DEVELOPMENT OF NEW MATERIALS

COMPASsCO2 Second Stakeholders Workshop

Next generation advanced materials for particle/supercritical CO_2 heat exchangers

Tom Blackburn, University of Birmingham, UK

September 25th, 2023
Hybrid Meeting: Hotel Anker, Marktheidenfeld, Germany & Zoom

Presentation Structure

- Material Candidates for the Heat Exchanger
- State of the Art Materials
- Novel Material Candidates
  - Chromium Nickel Aluminides
    - Coarsening Kinetics
    - High Temperature Compression
  - Chromium Silicides
    - Coating Procedure
    - Coating Oxidation Performance
- Conclusions and Future Prospective

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State of the Art materials

- Materials selected on basis of:
  - High Temperature (<900°C external)
  - sCO_2 corrosive environment
  - High Pressure (25MPa) sCO_2
  - Erosive ceramic particles
  - Good Thermal conductivity

- Steels: P92
  Sanicro 25
- Nickel: Inconel 740
  Inconel 617
  Haynes 282
- Novel Chromium alloys

Material candidates for solar sCO_2 Brayton cycles

Deliverable Number 1.3

WP1 "Materials operation conditions and their feasibility studies"

Date: January, 2021

Deliverable type: Report

Dissemination level: Confidential

Lead participant: DECHEMA-Forschungsinstitut

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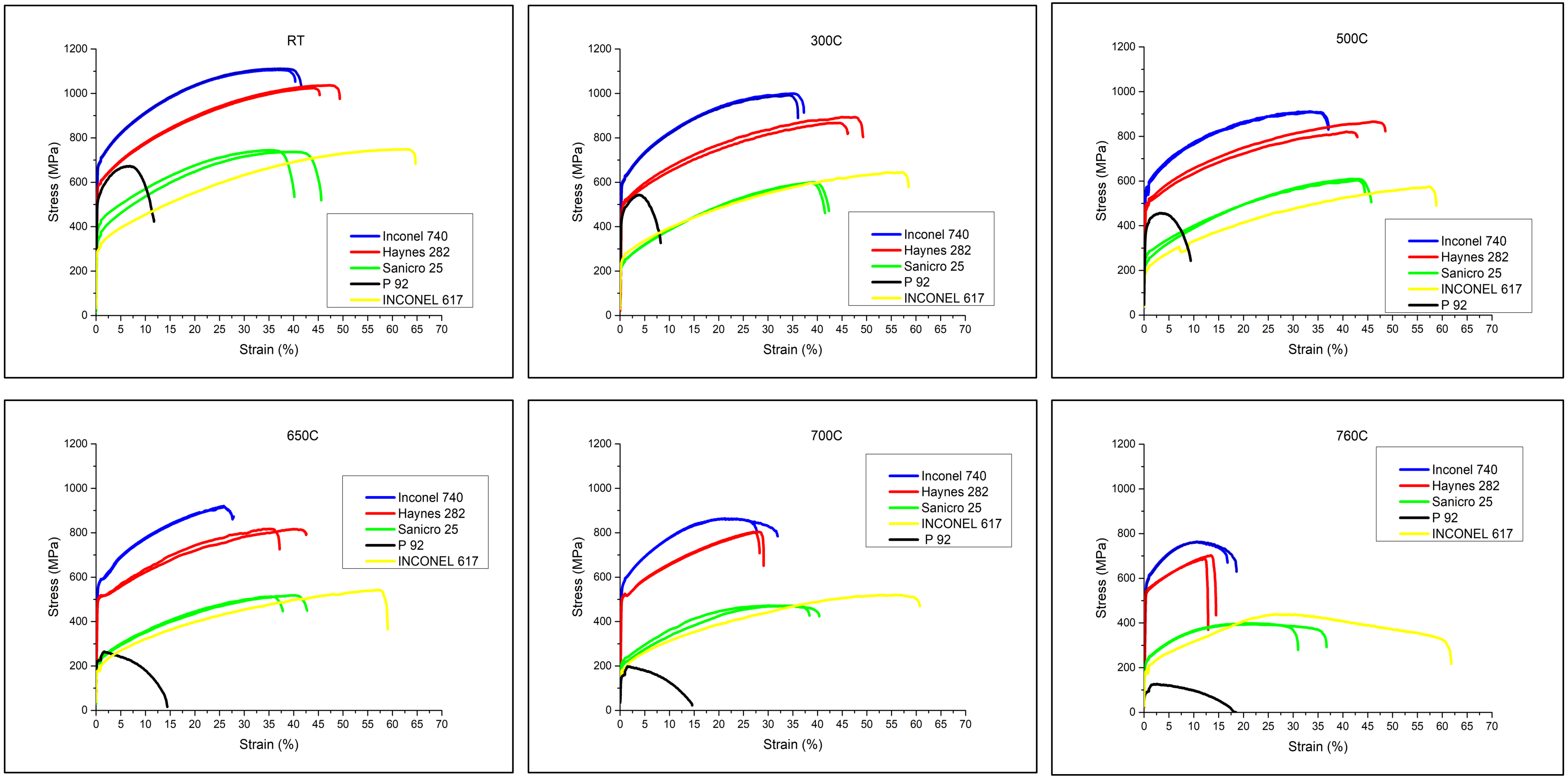
State of the art materials: Mechanical Properties (Tensile Tests)

