Components' and Materials' Performance for Advanced Solar Supercritical CO_2 Powerplants (COMPASsCO$_2$)

MATERIALS INNOVATION: NOVEL ALLOYS DESIGN FOR THE EXTREME CONDITIONS OF CST

Tom Blackburn (UoB), Michael Kerbstadt (Dechema)

COMPASsCO2 Final Workshop

Back to the Future: A Forward-Thinking Approach to Concentrating Solar Technologies - Key Takeaways from the COMPASsCO$_2$ Project

April 24th, 2025

9h30 – 14h30 CEST

Husinec u Řeže, Czech Republic & Online lifesize

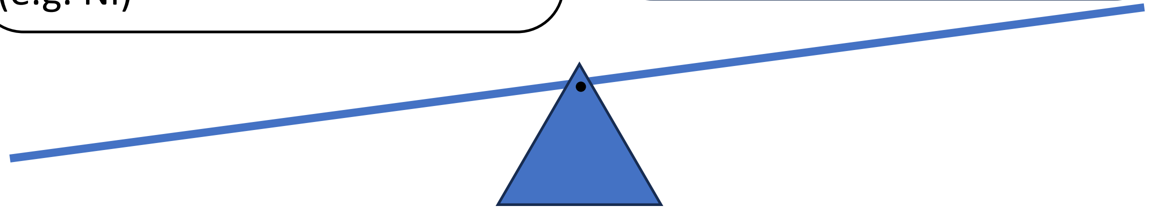
Presentation Structure

- Development of Cr-NiAl
  - Microstructure + Coarsening
  - High Temperature Mechanical Testing
  - High Temperature Exposures
- Development of Cr-Cr_3Si
  - Diffusion Coatings
  - Applications Beyond CSP
  - Upscaling
- ICME Alloy Screening
  - AI Model
  - Experimental Model Validation

Chromium BCC Superalloy

Why Chromium?

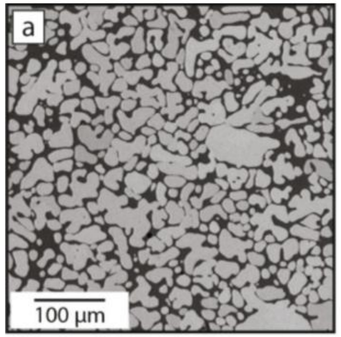
Strengths	Challenges
+ High Melting Point	- Mechanical properties at HT
+ Oxidation Resistant <900°C	- Creep resistance
+ Good Thermal Conductivity	- DBTT > RT
+ Cheaper than other metals used for high temperatures (e.g. Ni)	- Oxidation Resistance >900°C
	- Nitride Embrittlement



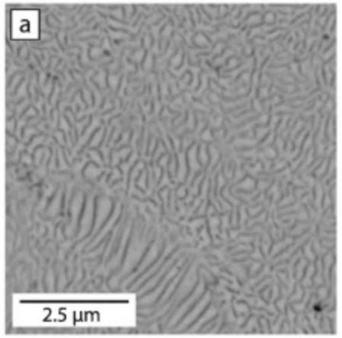
Approach 1

BCC-BCC → Cr (A2) strengthened by ordered bcc precipitates

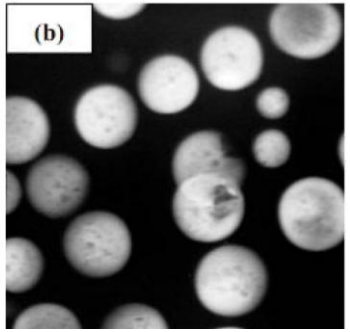
W-TiFe (A2-B2)[1]



Ti-TiFe (A2-B2)[2]

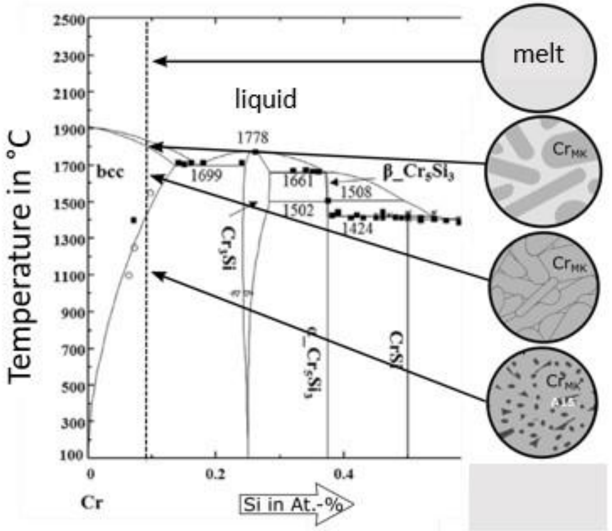


Fe-NiAl (A2-B2)[3]

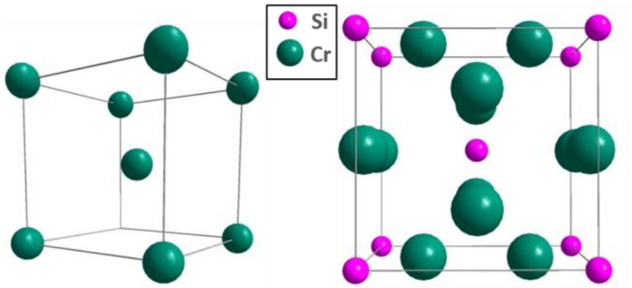


Approach 2

$Cr-Cr_3Si$ → Cr (A2) strengthened by A15 precipitates



[Cr-Si Phase diagram of the Cr-Si system revised by Oka]



bcc Cr_{ss} A15 Cr_3Si

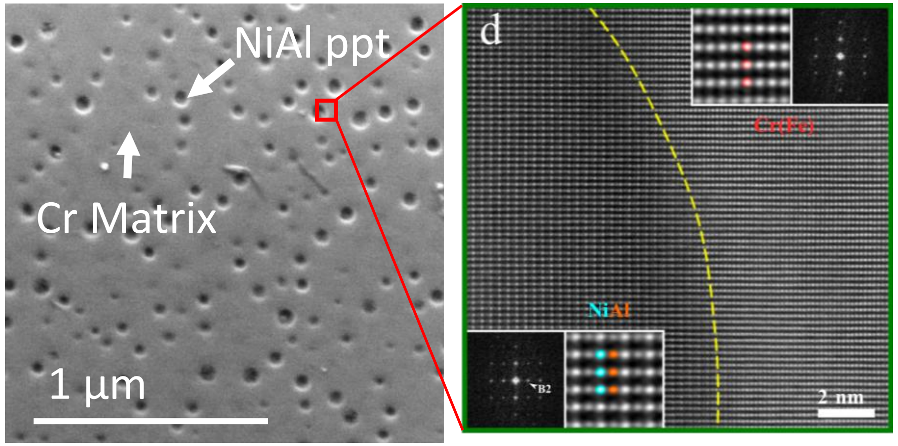
[A. S. Ulrich, PhD Thesis, University of Bayreuth, 2020]

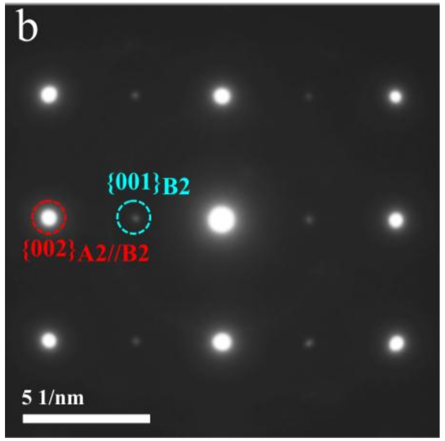
[1]A. Knowles et al. / Applied Materials Today 23 (2021) 101014
[2]A. Knowles et al. / Scripta Materialia 140 (2017) 71–75
[3]Z. K. Teng et al. / Scripta Materialia 63 (2010) 61–64

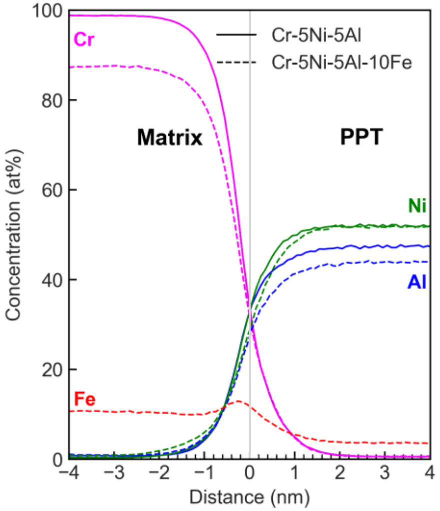
Cr-NiAl

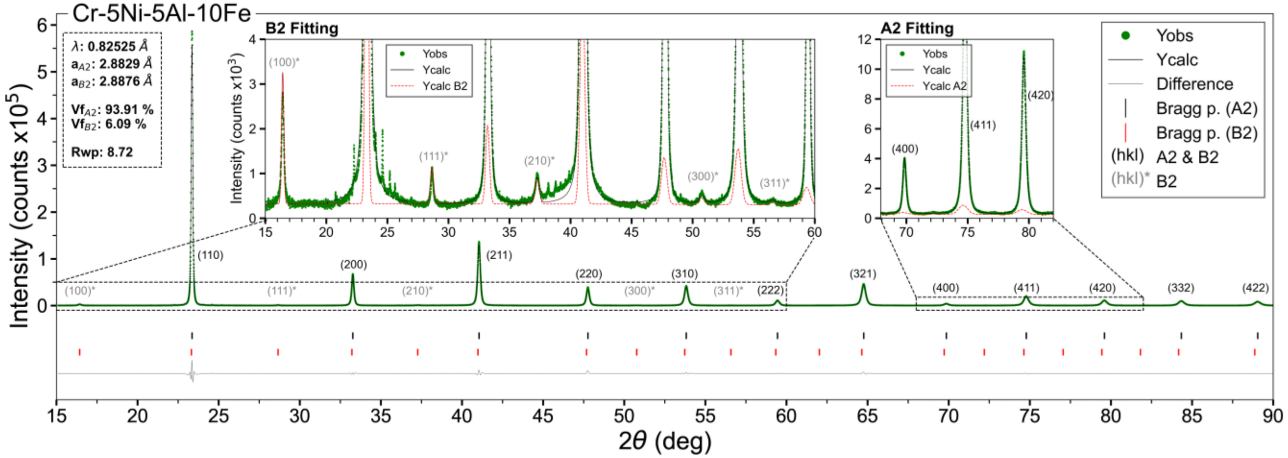
Tom Blackburn (UoB)

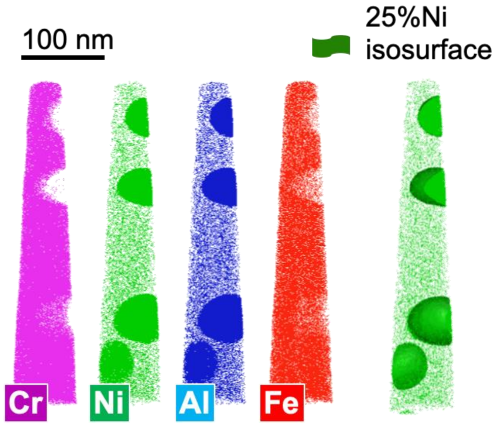
Nano-Scale Precipitate with Low Misfit







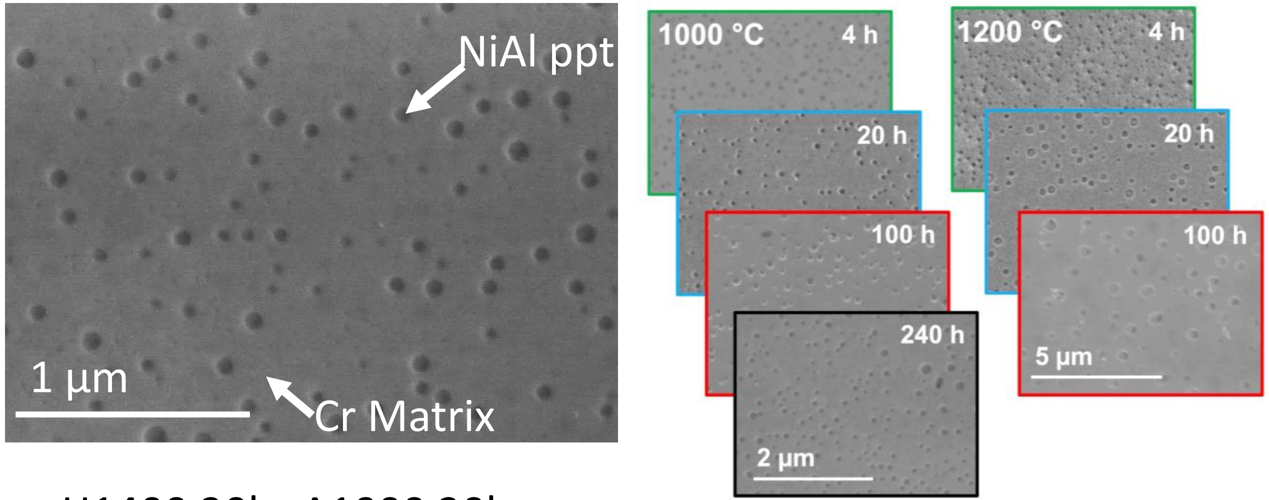




- ➢Coherent precipitates with misfit ±0.1%
- ➢Low solubility of NiAl in matrix and low solubility of CrFe in precipitate
- ➢Iron shell formed

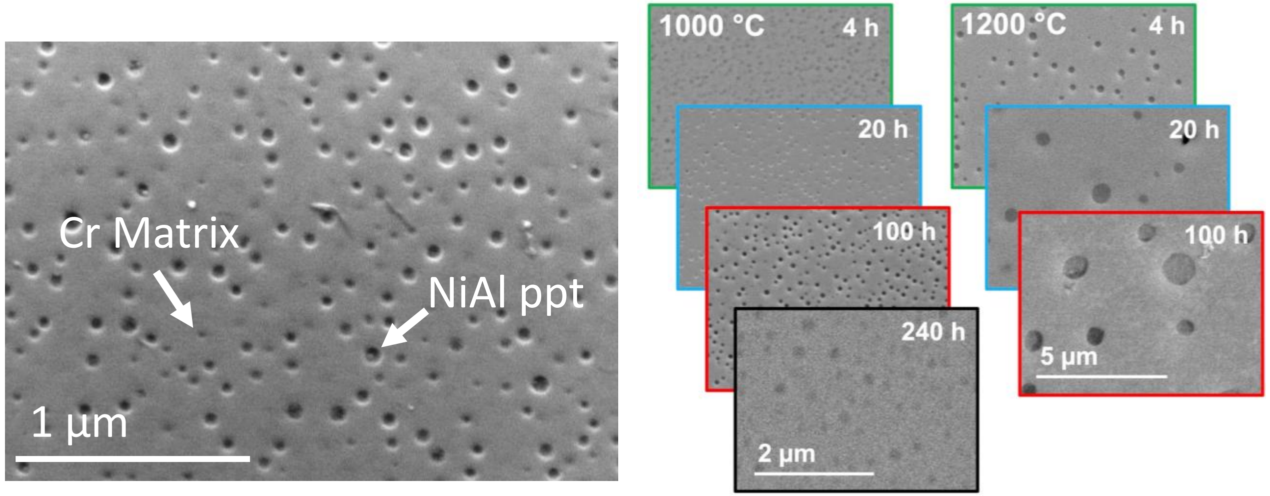
Slow Coarsening Kinetics of Cr-Superalloys

