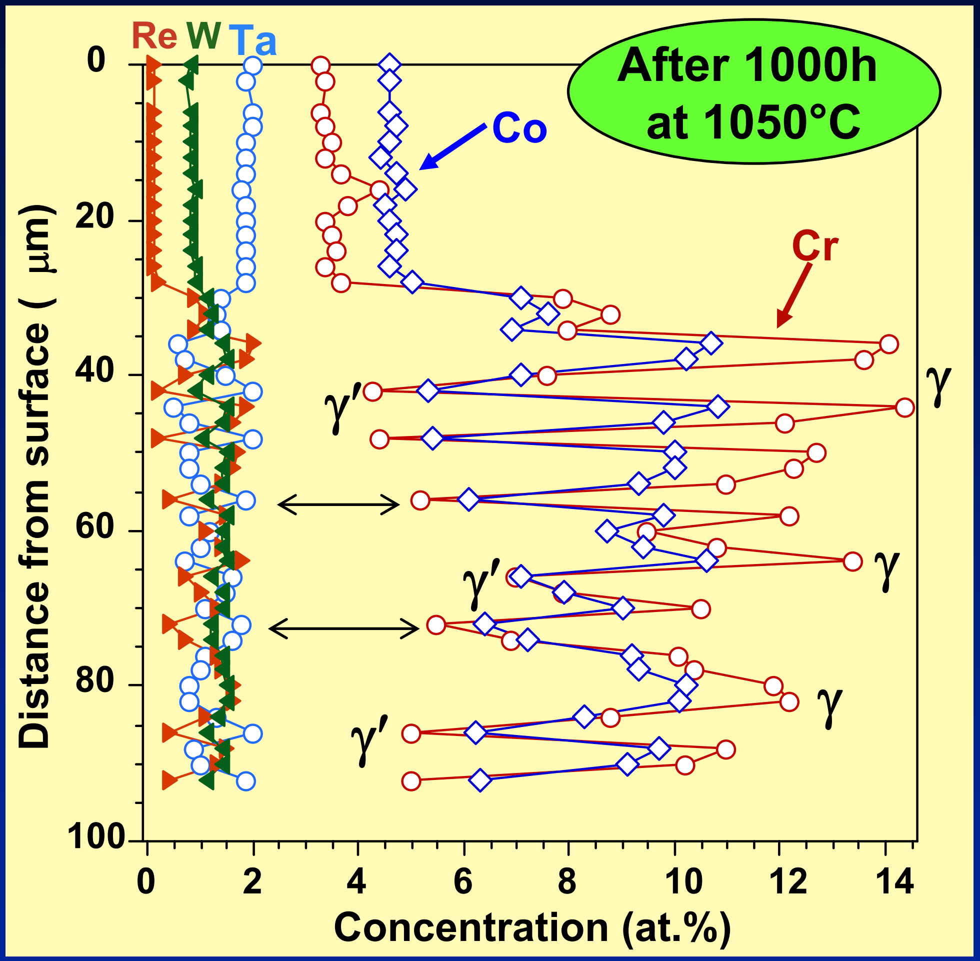




- Increased coarsening of γ′
- Formation of an interdiffusion zone between the coating & substrate consisting of Pt-enriched γ′ precipitates in γ

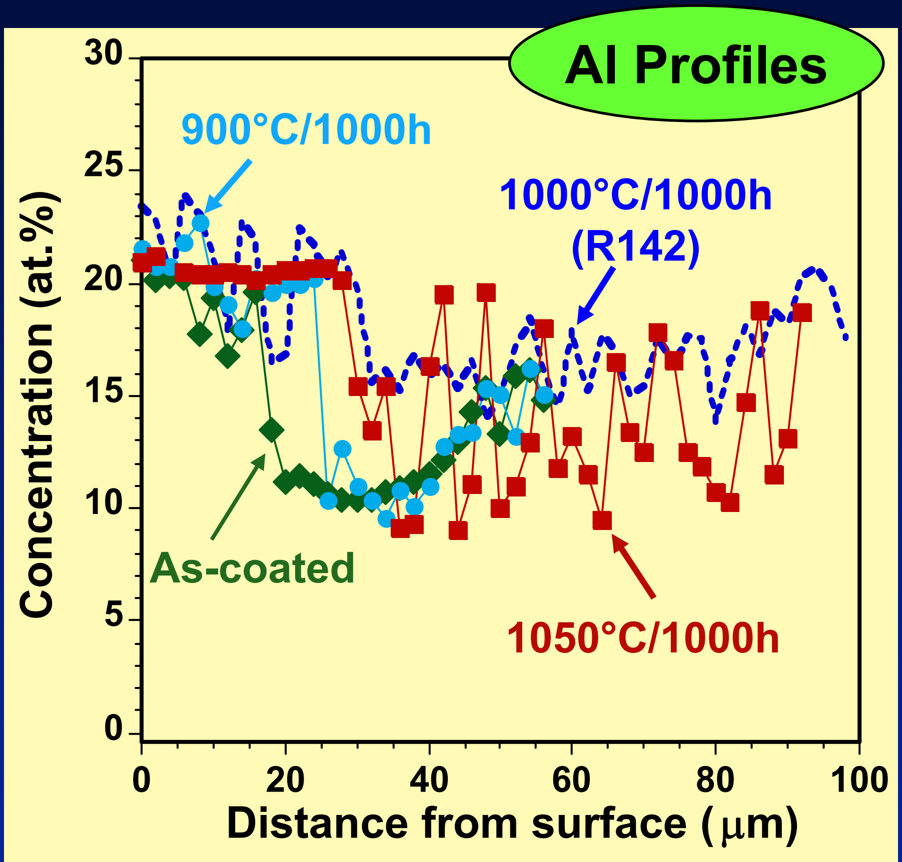
Distribution of alloying elements in interdiffusion zone can be correlated to their partitioning in γ and γ′