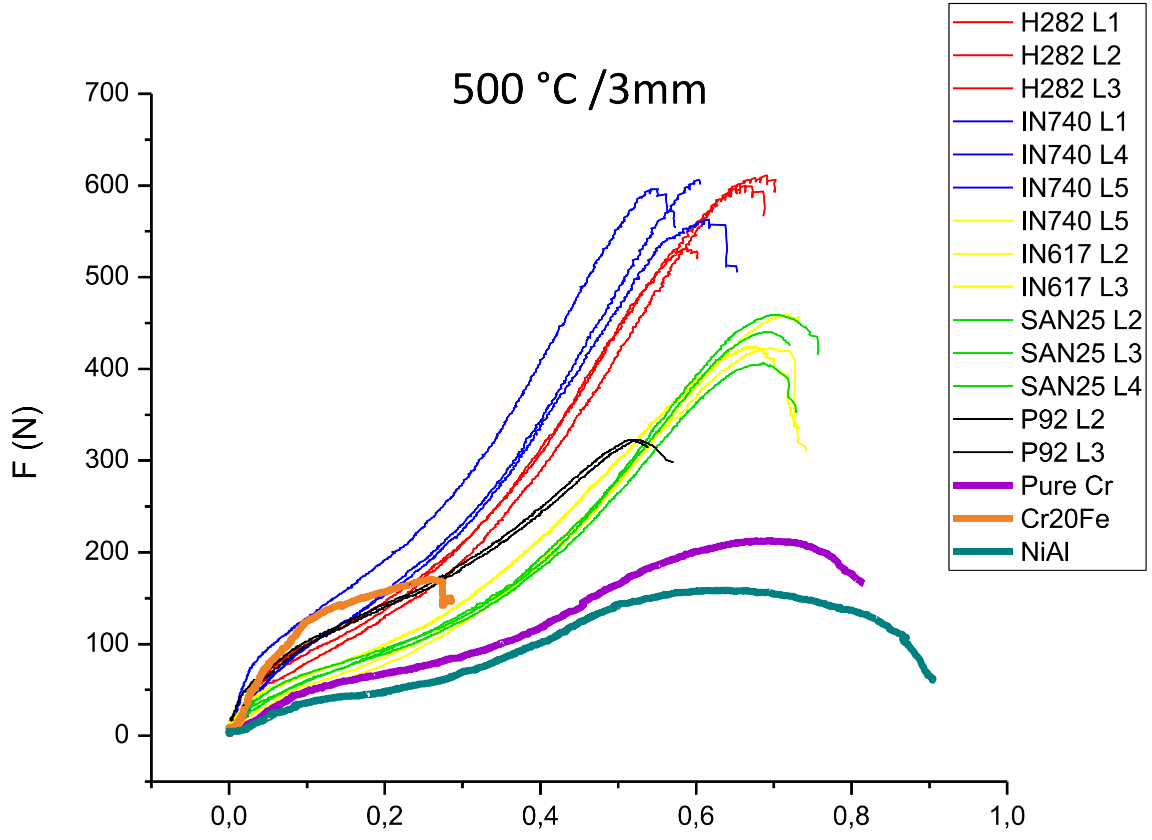


Source: COMPASsCO2

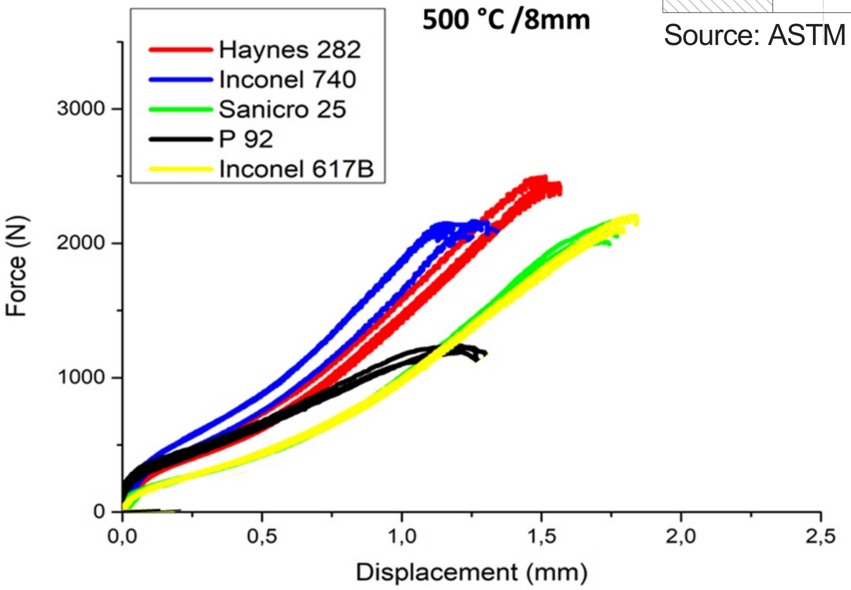
- In740 has the highest yield strength
- In617 shows greatest ductility at all temperatures
- Ni Superalloys show superior mechanical properties over Stainless steel and martensitic steels

Small Punch Testing of State of the Art materials

SP (3mm) vs. SP (8mm)



Source: COMPASsCO2



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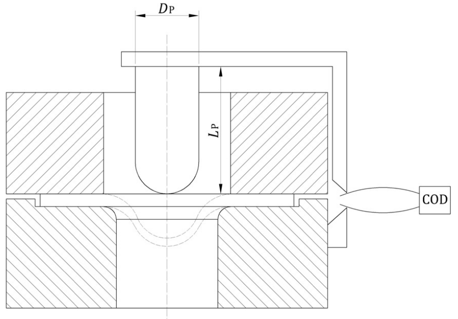

Source: ASTM 10371:2021

- IN740: higher yield stress
- H282 and IN617 show more ductility
- Similar correlations observed in 3 mmØ and 8 mmØ
- Initial investigation of Cr alloys

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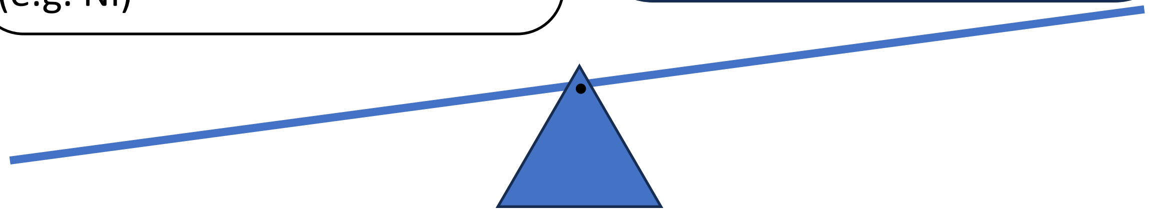
Chromium BCC Superalloy

Why Chromium?

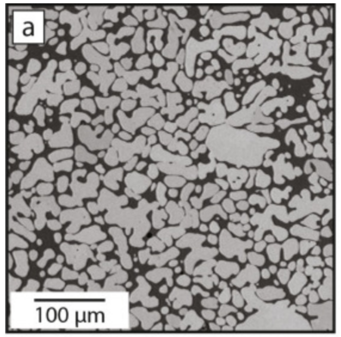
Strengths	Challenges
+ High Melting Point	- Mechanical properties at HT
+ Oxidation Resistant <900°C	- Creep resistance
+ Good Thermal Conductivity	- DBTT > RT
+ Cheaper than other metals used for high temperatures (e.g. Ni)	- Oxidation Resistance >900°C
	- Nitride Embrittlement



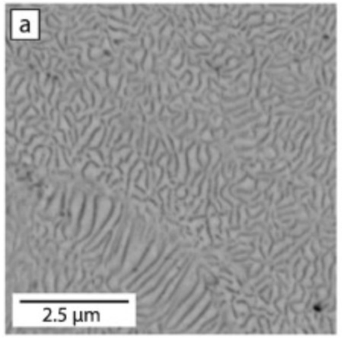
Approach 1

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

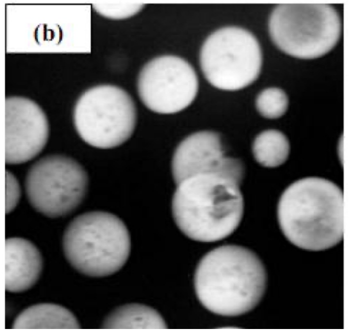
W-TiFe (A2-B2)[1]



Ti-TiFe (A2-B2)[2]

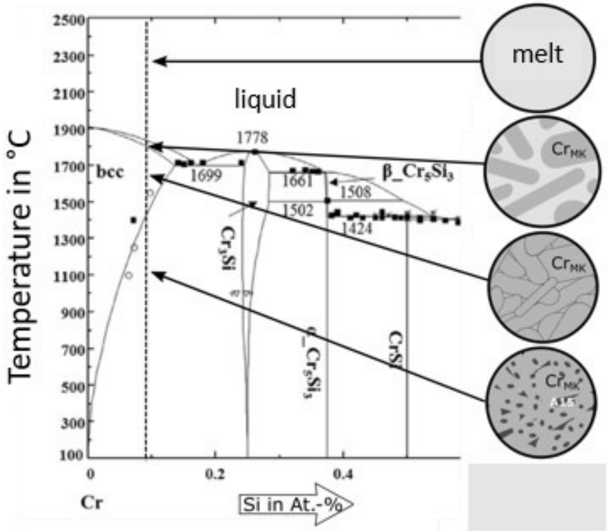


Fe-NiAl (A2-B2)[3]

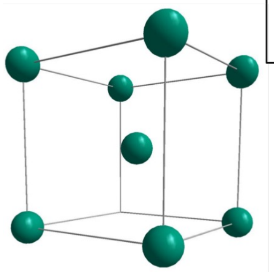


Approach 2

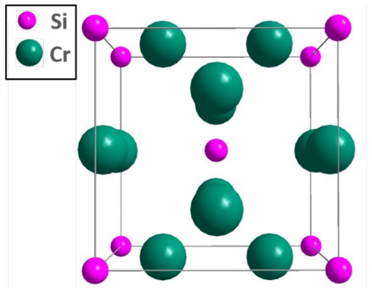
$Cr-Cr_3Si$ → Cr (A2) strengthened by A15 precipitates



