SafeG

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Structural materials
testing in media

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EXECUTIVE SUMMARY

The successful deployment of Generation IV (GIV) nuclear systems, such as the Gas-cooled Fast Reactor (GFR), depends critically on the availability of materials capable of withstanding the extreme conditions expected in these environments. This study aimed to evaluate the durability and behavior of selected structural materials under prolonged exposure to high temperatures, with a focus on simulating the GFR's helium gas coolant environment.

Structural material selection and testing in the simulated GFR´s environment is the main topic of this report. Candidate materials for the internals have been selected and the list was further optimized according to the design needs of WP1, WP3 based on desired material properties and expected conditions. Different AM technologies, including arc and laser energy sources, and powder and wire feedstock materials have been evaluated and used for the ODS FeCrAl and high nickel-based alloy IN 617 samples manufacturing. The evaluation successfully met its objective of assessing these materials' performance in high-temperature, helium-cooled environments similar to those in GFR systems. Notably, the newly developed AM IN617 manufactured via the LPBF process showed promising oxidation resistance, though further research is needed to optimize the powder manufacturing process and fully harness its potential for advanced reactor applications.

In conclusion, this study provides valuable data supporting the selection of advanced materials for GIV systems, contributing to the development of structural components that can endure the harsh operational conditions anticipated in next-generation nuclear reactors. Further optimization of additive manufacturing processes and material formulations will be essential in advancing these technologies for commercial deployment.

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1 INTRODUCTION

The development of Gas Fast Reactors (GFRs), a type of Generation IV nuclear reactor, faces several significant technical and operational challenges. These challenges stem from the unique design and operating conditions of GFRs, which use high-temperature gas (typically helium) as a coolant and fast neutrons for nuclear fission. Some of the key challenges include:

1. Fuel Development:

High-Temperature Stability: GFRs operate at very high temperatures (up to 850°C or more), so the fuel must be able to withstand these conditions without degradation. Traditional fuel materials (like UO_2) are not suitable for these extreme conditions, requiring advanced fuel forms like carbide, nitride, or metallic fuels.

Cladding Materials: The cladding (which encloses the fuel) must be resistant to radiation damage, high temperatures, and chemical interactions with the gas coolant. Finding materials that can maintain structural integrity in such an environment is a major challenge.

Fast Neutron Environment: In a fast neutron spectrum, fuel must be enriched to much higher levels of fissile material, and fuel cycle management (reprocessing, breeding, etc.) is more complex.

2. High-Temperature Materials:

Structural Materials: The reactor core components, including the reactor vessel, must be able to handle the high operating temperatures and radiation environment without undergoing significant degradation. Materials such as advanced ceramics, refractory metals, or composites are being explored, but long-term durability and performance are still issues.

Thermal Fatigue and Creep: At high temperatures, materials are more prone to creep (slow deformation under stress) and thermal fatigue. Ensuring the reliability of materials over the reactor's lifetime is a critical design concern.

3. Helium Coolant Management:

Leakage Control: Helium, the primary coolant in GFRs, is an inert gas that operates at high pressure. Its small atomic size makes it prone to leakage through materials, seals, and joints. Preventing helium loss while maintaining high pressure is a significant engineering challenge.

Heat Transfer Efficiency: While helium has favorable properties as a coolant (e.g., it is inert and does not activate easily), its heat capacity and heat transfer coefficient are relatively low compared to liquids like water or sodium. Achieving efficient heat removal requires high coolant flow rates and advanced heat exchanger designs.

4. Safety Systems:

Decay Heat Removal: In the event of a shutdown or accident, GFRs must be able to safely remove decay heat to prevent overheating. Traditional passive cooling mechanisms (used in other reactor types) are harder to implement in a gas-cooled system. This requires innovative passive or active decay heat removal systems that can function effectively under both normal and emergency conditions.

Core Design and Reactivity Control: Fast reactors have higher neutron fluxes and more complex reactivity control compared to thermal reactors. Ensuring that reactivity can be controlled effectively and safely, especially under accident conditions, is a key challenge.

