COMPONENTS' AND MATERIALS' PERFORMANCE FOR ADVANCED SOLAR SUPERCRITICAL CO2 POWERPLANTS

# Production of optimised steel / Ni substrates with advanced Cr aluminide/silicide coatings, coupons for WP4

**Deliverable Number: 3.3**

**WP3:** Development of metals

**Date**: June 2nd, 2023

**Deliverable type**: Report

**Dissemination level**: Public

**Lead participant**: OCAS

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

## AUTHORS


| Name | Organization |
|---|---|
| Krista Van den bergh | OCAS |
| Michael Kerbstadt, Ceyhun Oskay, Emma White, Mathias Galetz | DFI |
| Kan Ma, Thomas Blackburn, Sandy Knowles | UoB |


## DOCUMENT HISTORY

| Version | Date | Change |
|---|---|---|
| 01 | April 30, 2023 | Initial version uploaded |
| | | |

## ABOUT THE PROJECT

COMPASsCO$_2$ is a 4-year HORIZON2020 project started on 1.11.2020. It is led by the German Aerospace Center (DLR), with eleven additional partners from seven European countries.

COMPASsCO$_2$ aims to integrate CSP particle systems into highly efficient s-CO$_2$ Brayton power cycles for electricity production. In COMPASsCO2, the key component for such an integration, i.e. the particle/s-CO$_2$ heat exchanger, will be validated in a relevant environment. To reach this goal, the consortium will produce tailored particle and alloy combinations that meet the extreme operating conditions in terms of temperature, pressure, abrasion and hot oxidation/carburization of the heat exchanger tubes and the particles moving around/across them. The proposed innovative CSP s-CO$_2$ Brayton cycle plants will be flexible, highly efficient, economic and 100% carbon neutral large-scale electricity producers.

The research focus of COMPASsCO2 is on three main technological improvements: development of new particles, development of new metal alloys and development of the heat exchanger section.

## DISCLAIMER

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

# TABLE OF CONTENTS

# LIST OF FIGURES



# LIST OF TABLES



# LIST OF ABBREVIATIONS

| | |
|---|---|
| COMPASsCO2 | Components' and Materials' Performance for Advanced Solar Supercritical CO2 Power Plants |
| Cr | Chromium |
| Cr-Si | Chromium Silicon |
| CSP | Concentrating Solar Power |
| EC | European Commission |
| EPMA | Electron probe microanalysis |
| EU | European Union |
| RHEA | refractory high-entropy alloys |
| $sCO_2$ | Supercritical Carbon Dioxide |
| SEM | Scanning electron microscopy |
| Si | Silicon |
| XRD | X-ray diffraction |
| | |

# 1 ABSTRACT

Work package 3 (WP3) focuses on the development of novel Cr-based alloys, Cr-NiAl and Cr-$Cr_3Si$ alloys, to obtain enhanced strength, erosion resistance, oxidation and corrosion resistance of metals and alloys for high-temperature environments. WP3 also investigates the possibility to turn the new alloys into diffusion coating on the state-of-the-art nickel superalloys and advanced austenitic steels.

For the targeted Cr-Si-based diffusion coatings, pack cementation is the current state-of-the-art application process. Within the work of Deliverable 3.3 a new coating process was developed which utilizes a slurry technique to obtain a Cr-Si diffusion coating. This new process has the high potential to be both economically more viable and to meet the technical requirements for wear and oxidation-resistant coating for heat exchanger tubes of a concentrated solar power (CSP) plant with solid particles as heat collecting medium and supercritical $CO_2$ on the power cycle. To apply the coating the aqueous slurry, which contains metallic Cr-Si particles, is deposited on the substrate surface. Afterwards, a heat treatment is carried out during which the coating forms by interdiffusion between the metallic particles from the slurry and the metal substrate. For sufficient diffusion rates to form a dense coating layer, the existence of a liquid phase is essential during the heat treatment. Cr-Si slurry coatings were successfully demonstrated for the preselected materials Sanicro 25, Inconel 617 and P92 from Work Package 1. For these, an enrichment of Cr and Si within a diffusion layer of a thickness > 50 µm could be achieved. Also, intermetallic Cr-Si-rich precipitates were observed within the layer, which led to an increased hardness when compared to the substrate materials. This was proven by microhardness measurements (HV 25) and is promising for improved resistance to the harsh heat exchanger environment. Cr-Si slurry-coated state-of-the-art coupons have been produced and delivered to WP4 for further environmental testing.