[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

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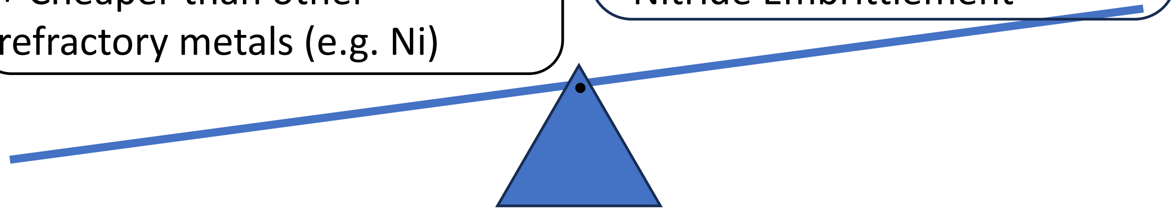
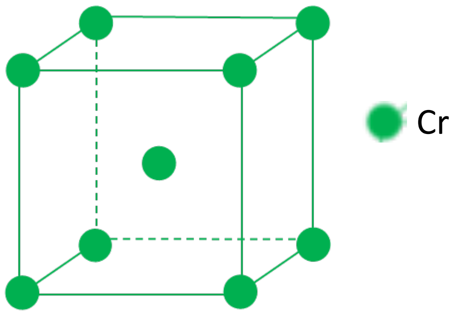
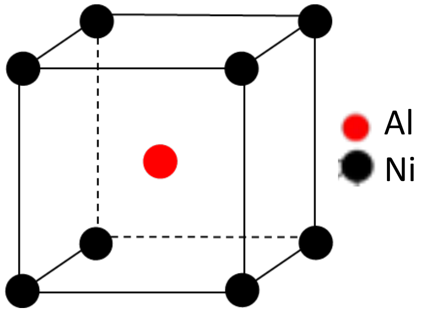
+ Cheaper than other refractory metals (e.g. Ni)	- Nitride Embrittlement





Cr A2 bcc matrix



B2 precipitates

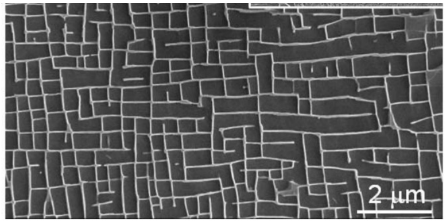
The BCC Superalloy Approach

FCC-FCC

γ-γ'

Ni-Ni_3Al

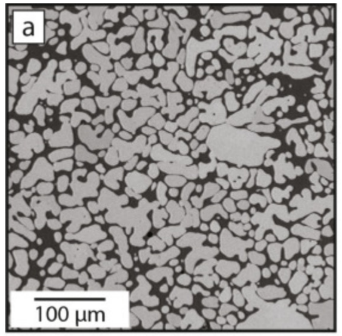
A1-L1$_2$



K. Park, P. Withey, Crystals 12 (2022)

BCC-BCC

W-TiFe (A2-B2)[1]



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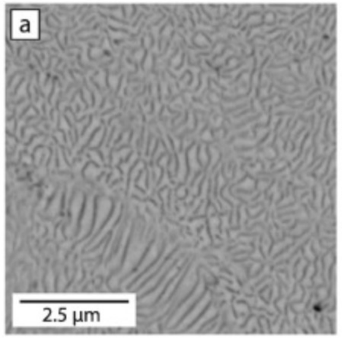

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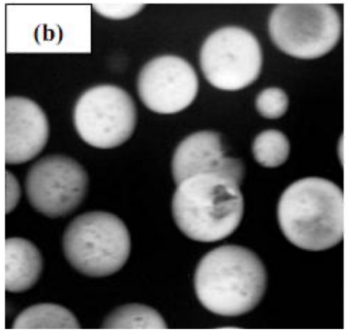

[1]A. Knowles et al. / Applied Materials Today 23 (2021) 101014
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Phase Diagram

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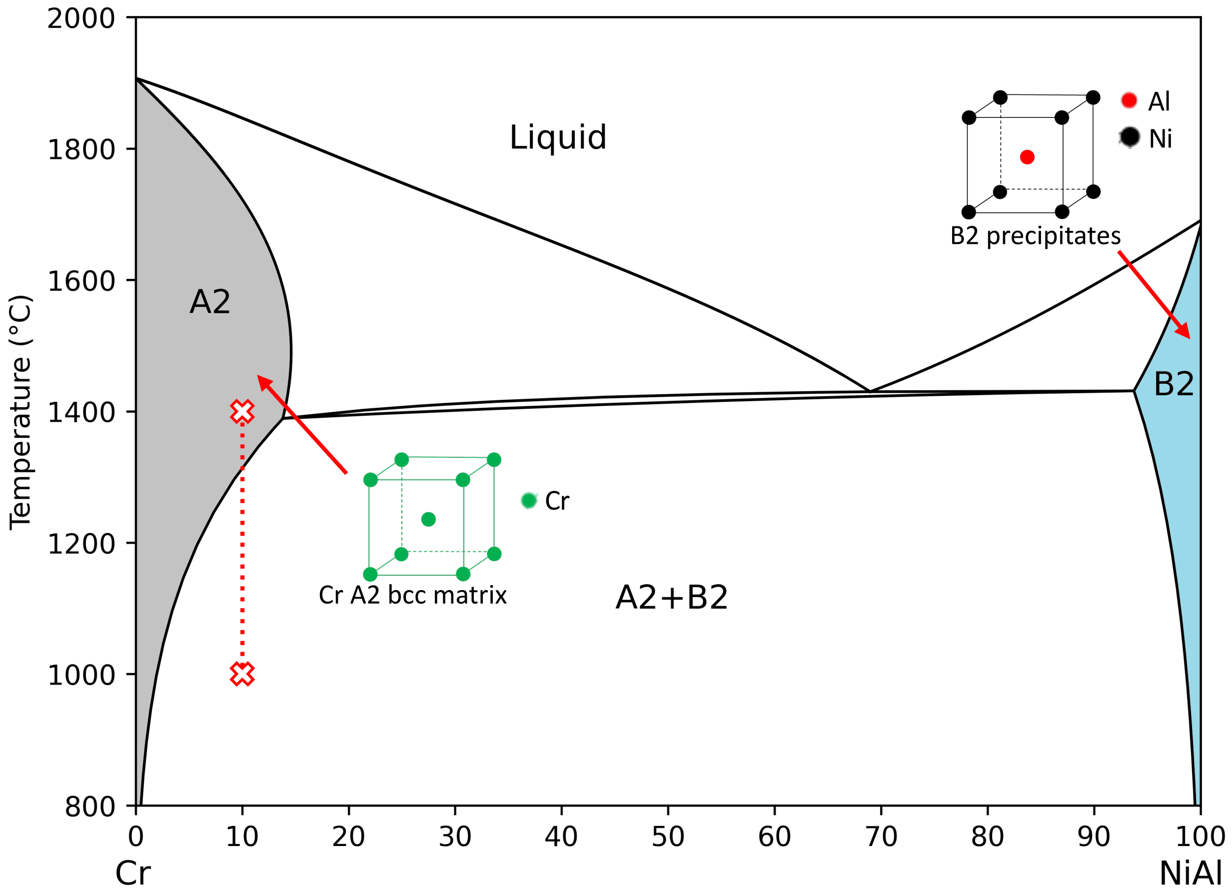
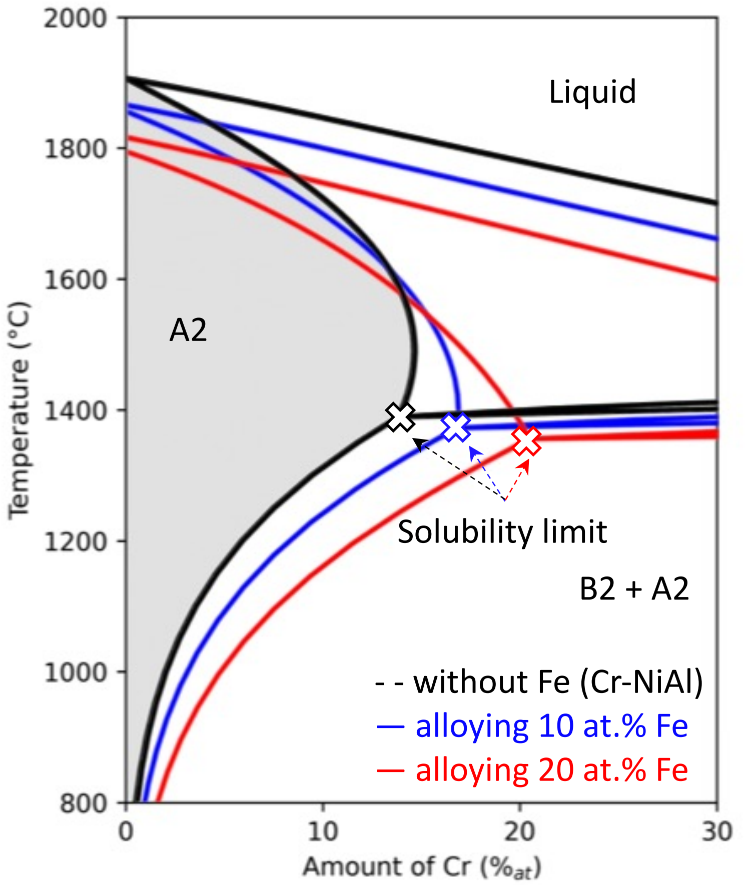


Source: COMPASsCO2

Addition of Fe



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.