5. Power Conversion Technology:

High-Efficiency Systems: GFRs aim to achieve high thermal efficiencies through gas-turbine power conversion systems (like Brayton cycles). However, these systems must be designed to

handle the high temperatures and pressures of the gas coolant while maintaining mechanical efficiency. Developing reliable and efficient gas-turbine technologies that integrate with GFRs is still an ongoing challenge.

6. Fuel Cycle and Waste Management:

Closed Fuel Cycle: GFRs are typically designed to operate in a closed fuel cycle, where spent fuel is reprocessed, and fissile material (like plutonium) is recycled. This adds complexity in terms of fuel reprocessing technology and handling of nuclear waste. Reprocessing technologies must be developed to manage high burn-up fuels and fast-spectrum fission products.

Minor Actinide Management: GFRs can transmute minor actinides (highly radiotoxic elements in spent fuel) into shorter-lived isotopes, reducing long-term nuclear waste. However, this requires precise control over fuel reprocessing and reactor operation, as well as further development of transmutation technology.

7. Economic Viability:

High Capital Costs: Developing advanced materials, fuel technologies, and safety systems for GFRs leads to high upfront capital costs. Achieving economic competitiveness with other reactor types (such as Light Water Reactors, LWRs) or alternative energy sources is a major challenge.

Long Development Time: The need for extensive testing and validation of new materials and technologies, combined with regulatory challenges, means that GFRs may take a long time to reach commercial viability, adding uncertainty to investment and deployment timelines.

8. Regulatory and Licensing Challenges:

Licensing Advanced Reactors: GFRs represent a novel reactor concept, and regulatory frameworks in many countries are not fully prepared for fast reactor designs. Developing the necessary safety standards, testing regimes, and licensing pathways is a significant challenge for GFR deployment.

Proliferation Risks: Fast reactors generally use higher-enriched fuel and have the capability to breed plutonium, raising concerns about nuclear proliferation. Ensuring that the fuel cycle is secure and proliferation-resistant requires careful planning and international oversight.

Conclusion:

Developing Gas Fast Reactors requires overcoming substantial challenges related to fuel and material development, safety system design, coolant management, and economic feasibility. Advances in high-temperature materials, fuel cycle technologies, and power conversion systems are critical to making GFRs a viable option for future nuclear energy production.

2   STRUCTURAL MATERIALS SELECTION FOR THE GAS-COOLED FAST REACTORS (GFR)

The Gas-Cooled Fast Reactor (GFR) is one of the six advanced nuclear reactor designs under the Generation IV International Forum (GIF). These reactors use a fast neutron spectrum and gas (typically helium) as the coolant. GFRs are designed to operate at high temperatures (up to 850°C and beyond), offering increased thermal efficiency and the potential for hydrogen production or other high-temperature applications. However, the extreme operating conditions, including high temperatures, fast neutron irradiation, and exposure to gas coolants, pose significant challenges for structural material selection.

The main goals in selecting structural materials for GFRs are to ensure:

- High-Temperature Strength: Materials must maintain mechanical integrity at elevated temperatures and pressure conditions without excessive creep or deformation.

- Thermal Conductivity and Expansion: High thermal conductivity helps in heat dissipation, while low thermal expansion reduces thermal stresses.

- Corrosion Resistance in gas environments: Resistance to oxidation, carburization, and other forms of high-temperature corrosion is critical, particularly in the presence of impurities in the coolant.

- Resistance to radiation damage and compatibility with fast neutron flux and helium gas: Structural materials are exposed to neutron irradiation in the reactor core, which can lead to embrittlement, swelling, and degradation over time.

Given these requirements, selecting the right materials for the reactor pressure vessel, fuel cladding, heat exchangers, and other critical components is essential.

Given these conditions, materials must withstand the combined effects of high temperatures, radiation, and corrosive environments.