For the targeted Cr-NiAl-based bulk alloys, the new alloys show high exceptional stability of the matrix-precipitate microstructure at 1000/1200°C and high yield strength (~ 320 MPa) at 1000 °C. Cr-NiAl bulk alloy coupons are in the preparation stage for delivery to WP4 in June.

# 2 DEVELOPMENT OF CR-SI SLURRY COATINGS

## 2.1 DEVELOPMENT PROCESS OF THE COATINGS

The target of task 3.3 was to apply Cr-Si-based coatings on some of the preselected state-of-the-art heat exchanger materials identified within WP1.

The purpose of the coating was to enrich Cr and Si in the surface area to improve the properties of the substrate materials to better withstand the harsh heat exchanger environment. It was desired to develop a process which can be economically viable and also meets the technical requirements for a concentrated solar power plant in terms of properties and geometries. For CSP plants with solid particles as heat collecting medium operating at 900 °C and supercritical CO2 on the power cycle at 250 Bar pressure the heat exchanger tubes are the component which needs the greatest improvement in properties and thus where a coating could be most beneficial. Therefore, the approach was to develop a new coating process using a slurry technique in contrast to the state-of-the-art pack cementation process used for typical Cr-based diffusion coatings. For pack cementation the parts/substrates are usually fully embedded into a powder mixture which is energy- and labor-intensive, requiring large furnaces with extensive fixturing to be heated up to high temperatures in order for the diffusion process to occur. Alternatively, slurry-based coatings do not require embedding into and heating of a big powder bed, nor such large furnaces (as more localized heat treatments can be used), and are thus a much more economical option, especially for the dimensions of the targeted heat exchanger tubes. The desired elements for a slurry coating are in the form of metallic powders and are mixed with a binder to form a slurry. Then the slurry is deposited on the material surface by dipping, brushing or spraying. The diffusion coating is then formed during a subsequent heat treatment by interdiffusion between the metallic particles from the slurry and the substrate. For sufficient diffusion rates during the heat treatment, the existence of a liquid phase at the interface of the substrate surface and the slurry particles is necessary. The general process is shown in Figure 1.

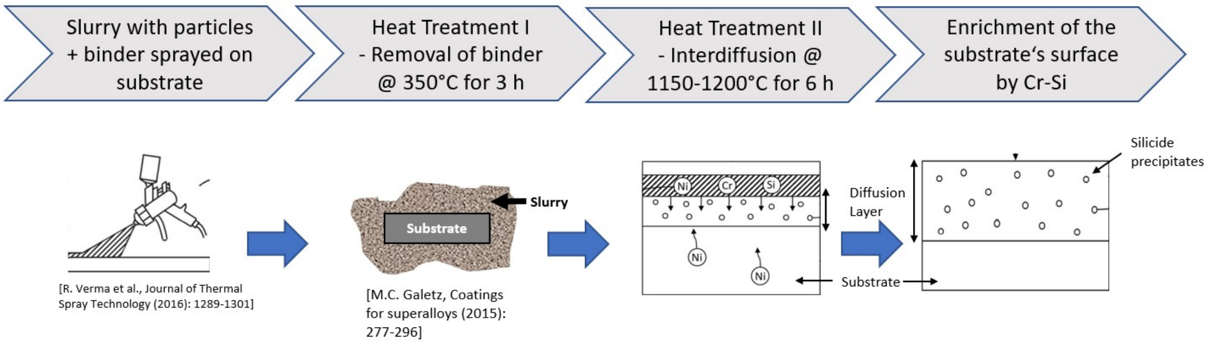


*Figure 1. Process chart of the newly developed Cr-Si slurry coating process.*

The main challenge of the process for a Cr-Si slurry is that the existence of a liquid phase during the heat treatment is highly necessary in order to achieve a dense coating. Because the lowest melting phase in the Cr-Si system melts at above 1300°C, alloying with a third element was required to get a sufficiently low melting phase. Therefore, the main challenge during the development process was to determine the right slurry composition and heat treatment parameters to obtain a dense diffusion layer.

