DECHEMA FORSCHUNGSINSTITUT

COMPASsCO_2

European Commission
HORIZON 2020

Chromium-Silicon Alloys with Fe and Ni for Structural High Temperature Applications

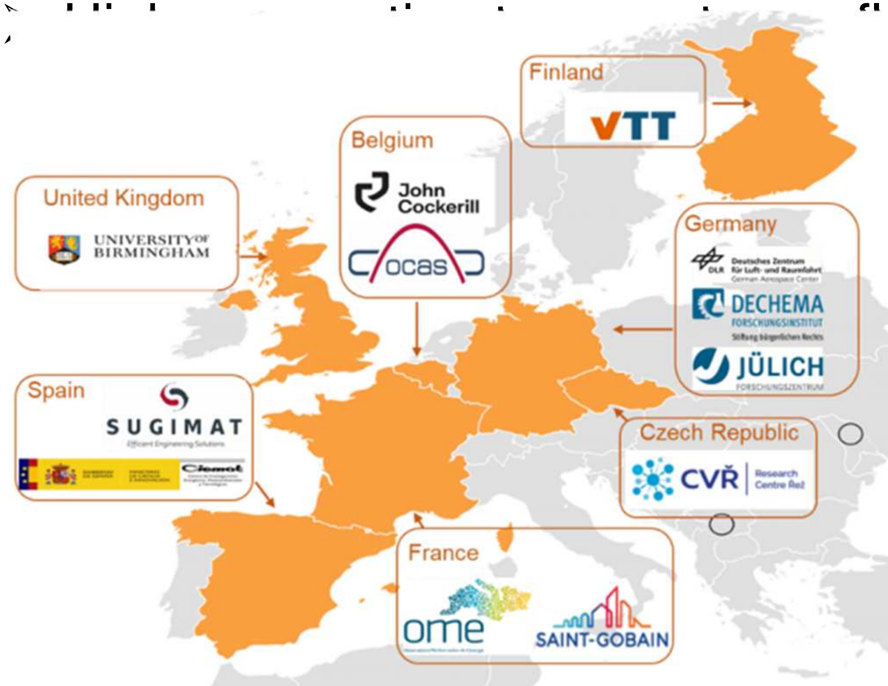
M. Kerbstadt, E. White, A. S. Ulrich, M. C. Galetz

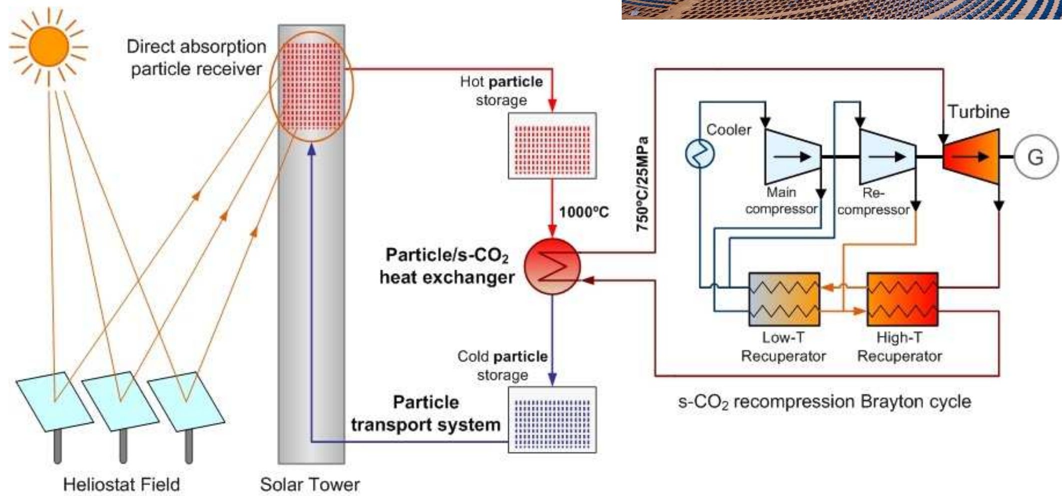
THIS PROJECT IS BEING FUNDED BY THE EUROPEAN UNION'S HORIZON 2020 RESEARCH AND INNOVATION PROGRAMME UNDER GRANT AGREEMENT NO 958418 COMPASsCO2

CompassCO2: Next Gen. Concentrated Solar Plants

- Difference to state-of-the-art: ceramic particles for heat storage and s-CO_2 as working medium in Brayton Cycle

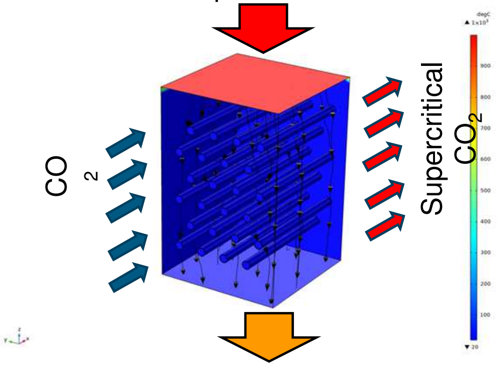
- flexible day and night use

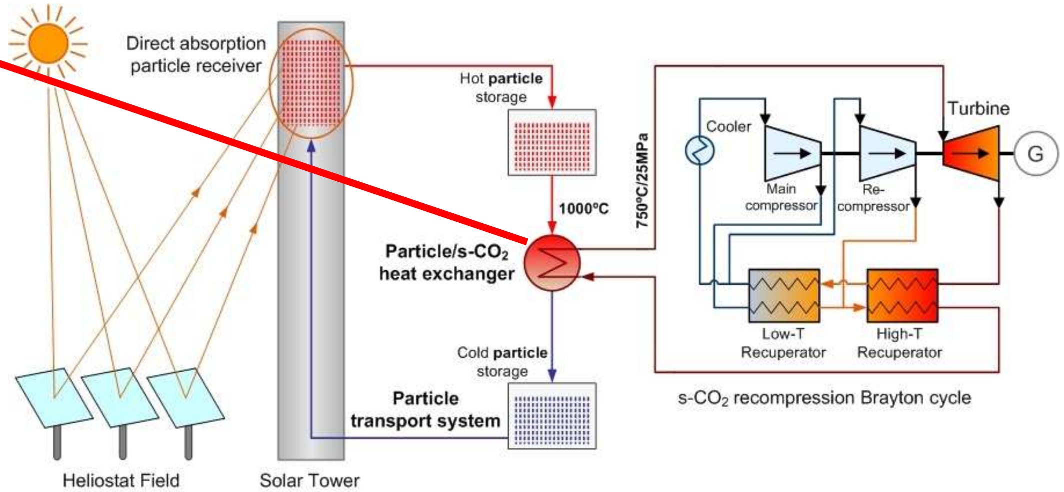




CompassCO2: Heat Exchanger

Heat exchanger (HX)





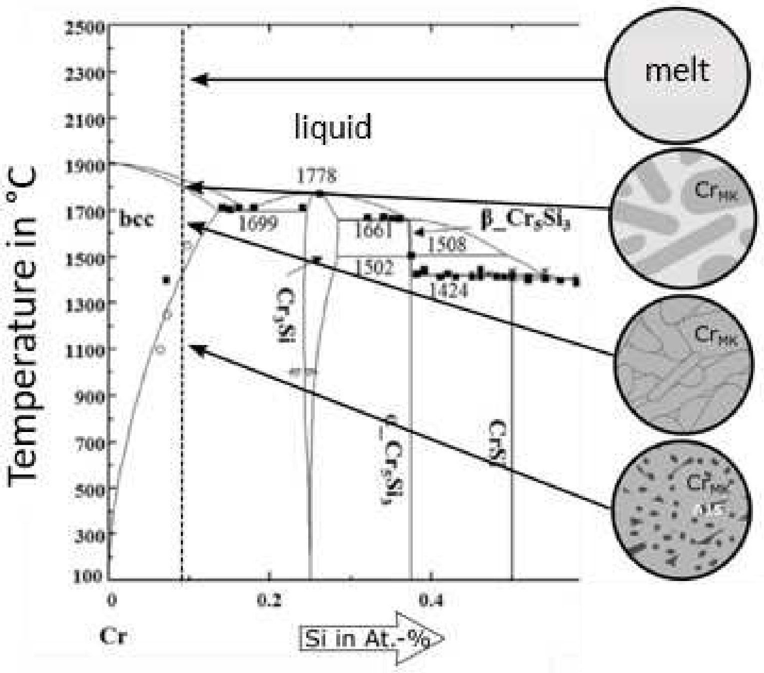
Challenges of structural materials of HX:

- **High temperature >700°C (strength)**
- **s-CO_2 environment (corrosion)**
- **Erosion due to particles (wear)**
- **High pressure ~20 MPa**