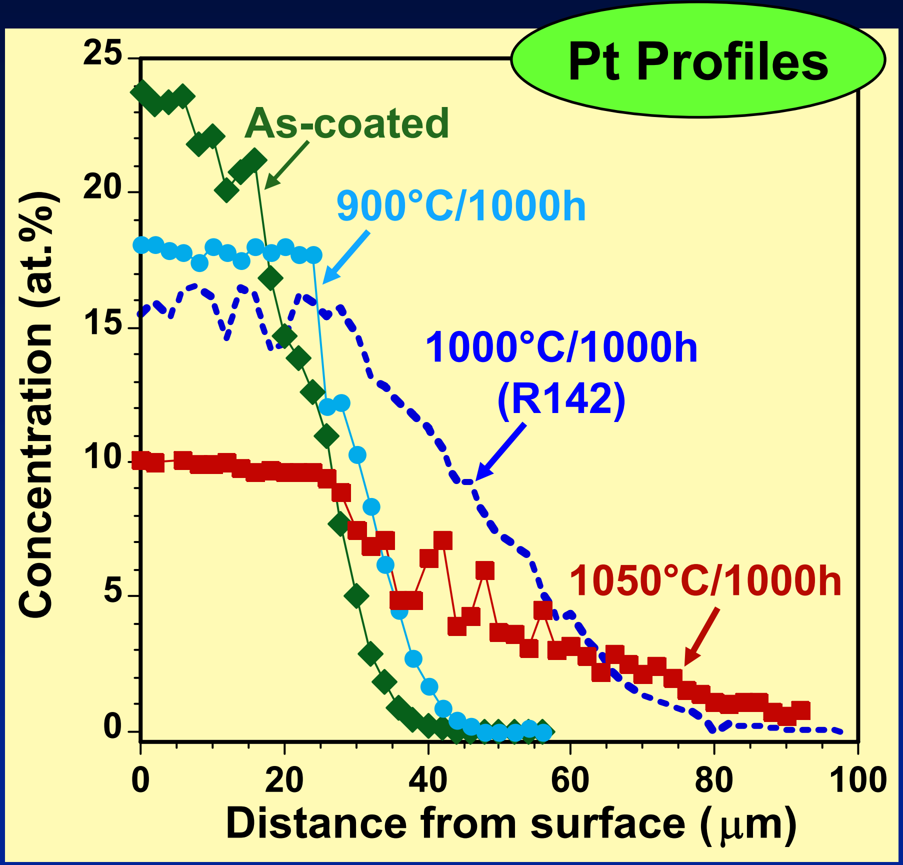




- Partitioning to γ′: Ta (Al, Pt)
- Partitioning to γ: Cr, Co, W, Re, & Mo
- Disruption of the original fine γ/γ′ microstructure may have an effect on thin-walled components

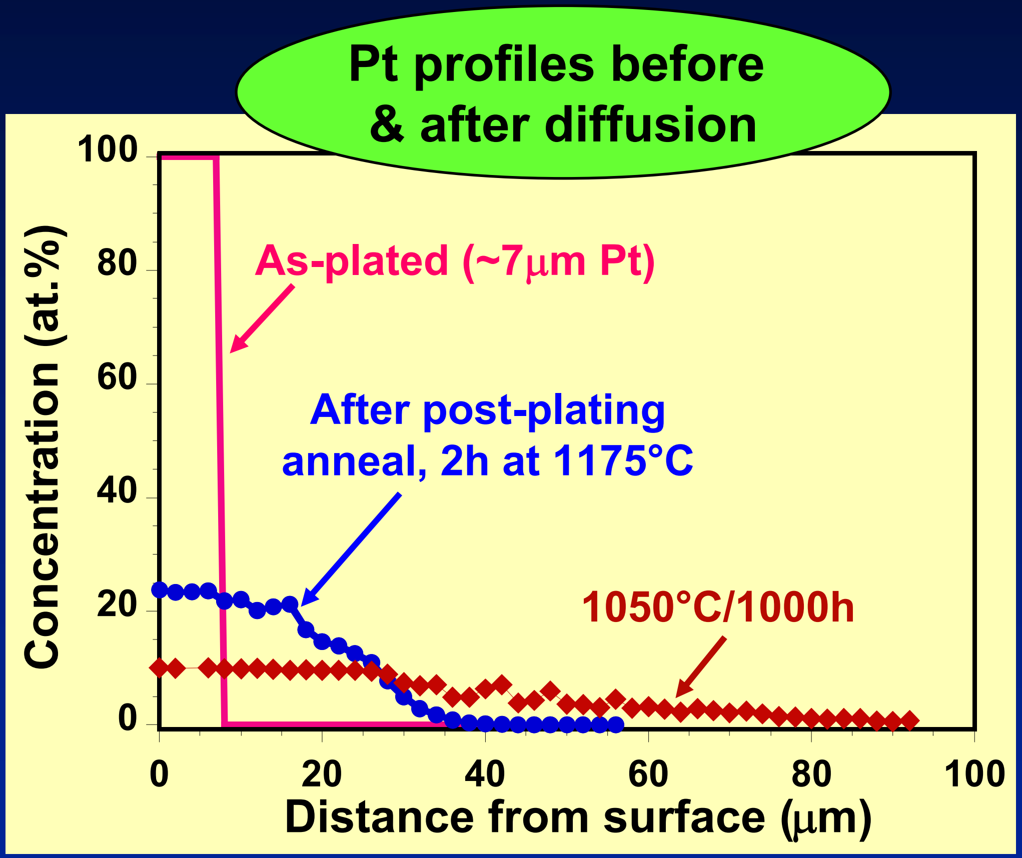
While the change in Al content was minimal, Pt loss to the substrate was evident after diffusion