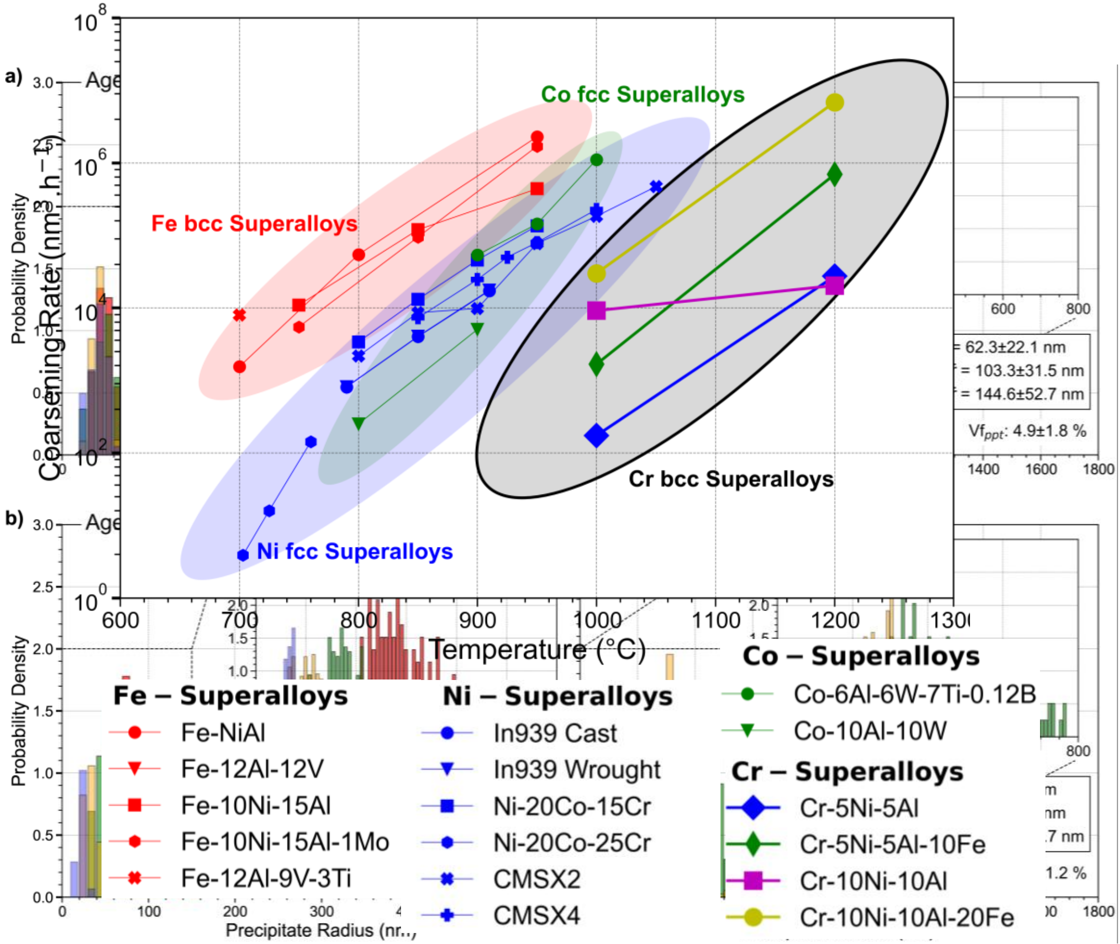
Cr-5Ni-5Al



H1400 20hr A1000 20hr

Cr-5Ni-5Al-10Fe



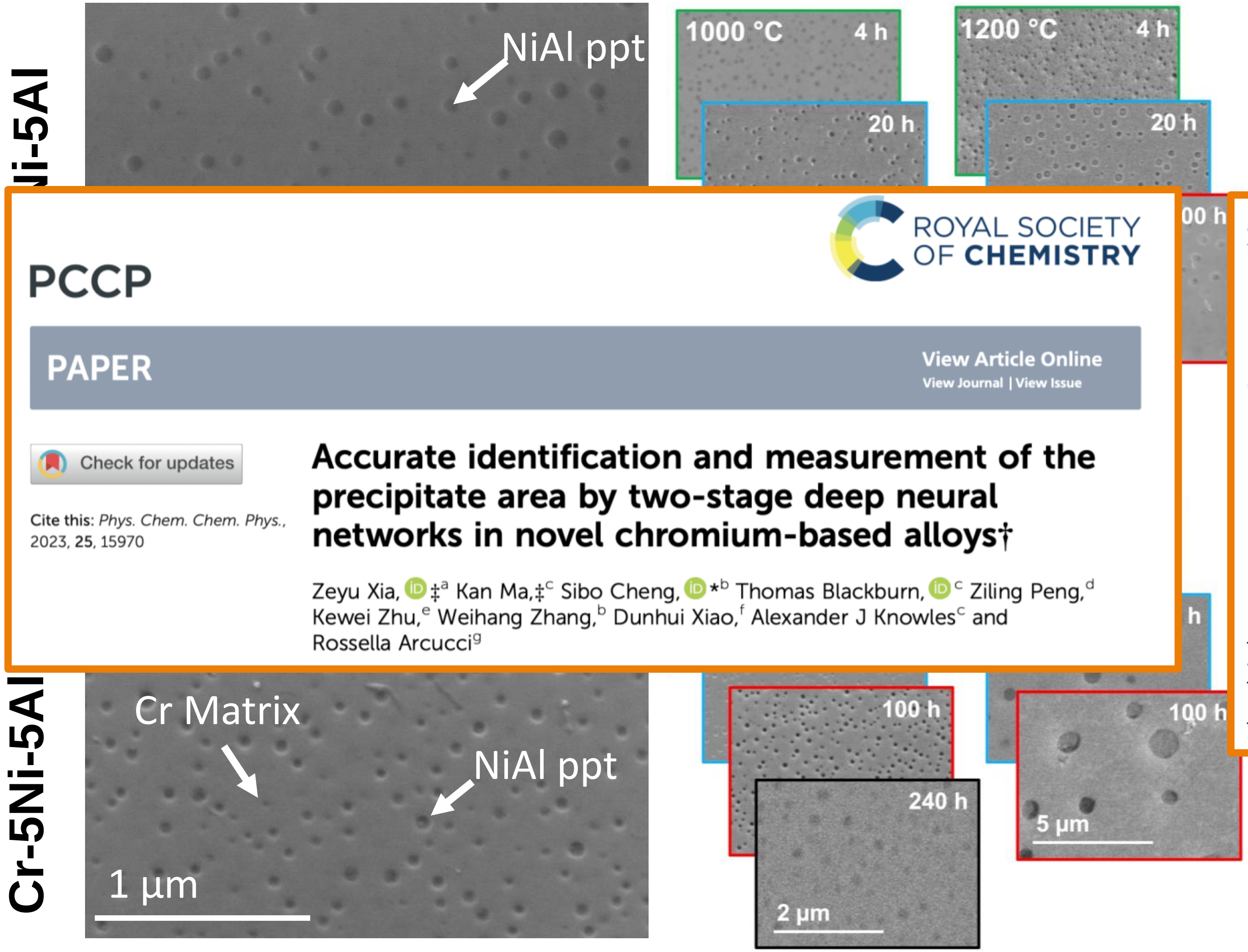


- Lower coarsening rate than Ferritic, Nickel and Cobalt superalloys
- 2 orders of magnitude lower rate at 1000°C over Ni superalloys

➢ Nano-scale ppts coarsen upon ageing

[1] K. Ma, T. Blackburn, J.P. Magnussen, M. Kerbstadt, P.A. Ferreirós, T. Pinomaa, C. Hofer, D.G. Hopkinson, S.J. Day, P.A.J. Bagot, M.P. Moody, M.C. Galetz, A.J. Knowles, Acta Materialia 257 (2023) 119183.

Slow Coarsening Kinetics of Cr-Superalloys



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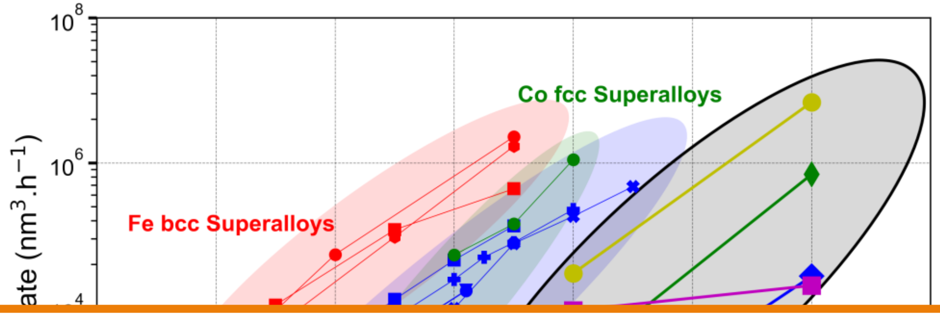
Accurate identification and measurement of the precipitate area by two-stage deep neural networks in novel chromium-based alloys†

Zeyu Xia,‡[a] Kan Ma,‡[c] Sibo Cheng,*[b] Thomas Blackburn,[c] Ziling Peng,[d] Kewei Zhu,[e] Weihang Zhang,[b] Dunhui Xiao,[f] Alexander J Knowles[c] and Rossella Arcucci[g]



ELSEVIER

Acta Materialia

Volume 257, 15 September 2023, 119183

Full length article

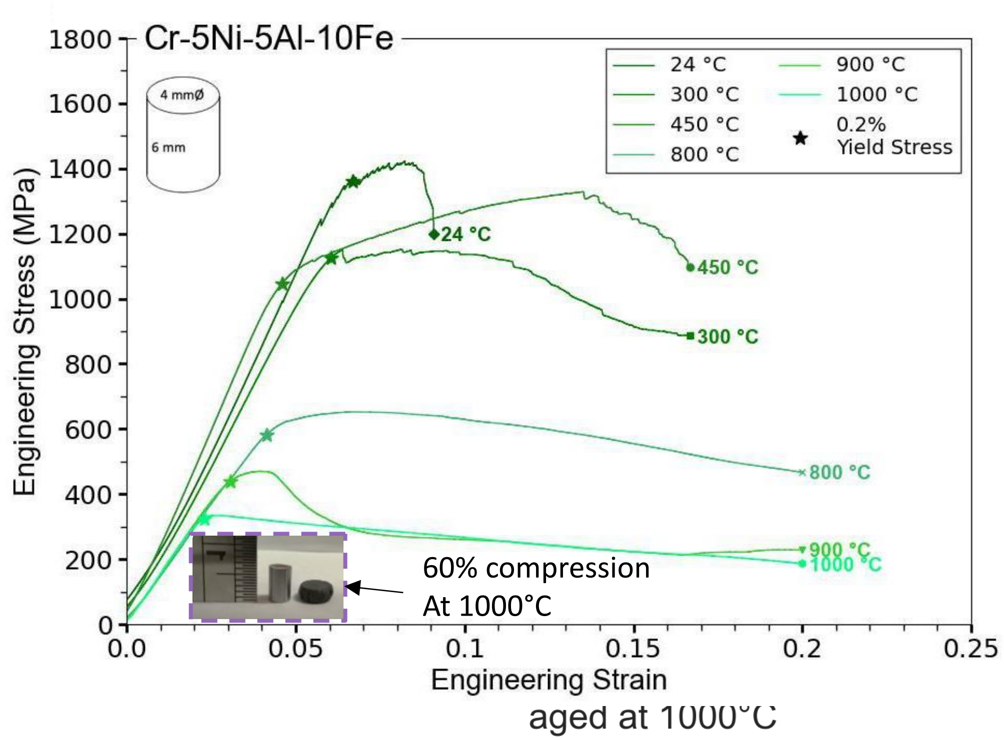
Chromium-based bcc-superalloys strengthened by iron supplements

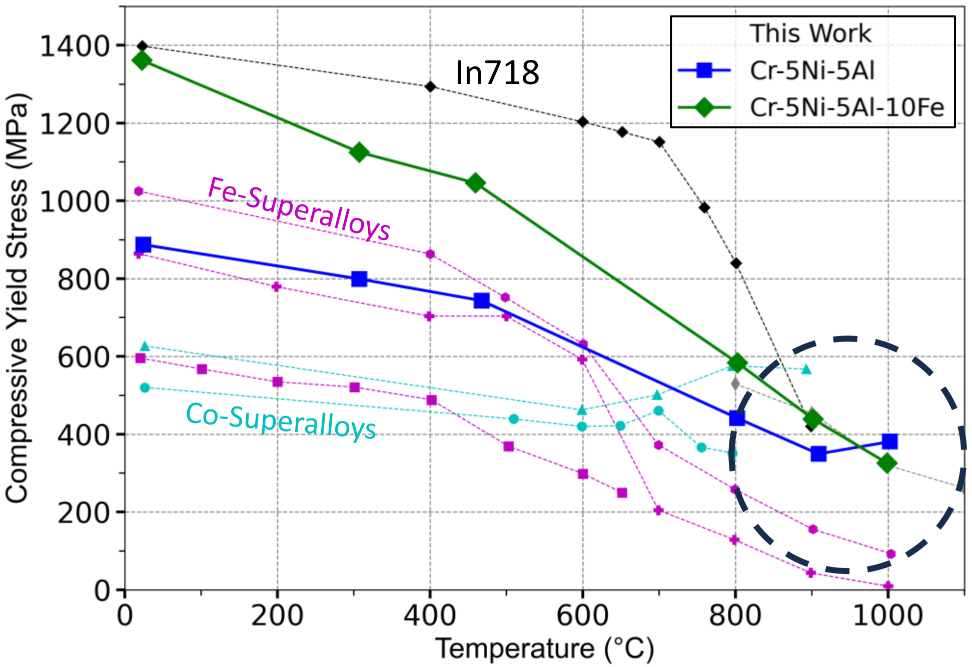
Kan Ma[a], Thomas Blackburn[a], Johan P. Magnussen[a], Michael Kerbstadt[b], Pedro A. Ferreirós[a c], Tatu Pinomaa[c], Christina Hofer[d], David G. Hopkinson[e], Sarah J. Day[e], Paul A.J. Bagot[d], Michael P. Moody[d], Mathias C. Galetz[b], Alexander J. Knowles[a]

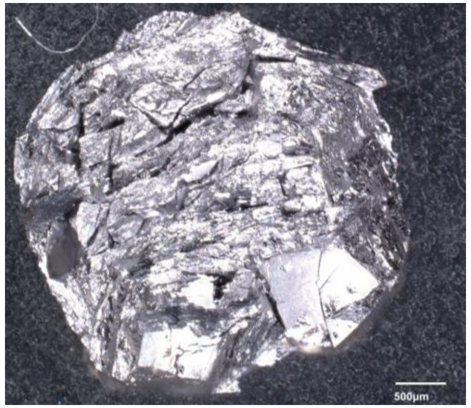
- Lower coarsening rate than Ferritic, Nickel and Cobalt superalloys
- 2 orders of magnitude lower rate at 1000°C over Ni superalloys

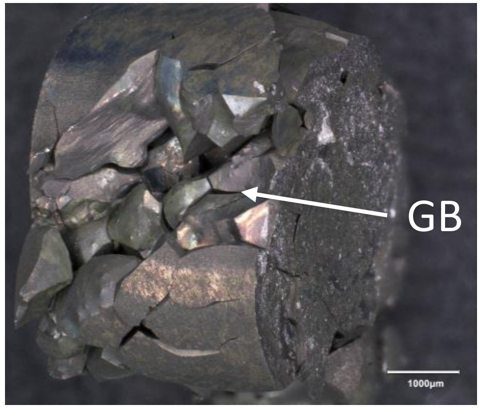
[1] K. Ma, T. Blackburn, J.P. Magnussen, M. Kerbstadt, P.A. Ferreirós, T. Pinomaa, C. Hofer, D.G. Hopkinson, S.J. Day, P.A.J. Bagot, M.P. Moody, M.C. Galetz, A.J. Knowles, Acta Materialia 257 (2023) 119183.