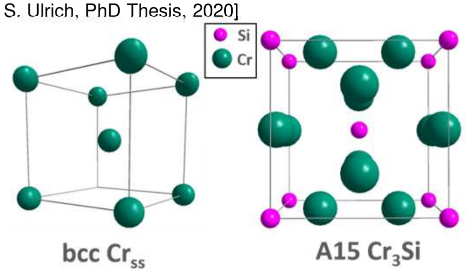
=> Cr-based materials

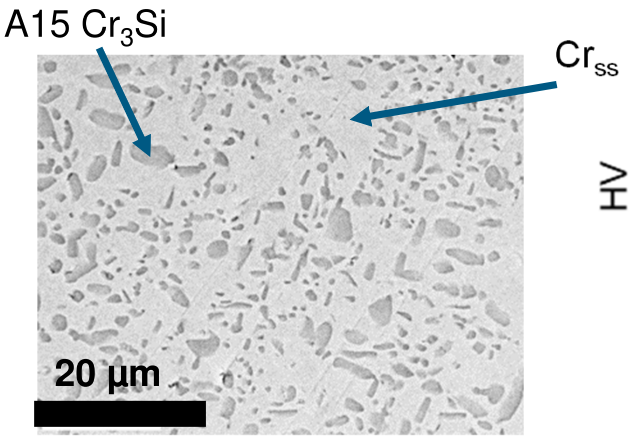
[www.compassco2.eu]

Candidate alloys: Heat Treatable Cr-Si Alloys



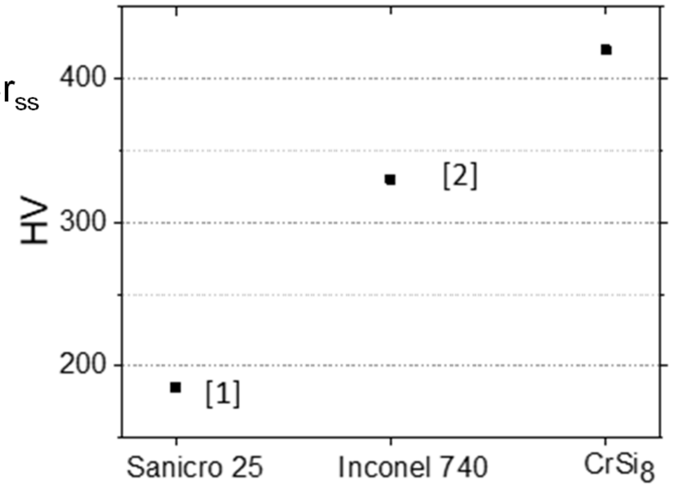
[A. S. Ulrich, PhD Thesis, 2020]





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

➢ 100 h @ 1200°C: Diffusion controlled precipitation of Cr_3Si-phase

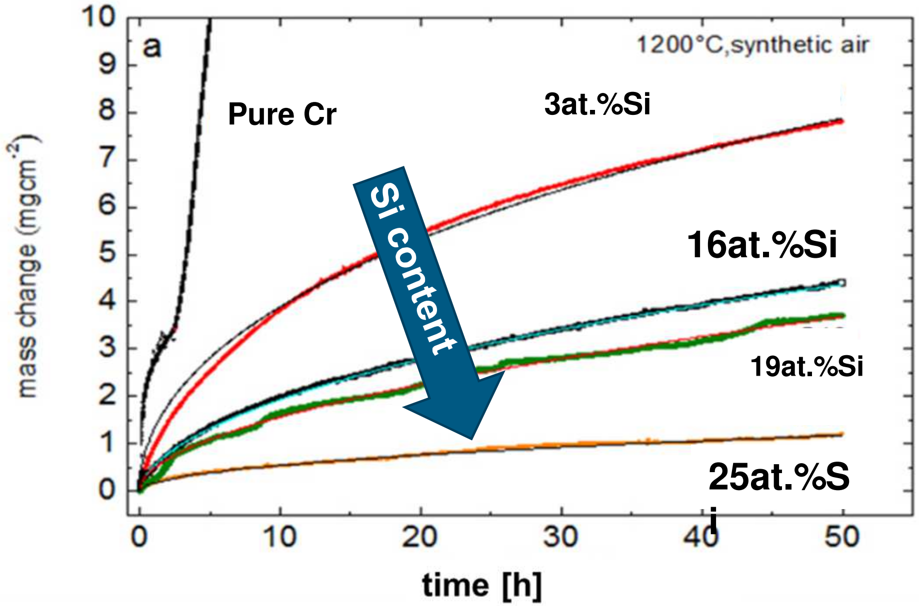


HV of $Cr_{90}Si_8$ compared to conventional materials*

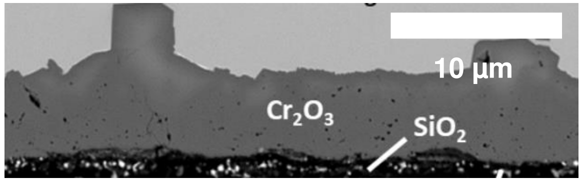
[1] https://www.materials.sandvik.com, January 2022
[2] https://www.azom.com, January 2022

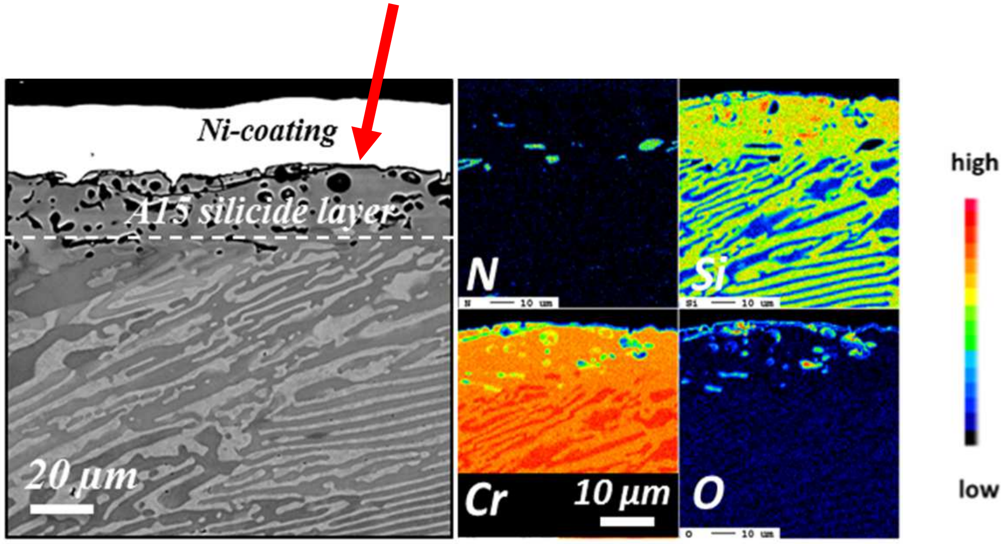
Cr-Si Alloys: Advantages

50h @ 1200°C, air



Si decreases oxidation rate but also ductility





$Cr_{84}Si_{16}$: Layered oxid scale + continous A15 Cr_3Si layer acts as a barrier to nitration

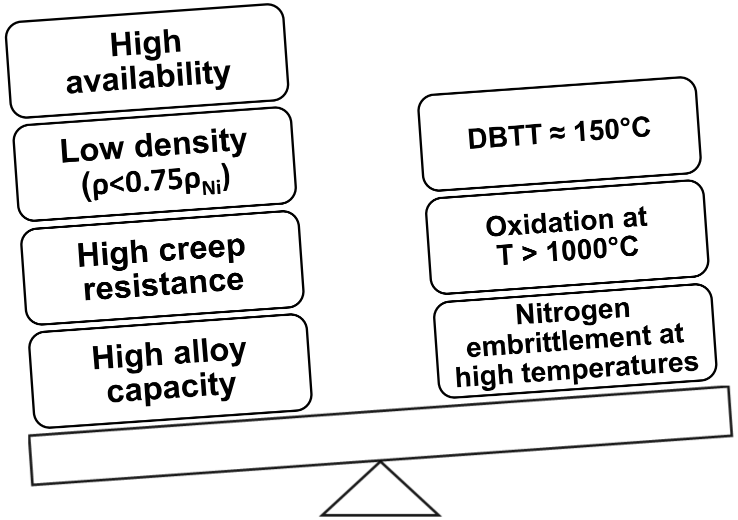
➢ Increasing amount of Si: improved oxidation and nitration resistance