- Al uphill diffusion was still effective after 1000h at 1050°C *(Hayashi et al., Metall. Mater. Trans., 2005)*
- Pt at coating surface: 23% → 18% → 15% → 10%
- Pt penetration depth: 40 → 44 → 79 → 98 μm

Interdiffusion in γ+γ′-coated superalloys is a multicomponent mulitphase diffusion problem

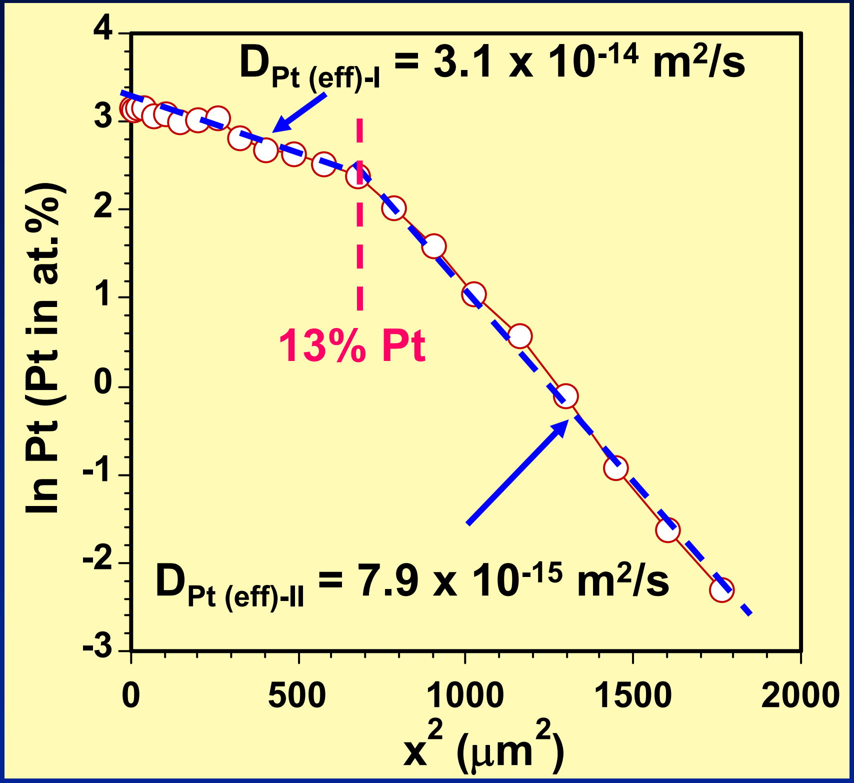


- Presence of γ and γ′
- Uphill Al diffusion
- Limited diffusivity data
- Diffusivities are likely concentration-dependent
- The γ+γ′-coated superalloy does not exhibit fixed terminal compositions as in the diffusion couple of γ+γ′ (Ni-20Al-22Pt) / γ+γ′ (Ni-14Al)

- The present case could be approximated as a thin film at the end of a semi-infinite bar

As-Annealed Condition: Thin Film Solution

After 2h post-plating anneal at 1175°C



Thin Film on a Semi-infinite Bar

$$C(x,t) = \frac{bc_0}{\sqrt{\pi D t}} e^{-\frac{x^2}{4Dt}}$$

b — **the film thickness (=7μm)**

c_0 — **original solute conc. (=100%)**

D: solute diffusivity; *x*: the diffusion distance; *t*: diffusion time

$$\ln C(x,t) = -\frac{1}{4Dt}x^2 + \ln\frac{bc_0}{\sqrt{\pi D t}}$$

(1) For x > 0, c → 0 as t → ∞; x = 0, c → ∞ as t → 0 **(2)** $\int_0^{+\infty} C(x,t)\,dx = bc_0$

- **For constant D, *lnC ~ x^2* should be a straight line; slope = -1/4Dt**
- **Plot of *$lnC_{(Pt)}$ ~ x^2* showed two linear portions**

Pt diffusivity data for γ and γ′ phases are available only for dilute Pt concentrations

In γ-Ni, Pt = ~3.2% $D_{Pt}(\gamma)\,(m^2 s^{-1}) = 9.2\times10^{-5}\exp(-291.2\ kJ\,mol^{-1}/RT)$

Karunaratne and Reed, *Acta. Mater.*, 2003

In γ′-Ni_3Al, Pt = ~2.1% $D_{Pt}(\gamma')\,(m^2 s^{-1}) = 7.8\times10^{-4}\exp(-323\ kJ\,mol^{-1}/RT)$

Minamino et al., *Defect Diff. Forum*, 1997

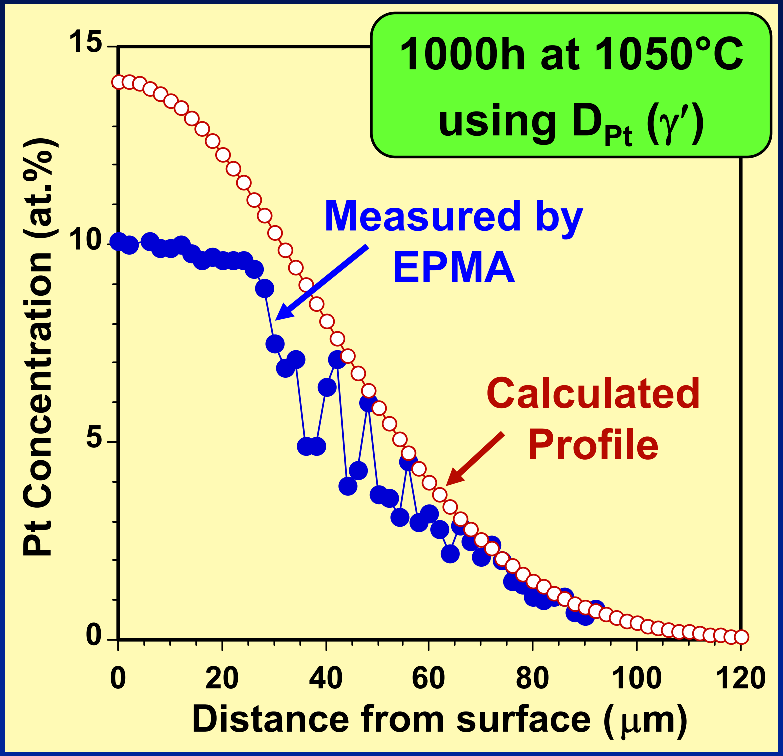
At 1175°C	Pt Diffusivity (m^2/s)
For diluted Pt in γ	2.8×10^{-15}
For diluted Pt in γ′	1.4×10^{-15}
Thin Film Solution (Linear Portion I)	3.1×10^{-14}
Thin Film Solution (Linear Portion II)	7.9×10^{-15}