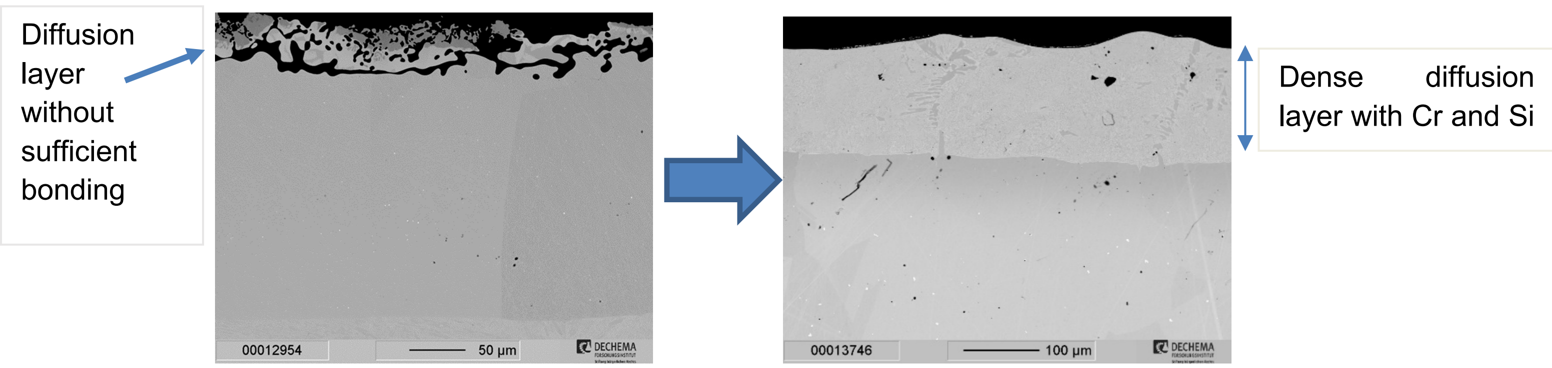


*Figure 2. Influence of the applied slurry composition on the resulting coating: left: slurry composition with $Cr_{75}Si_{25}$ (at.-%), right: alloyed slurry composition with a lower melting point.*

In Figure 2 two exemplary cross-sections of a coating applied on Sanicro 25 are shown. For the left cross-section in Figure 2, a slurry containing 75 at.-% Cr and 25 at.% Si was applied. Due to the lack of a liquid phase and thus insufficient interdiffusion, the coating was porous and non-adherent. In the right cross-section of Figure 2 is an adjusted slurry composition, containing 60 at.% Cr, 20 at.% Si and 20 at.%X. The reduced melting point by alloying within the slurry mixture enabled higher interdiffusion rates so that a dense coating was formed. As this newly developed coating process by the slurry technique represents an innovative and new alternative to apply Cr-Si-based diffusion coatings, a patent („Verfahren zur Diffusionsbeschichtung mit einem Cr-Si-haltigen Schlicker", reference number 10 2022 112 093.7) was applied for within the EU.

So far the investigated substrates for the Cr-Si slurry diffusion coating include P92 (ferritic steel), Sanicro 25 (austenitic steel) and Inconel 740 (Ni-based superalloy). The conducted investigations included phase analysis by SEM (Scanning electron microscopy), XRD (X-ray diffraction) and EPMA (Electron probe microanalysis) for the various coatings, as well as hardness measurements. Representative images of the cross-sections of the final coatings, as delivered for the testing program in WP4, are shown in the following (Figures 3-5):

Cr-Si coating on P92:

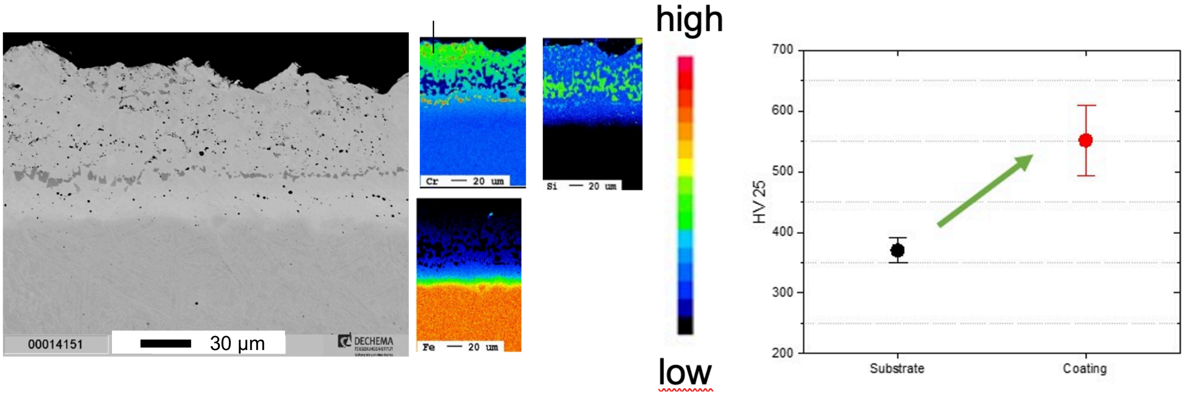


*Figure 3. Cross-section of the Cr-Si-slurry coating on P92, applied with a slurry composition of Cr-Si-X (left) and results of microhardness measurements (right).*

Cr-Si coating on Sanicro 25:

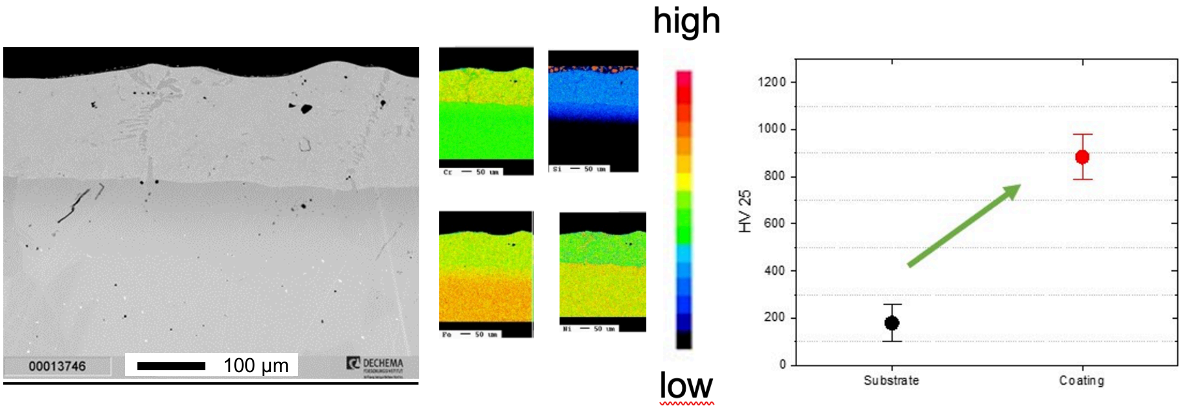


*Figure 4. Cross-section of the Cr-Si-slurry coating on Sanicro 25, applied with a slurry composition of Cr-Si-X (left) and results of microhardness measurements (right).*

Cr-Si coating on Inconel 617b:

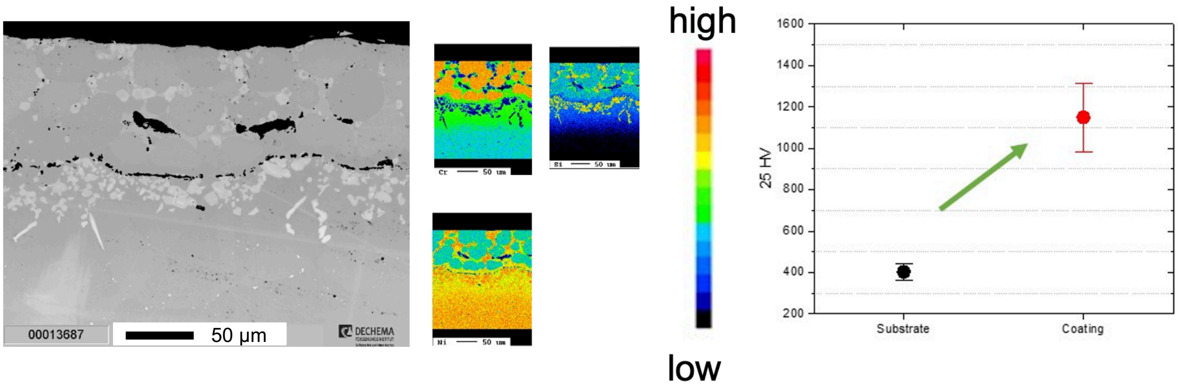


*Figure 5. Cross-section of the Cr-Si-slurry coating on Inconel 617b, applied with a slurry composition of Cr-Si-X (left) and results of microhardness measurements (right).*

For all of these coatings a dense diffusion layer with a thickness of >50 µm can be observed. As the EPMA images show, the targeted enrichment of Cr and Si within the diffusion layer was achieved. Also intermetallic Cr-Si-rich precipitates can be observed within these layers, which led to an increased hardness when compared to the bare substrate materials. This increased hardness is promising for wear resistant behavior within the heat exchanger environment.

## 2.2 PRODUCTION OF CR-SI COATED COUPONS FOR WP 4 TESTING PROGRAM

In order to test and validate the suitability and resistance of the coatings within the targeted heat exchanger environment, samples for the various tests in WP 4 were prepared. An overview of the delivered samples for each test is given in Table 1. The coupon geometry and some examples of delivered coupons are shown in Figure 6 and Figure 7.

*Table 1. Produced and delivered Cr-Si-coated samples for the WP4 testing program.*

| Test | Deliver to | Coated substrates |
|---|---|---|
| Oxidation | FZJ | Inconel 617b (20 x), Sanicro 25 (20 x) and P92 (10 x) |
| $CO_2$ | CIEMAT | Inconel 617b (20 x) and Sanicro 25 (20 x) |
| $sCO_2$ | CVR | Inconel 617b (4 x), Sanicro 25 (4 x), Haynes 282 (4 x) and P92 (4 x) |
| Erosion | FZJ | Inconel 617b (10 x), Sanicro 25 (10 x) and P92 (10 x) |
| Erosion | CIEMAT | Haynes 282 (8 x) and P92 (8 x) |