A. Soleimani Dorcheh, W. Donner, M. C. Galetz, Materials and Corrosion, 2014

Cr-Based Alloys: Potentials and Challenges

DECHEMA FORSCHUNGSINSTITUT

Possibilities | ***Challenges***

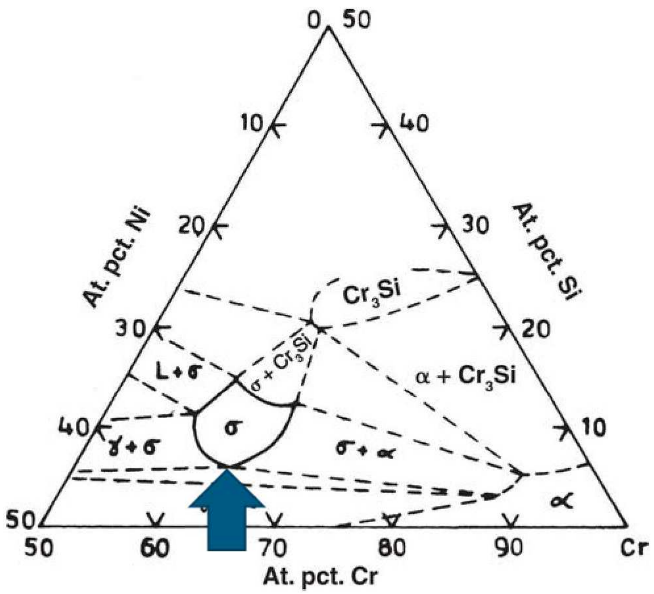


A. Soleimani Dorcheh, W. Donner, M. C. Galetz, Materials and Corrosion, 2014

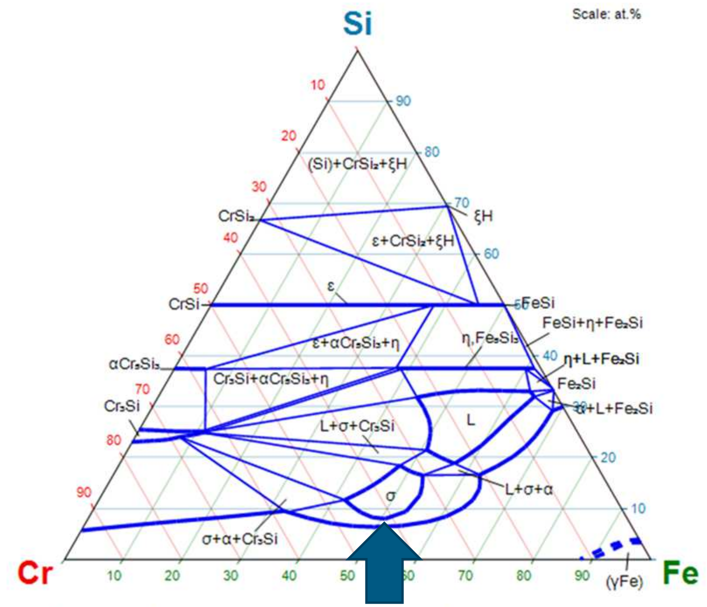
Alloying with Iron and Nickel

DECHEMA FORSCHUNGSINSTITUT

Sigma-formers (might) have a ductilizing effect? **Rhenium effect**



Cr-Si-Ni @ 1175°C, K.P. Gupta, Journal of Phase Equilibria and Diffusion Vol. 27 No. 5 2006

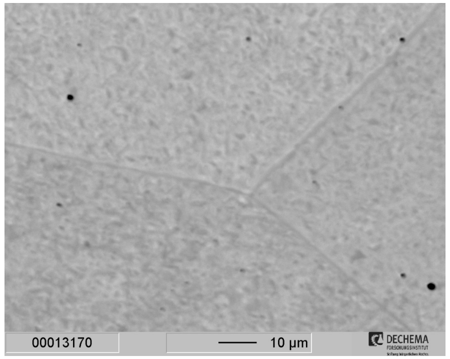


MSI Fig. 10: Calculated isothermal section at 1150°C

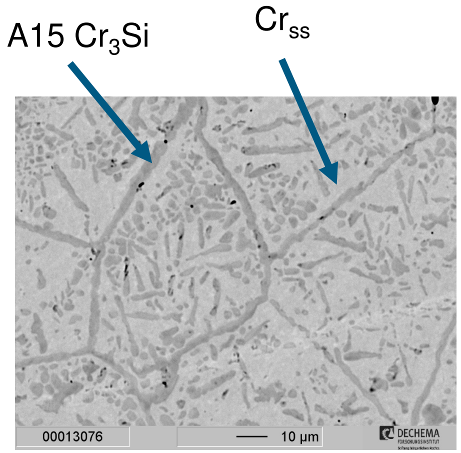
Cr-Si-Fe @ 1150°C, Materials Science International Team, MSIT ®1 , A. Watson et. al

*Klopp W.D., Review of Ductilizing of Group VIA Elements by Rhenium and Other Solutes. National Aeronautics and Space Administration, 1968 [1]
*Gilbert A., Allen B.C., Reid C.N., An investigation of mechanical properties of chromium, chromium-rhenium, and derived alloys; NASA CR-118, (1964) [2]
*Stephens J.R.; Klopp W.D., Ductility Mechanisms and Superplasticity in Chromium Alloys. National Aeronautics [3]