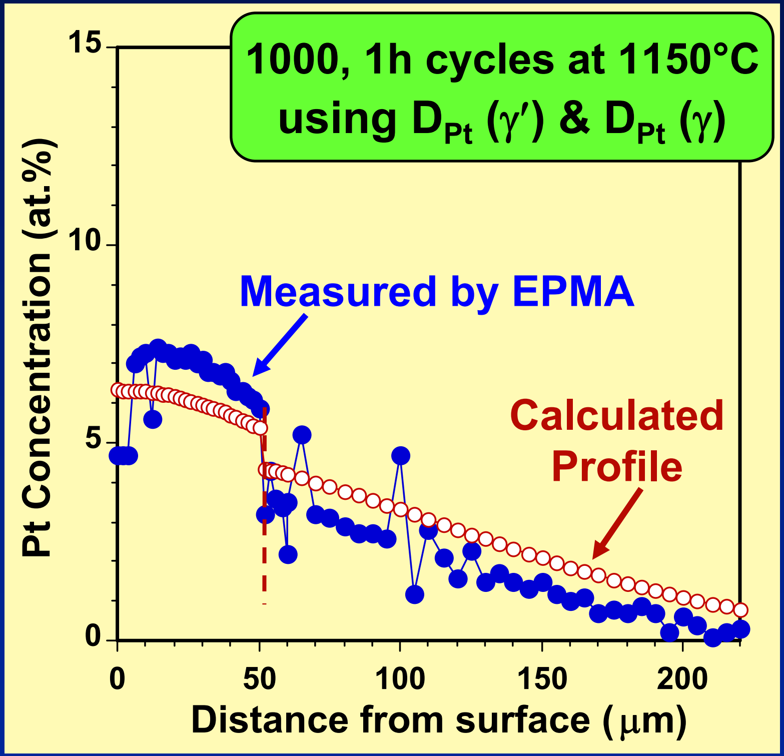
- The Pt diffusivity appears to be a function of Pt concentration

Calculated Pt Profiles after Thermal Exposure

- Post-plating anneal: 2h at T_1 (1175°C) ⟶ t_1 at T_2
- Diffusion test: t_2 at T_2

$t = t_1 + t_2$





- The calculated Pt profile fits better for more extensive interdiffusion where the Pt level (≈ 5%) is close to diluted concentrations
- Interactions between Pt & other elements were not taken into account

Estimated Pt Diffusion Depth after Diffusion

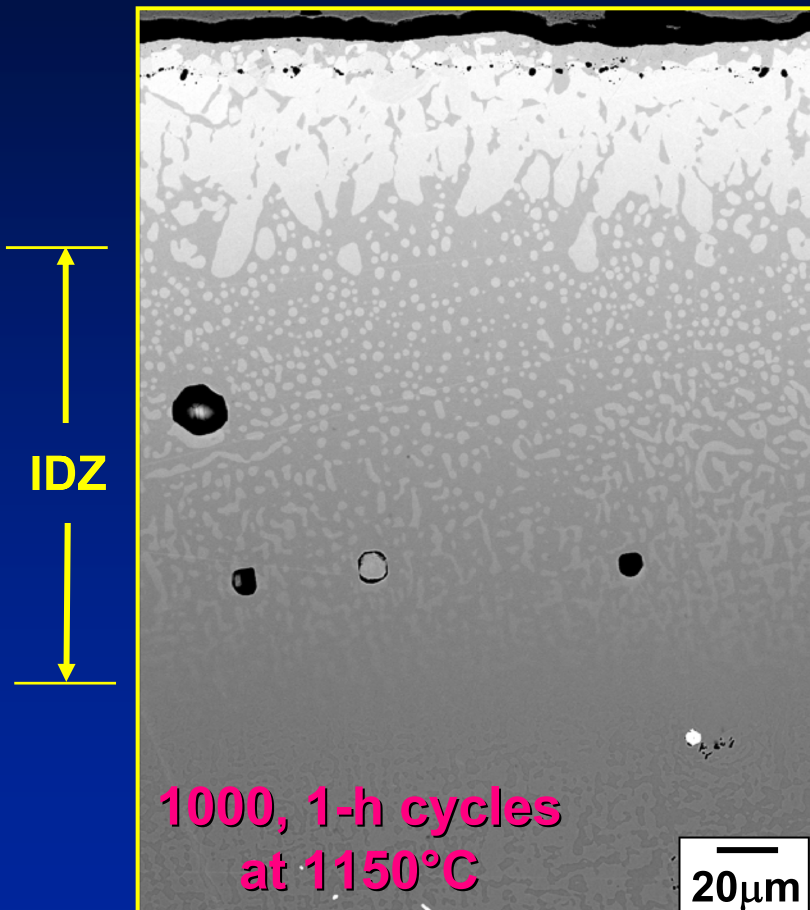
$$Pt\ Diffusion\ Depth = x_0 + \Delta x = x_0 + 2\sqrt{Dt}$$