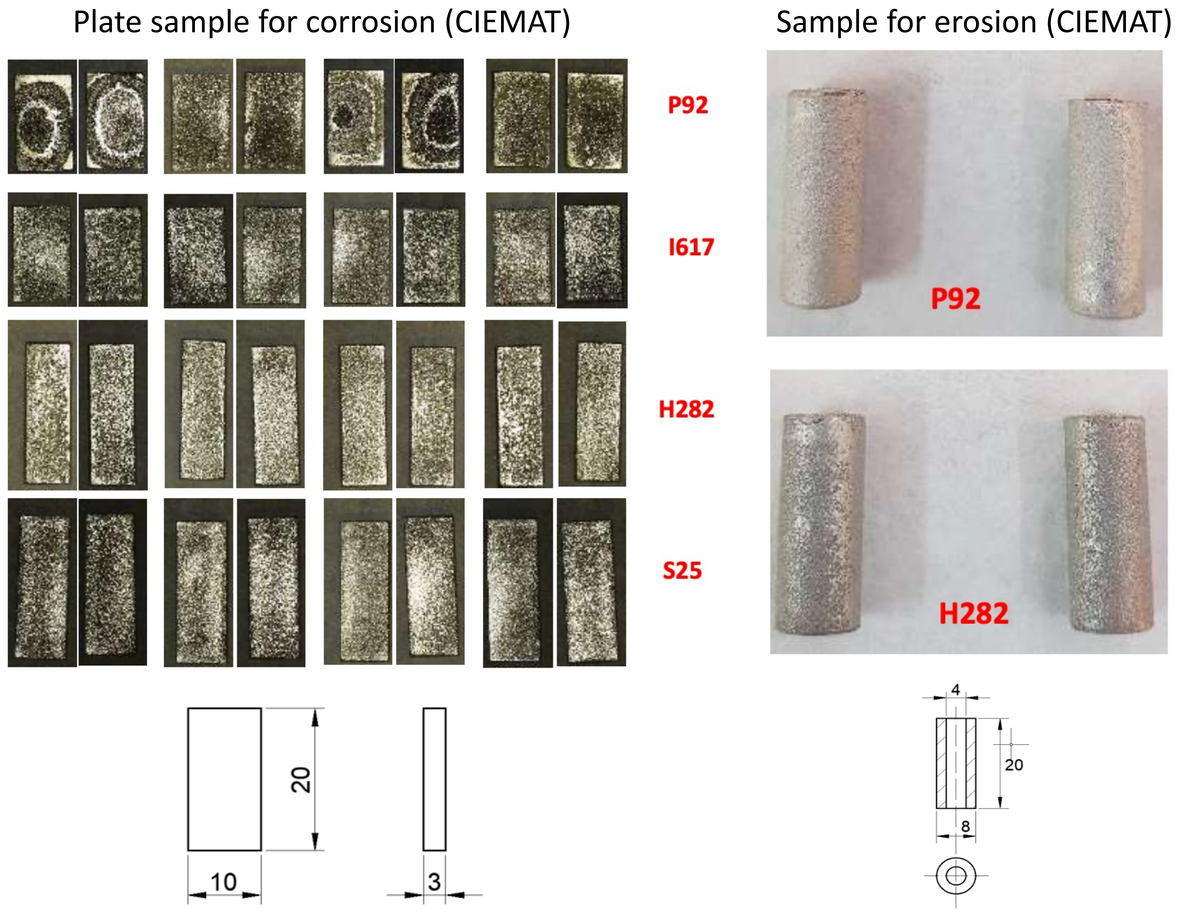


*Figure 6 Examples of coated sample delivered to CIEMAT for corrosion and erosion tests.*

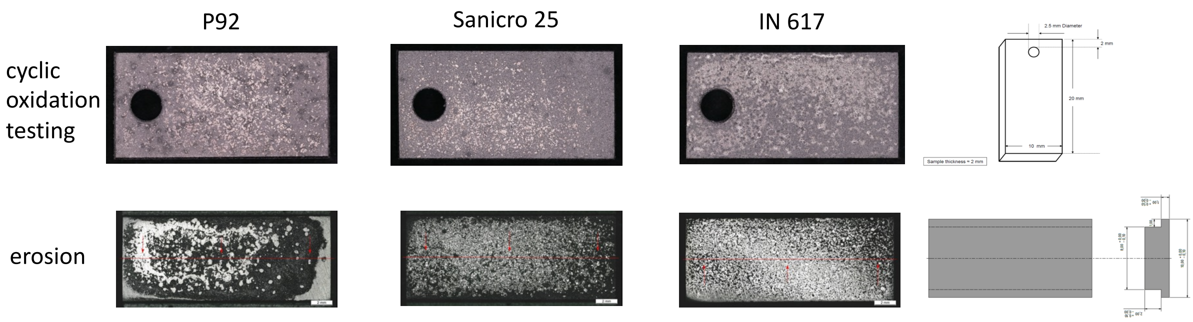


*Figure 7 Examples of coated sample delivered to FZJ for corrosion and erosion tests.*

# 3 DEVELOPMENT OF CR-NIAL SUPERALLOYS

## 3.1 DEVELOPMENT OF THE NOVEL CR-BASED BCC-SUPERALLOYS

The target of task 3.1 was to develop bulk Cr-NiAl alloys as candidate materials for the heat exchanger identified within WP1. The purpose of the alloy development was to produce alloys based on Cr with good microstructure stability and strength at temperatures >800°C. The Cr-NiAl alloys follows a "bcc-superalloy" design strategy. The alloys compromise nano-scale ordered-bcc intermetallic precipitates (e.g. NiAl) in a disordered-bcc matrix (Cr), which is expected to enable good recombination of ductility and high-temperature properties (strength and creep resistance). Figure 8 shows the pseudo-binary phase diagram of Cr-NiAl system. The alloy design is enabled by the fact that the alloy can be homogenised at a higher temperature followed by an ageing treatment at a lower temperature to produce finely distributed precipitates. Figure 8 also presents the microstructure of a Cr-5Ni-5Al-10Fe alloy (at.%) after ageing. The A2+B2 microstructure was successfully produced. Fe is added into the alloy to increase the solubility of Ni and Al for a higher precipitate volume fraction.