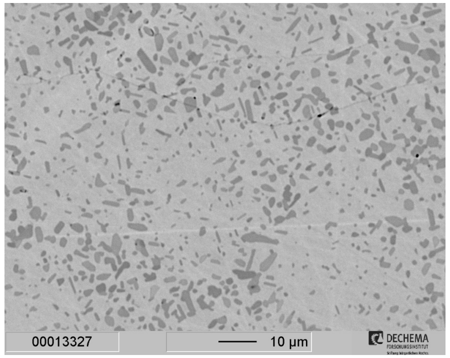
Alloying: Fe



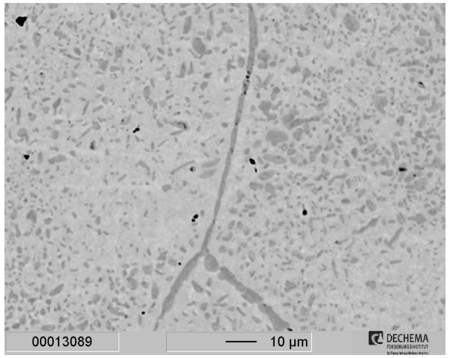
$Cr_{92}Si_8$



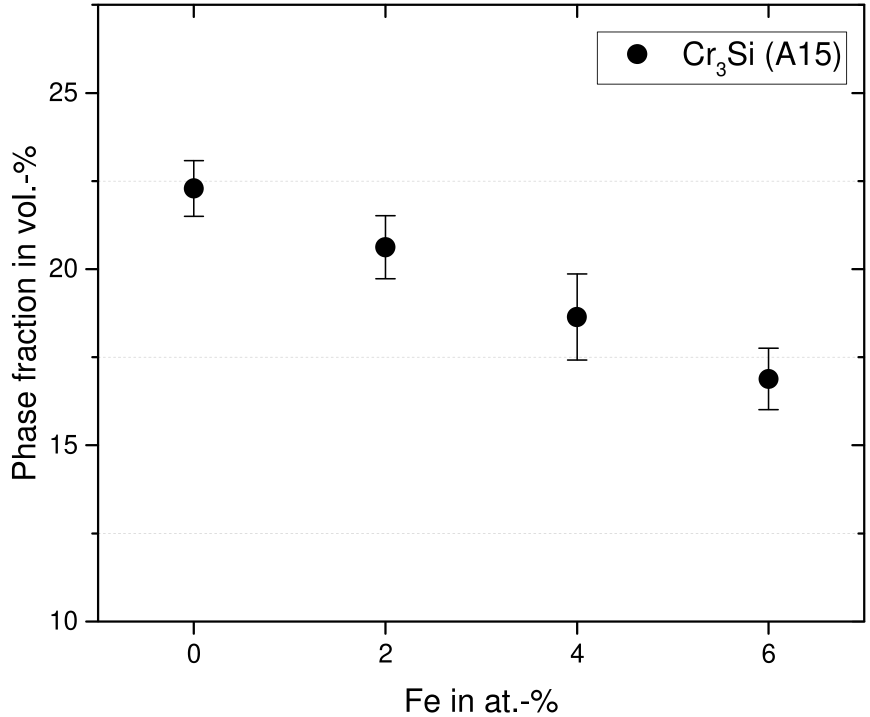
$Cr_{90}Si_8Fe_2$



$Cr_{88}Si_8Fe_4$



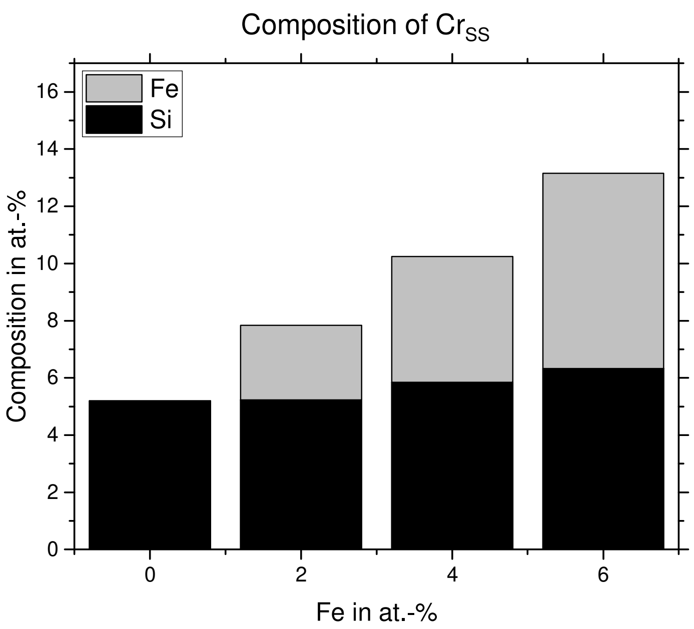
$Cr_{86}Si_8Fe_6$

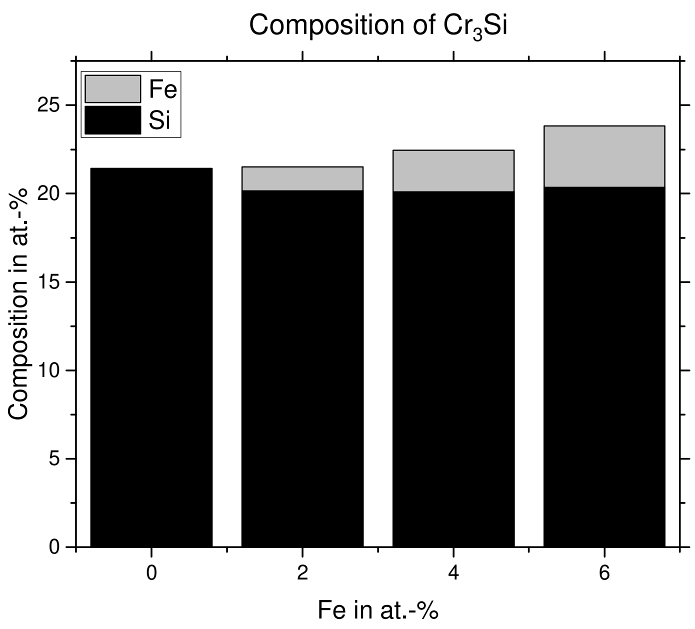


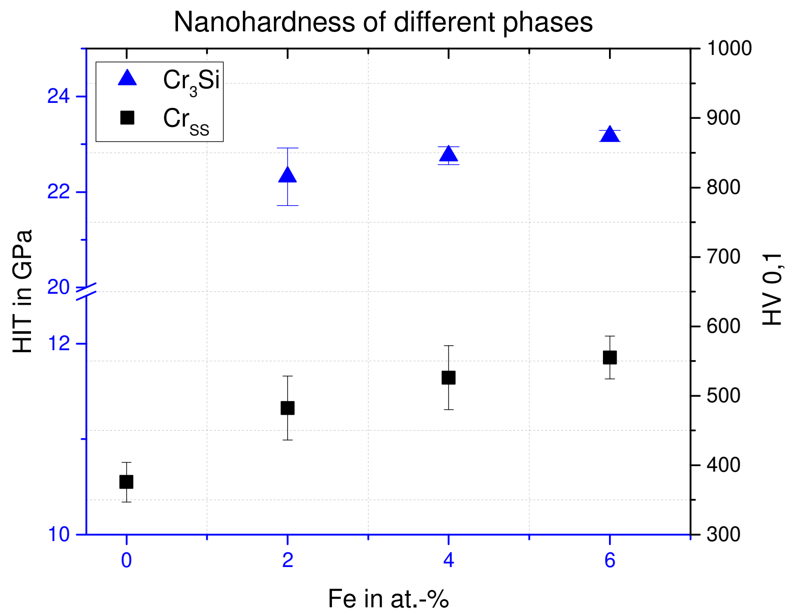
Cr_3Si fraction with of Fe amount

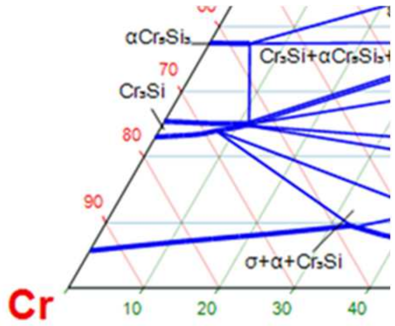
- Formation of desired two-phase microstructure
- Decreasing fraction of A15-precipitates with increasing amount of Fe

Cr-Si-Fe









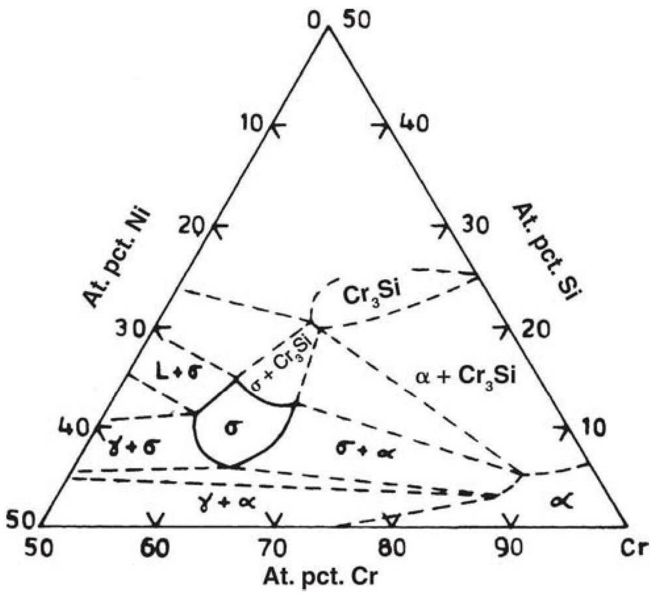
- ➢ Fe substitutes Cr in both phases, solubility of Si in Cr_{SS} increases with Fe, decreases in A15)
- ➢ **Hardness of both phases increases**

Alloying with Iron and Nickel

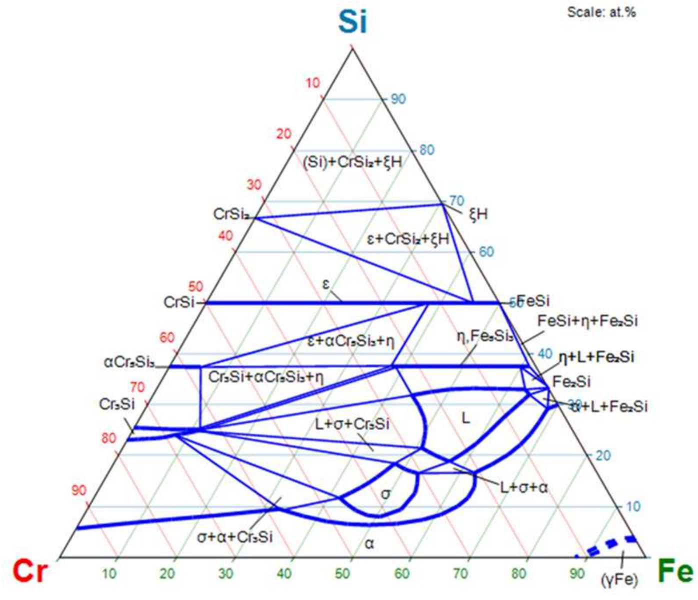
DECHEMA FORSCHUNGSINSTITUT

Fe and **Ni**

→Systems interesting for development of Cr/Si diffusion coatings on Fe-/Ni-based substrates



Cr-Si-Ni @ 1175°C, K.P. Gupta, Journal of Phase Equilibria and Diffusion Vol. 27 No. 5 2006