Condition		From Pt Profile (μm)	Calculated Depth (μm)		Substrate Alloy
T (°C)	t (h)		D_{Pt} (γ′)	D_{Pt} (γ)	
900	1000	44	45	50	N5
1000	1000	79	65	78	R142
	2000	90	73	93	N5
1050	1000	98	82	103	
1150	1000, 1h	205	160	200	
900	40,000	—	81	113	X_0 = 40μm
1050	15,000	—	209	288	

- For limited interdiffusion, estimation using D_{Pt} (γ′) is closer to the experimental value
- For extensive interdiffusion, estimation using D_{Pt} (γ) gives a better fit
- The thin film equation was not used because $c \rightarrow 0$ at $x \rightarrow \infty$

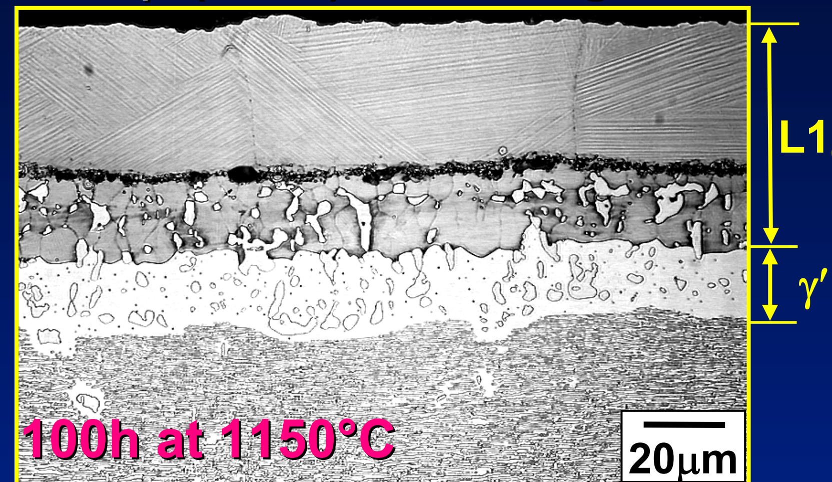
Comparison of Microstructural Stability between γ+γ′ & β-(Ni,Pt)Al Coatings

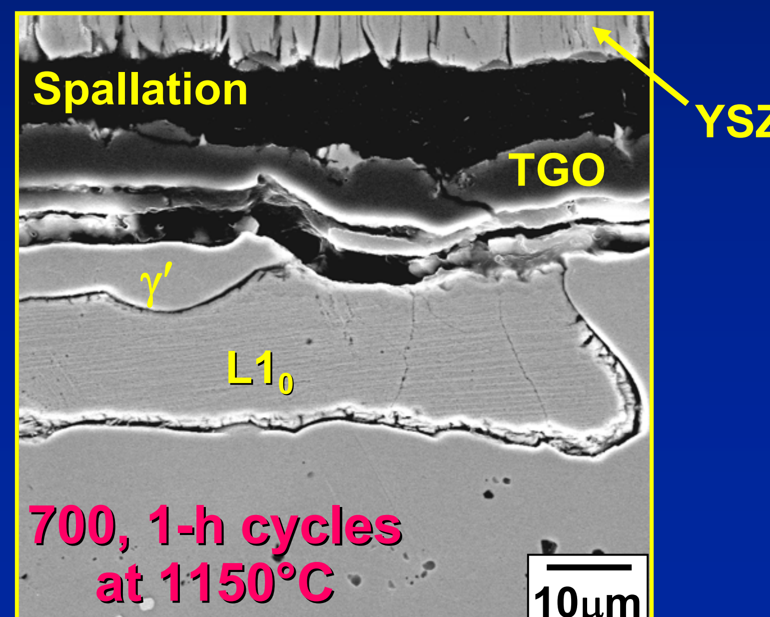
γ+γ′ Coatings



Adapted from Haynes et al., submitted to *Surf. Coat. Technol.*, 2008

β-(Ni,Pt)Al Coating





Preliminary Evaluation of Oxidation Performance of Different Types of $\gamma+\gamma'$ Coatings

- **Pt-diffused $\gamma+\gamma'$ coatings (Simple $\gamma+\gamma'$)**
  - Electroplating ~ 7μm Pt, vacuum annealing for 2h at 1175°C (18-20 at.% Al)
- **Modified $\gamma+\gamma'$ coatings**
  - Increased Al content (22-25 at.%) via a secondary aluminizing step *(Deodeshmukh, Mu, & Gleeson, Surf. Coat. Technol., 2006)*
  - Pack cementation for 0-30 min at 1050°C (Stacy et al., *Surf. Coat. Technol.*, 2007)
  - With and without Hf doping