Microstructure Cr-5Ni-5Al and Cr-5Ni-5Al-10Fe [1]

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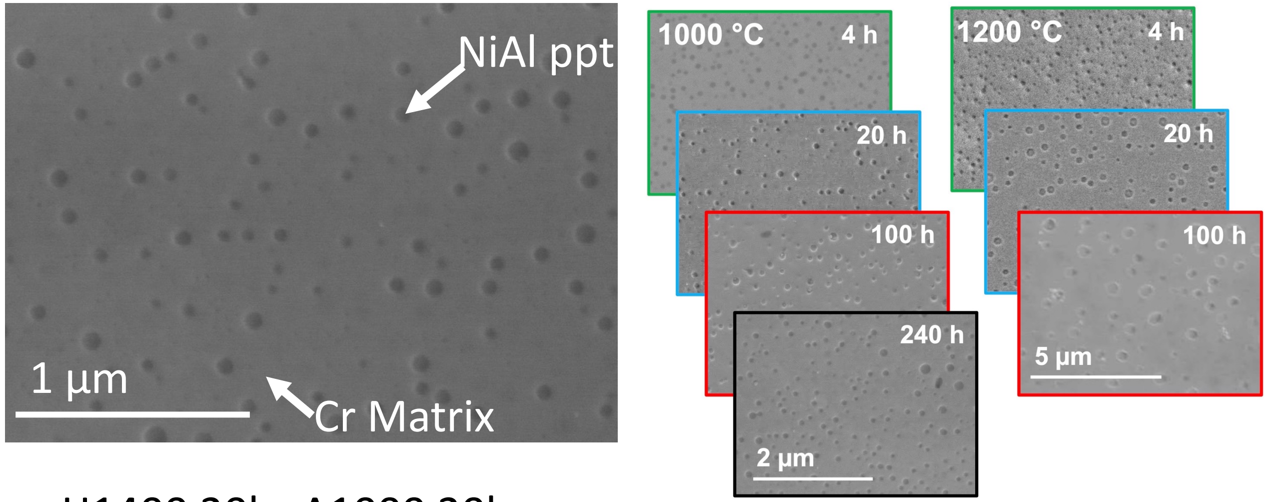
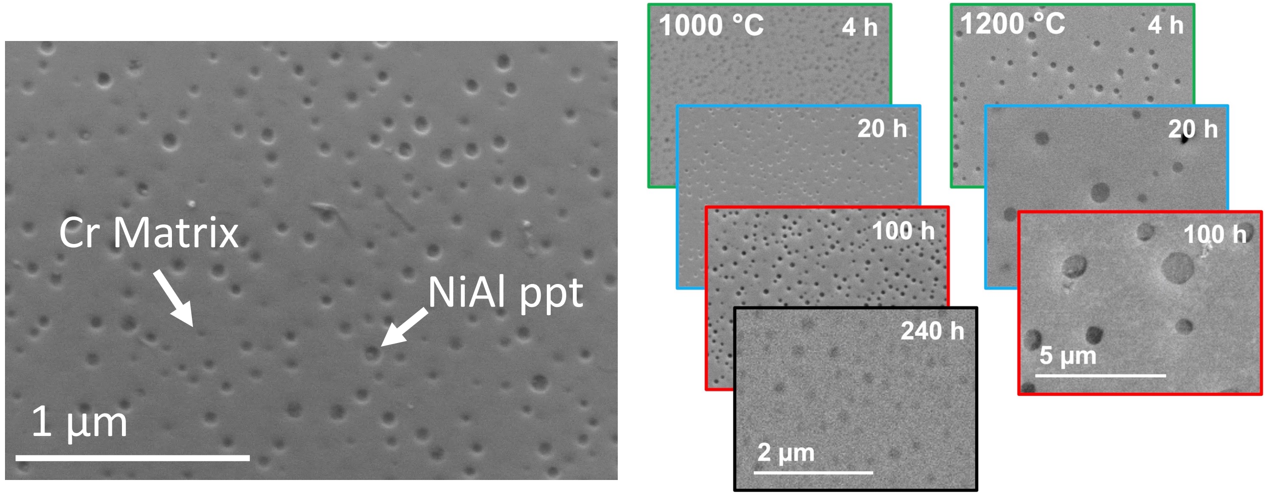
Cr-5Ni-5Al



H1400 20hr A1000 20hr

Cr-5Ni-5Al-10Fe



[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.

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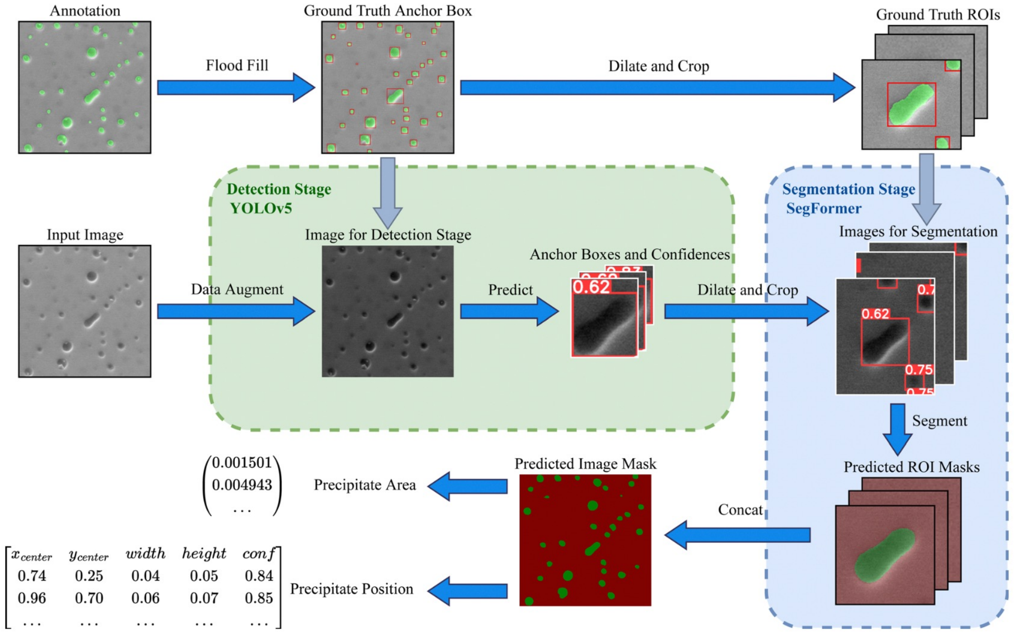
Cite this: *Phys. Chem. Chem. Phys.*, 2023, **25**, 15970

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]