Retained Flow Stress at 1000 °C







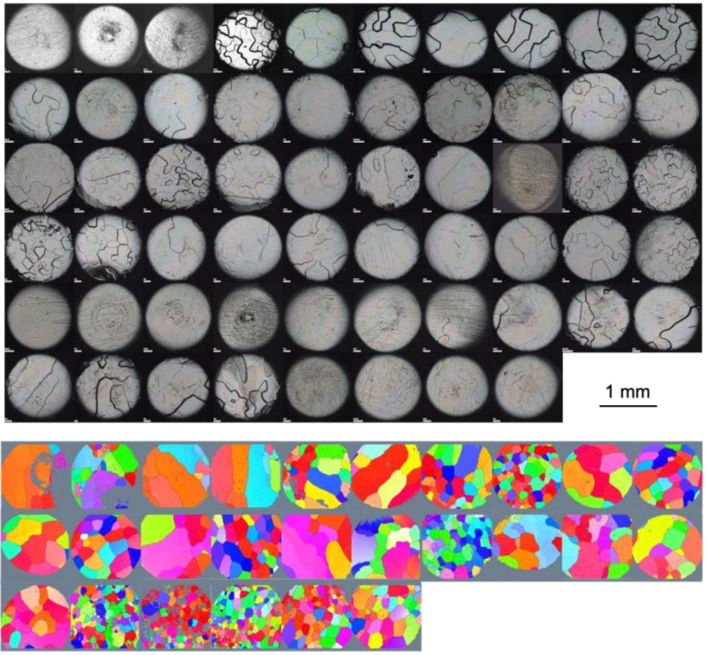


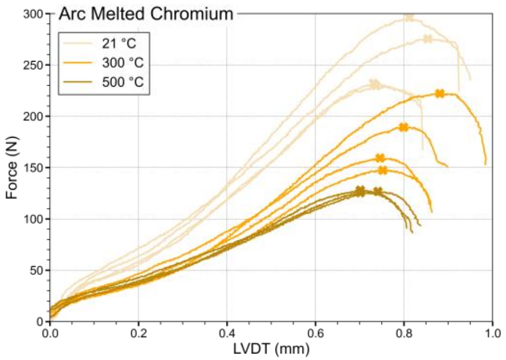
- ➢Very hard → Age softening
- ➢Compressive plasticity >300 °C

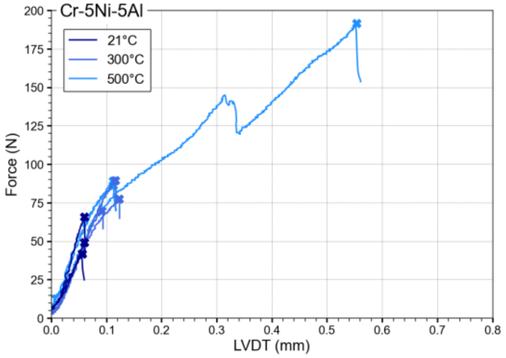
- ➢Retained high temperature yield stress
- ➢Grain boundary failure

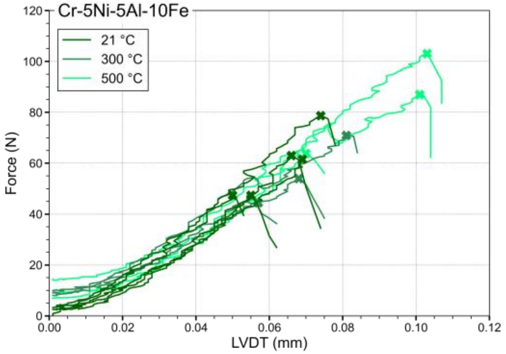
Sub-scale Small Punch Testing

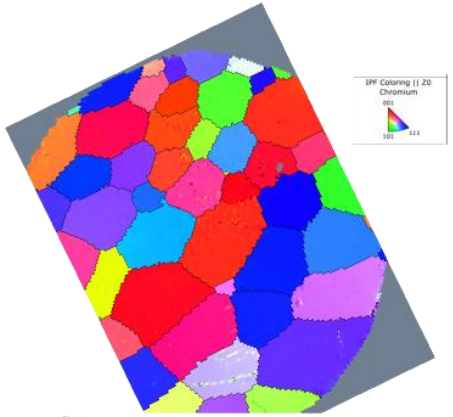
Pure Chromium



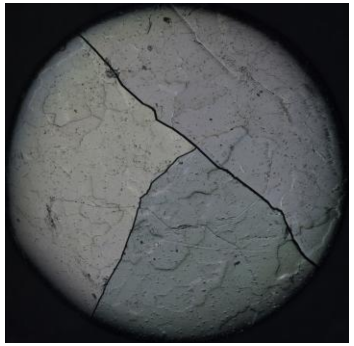


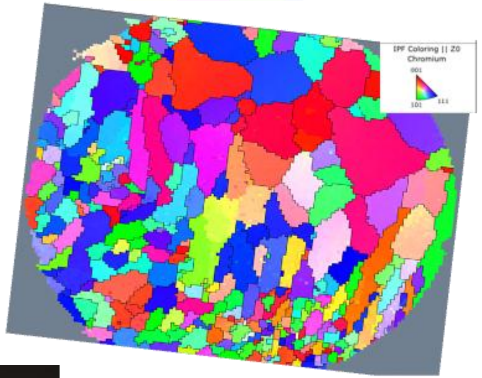




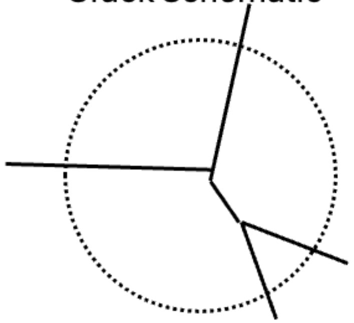


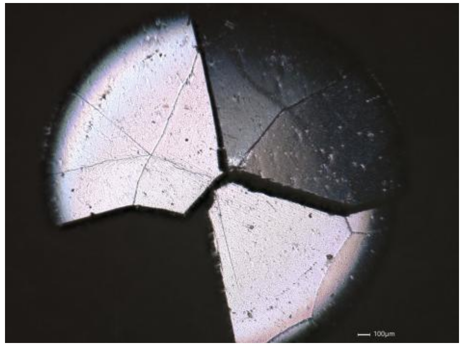
Crack Schematic





Crack Schematic





- Attempt to corelate failure to gran structure
- The brittle does not allow the estimation of SP parameters.

- Heat treatment in Ar/5%H_2 removed impurities
- GB NiAl Weakness

In Memoriam

We will never forget his great dedication and his daily work in the Mechanical Behaviour Unit for 32 years specially on the small punch testing technique

Daniel Plaza

1971-2025

Gone but not forgotten.

Diffusion Controlled Parabolic Growth Kinetics

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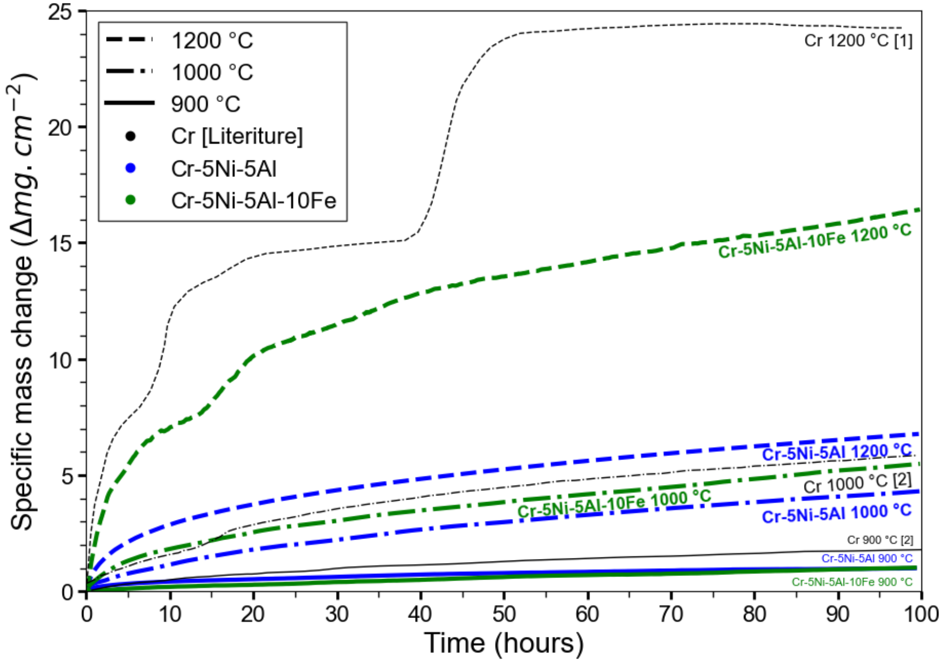
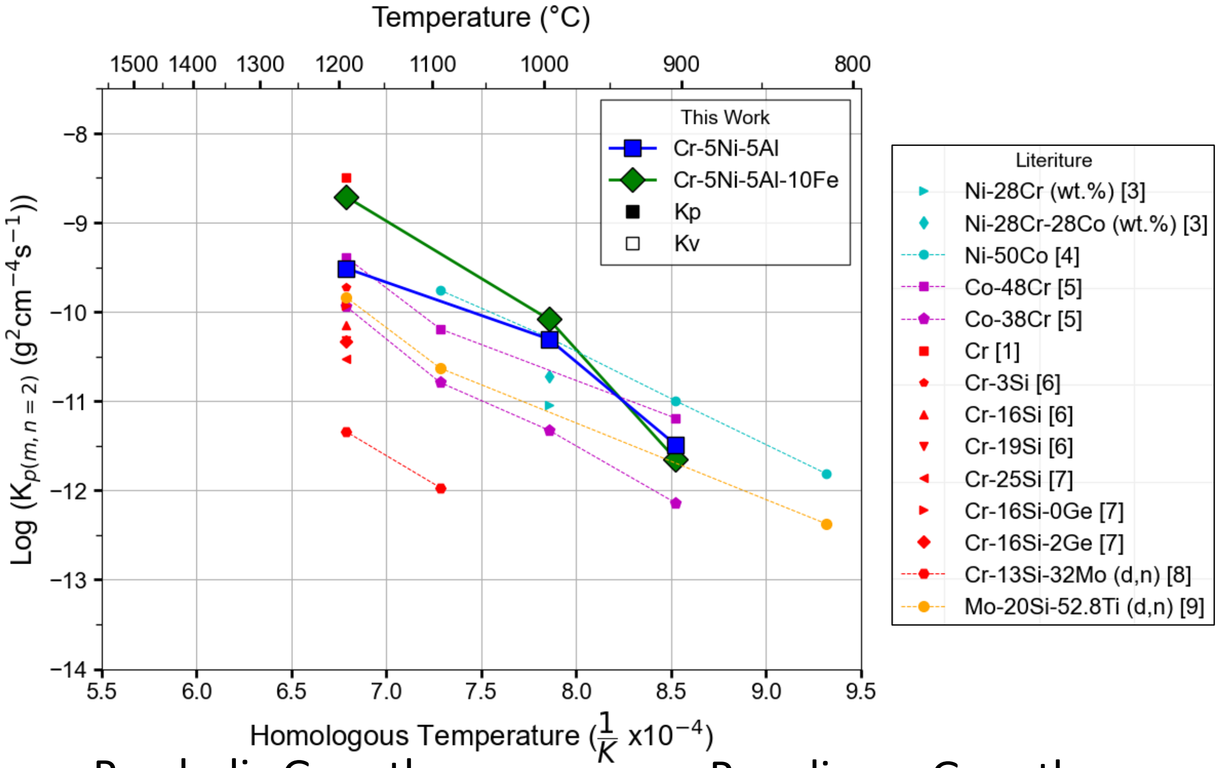


[1] A. S. Ulrich, P. Pfizenmaier, A. Solimani, U. Glatzel, and M. C. Galetz, "Improving the oxidation resistance of cr-si-based alloys by ternary alloying,"
[2] I. Murris, Y. P. Jacob, V. A. C. Haanappel, and M. F. Stroosnijder, "High-temperature oxidation behavior of chromium: Effect of different batches,"



- Reduced mass gain over pure chromium
- Parabolic growth at 900 and 1000 °C
  → para-linear at 1200 °C
- Comparable K_p to nickel-based systems
- Not as resistant as $Cr\text{-}Cr_3Si$

Parabolic Growth

$$\left(\frac{\Delta m}{A}\right)^n = k_{p(m,n)} \cdot t$$

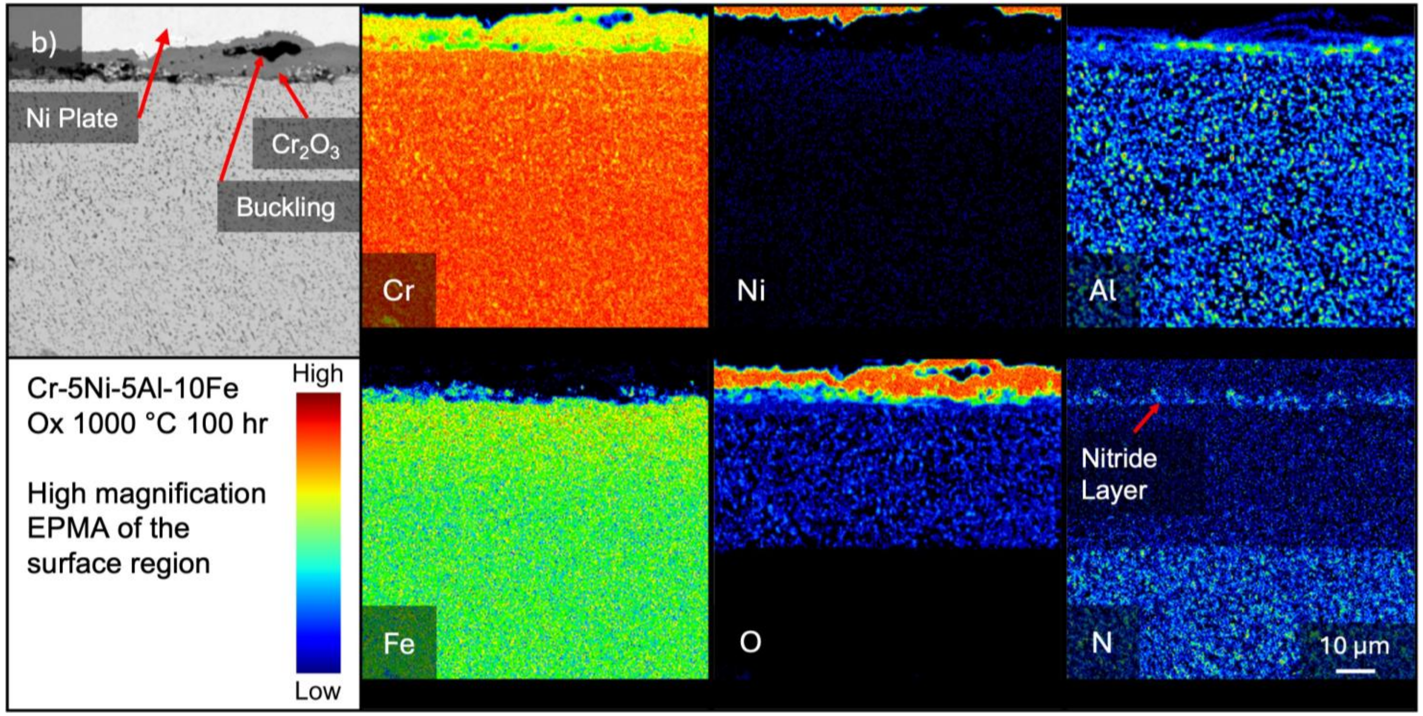
Para-linear Growth

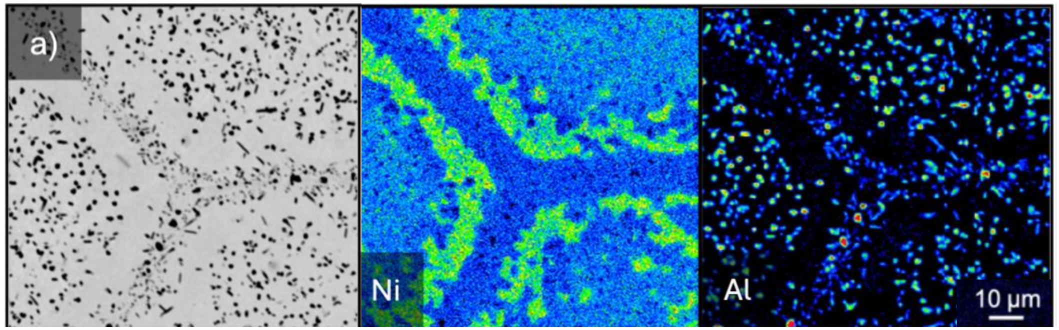
$$\left(\frac{\Delta m}{A}\right) = (k_p t)^{0.5} - k_v t$$