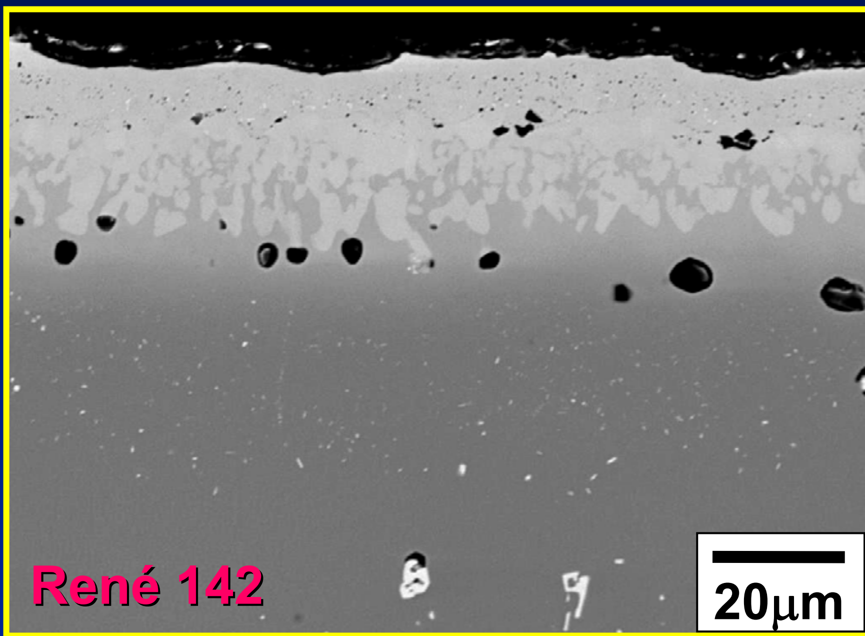
Modified $\gamma+\gamma'$+Hf

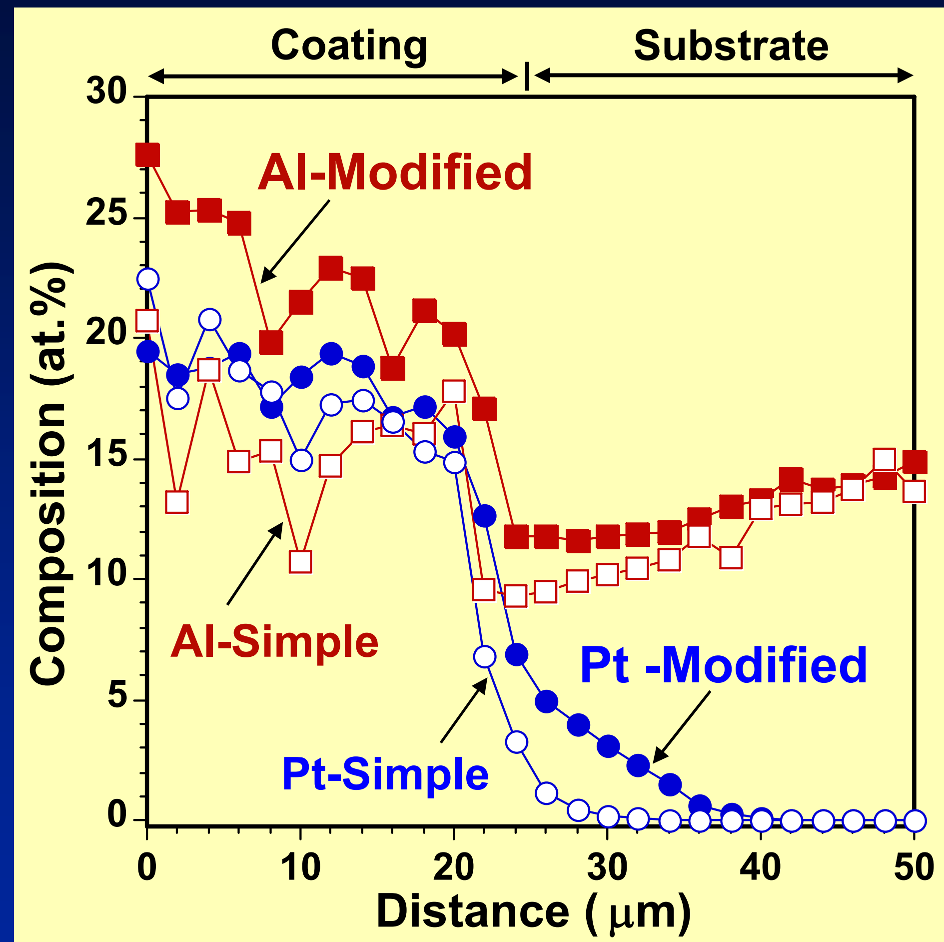
Modified $\gamma+\gamma'$

Simple and Modified γ+γ′ coatings

Modified γ+γ′ coatings

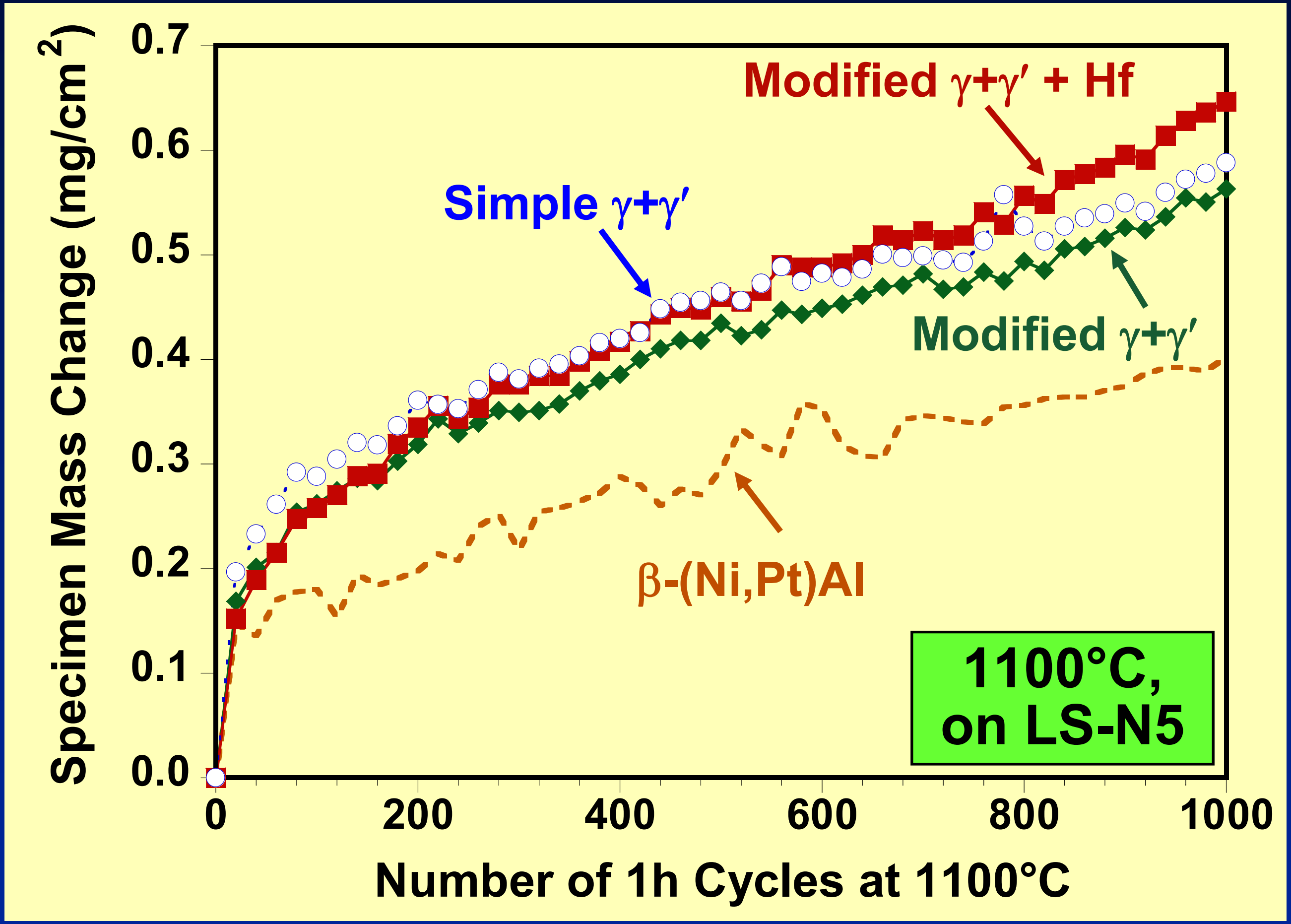
(Stacy et al., *Surf. Coat. Technol.*, 2007)