COMPASsCO2

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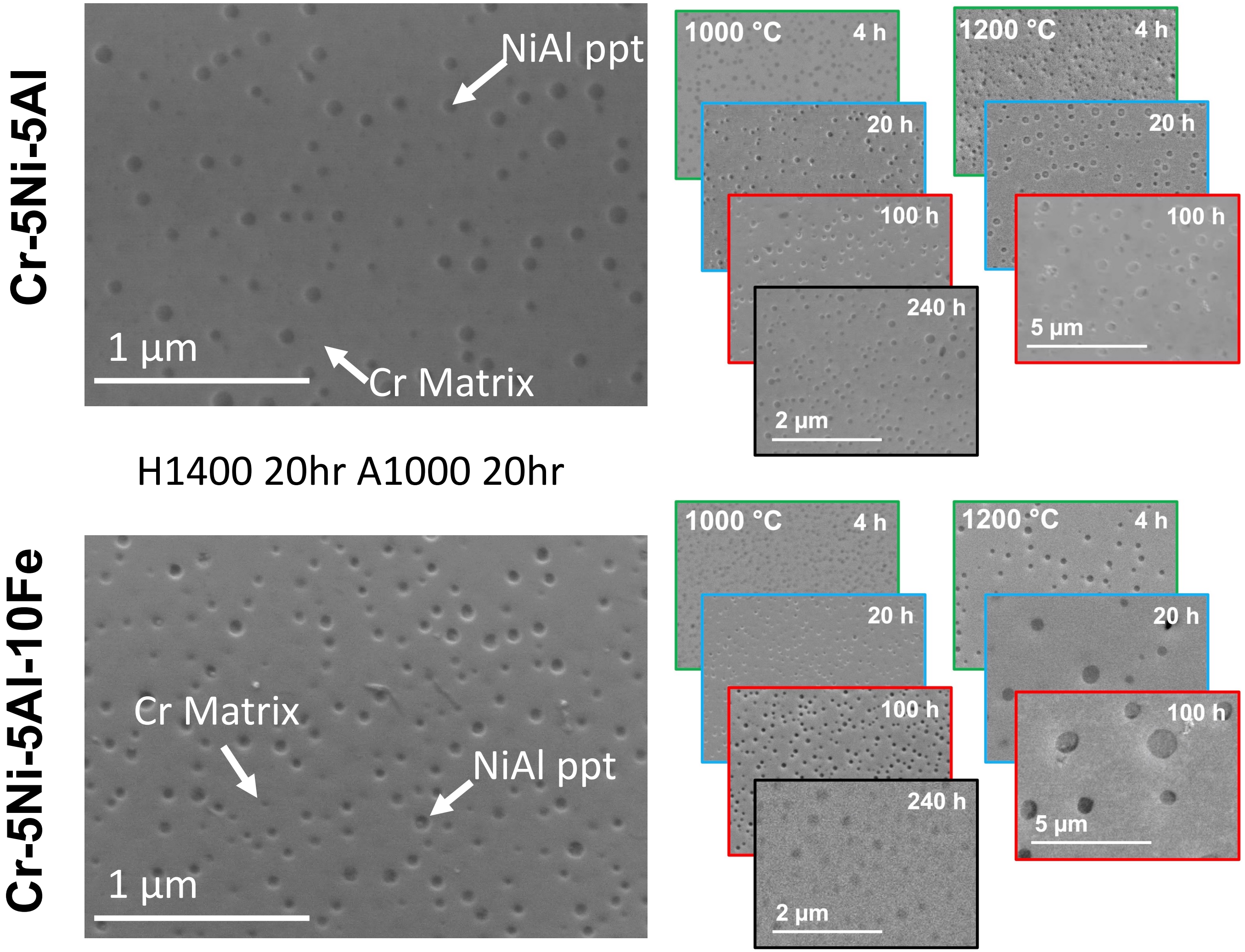
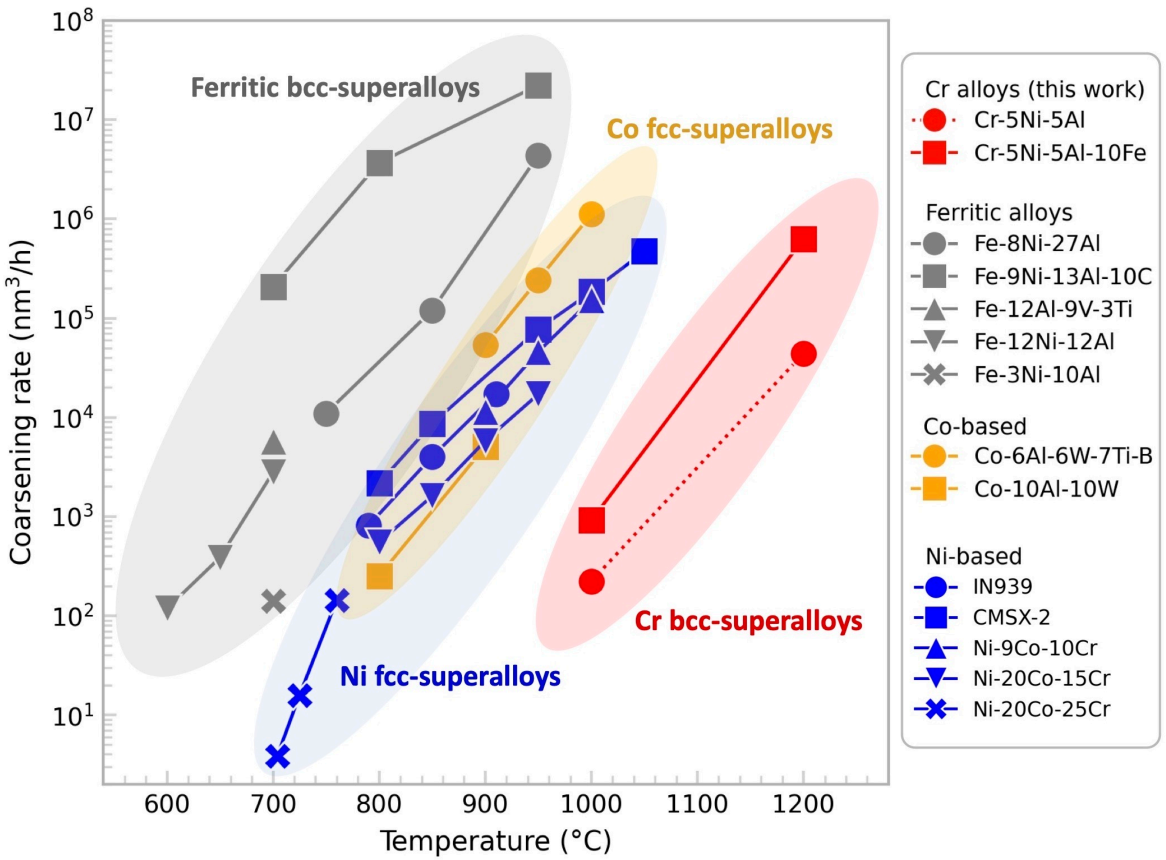
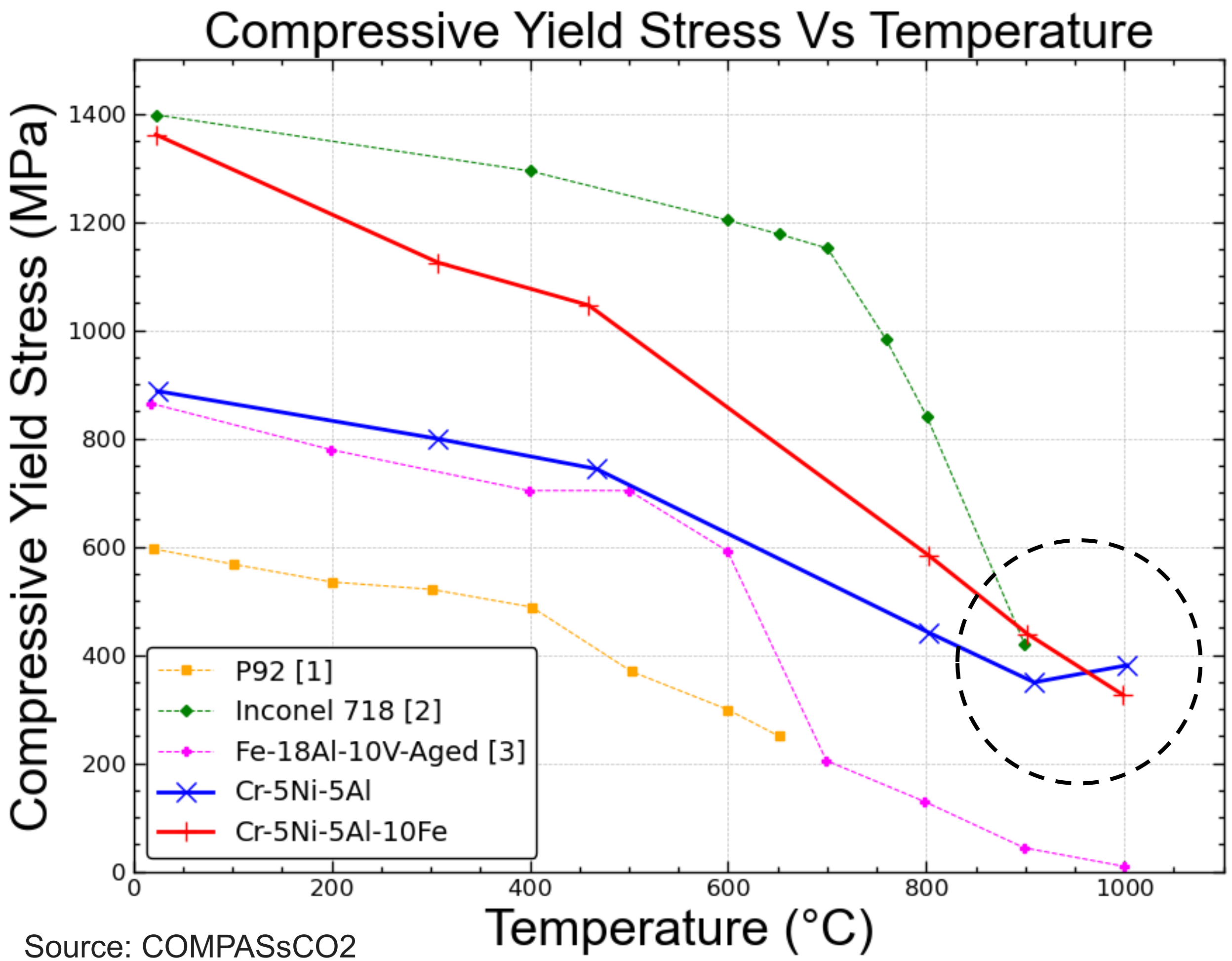