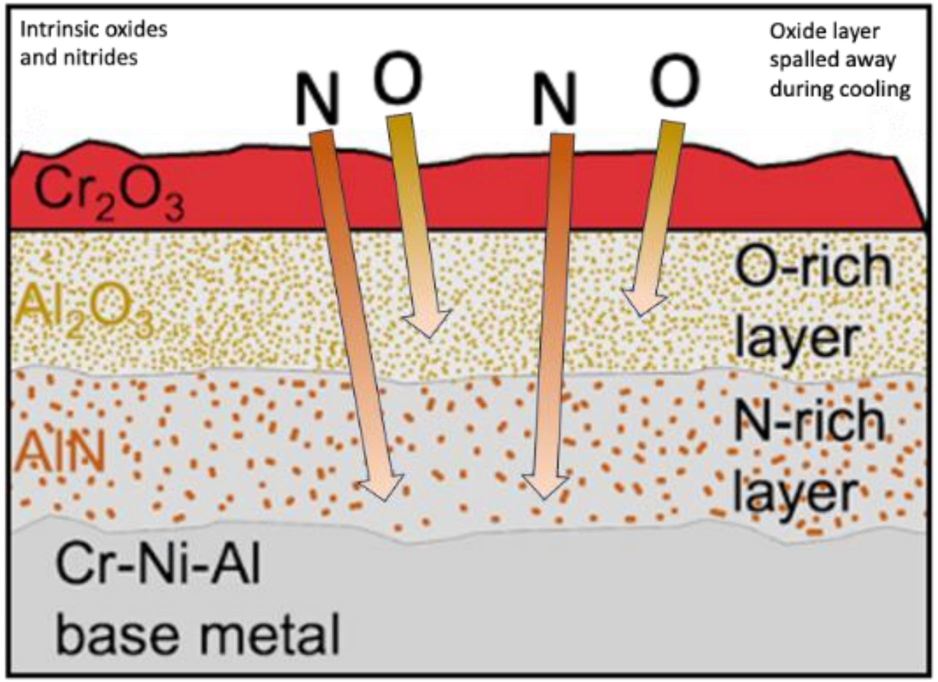
Specific mass change — Parabolic term — Velocitising term

[3] B. Li and B. Gleeson, "Effects of silicon on the oxidation behavior of ni-base chromia-forming alloys,"
[4] G. M. Ecer and G. H. Meier, "Oxidation of high-chromium ni-cr alloys,"
[5] C. A. Phalnikar, E. B. Evans, and W. M. Baldwin, "High temperature scaling of cobalt-chromium alloys,"
[6] A. Soleimani-Dorcheh and M. C. Galetz, "Oxidation and nitridation behavior of cr–si alloys in air at 1473 k,"
[7] A. Soleimani Dorcheh and M. C. Galetz, "Oxidation–nitridation mechanism in eutectic cr-silicide alloy and its mitigation by germanium alloying,"
[8] F. Hinrichs, A. Kauffmann, A. S. Tirunilai, et al., "A novel nitridation- and pesting-resistant cr-si- mo alloy,"
[9] S. Obert, A. Kauffmann, S. Seils, et al., "Microstructural and chemical constitution of the oxide scale formed on a pesting-resistant mo-si-ti alloy,"

Non-Protective Cr_2O_3 Scale

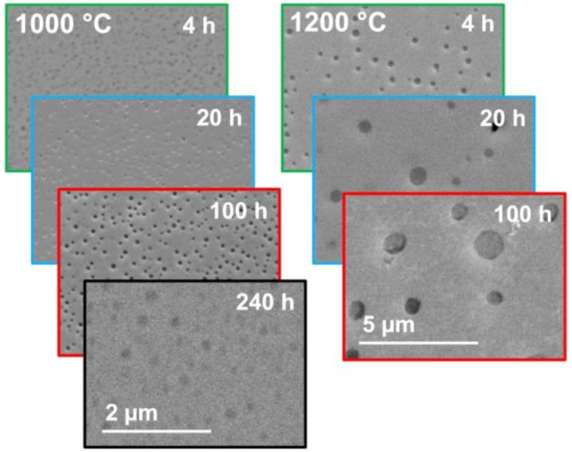




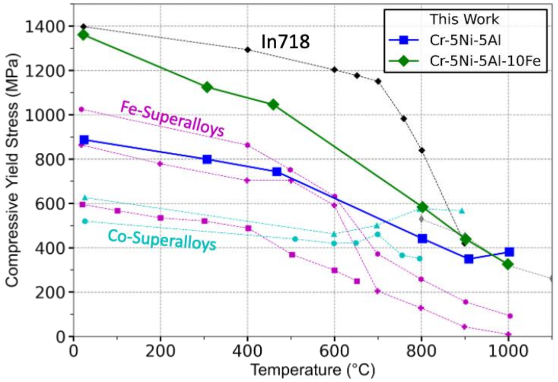


- Non-protective Cr_2O_3 scale formed
- Inward diffusion of Oxygen and Nitrogen
- Reacts with Al → dissolution of B2

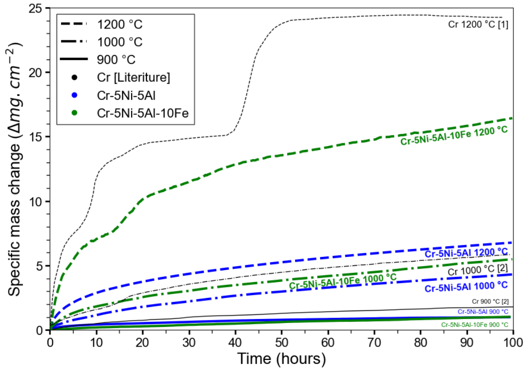
Take Home Messages



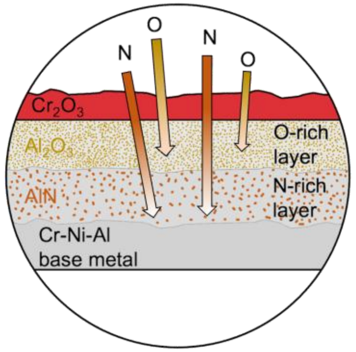
- Nano-scale coherent precipitates with slow coarsening rate



- Retained high temperature compressive yield stress



- Parabolic growth at 900 and 1000 °C beyond which para-linear kinetics prevail



- Non-protective Cr_2O_3 scale formation → Internal attack of Al

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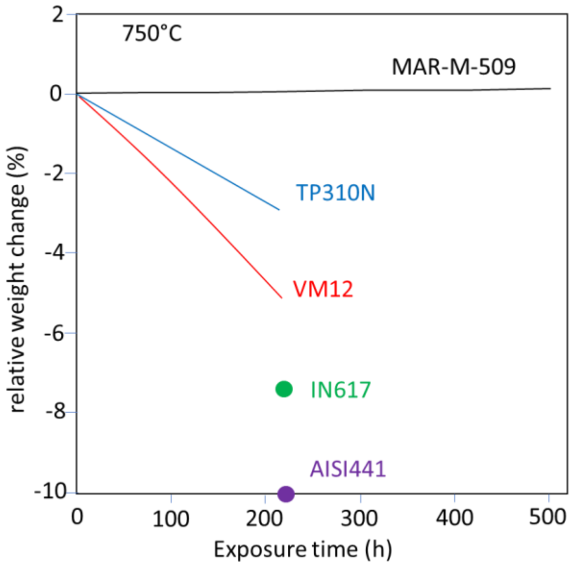
Cr-Cr_3Si

Michael Kerbstadt (Dechema)

Motivation: Cr-Si Diffusion Coatings

- Ni- and Fe-base: Limited lifetime in harsh heat exchanger environment

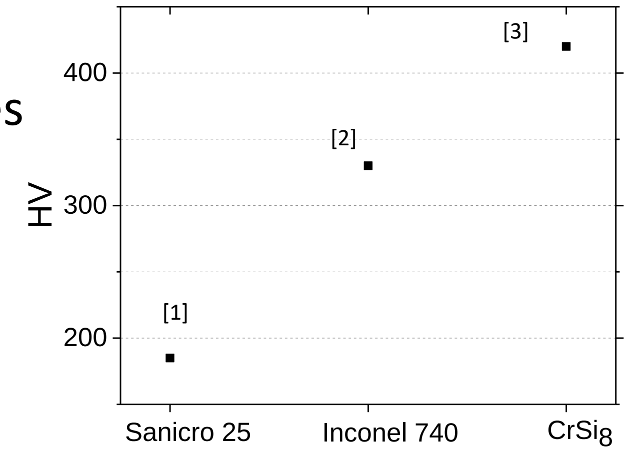
→Cr/Si diffusion coatings for extended properties



T. Galiullin, B. Gobereit, D. Naumenko, R. Buck, L. Amsbeck, M. Neises-von Puttkamer, W.J. Quadakkers, „High temperature oxidation and erosion of candidate materials for particle receivers of concentrated solar power tower systems", Solar Energy 188(2019) 883-889

- Significantly mass loss after already 200 h

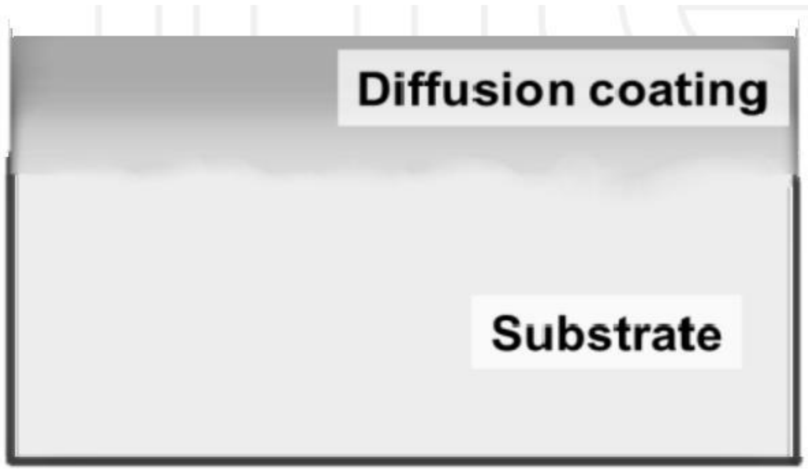
- Si: formation of hard silicide phases → erosion resistance



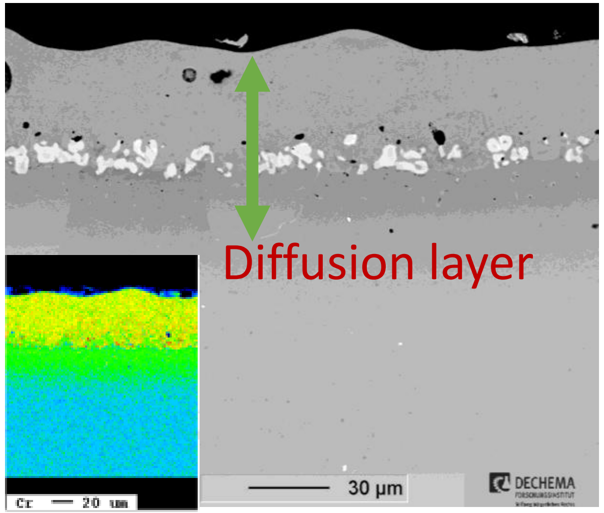
HV of $CrSi_8$ compared to conventional heat exchanger materials*

[1] https://www.materials.sandvik.com, January 2022
[2] https://www.azom.com, January 2022
[3] Ulrich, Anke S., et al., Int. J. Refract. Hard Met. 76 (2018): 72-81.

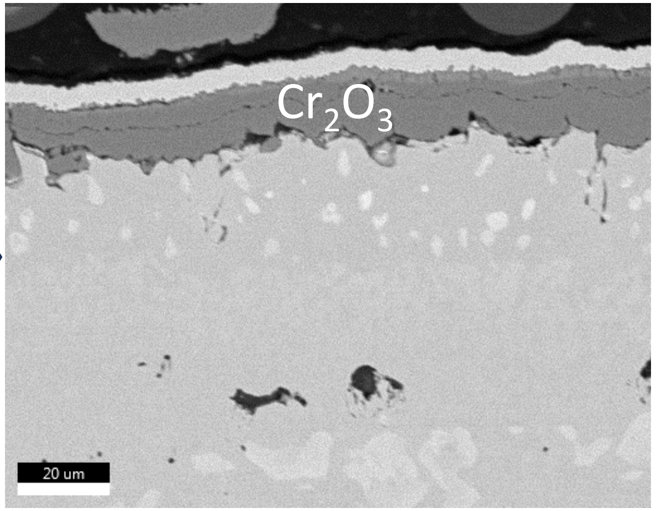
Diffusion Coatings



[M.C. Galetz, Coatings for superalloys (2015): 277-296]



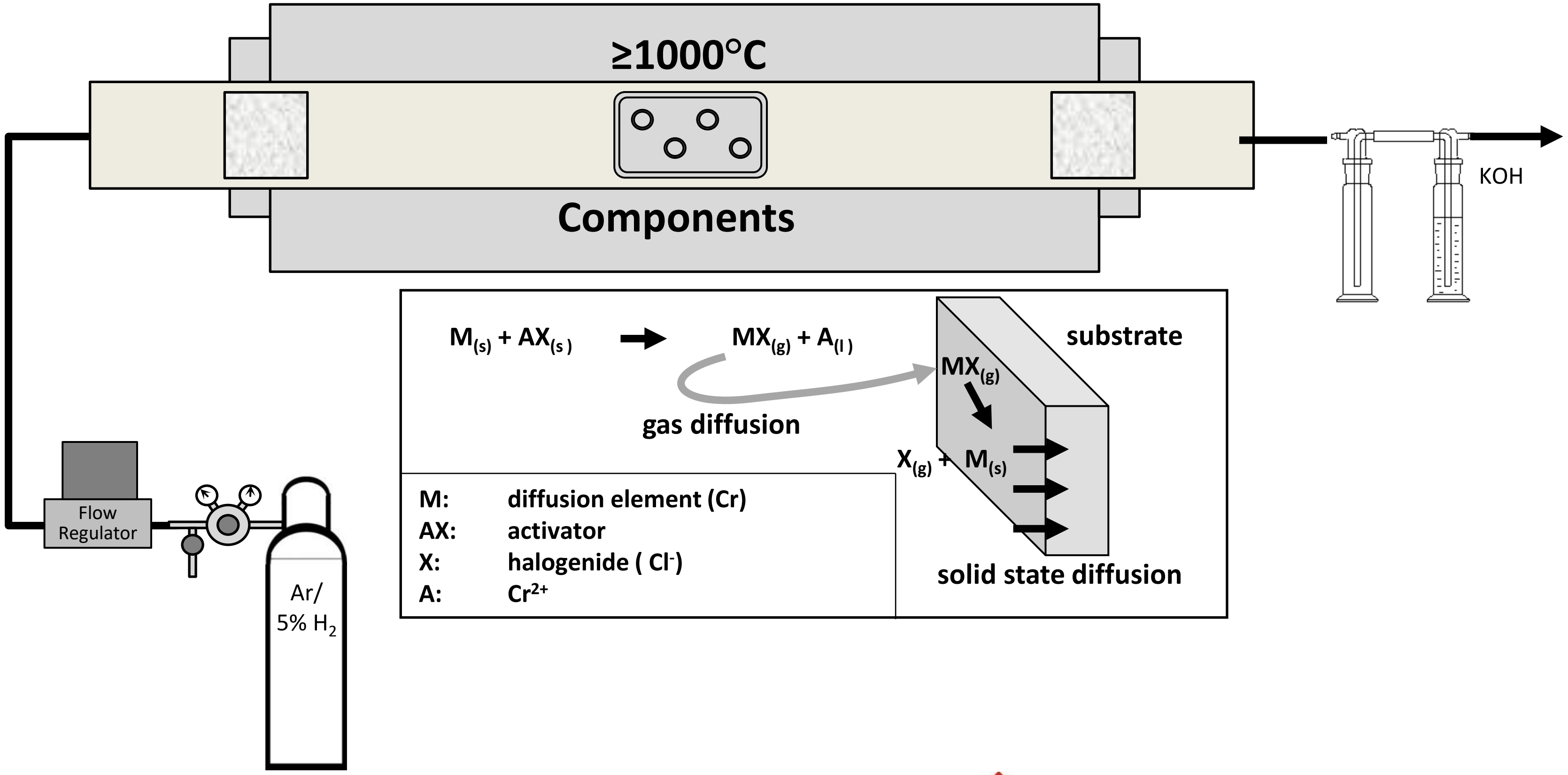
Schematic of diffusion coating



Selective oxidation of Cr

- Enrichment of surface region by protective elements (Al, Cr, Si) → selective oxidation