- **Coating Thickness: 30-40 μm**
- **The Al content was increased from 20 to 26 at% in the modified γ+γ′ coating**

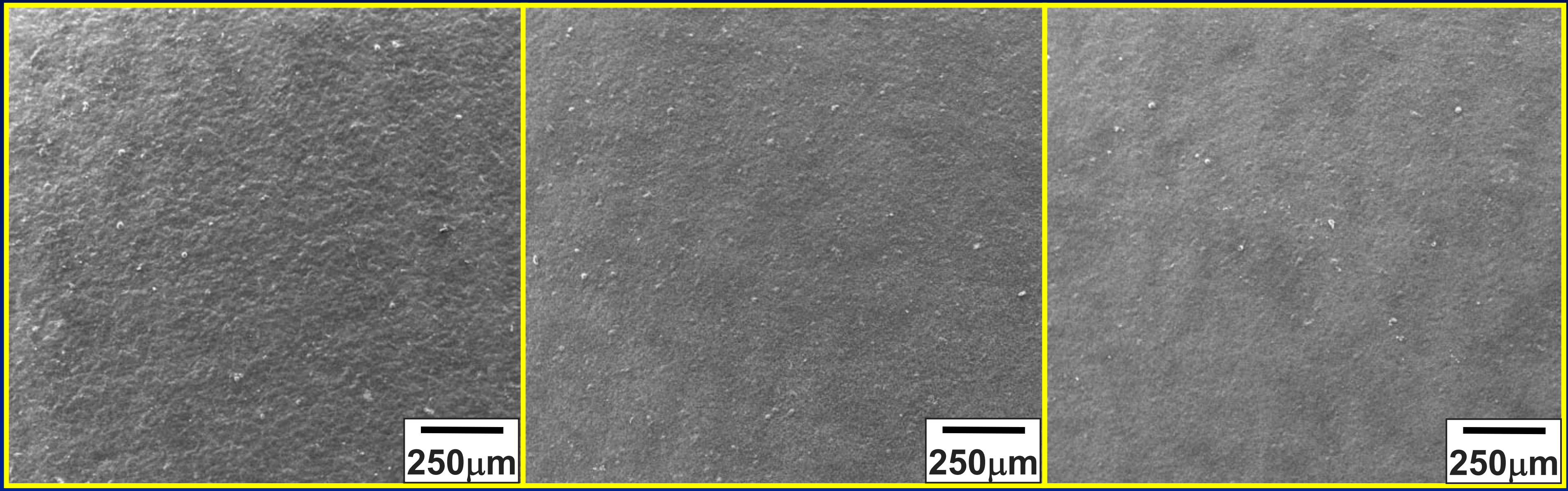
Cyclic Oxidation Performance of Simple and Modified γ+γ′ Coatings at 1100°C



- Simple & modified γ+γ′ coatings registered similar mass gains, but higher than the β-(Ni,Pt)Al coating
- The Hf level introduced during pack cemention was not optimal