- Lower coarsening rate than Ferritic, Nickel and Cobalt superalloys
- 2 orders of magnitude lower rate at 1000°C over Ni superalloys

[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.

Yield Stress



Source: COMPASsCO2

- No significant drop off in strength
- Higher strength over Ni superalloys at 1000°C

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]

This work has been published:
K. Ma, T. Blackburn, J.P. Magnussen, M. Kerbstadt, P.A. Ferreirós, T. Pinomaa, C. Hofer, D.G. Hopkinson, S.J. Day, P.A. Bagot, *Acta Materialia*, 257, **2023**, 119183.

[1] https://www.jstage.jst.go.jp/article/isijinternational/56/9/56_ISIJINT-2016-097/_pdf/-char/en
[2]https://reader.elsevier.com/reader/sd/pii/S0921509316314071?token=1949412CCA518C81737CC1B68030E005CF2A0387C33BA5D4FA43B354A00B07F2F311D086BBDC5B7B2ED2454560247724&originRegion=eu-west-1&originCreation=20230223152235
[3]https://reader.elsevier.com/reader/sd/pii/S0966979516300450?token=FBECCA4462F7AB823961272CB29FF8EA3EFD96253210FBB2FD080930E0EB90CFFC76C5AA9D430984A76C7CF847331C51&originRegion=eu-west-1&originCreation=20230306090121

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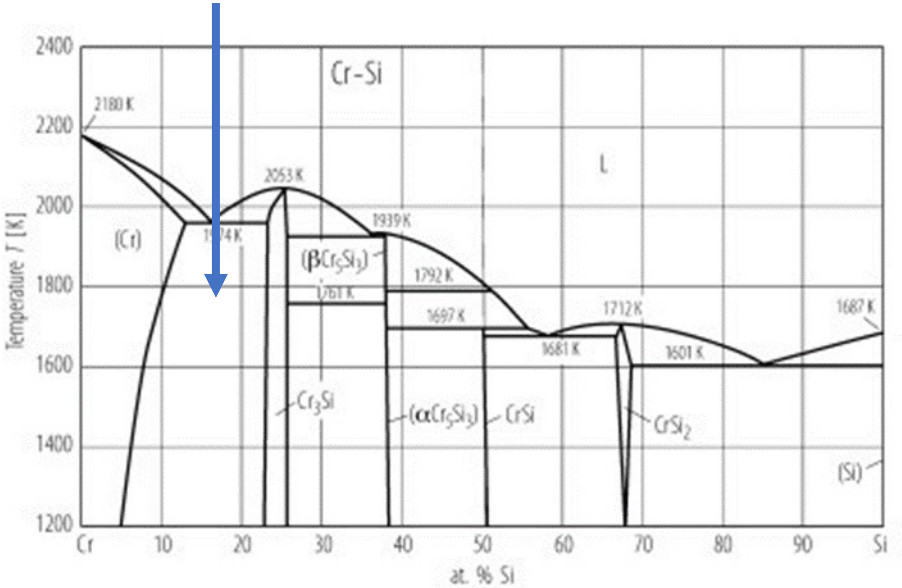
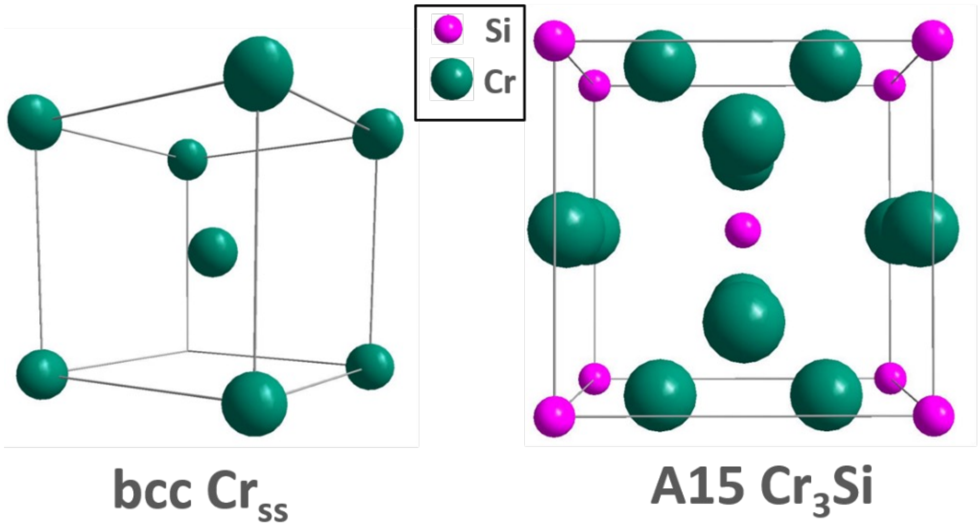
Approach 2: $Cr\text{-}Cr_3Si$

- Approach: Cr-based materials alloyed by silicon
- Cr_2O_3 scale for **oxidation/carburization resistance**, precipitation of hard intermetallic silicides for **erosion resistance**

$Cr_{ss} + Cr_3Si$



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

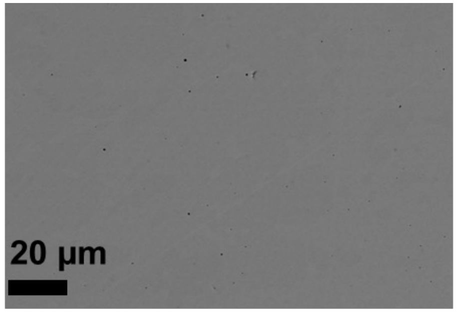


[A. S. Ulrich, PhD Thesis, University of Bayreuth, 2020]

- Two phase microstructure: toughening bcc Cr_{ss} + strengthening A15 Cr_3Si precipitates

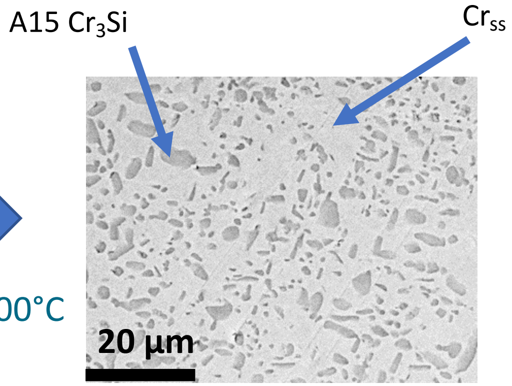
Material Selection for HEX Tubes: Cr_{ss}-Cr_3Si System

- Heat treatment 100 h @ 1200°C: diffusion controlled precipitation of Cr_3Si-phase