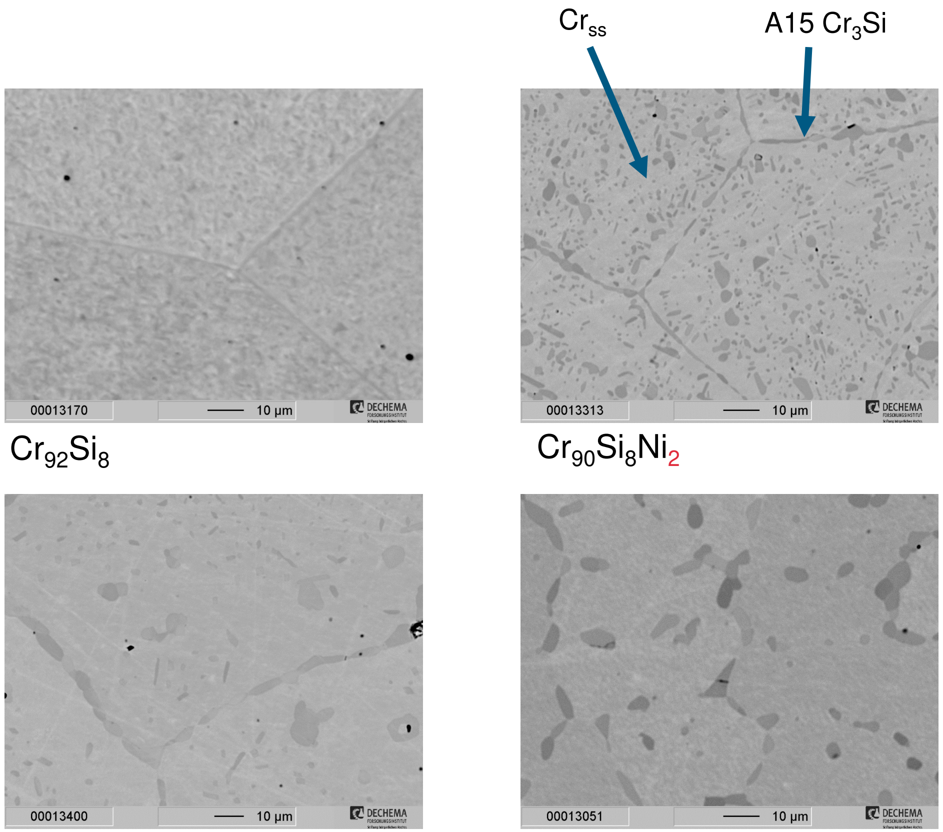
MSI Fig. 10: Calculated isothermal section at 1150°C

Cr-Si-Fe @ 1150°C, Materials Science International Team, MSIT ®1 , A. Watson et. al

Sigma-formers migh have a ductilizing effect (Rhenium effect)

*Klopp W.D., Review of Ductilizing of Group VIA Elements by Rhenium and Other Solutes. National Aeronautics and Space Administration, 1968 [1]
*Gilbert A., Allen B.C., Reid C.N., An investigation of mechanical properties of chromium, chromium-rhenium, and derived alloys; NASA CR-118, (1964) [2]
*Stephens J.R.; Klopp W.D., Ductility Mechanisms and Superplasticity in Chromium Alloys. National Aeronautics [3]

Alloying Ni

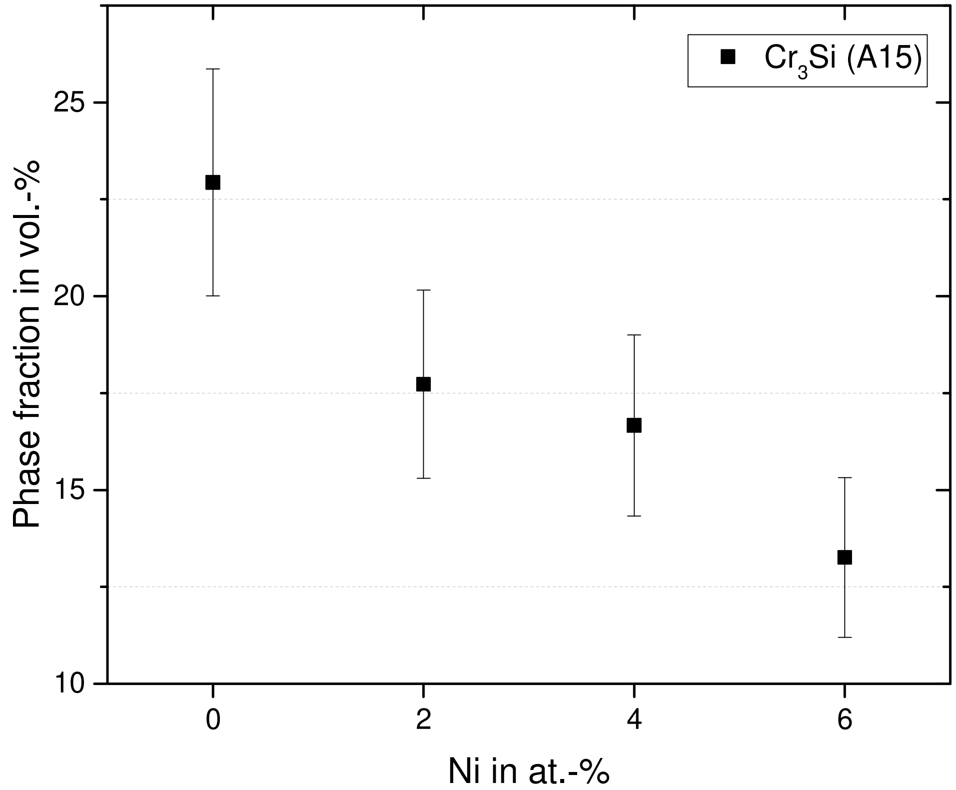


$Cr_{92}Si_8$

$Cr_{90}Si_8Ni_2$

$Cr_{88}Si_8Ni_4$

$Cr_{86}Si_8Ni_6$

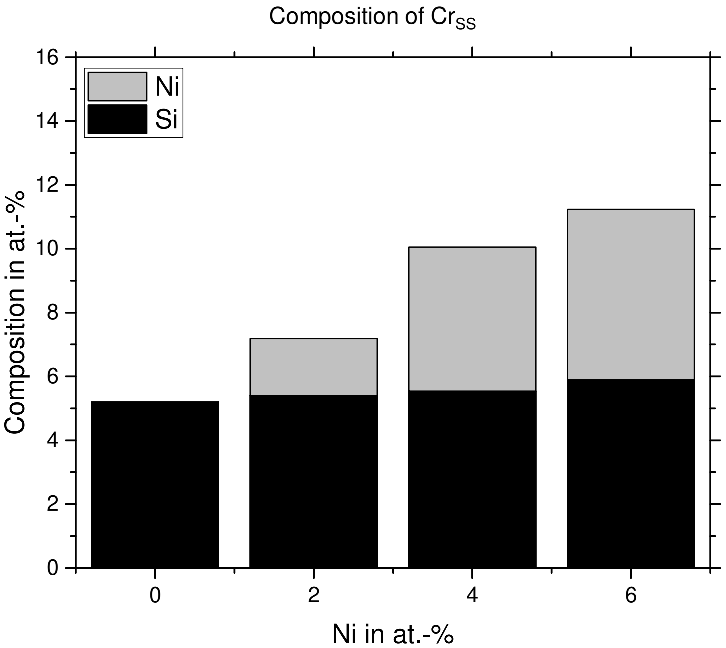


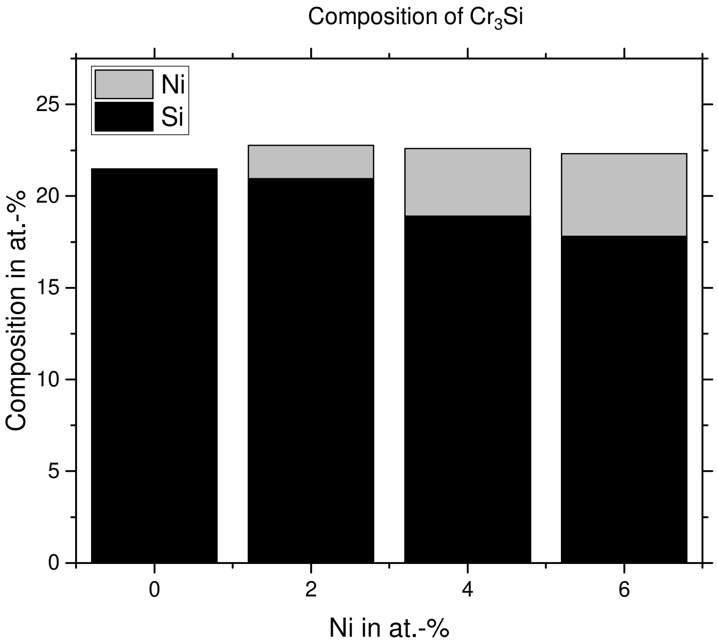
Cr_3Si fraction in dependence of Ni amount