Visual Comparison of Surface Roughness

After 1000, 1h cycles at 1100°C, on LS-N5

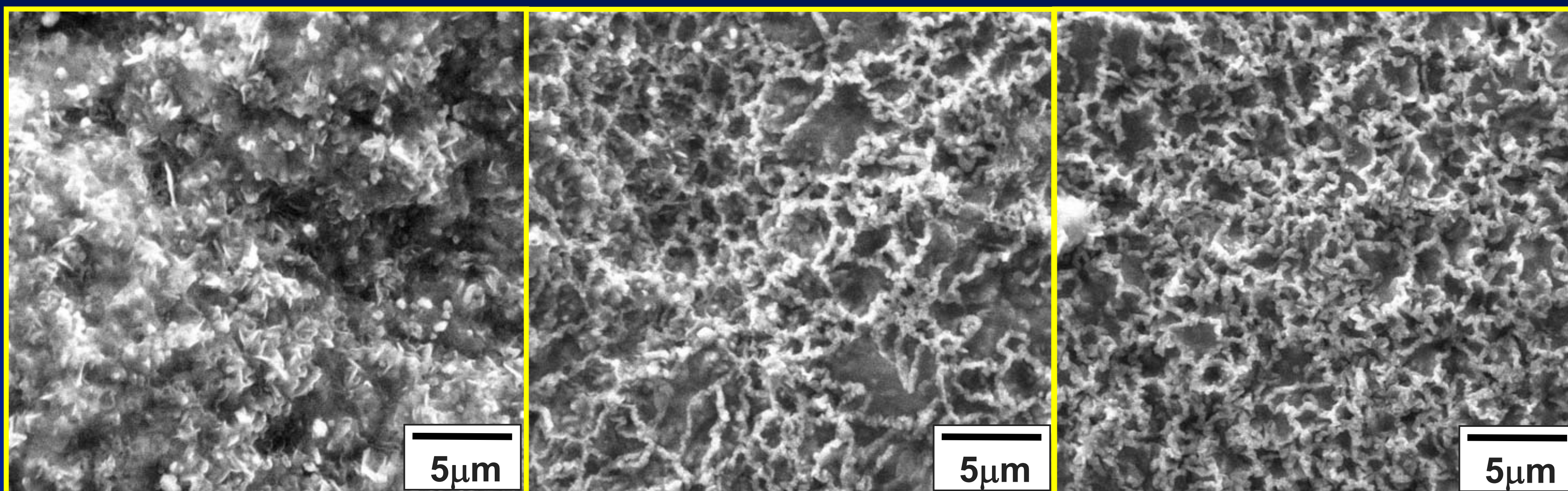


Simple $\gamma+\gamma'$ | **Modified $\gamma+\gamma'$** | **Modified $\gamma+\gamma'$ + Hf**

- Upon visual inspection the modified $\gamma+\gamma'$ coatings appeared to be more planar
- The modified + Hf was the flattest among all the samples

Simple and modified $\gamma+\gamma'$ coatings exhibited different scale morphologies

After 1000, 1h cycles at 1100°C, on LS-N5

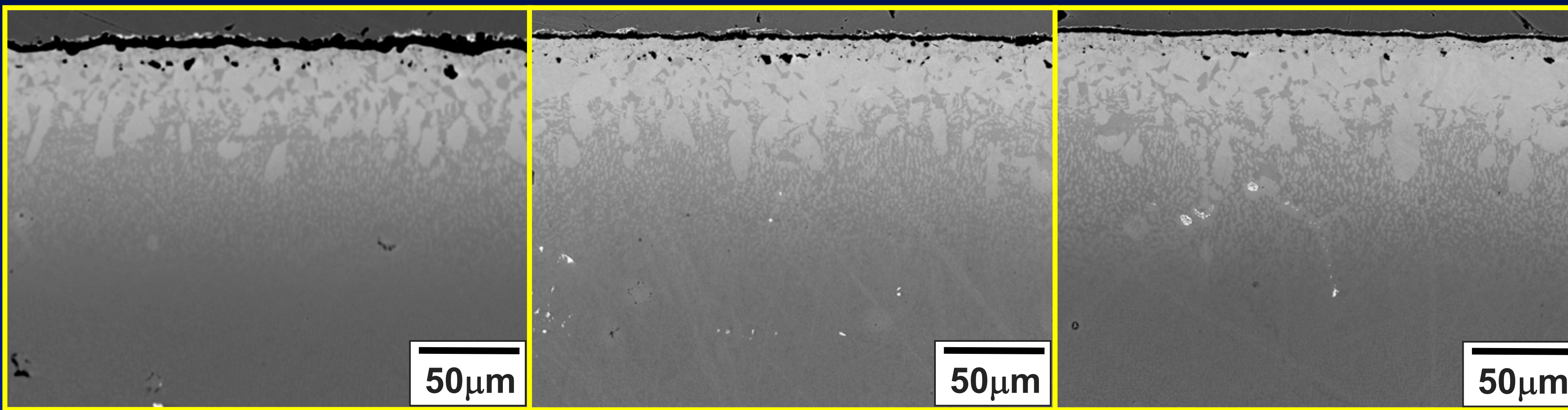


Simple $\gamma+\gamma'$ | Modified $\gamma+\gamma'$ | Modified $\gamma+\gamma'$ + Hf

- **Some extent of ridge-like structure on the modified $\gamma+\gamma'$ coatings, consistent with oxidation of Ni-22Al-20Pt at 1150°C** (Hayashi, et al., *Mater. Sci. Forum*, 2006)

Cross-Sectional Observation of Oxidized Coatings

After 1000, 1h cycles at 1100°C, on LS-N5



Simple $\gamma+\gamma'$ (4.4μm)

Modified $\gamma+\gamma'$ (2.4μm)

Modified $\gamma+\gamma'$ + Hf (2.6μm)

- The Al_2O_3 scales formed on modified $\gamma+\gamma'$ coatings were thinner
- Cross-sectional observations were consistent with surface roughness

Summary

- Interdiffusion between Pt-Diffused $\gamma+\gamma'$ Coatings & Superalloy Substrates at 900-1050°C
  – Interdiffusion & microstructural evolution were minimal at 900°C, but became more significant at ≥ 1000°C
  – The predicted Pt profile using thin film solution showed reasonable agreement for the $\gamma+\gamma'$ coatings after extended diffusion
  – The estimated Pt penetration depth agreed well with the experimental results
- Cyclic Oxidation Performance of Different $\gamma+\gamma'$ Coatings
  – The modified $\gamma+\gamma'$ coatings containing higher Al exhibited slightly lower mass gains and thinner Al_2O_3 scales
  – The Hf level in the $\gamma+\gamma'$ coatings needs to be optimized

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