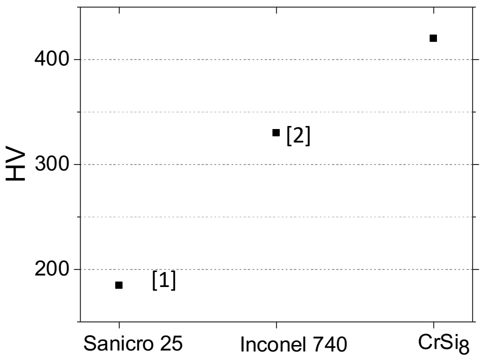


As cast: oversaturated single phase Cr_{SS}

100 h @ 1200°C

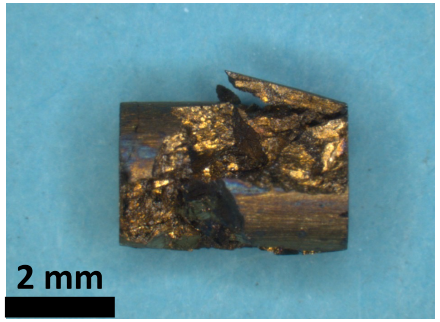


$Cr_{88}Si_8$: Two-phase microstructure Cr_{ss} + A15 Cr_3Si



HV of $Cr_{90}Si_8$ compared to conventional materials*

[1] https://www.materials.sandvik.com, January 2022
[2] https://www.azom.com, January 2022



Fracture pattern after compression test @ 700°C

- Increased hardness by precipitation hardening → promising for improved erosion behavior
- Brittleness and manufacturing main challenges → application as coatings

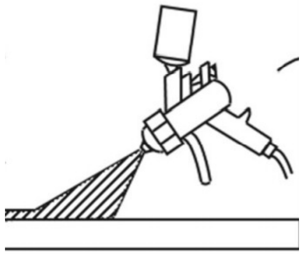
Source: COMPASsCO2

Process Chart of Cr-Si Slurry Coating

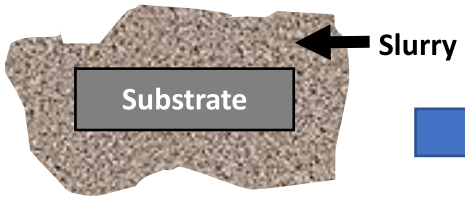
*Patent pending

- Newly developed coating process by the slurry technique for applying Cr-Si diffusion coatings

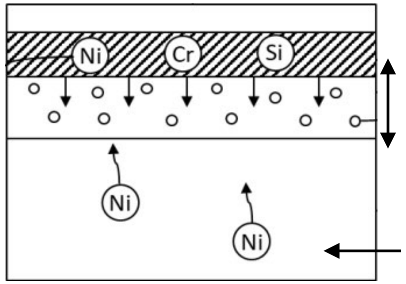
Slurry with particles + binder sprayed on substrate → Heat Treatment I - Removal of binder @ 350°C for 3 h → Heat Treatment II - Interdiffusion @ 1150-1200°C for 6 h → Enrichment of the substrate‘s surface by Cr-Si



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



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



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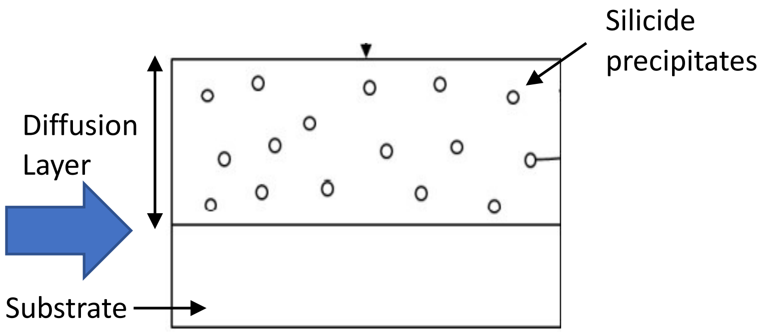


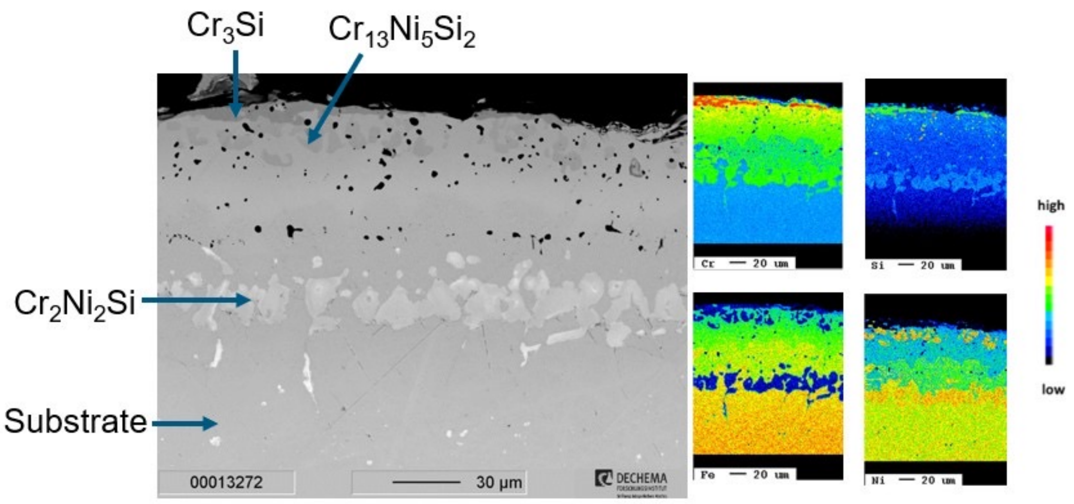
Source: COMPASsCO2

- Enrichment of Cr and Si in surface zone to specifically modify the properties

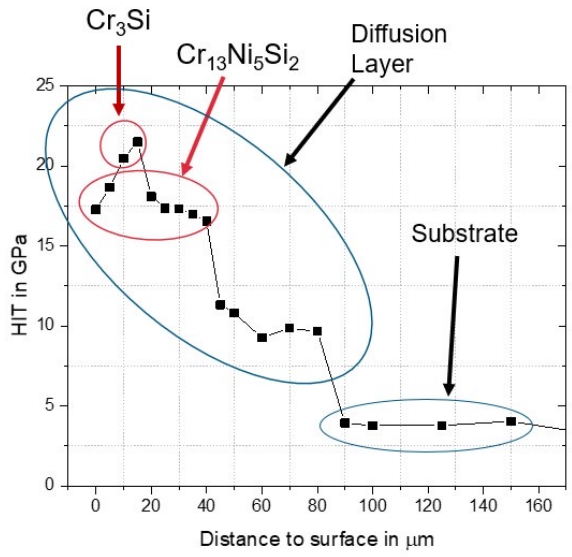
Cr-Si Coatings: Cross-sections

Austenitic steel: Sanicro 25

- Enrichment of Cr and Si in a layer of about 100 µm
- Diffusion layer: high increase of hardness compared to substrate

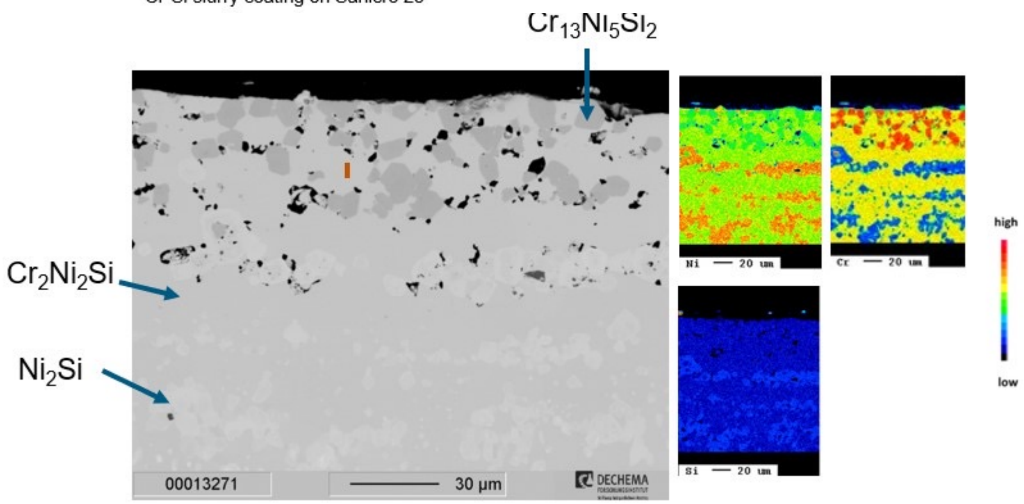


Cr-Si slurry coating on Sanicro 25



Ni-based alloy: Inconel 740

- Enrichment of Cr and Si in a layer of about 200 µm
- Diffusion layer: high increase of hardness compared to substrate