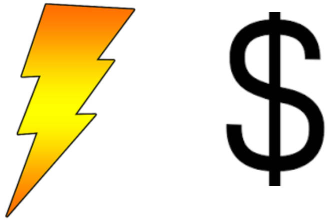
State of the art Process: Pack Cementation



- Use of harmful (+ expensive) halogenids

- Huge powder waste

- Additional heat treatment necessary

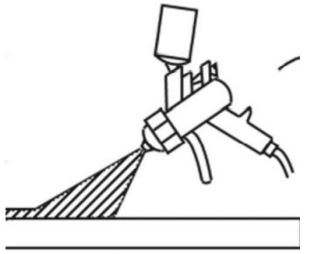


Novel Cr-Si Slurry Coating

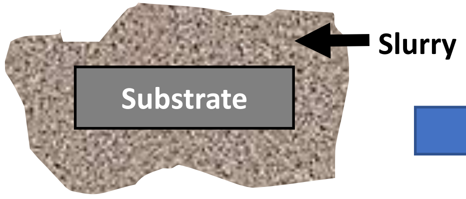
- Challenge: T_m of Cr > 1900°C → Cr-Ni-**Si**: ternary eutectic at 1077°C[1]

[2]Patent applied

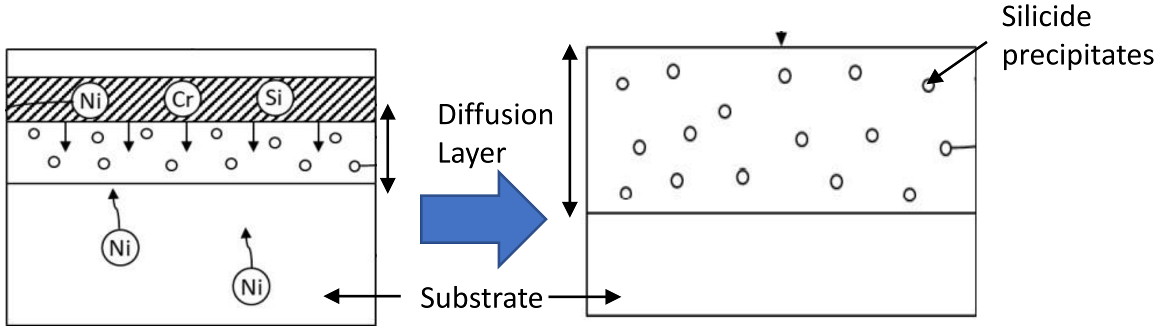
1. Slurry with particles + binder sprayed on substrate
2. Heat Treatment I - Removal of binder @ 350°C for 3 h
3. Heat Treatment II - Interdiffusion @ 1150-1200°C for 4 h
4. Enrichment of the substrate‘s surface by Cr-Si



R. Verma et al., Journal of Thermal Spray Technology (2016): 1289-1301



[M.C. Galetz, Coatings for superalloys (2015): 277-296]



- No use of halogenid activators + localised recoating after damage possible

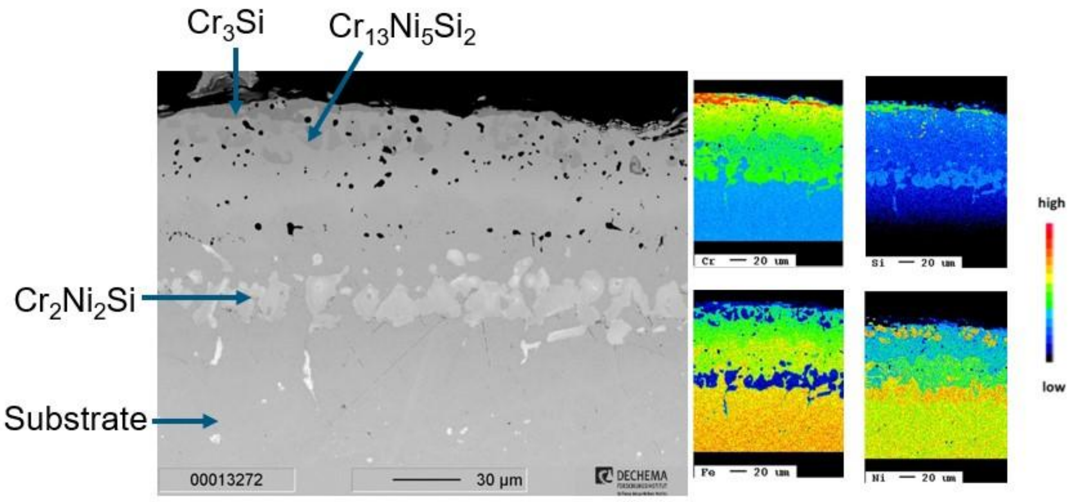
[1]E. Lugscheider et al.,*Thermochimica Acta*, vol. 29, no. 2, pp. 323-226, 1979.

[2]Kerbstadt, M.; Galetz, M.C. Verfahren zur Diffusionsbeschichtung mit einem Cr-Si-haltigen Schlicker. German Patent 2022.

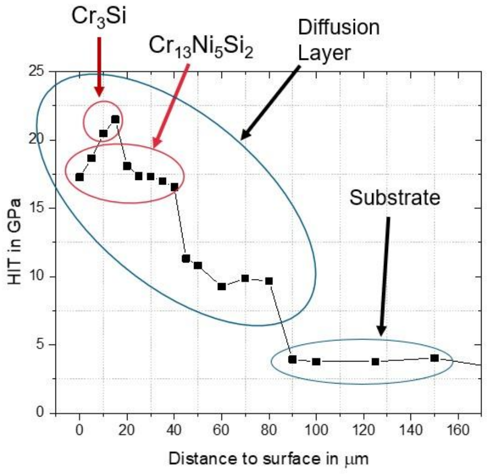
Cr/Si-coated Cross-Sections

Austenitic steel: Sanicro 25

- Enrichment of Cr and Si in a layer of about 100 µm
- Formation of intermetallic layer

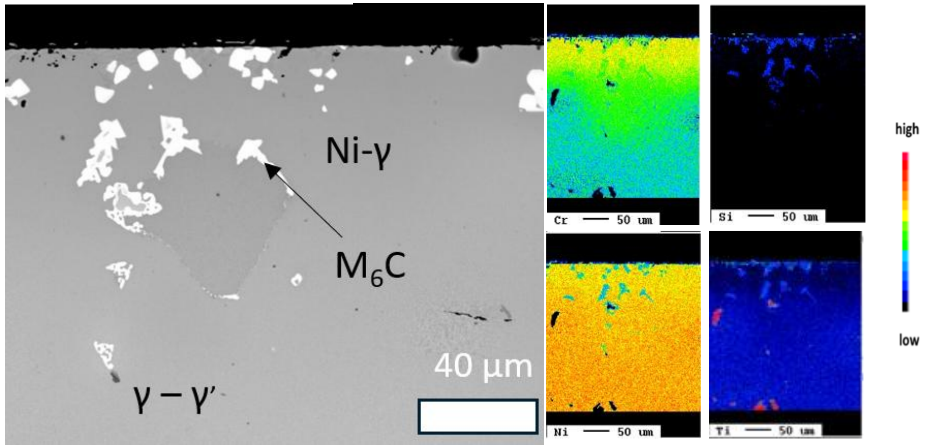


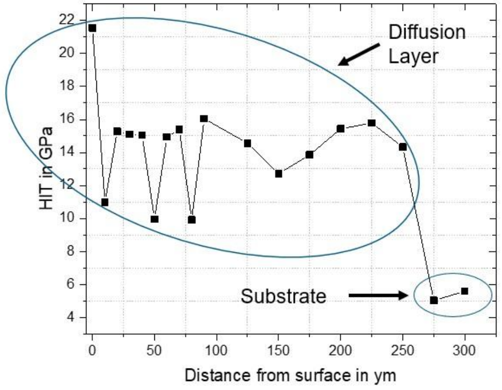
Cr-Si slurry coating on Sanicro 25



Ni-based alloy: Rene 80

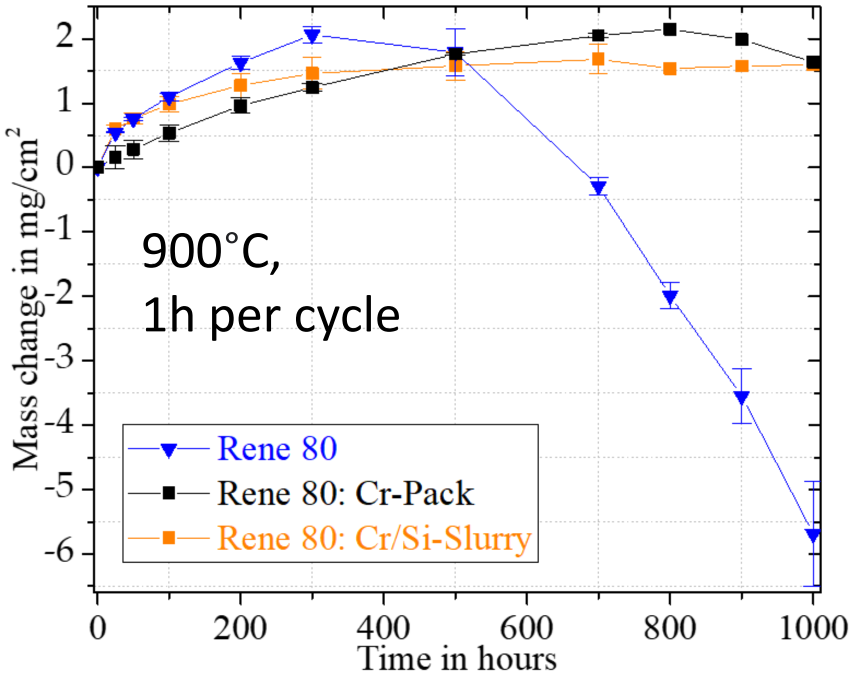
- Enrichment of Cr and Si in a layer of about 200 µm
- Enriched Ni-γ with Si-rich precipitates