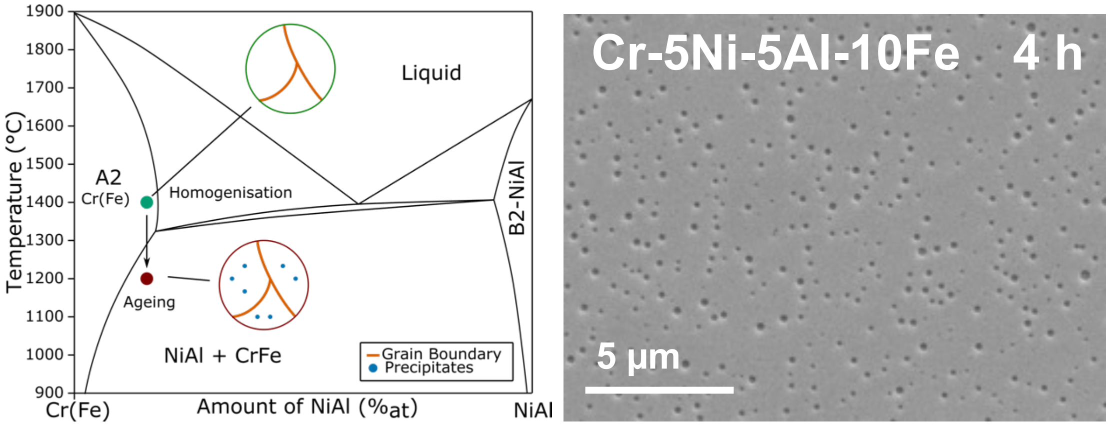


*Figure 8. (left) Pseudo-binary phase diagram of Cr(Fe)-NiAl system showing the design of Cr(Fe)-NiAl alloy. (right) SEM micrograph showing the microstructure of a Cr-5Ni-5Al-10Fe alloy (at.%) homogenised at 1400°C for 20 hours and aged at 1000°C for 4 hours.*

Microstructure characterization and hot compression testing have been performed to evaluate the microstructure stability and strength of the Cr(Fe)-NiAl alloys at high temperatures.

First, precipitates grow and coarsen at high temperatures, so the microstructure evolves. The stability of the microstructure is important to maintain the strength and creep resistance. The precipitate coarsening rate which describes the kinetics of precipitate size is investigated in WP3. Figure 9 shows the precipitate coarsening rate of Cr(Fe)-NiAl alloys as a function of temperature compared to other superalloys. The remarkably low coarsening rates demonstrate good microstructural stability at T>1000°C , which is optimal for creep resistance and ensures a longer service life of the alloy.

Second, the yield strength of the Cr(Fe)-NiAl alloys at temperature >800°C is studied using hot-compression in DECHEMA and the results are shown in Figure 9. The Cr-superalloy design offers a significant improvement of strength at T > 800°C compared to pure Cr, a Ni-superalloy (Inconel 718), and a Co-superalloy. Although the CMSX-4 Ni-superalloy show higher yield strength than Cr- superalloys at T>800 °C, a large amount of refractory elements including rhenium (~3%), tantalum (>5%) and tungsten (>5%) are alloyed into CMSX alloys to achieve their exceptional high-temperature strength. In addition, Cr-superalloys also exhibit high strength compared to some novel alloys such as Fe-superalloys and refractory alloys (vanadium-based, tantalum-based alloys) and are comparable to some refractory high-entropy alloys (RHEA). Adding iron increases the yield strength of the Cr-NiAl alloys but also increases the coarsening rate. Therefore, a comprise of Fe addition should be considered to achieve balanced properties.