Cr-Si slurry coating on Inconel 740

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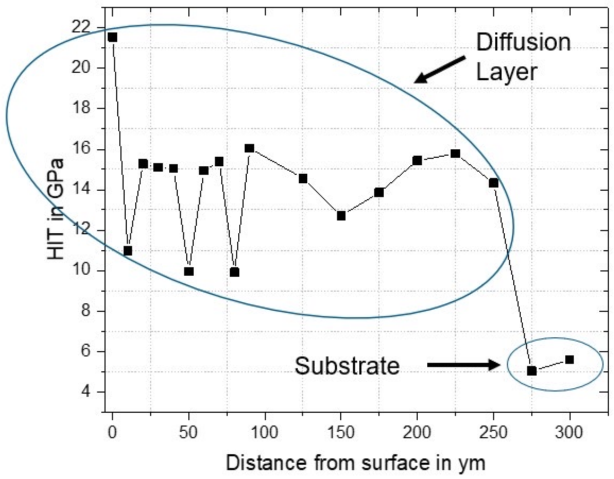

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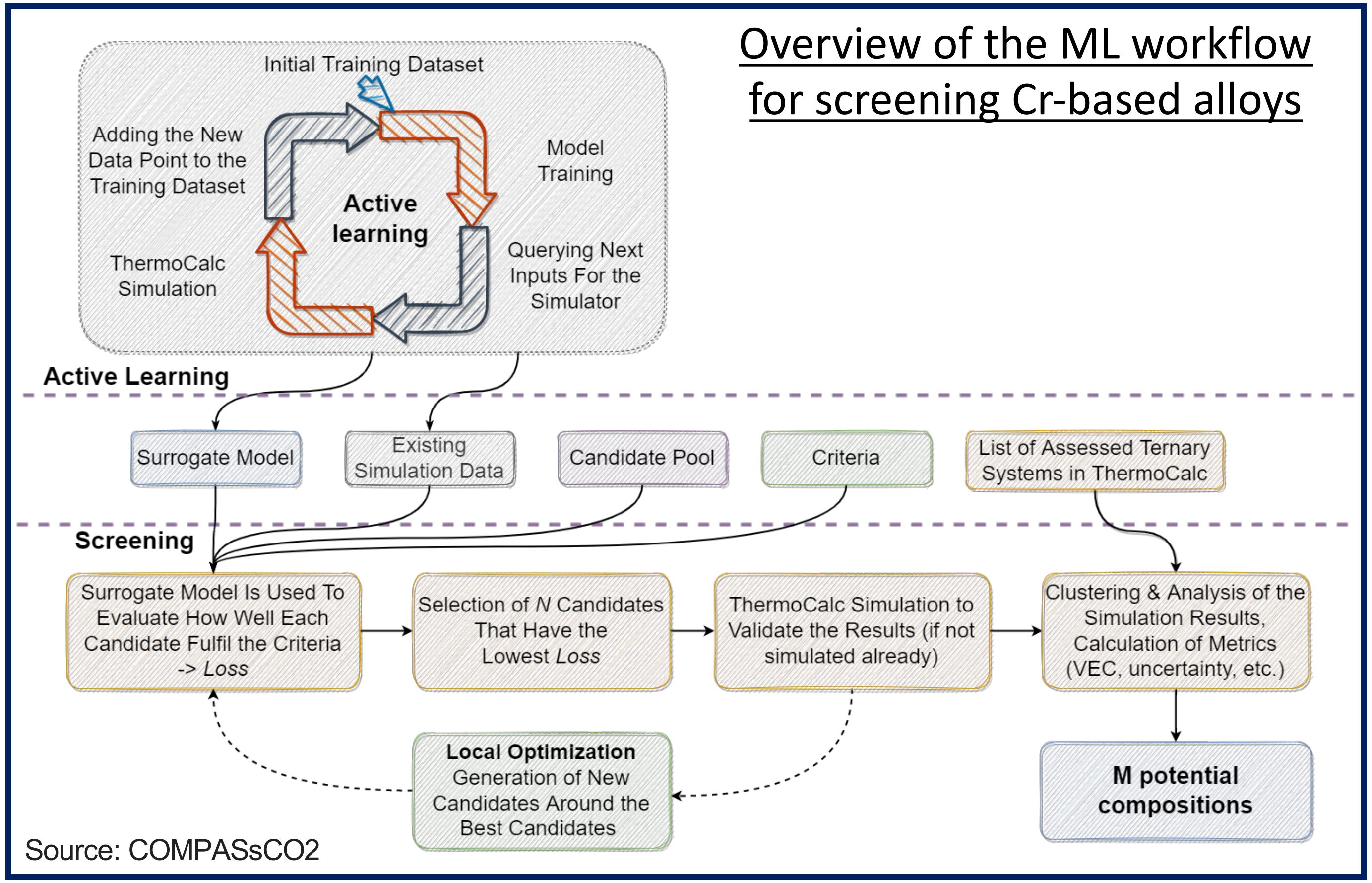
ML high-throughput screening of BCC Cr-alloys

- VTT have developed a machine learning (ML) tool for screening large composition spaces rapidly using computational thermodynamics accelerated to find suitable Cr-based alloys



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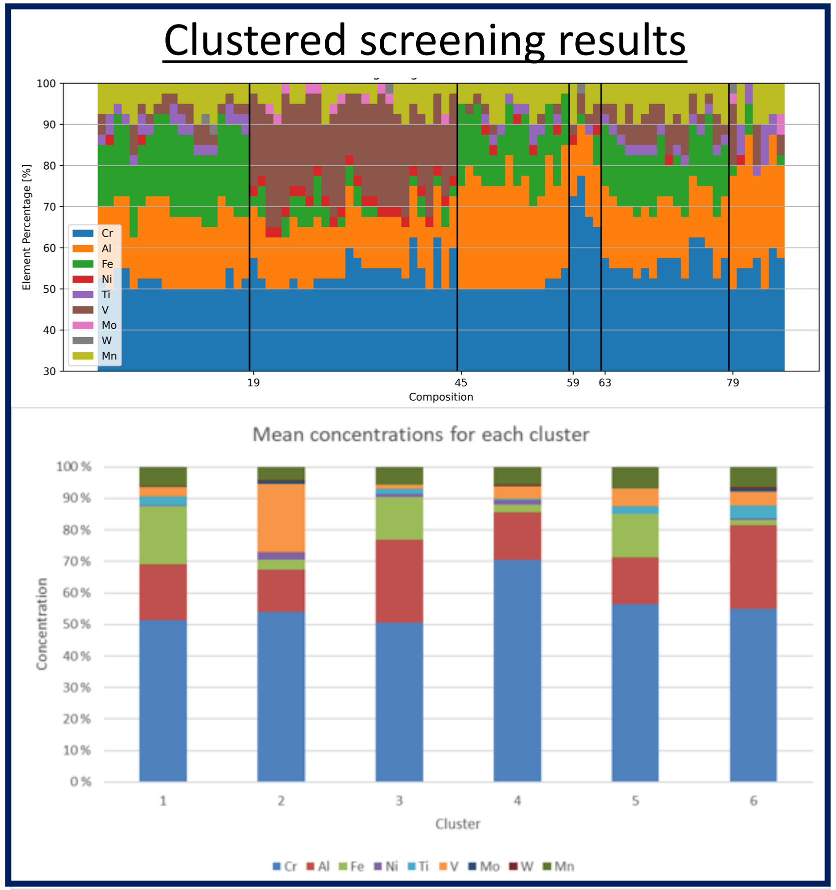

Conclusions and Perspectives

- State of the art materials identified and mechanically tested
- Cr-NiAl alloys have low coarsening rate & retain high temperature strength, even outperforming some Ni-superalloys
- Cr-Si pack-cementation slurry coating process proving successful, and provides a protective oxidation barrier on SOA Fe/Ni alloys

- Ongoing high throughput CALPHAD simulations by VTT, alloys being produced and tested at UoB
- Room temperature ductility of Cr continues to be addressed

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This project has received funding from the European Union's Horizon 2020 Research and Innovation Action (RIA) under grant agreement No. **958418.**

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