*M. Kerbstadt et. al, Materials 16.23 (2023): p. 7480

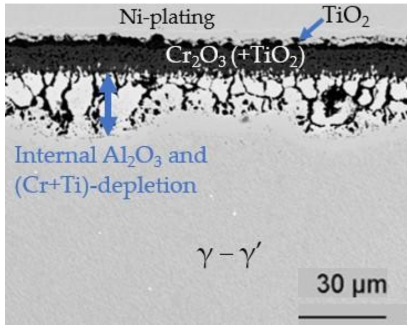
Oxidation Performance

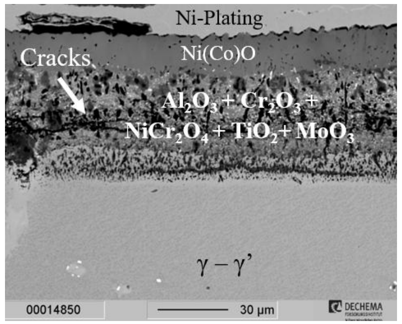


After 300 h

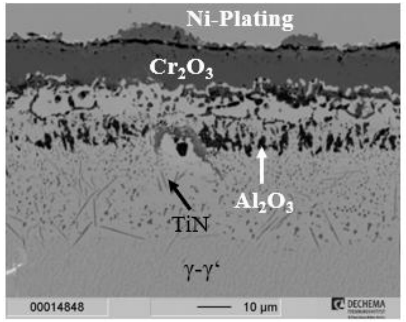
After 1000 h

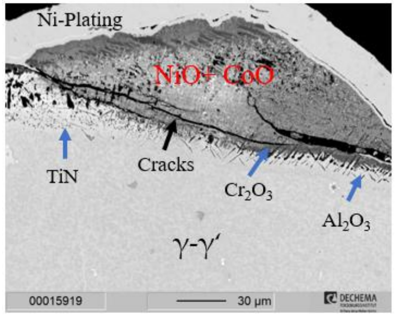
Uncoated



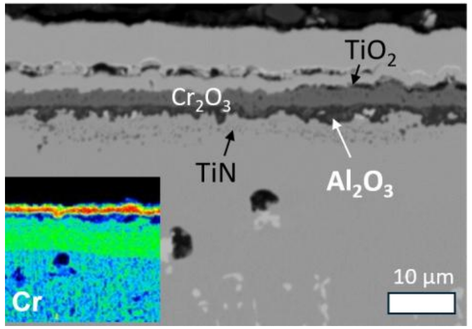


Cr-Pack

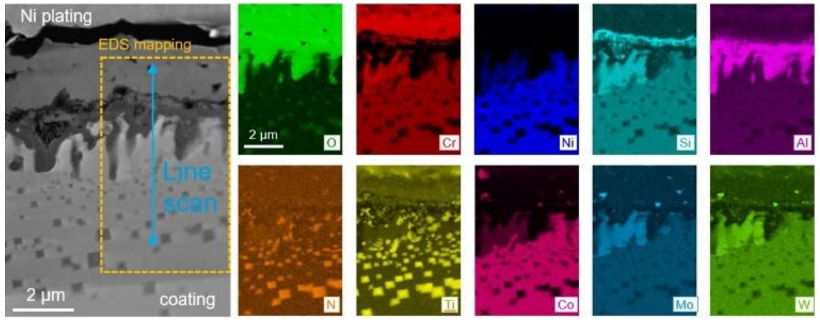




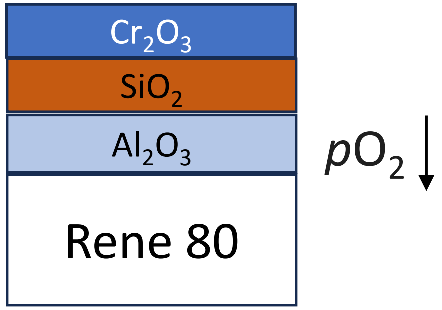
Cr-Si Slurry



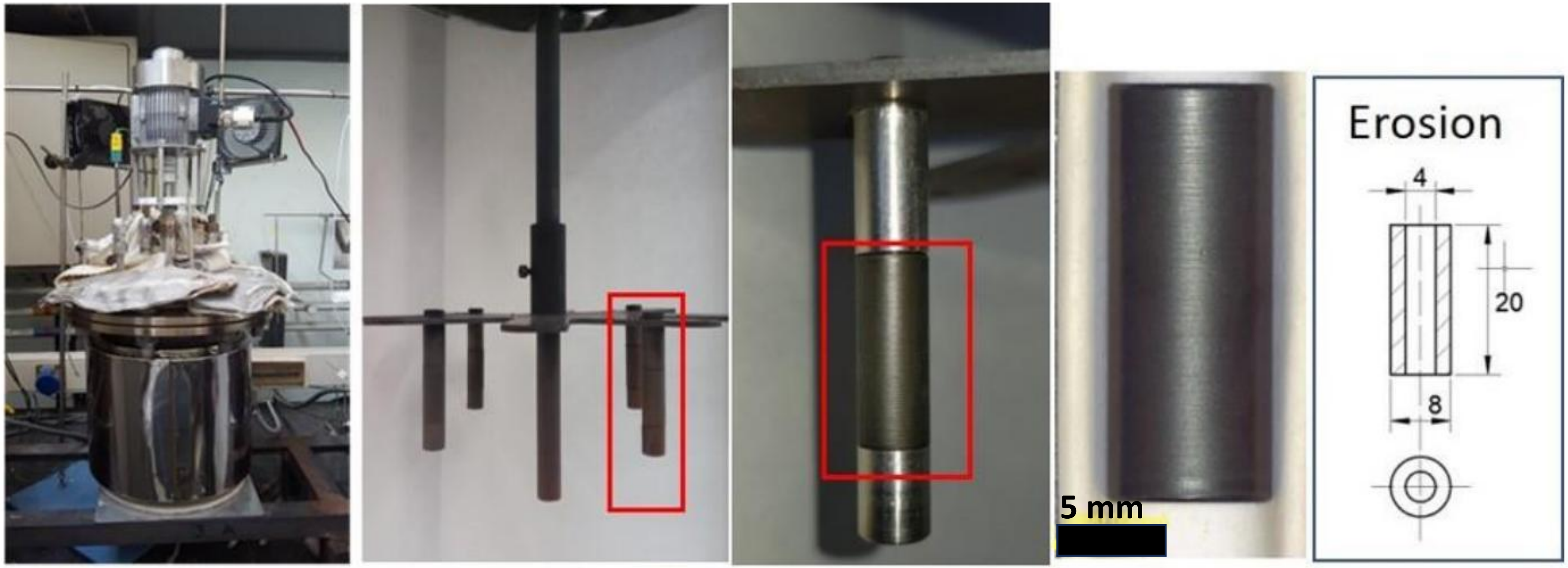
After 1000 h



TEM-analysis



Erosion Test at Ciemat

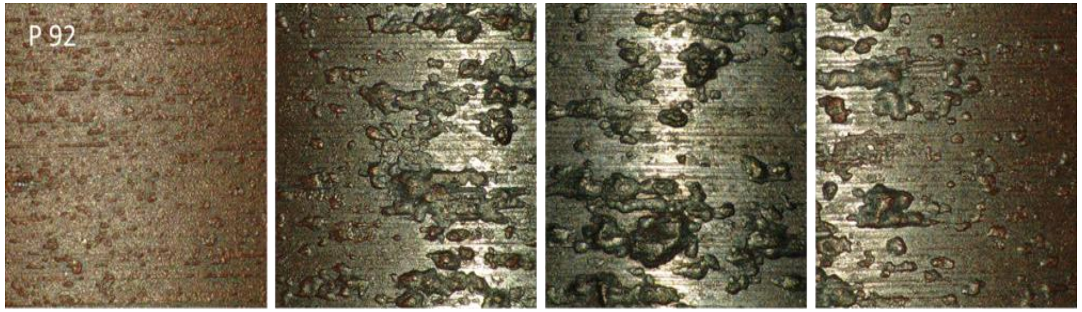


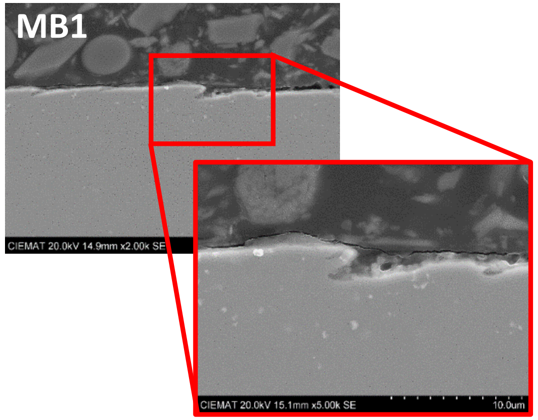
Erosion Tests at CIEMAT

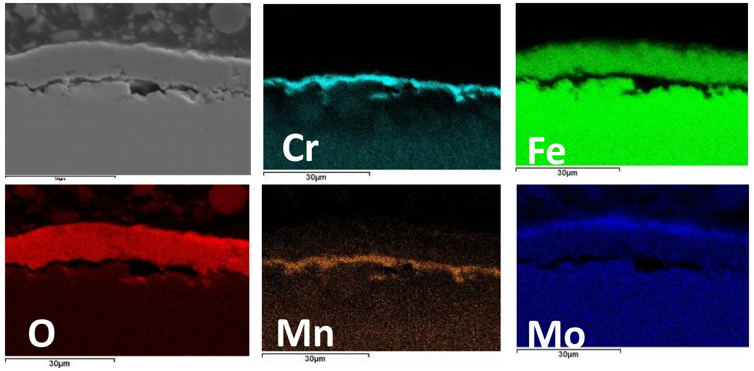
GOBIERNO DE ESPAÑA
MINISTERIO DE CIENCIA E INNOVACIÓN
Ciemat
Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

FerOx-5mm/s-700°C, 250h

Uncoated P92

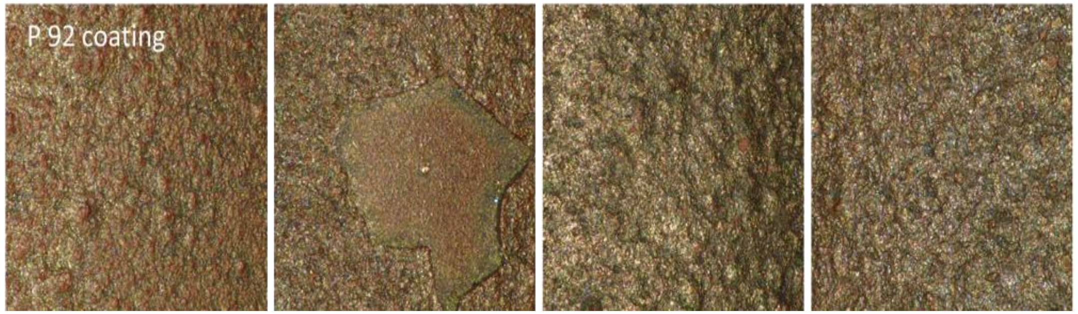


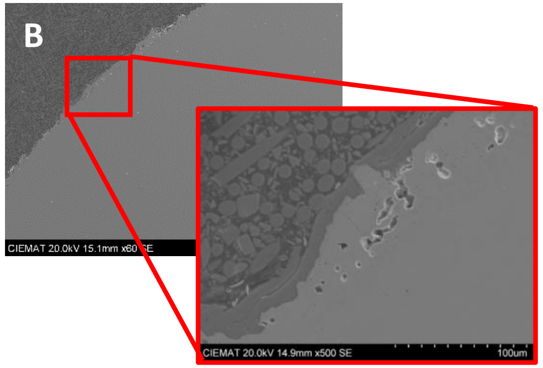


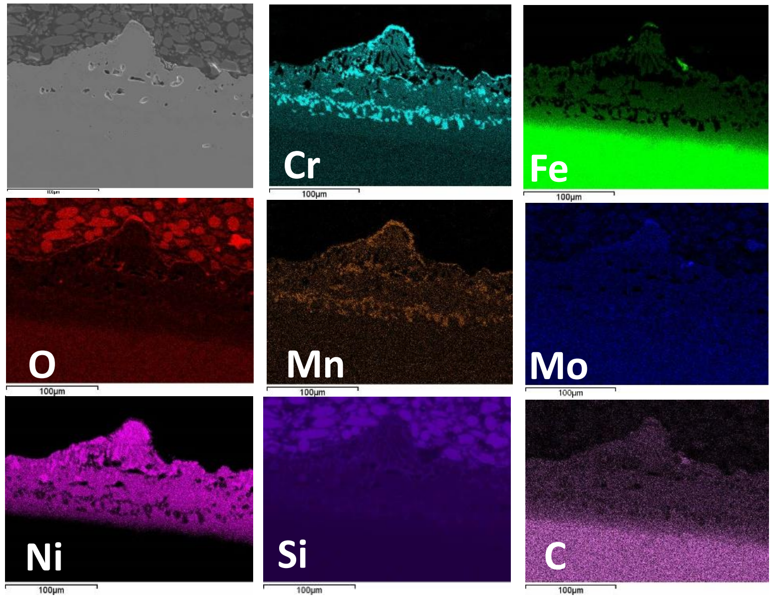


- Metall loss + Fe-Oxide formation

Cr/Si-coated P92







- Clear beneficial effect of the coating
- EDS analysis reveals thin oxide layer and only partial loss of the coating

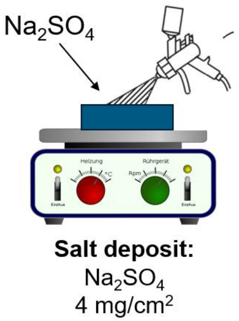
Cr/Si coatings beyond CSP

https://www.pv-magazine.com/2017/09/19/shanghai-electric-acwa-to-build-700-mw-csp-plant-phase-four-of-raschid-al-maktum-solar-park/

https://www.oerlikon.com/balzers/global/de/portfolio/

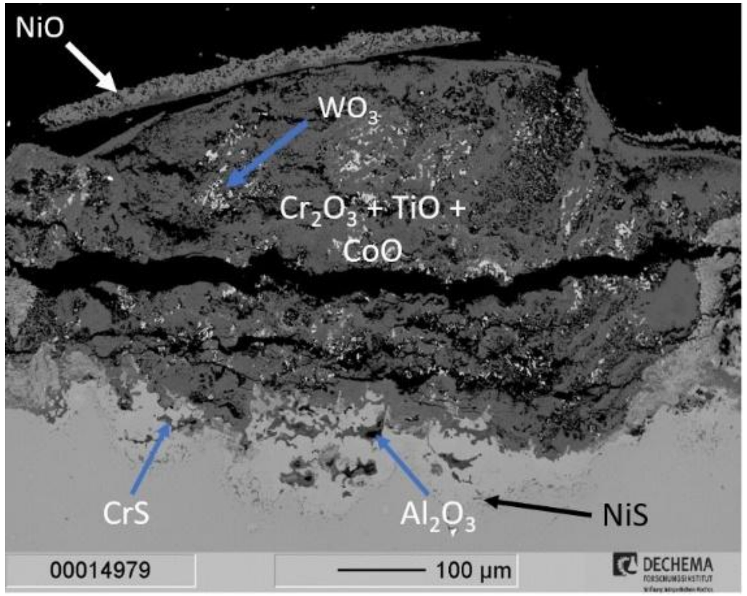
https://ndtsupply.com/magnetite-inspection-of-superheat-tubes-in-a-boiler-with-low-frequency-electromagnetic-technique-lfet.html

Cr/Si coatings beyond CSP: hot corrosion environments



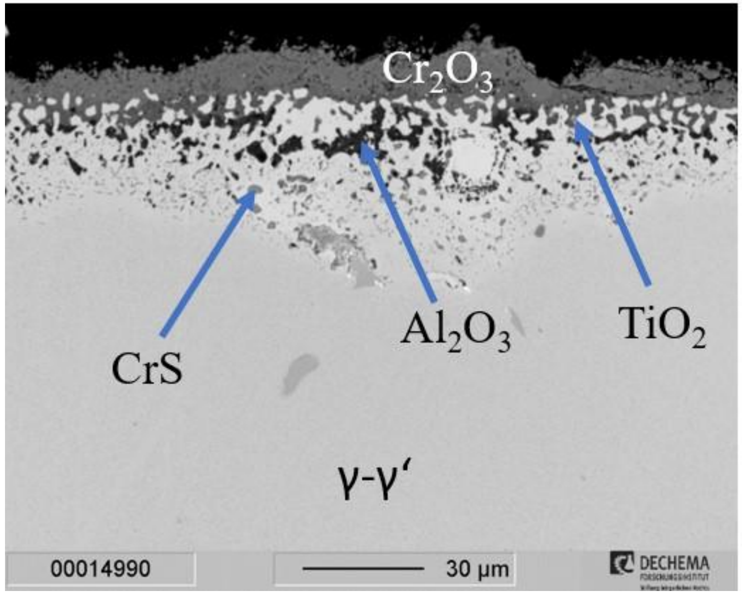
- Deposition of 4 mg/cm^2 Na_2SO_4, 900 °C for 300 hours at 0.1 vol.% SO_2 synthetic air

Rene 80



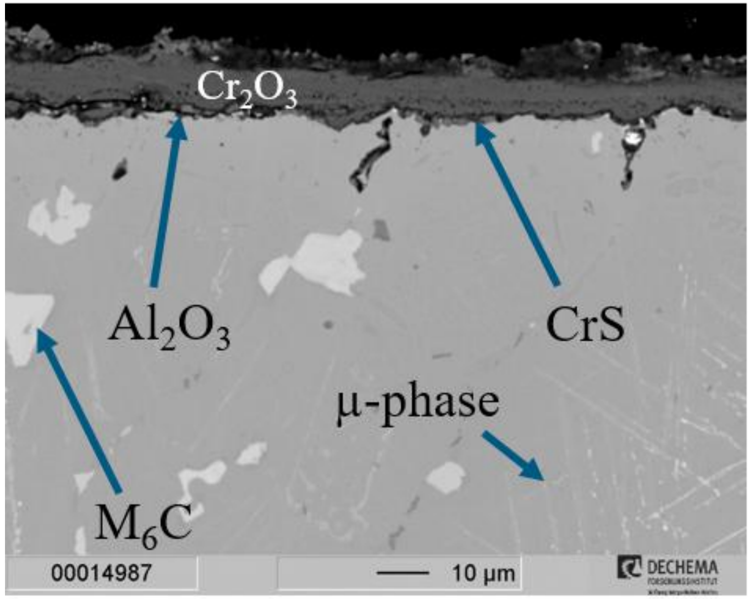
after 24 hours

Rene 80:Cr-coated by pack



after 300 hours

Rene 80: Cr/Si-coated



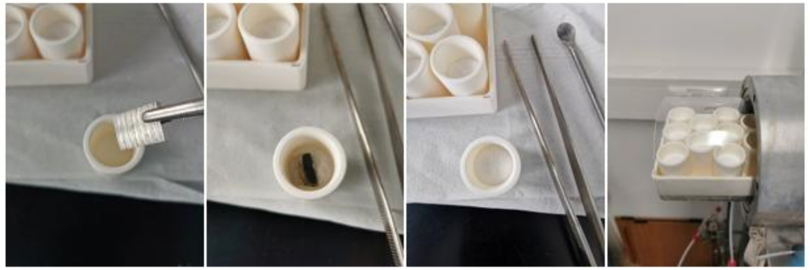
after 300 hours

- Uncoated Rene 80: catastrophic corrosion attack within short exposure times
- Cr/Si-coatings: no internal sulfidation or oxidation → Al_2O_3-subscale + defined CrS-film

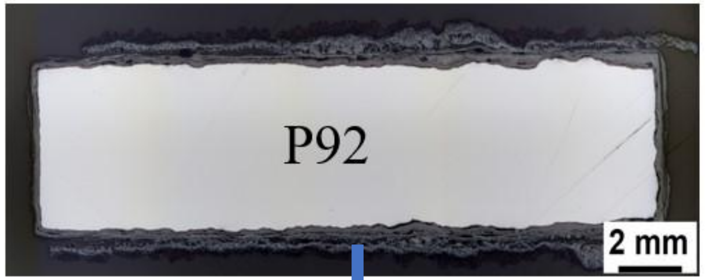
*M. Kerbstadt et al. High Temperature Corrosion of mater. (2024): p.1-13