2.1   Key Materials for GFRs

Several groups of materials based on their deployment in the reactor have been selected. Nickel-based alloys (Alloy 617, Haynes 230, Alloy 625,690) and titanium-based alloys for the high temperature out of core components. The development approach is to rely on technologies developed for the VHTR for structures, materials, components, and power conversion systems. A qualification Code Case for Alloy 617 to allow construction of components has been submitted. Due to high irradiation doses, other heat-resistant materials need to be considered for in-core applications and insulation. The spectrum is wide, ranging from refractory metals (e.g., molybdenum or vanadium) to ceramics. The latter generally offers very attractive properties in terms of both the stability to high temperatures and the resistance against wear and corrosion/erosion. However, both properties are counterbalanced by brittleness and a core design. Materials and their manufacturing technologies including fuel cladding are still being developed. Advanced ceramic or metallic refractory materials, which can be considered for cladding or other applications in GFRs to mitigate corrosion effects, include ODS -Mo, high entropy alloys (HEAs), and MAX phases. The high entropy alloys (HEAs) have attracted great attention in recent years as very promising materials with high resistance against radiation damage and high-temperature properties. The main candidate for GFR cladding, which has also

been extensively studied is the ceramic composite SiCf/SiC, i.e., silicon carbide fibres in the silicon carbide matrix. However, the design rules and joining technique of SiCf/SiC cladding also need to be developed.

2.1.1 Ferritic-Martensitic Steels

Ferritic-martensitic steels are considered a candidate material for high-temperature reactor environments due to their strength and good resistance to radiation-induced swelling compared to austenitic steels. These steels are well-suited for core components that experience high neutron flux.

Characteristics:

- Excellent thermal conductivity and low thermal expansion, which reduce thermal stress.
- Good mechanical strength at elevated temperatures.
- High resistance to radiation-induced swelling and embrittlement.
- Moderate oxidation and carburization resistance, though they may require protective coatings to enhance performance.

Example Alloys:

9Cr-1Mo (Grade 91 steel): This alloy is commonly used in high-temperature, radiation-exposed environments due to its excellent mechanical strength and thermal properties.

HT-9: Another ferritic-martensitic steel that offers good resistance to radiation damage and is used in nuclear applications.

Applications: Ferritic-martensitic steels are often used for structural components like the reactor vessel, and internal support structures, where mechanical strength and radiation resistance are key.

2.1.2 Nickel-Based alloys

Nickel-based superalloys are extensively used in the nuclear industry due to their exceptional mechanical properties, resistance to high-temperature corrosion, and ability to maintain strength and stability in harsh environments, including those with high radiation exposure. These alloys are primarily employed in advanced nuclear reactors, nuclear power plants, and related systems where high temperatures, radiation, and corrosive environments are present. Below are the key applications of nickel-based superalloys in the nuclear industry:

Characteristics:

- High-temperature strength and creep resistance.
- Excellent oxidation resistance, even in the presence of small amounts of impurities like oxygen and carbon dioxide in the helium coolant.
- Reasonable resistance to neutron irradiation, though they tend to suffer from embrittlement over time due to exposure to fast neutrons.
- Creep Resistance: Nickel-based superalloys maintain mechanical strength and resist creep deformation under sustained high temperatures and stress, critical for long-term reactor operation.

- Long-Term Stability: These materials are designed for the long service life required in nuclear reactors, often spanning several decades without significant degradation.
- High cost and complex fabrication processes.

Example Alloys:

Inconel 617: Known for its high strength and resistance to oxidation and carburization at extreme temperatures. Inconel Alloy 617 (UNS N06617) 52Ni-22Cr-13Co-9Mo is the leading candidate material for the intermediate heat exchanger in GFRs. An ASME Task Group on Alloy 617 Qualification has drafted a Code Case for Alloy 617 to allow the construction of components for nuclear applications.