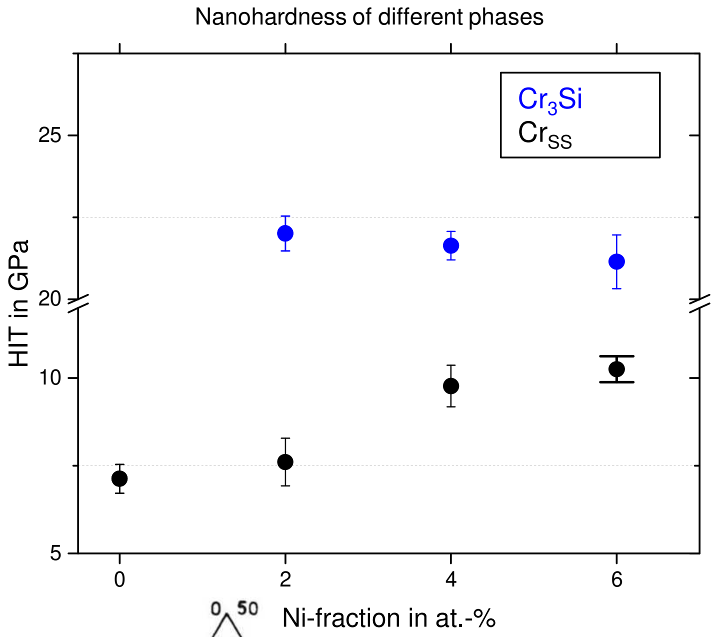
- Formation of the desired two-phase microstructure
- Decreasing fraction of A15 with increased amount of Ni

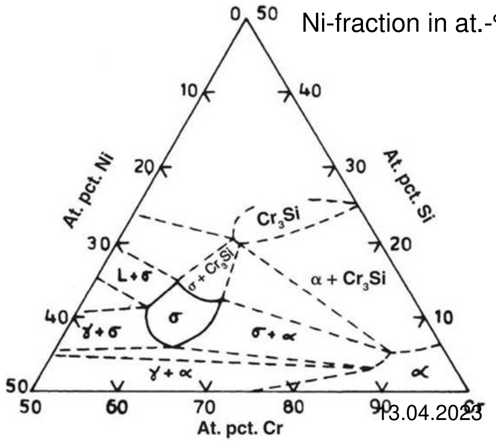
Cr-Si-Ni: Phase Analysis

DECHEMA FORSCHUNGSINSTITUT





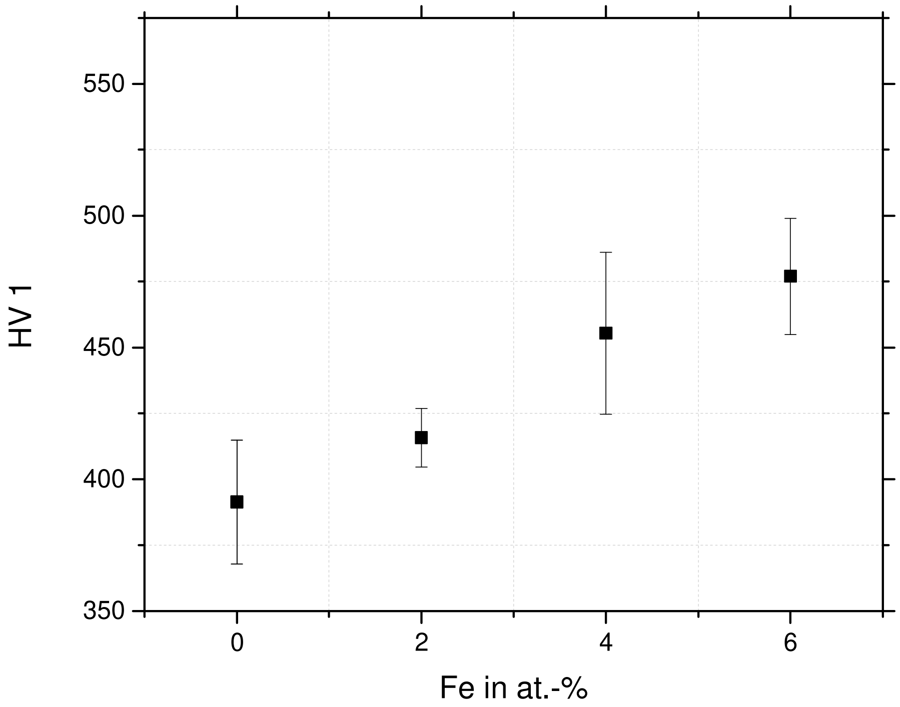




- Ni changes stichometry in Cr_3Si (Ni might substitute Si and Cr)
- **Hardness of Cr_3Si decreases with Ni and of Cr_{SS} increases**

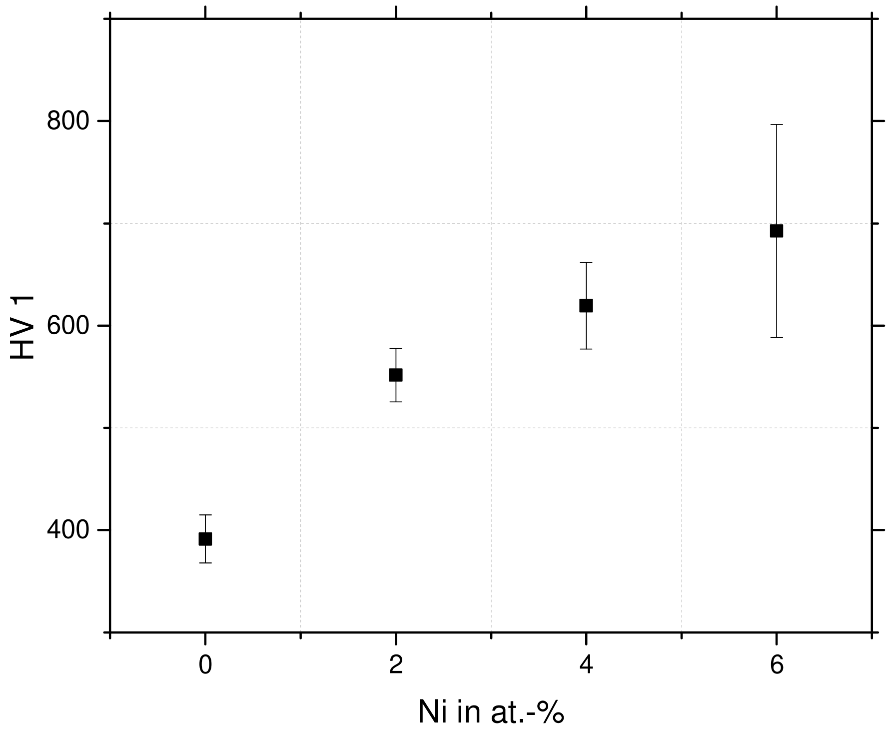
Microhardness

Cr-Fe-Si



- Microhardness increased by 28%

Cr-Si-Ni



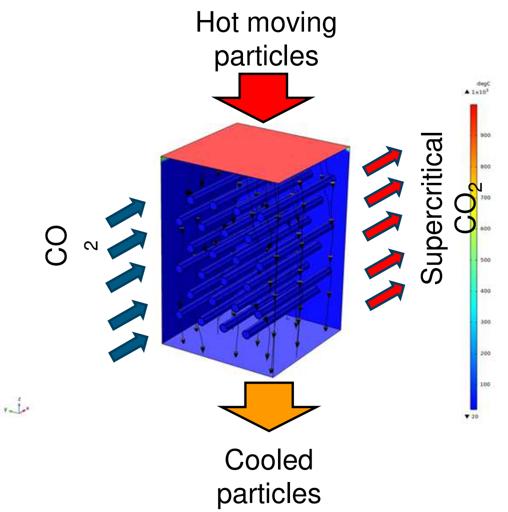
- Microhardness increased by 75%

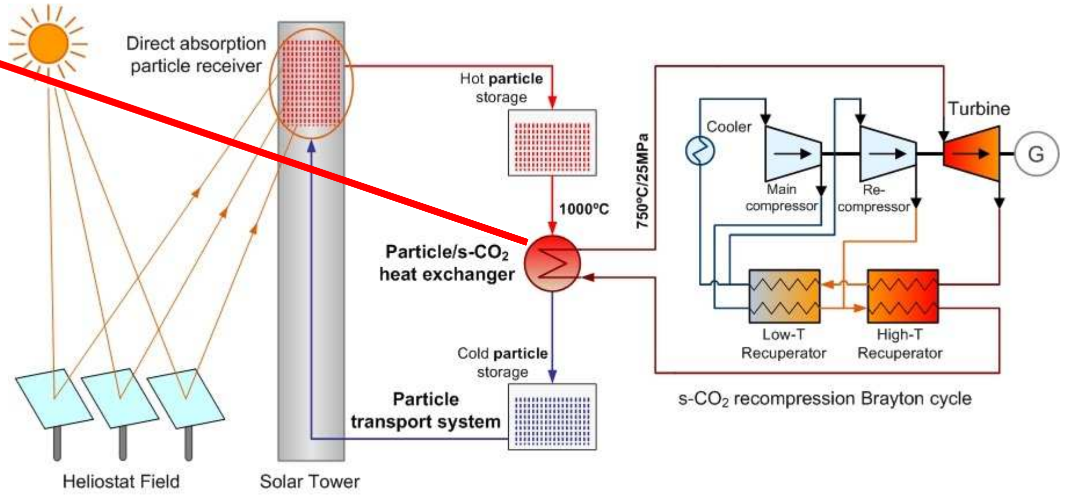
-> Ni much stronger Cr(ss)-hardener

CompassCO2: Heat Exchanger

DECHEMA FORSCHUNGSINSTITUT

Heat exchanger (HX)