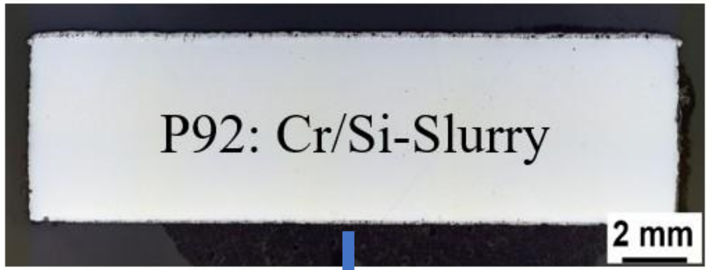
Cr-Si Coatings: Application beyond CSP

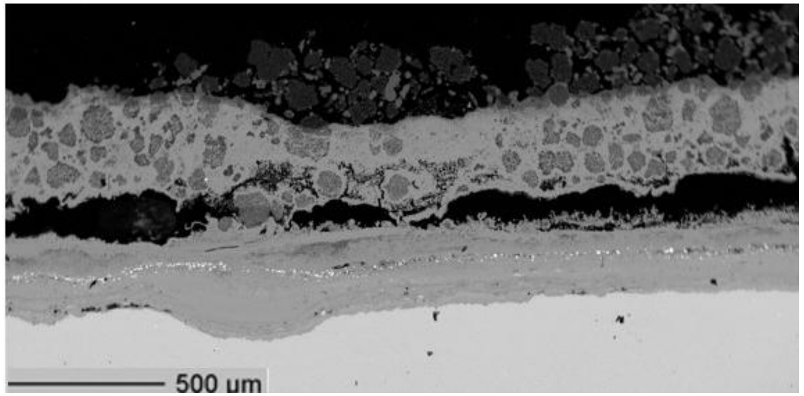
- Sewage sludge combustion
- Corrosion test of P92: 625° C for 5000 h



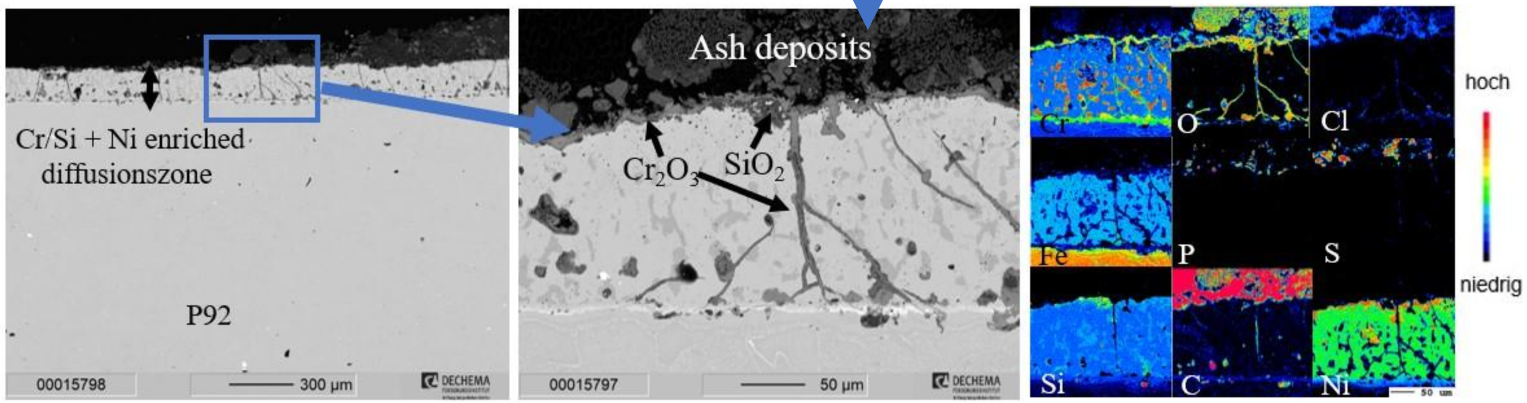
Samples covered with 10g of combustion ashes







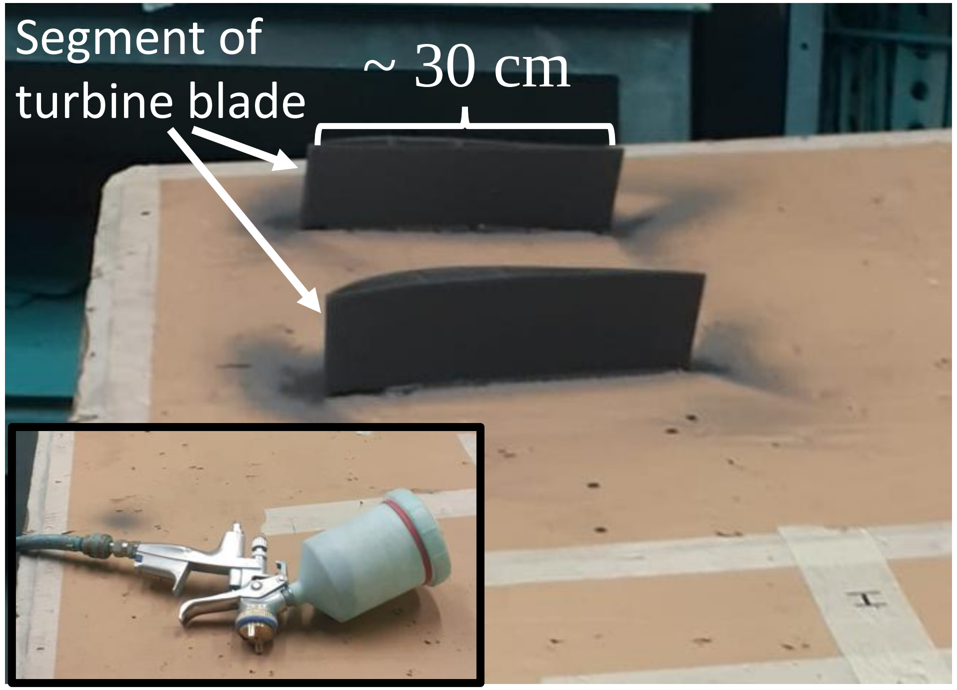
P92/Pack after 5000 h: catastrophic corrosion attack

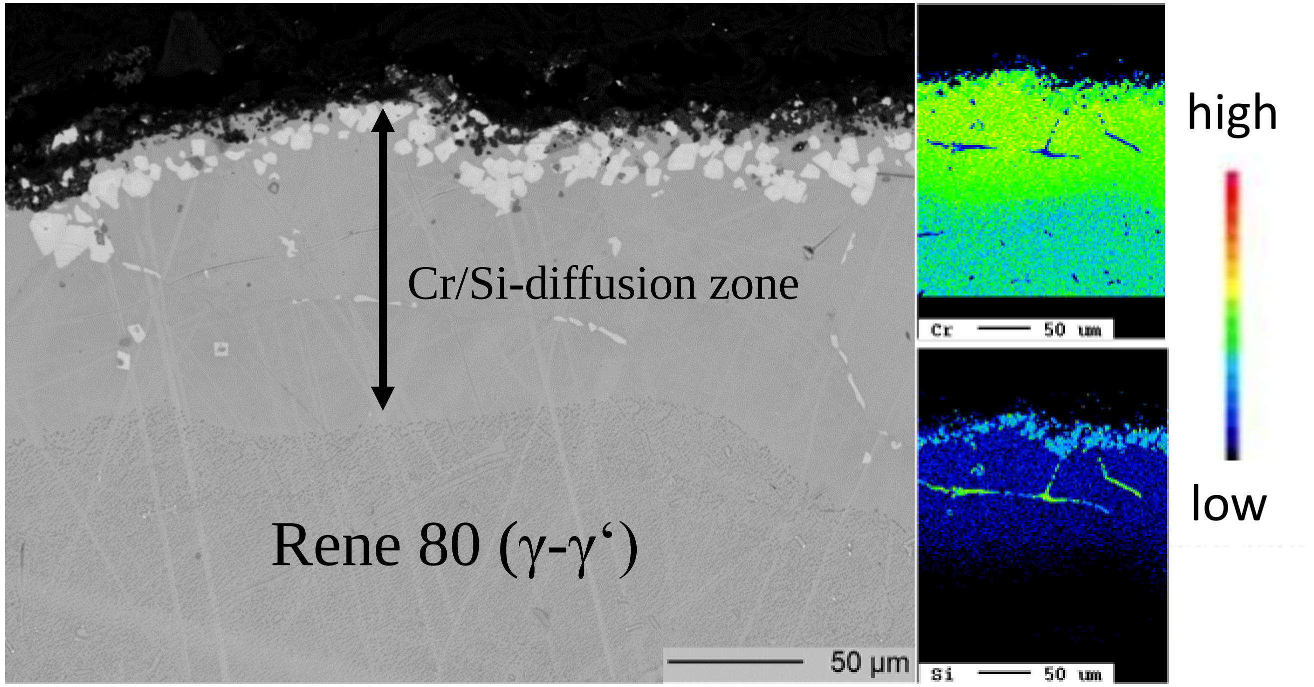


Cr-Si coating after 5000 h: no corrosion attack visible

Up scaling for industrial application

- Based on their properties, the coatings have attracted interest especially for turbine applications



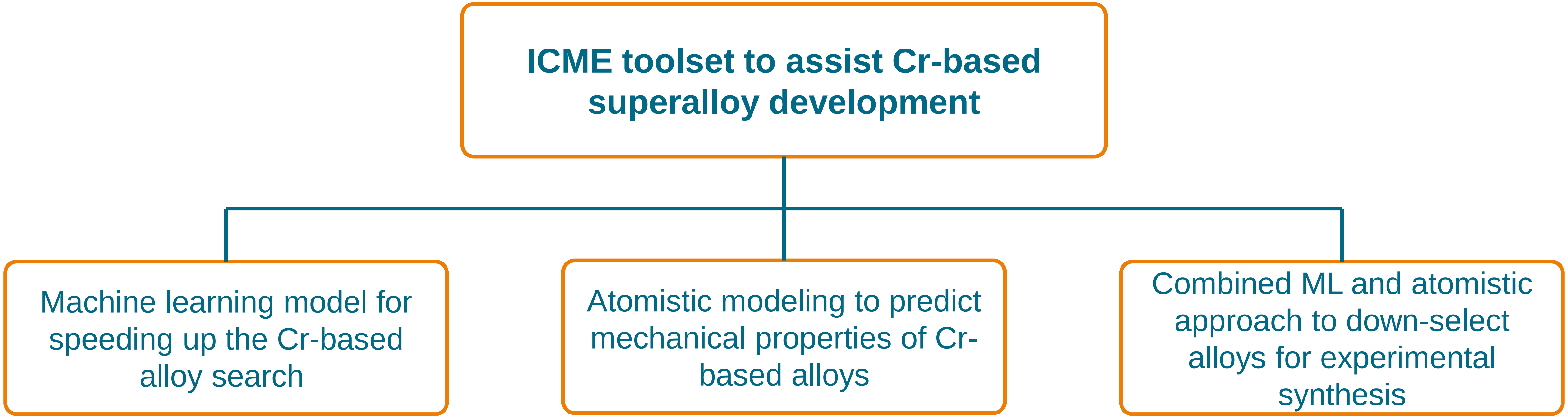


- Coatings applied in industrial production during material heat treatment process

High Throughput Modelling Approach

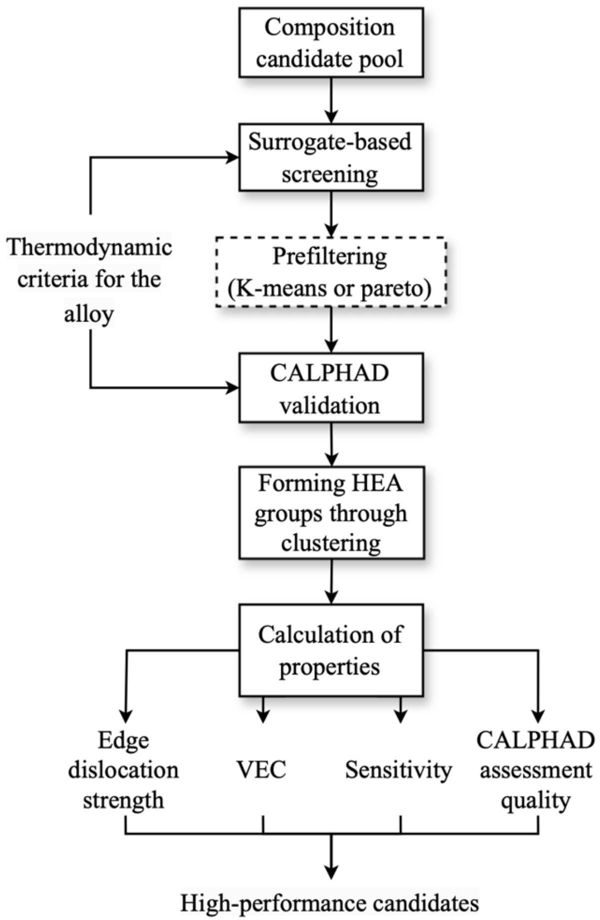
Task 3.6 objective for VTT

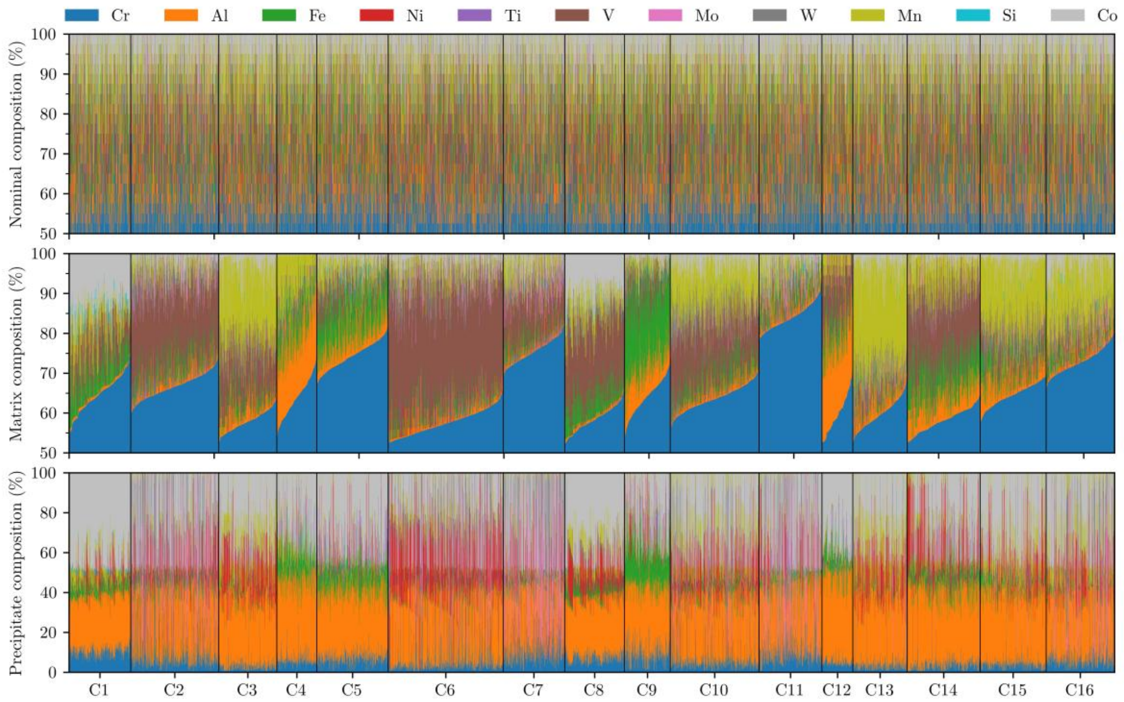
- VTT will develop materials modeling workflows that will assists the experimental partners in realizing Cr-based superalloys with suitable properties