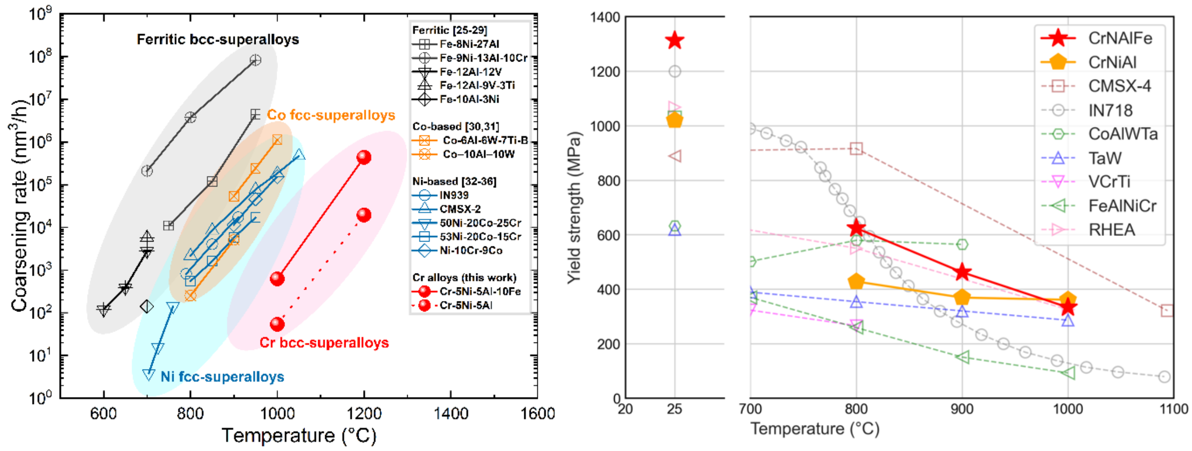


*Figure 9. (left) coarsening rate of precipitate in various types of superalloys and (right) room-temperature and high-temperature strength of various alloys for high-temperature applications.*

Initial attempts have been made to turn the Cr-NiAl alloy into diffusion coating using the slurry coating technique developed in Task 3.3. However, no compact coating was formed on the substrate of the state-of-the-art materials. Further composition tuning is required to enable the coating of Cr-NiAl.

The Cr-NiAl alloys show compression ductility at high temperatures which is of great interest for application as bulk materials. For further environmental testing in WP4, bulk pure Cr, Cr-5Ni-5Al (iron-free) and Cr-5Ni-5Al-10Fe alloys are selected to study the environmental behaviour of the Cr-NiAl alloys and also investigate the influence of the alloy design (bcc-superalloy and Fe-addition) on the oxidation/corrosion/erosion resistance.

## 3.2 PLANNED PRODUCTION OF CR-NIAL BULK ALLOY COUPONS FOR WP 4 TESTING PROGRAM

In order to test and validate the suitability and resistance of the bulk alloys within the targeted heat exchanger environment, samples for the various tests in WP 4 are in preparation. An overview of the samples planned for test in WP4 is given in Table 2.

*Table 2. Planned Cr-NiAl samples for the WP4 testing program.*

| Test | Planned delivery date | Deliver to | Samples composition |
|---|---|---|---|
| Oxidation | June 2023 | FZJ | Cr, Cr-5Ni-5Al and Cr-5Ni-5Al-10Fe (x20 each) |
| $CO_2$ | June 2023 | CIEMAT | Cr, Cr-5Ni-5Al and Cr-5Ni-5Al-10Fe (x5 each) |
| Oxidation | June 2023 | CIEMAT | Cr, Cr-5Ni-5Al and Cr-5Ni-5Al-10Fe (x5 each) |
| $sCO_2$ | June 2023 | CVR | Cr, Cr-5Ni-5Al and Cr-5Ni-5Al-10Fe (x19 each) |
| Erosion | June 2023 | FZJ | Cr, Cr-5Ni-5Al and Cr-5Ni-5Al-10Fe (x8 each) |
| Erosion | June 2023 | CIEMAT | Cr, Cr-5Ni-5Al and Cr-5Ni-5Al-10Fe (x8 each) |