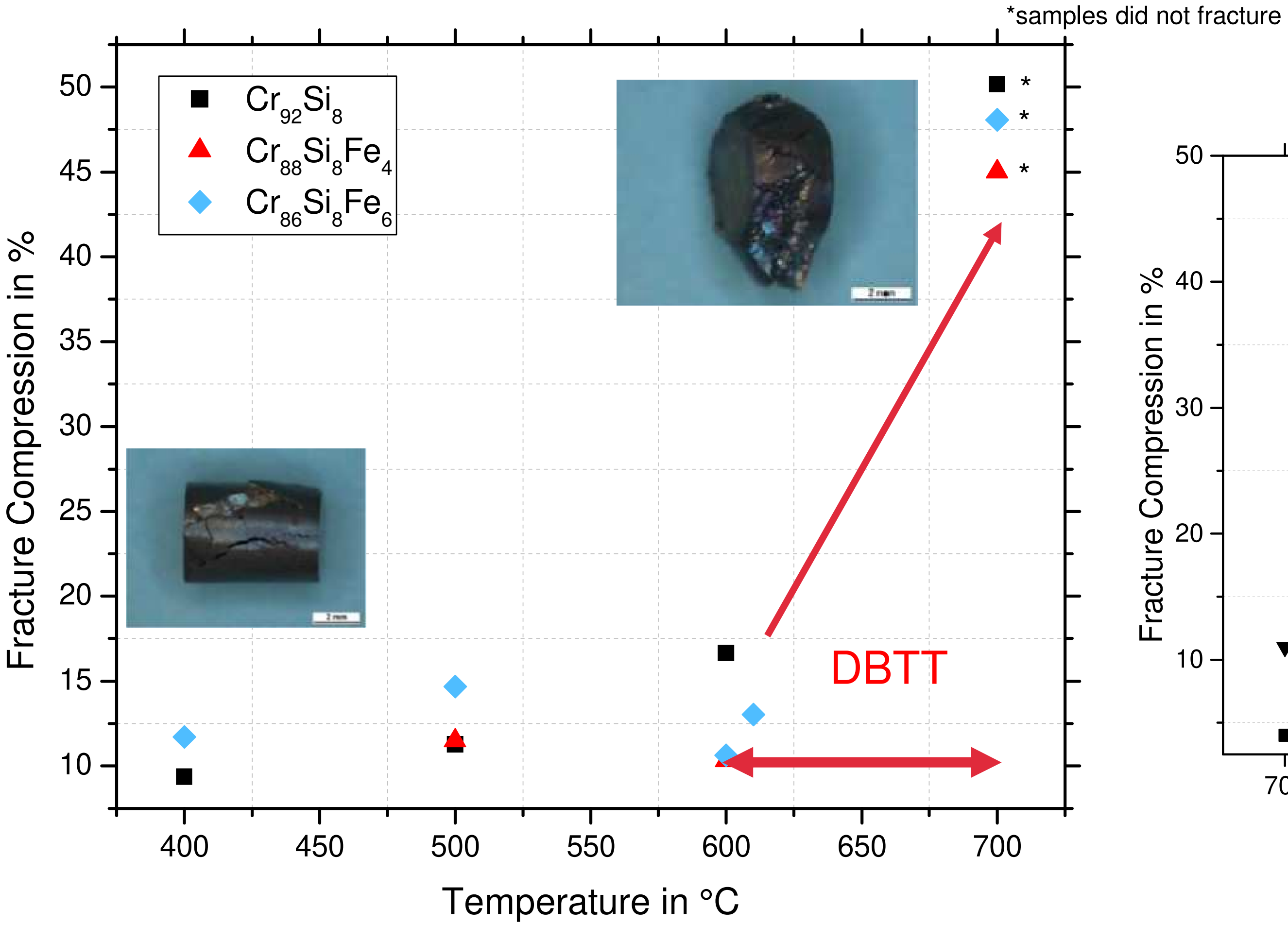
[www.compassco2.eu]

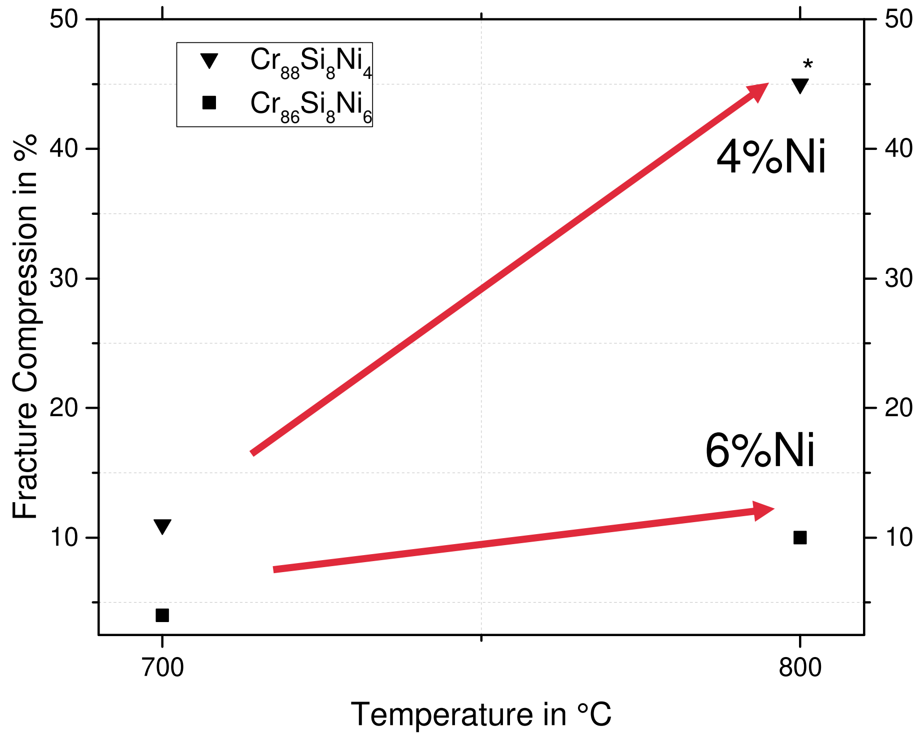
Challenges of structural materials of HX:

- **High temperature >700°C (strength)**
- **s-CO_2 environment (corrosion)**
- **Erosion due to particles (wear)**
- **High pressure ~20 MPa**

=> Cr-based materials

Cr-Si-Fe: DBTT by Compression Tests

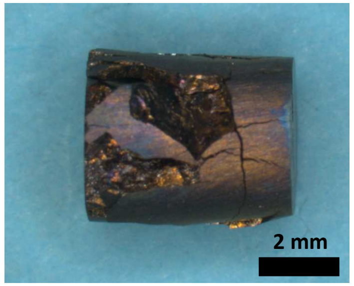




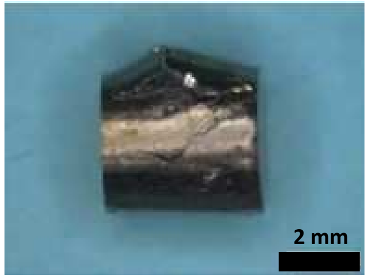
➢ DBTT tested alloys with and without Fe between 600 and 700°C, > 4% Ni increases DBTT

Challenge: Ductile to Brittle Transition Temperature

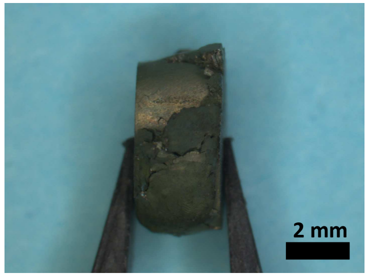
- DBTT was determined by compression tests at different temperatures