Machine learning accelerated thermodynamic search of Cr-based BCC-B2 superalloys

- Computational tool for rapid screening of Cr-based alloys using ML-accelerated computational thermodynamics

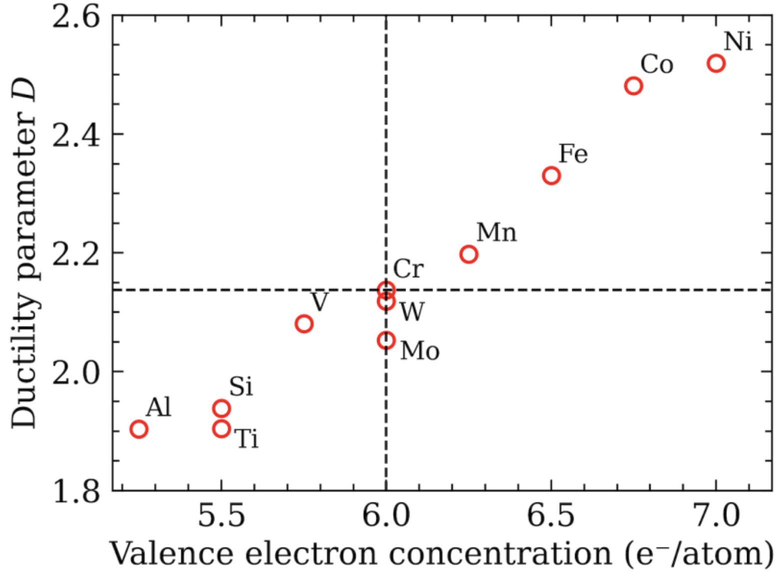




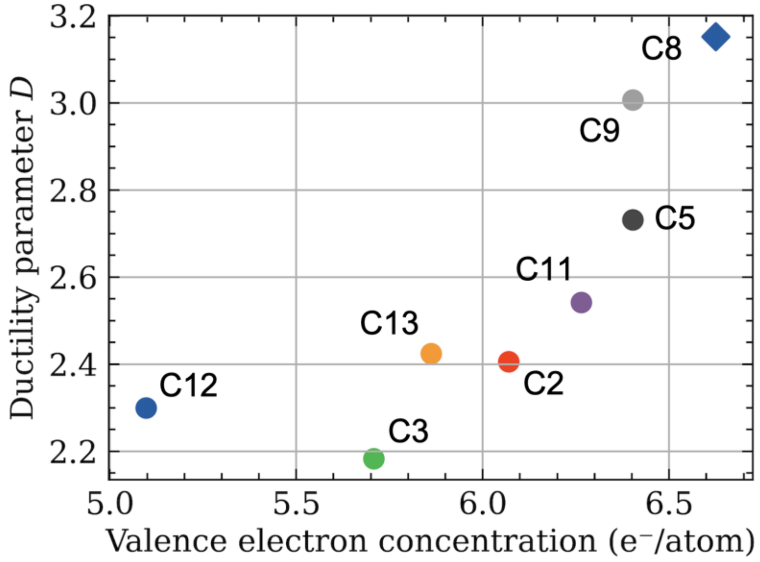
- 15,000 alloys identified from 300 million compositions that meet Cr superalloy criteria

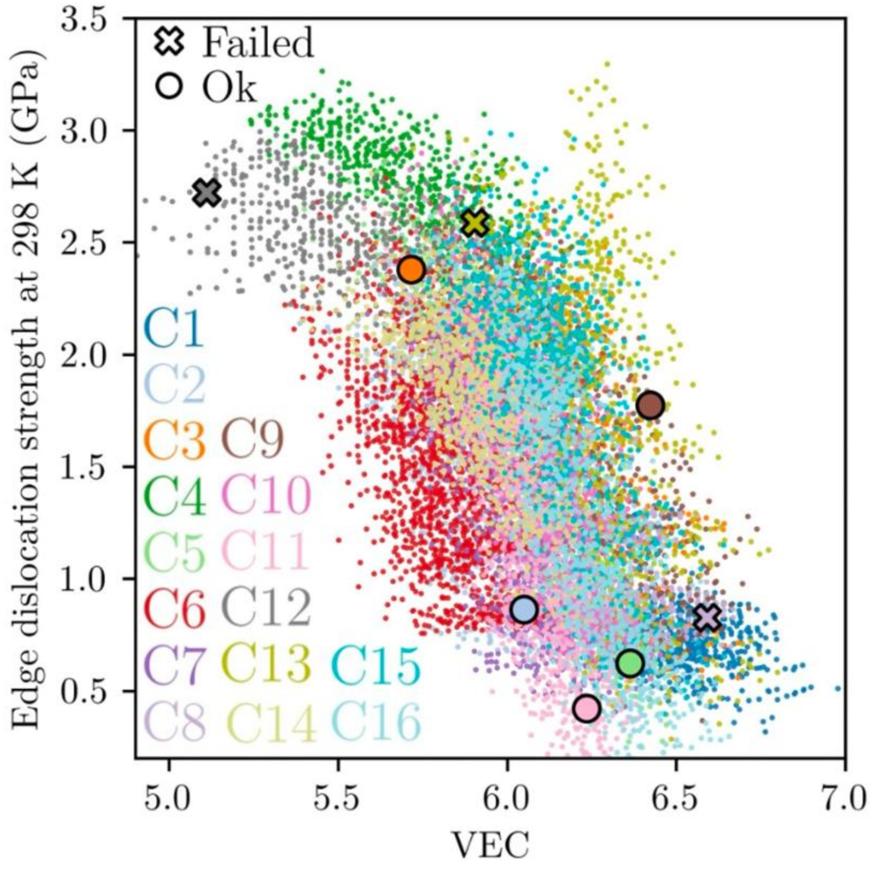
Ab-initio predictions of the ductility

Binary Cr-X



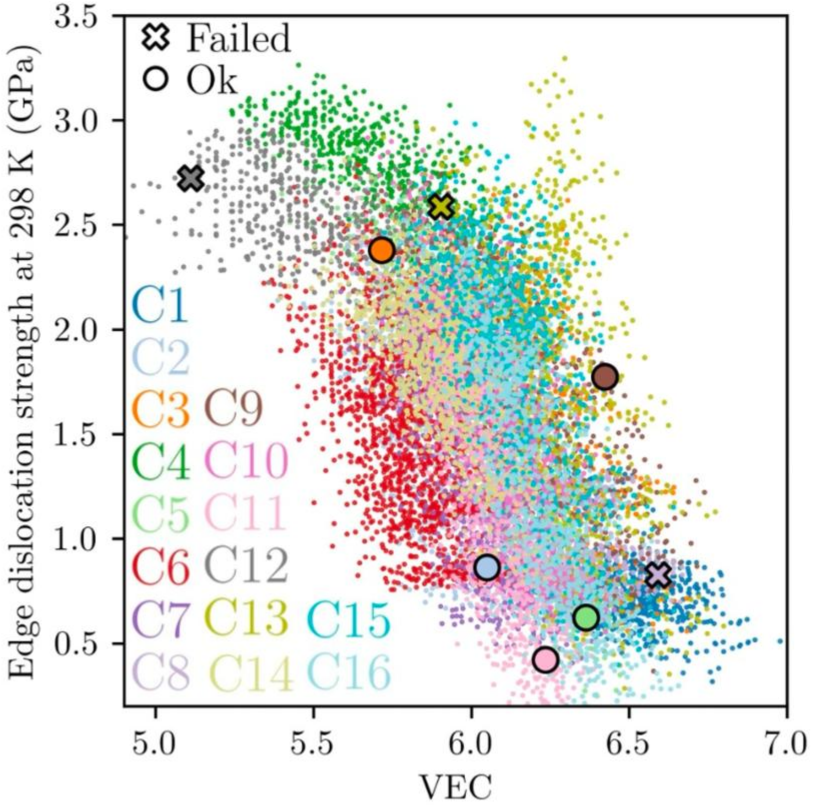
Matrix phase of alloys



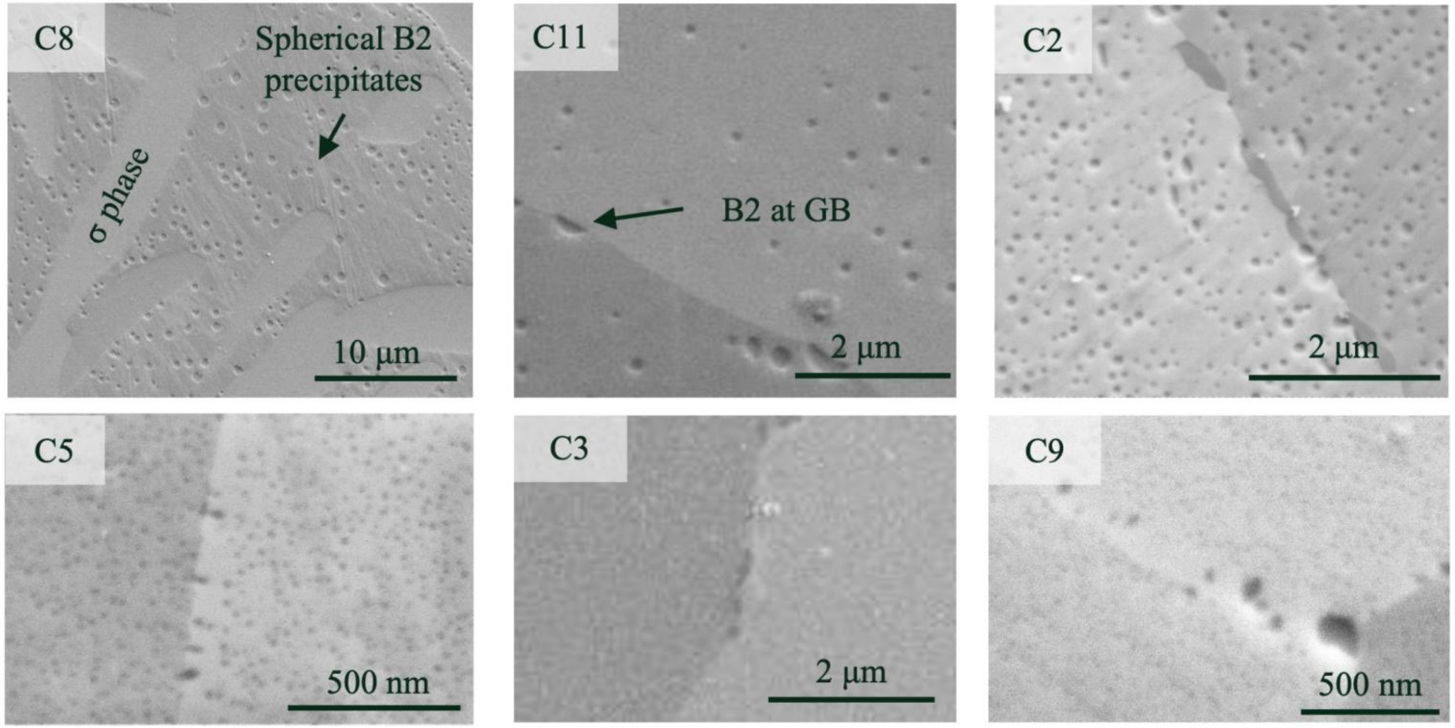


- ➢ Rice parameter D predicts cleavage vs. dislocation emission at crack tip
- ➢ For Cr-based alloys, D increases with valence electron concentration (VEC)

Down selected alloys for experimental synthesis



Alloys synthesized by University of Birmingham



- Eight alloys selected for synthesis based on their predicted mechanical properties
- Five out of eight successfully produced Cr-based BCC-B2 microstructure

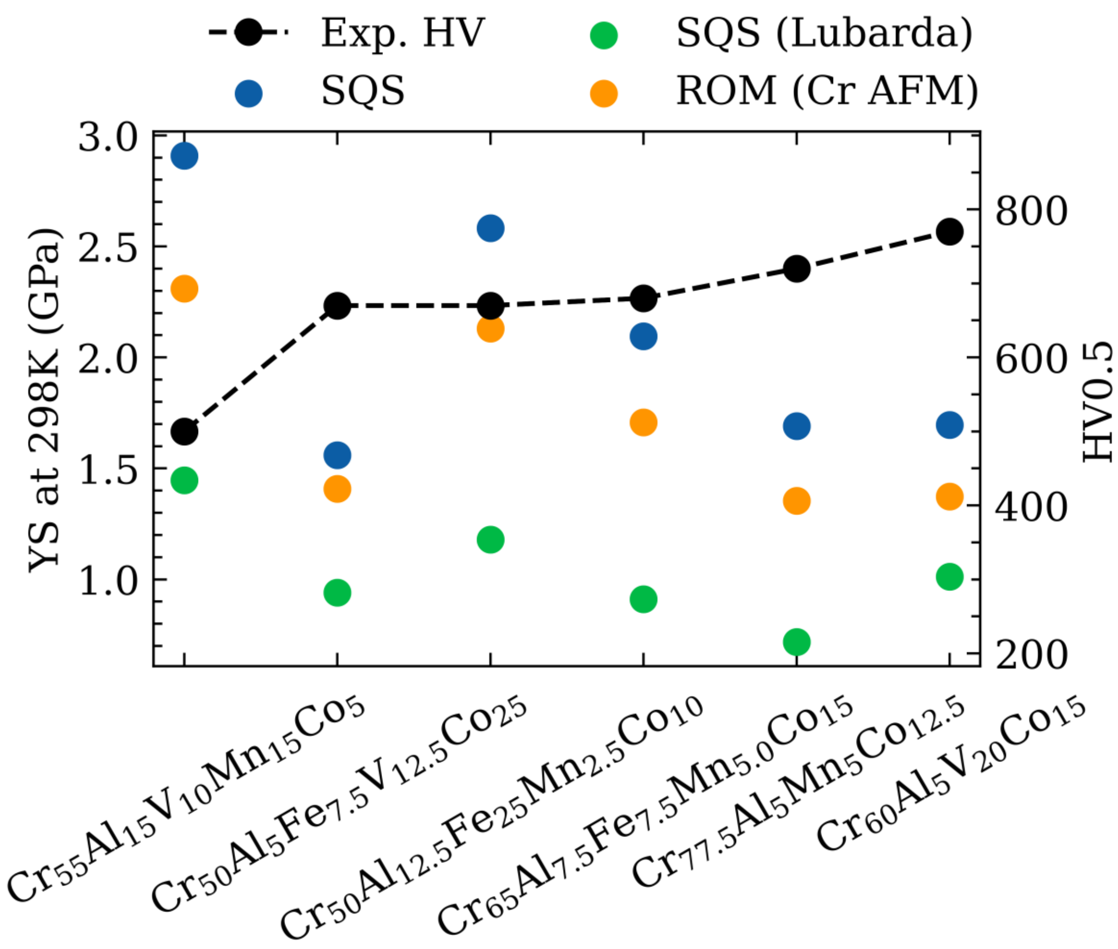
Mechanical properties of the matrix phase of the alloys

- Yield strength predicted via Maresca–Curtin edge dislocation theory
  - Strength linked to solute misfit volume vs. alloy volume

For Cr-based alloys:

- V-W-Mo large misfit
  - Edge dislocation strengthening
- Fe-Co-Mn small misfit
  - Screw dislocation strengthening

- Effect of Al is unclear



Conclusions and Perspectives

- Mechanical property predictions need further theoretical and experimental assessment
- Trapping of GB embrittling elements to precipitate-matrix interfaces?
- Finalizing paper on high-throughput screening of chromium-based high-entropy superalloys

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THANK YOU

contact@compassco2.eu

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