Fracture pattern for $Cr_{92}Si_8$ after compression test @ 500°C



Fracture pattern for $Cr_{92}Si_8$ after compression test @ 600°C



Fracture pattern for $Cr_{92}Si_8$ after compression test @ 700°C

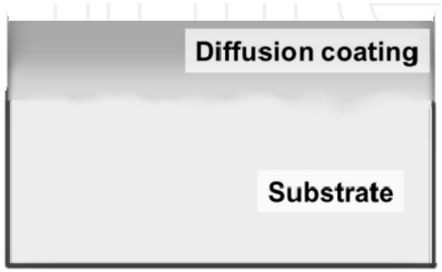
- Up to temperatures to 700°C very limited deformation → DBTT between 600°C and 700°C; no improvements by alloying with Fe and Ni

Coatings

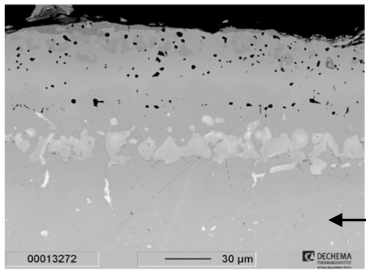
	Fe	Ni
Fraction of Cr_3Si	22 % ↓	41% ↓
Microhardness	28 % ↑	75% ↑
DBTT	→	↑

→ "Make or break" criteria for structural applications → Development of Cr-Si coatings on state of the art materials as substrates

→Development of Cr/Si diffusion coatings on Fe and Ni-base materials



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



Cr/Si diffusion layer with Cr_3Si precipitates

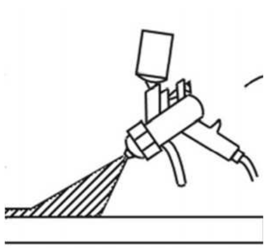
Ni-base alloy

Cr-Si Slurry Coating

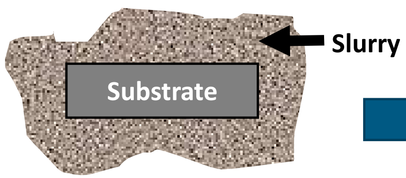
*Patent applied

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

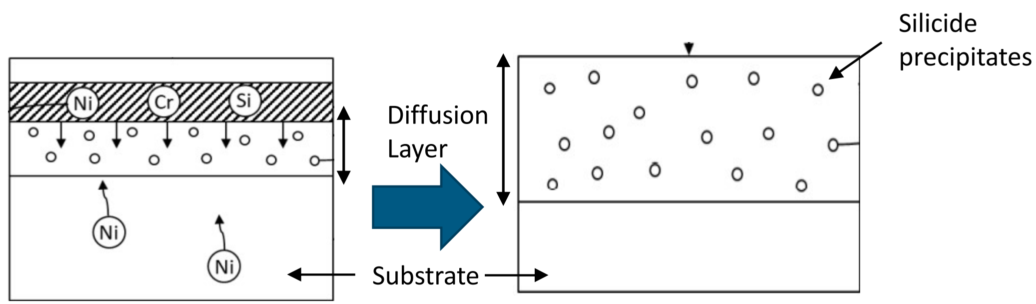
Slurry with particles + binder sprayed on substrate → Heat Treatment I - Removal of binder @ 350°C for 3 h → Heat Treatment II - Interdiffusion @ 1150-1200°C for 6 h → Enrichment of the substrate‘s surface by Cr-Si



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



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

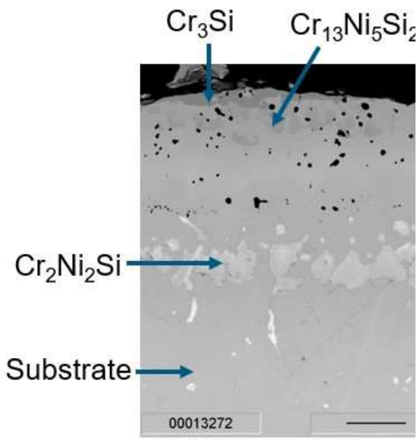


- Enrichment of Cr and Si in surface zone to specifically modify the properties

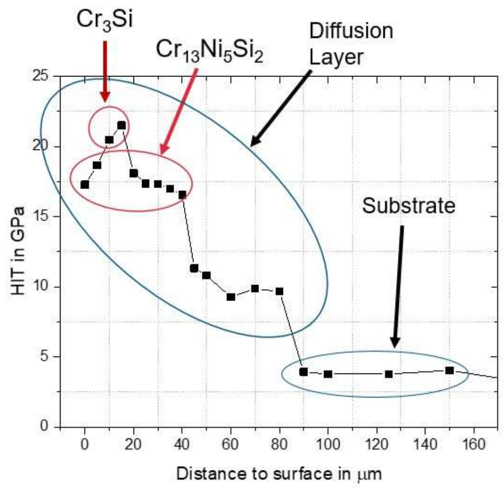
Cr-Si Coatings: Cross-sections

<u>Austenitic steel</u>: Sanicro 25

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

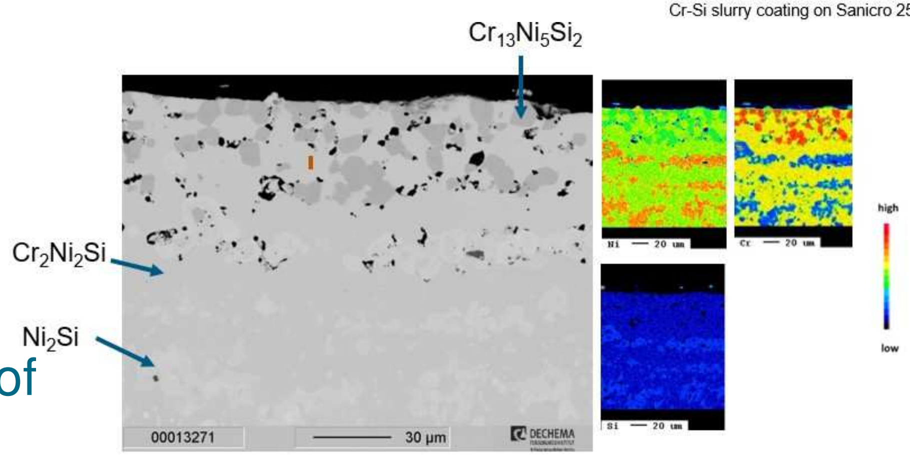


Cr-Si slurry coating on Sanicro 25

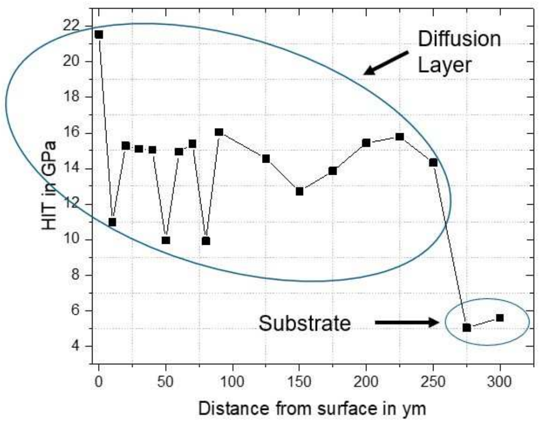


<u>Ni-based alloy</u>: Inconel 740

- 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

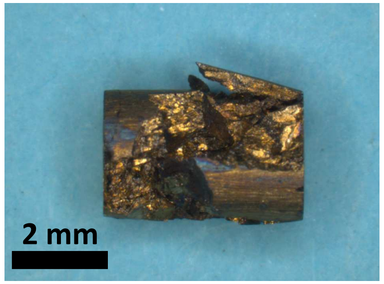


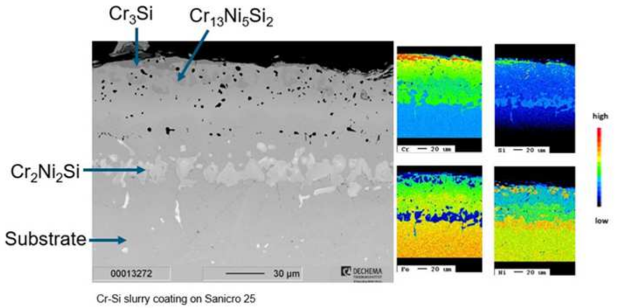
Conclusions and next steps

DECHEMA FORSCHUNGSINSTITUT

- Cr-Si alloys show high potential for high temperature applications

- Mechanical properties and in particular DBTT remains „make or break“ criteria for structural applications





- ***CSP-application: Use Cr-Si in the form of diffusion coatings on state-of-the-art materials: Novel slurry process successfully developed***
- Next Step: Testing of coatings in CSP heat exchanger environment

COMPASSCO2 project website
https://www.compassco2.eu