Alloy 800H: is a high-temperature nickel-iron-chromium alloy that is a variant of Incoloy 800 with improved mechanical properties at elevated temperatures. It is specifically designed for use in extreme environments, such as high-temperature and corrosive atmospheres Its high creep strength, resistance to carburization and nitridation, thermal fatigue resistance, and ability to maintain mechanical properties under harsh conditions make it a reliable material for use in heat exchangers, core internals, piping, and steam generator tubing. Its excellent performance in the chemically inert, high-temperature helium environment ensures its critical role in the safe and efficient operation of next-generation nuclear reactors.

Haynes 230: Another high-performance nickel-based alloy, prized for its oxidation resistance and ability to retain strength at temperatures exceeding 800°C.

Hastelloy X and Inconel 625: known for their excellent oxidation resistance and thermal stability, making them an ideal candidate for components exposed to high-temperature environments.

Applications:

Nickel-based superalloys may be used in the reactor core, heat exchangers, or other components where both high temperature and oxidation resistance are critical. Specific alloys used: Alloy 800, Inconel 625, and Hastelloy X are typically used in heat exchangers and steam generators due to their excellent high-temperature properties. Inconel 713, Rene 80, and Udimet 700 are examples of nickel-based superalloys used in turbines due to their superior high-temperature performance. Nickel-based superalloys are also considered for use in nuclear waste containment due to their ability to withstand long-term exposure to corrosive environments such as saline groundwater or acidic solutions, ensuring that nuclear waste is safely contained. The Alloy 800 was used in steam generators of pressurized water reactors of German design, SUPERPHENIX sodium fast reactor, and Alloy 800H forge by FOMAS is also currently used in the only operating HTR reactor in the world, the Chinese HTR-PM.

2.1.3 Austenitic Stainless Steels

Austenitic stainless steels are often used in nuclear applications because of their corrosion resistance and mechanical properties at elevated temperatures, but they are more susceptible to radiation damage compared to ferritic steels.

Characteristics:

- Good high-temperature oxidation resistance.
- High toughness and ductility at elevated temperatures.

- Susceptible to radiation-induced swelling, which limits their use in the core of fast reactors.

Example Alloys:

316L Stainless Steel: A low-carbon variant of 316 stainless steel with improved corrosion resistance and good high-temperature performance.

304 Stainless Steel: A commonly used austenitic steel that offers good oxidation resistance but may suffer from swelling under fast neutron exposure.

321 Stainless Steel: SS 321 is a titanium-stabilized austenitic stainless steel which offers as its main advantage an excellent resistance to intergranular corrosion following exposure to temperatures in the chromium carbide precipitation range from 427 to 816°C. It offers excellent resistance to oxidation and general corrosion, particularly in aqueous environments. It is commonly used in high-temperature environments, including the nuclear industry.

Applications: Austenitic stainless steels are typically used in non-core components, such as piping, heat exchanger tubing, and the reactor vessel in lower radiation zones. Protective coatings are often applied to enhance their performance in high-temperature environments.

2.1.4 Ceramic and Carbon-Based Materials

Ceramics and carbon-based materials offer unique advantages in GFRs, especially in terms of their high-temperature stability and resistance to radiation.

Silicon Carbide (SiC):

SiC and SiC composites are candidates for fuel cladding and other high-temperature components. They offer exceptional high-temperature stability, radiation resistance, and low neutron absorption. SiC can tolerate temperatures up to 1600°C and is highly resistant to oxidation and corrosion. For nuclear applications, the critical feasibility properties of SiC-based ceramic composites strongly depend on their fabrication methods. The main candidate for GFR cladding, which has also been extensively studied is the ceramic composite SiCf/SiC, i.e., silicon carbide fibres in the silicon carbide matrix. However, the design rules and joining technique of SiCf/SiC cladding also need to be developed.

The CEA Sandwich Design Since 2002, CEA (the French Alternative and Atomic Energies Commission) has been running a large R&D program for the design of SiCf/SiC fuel cladding. CEA is proposing an innovative design using a porous carbon fiber seal (Vf = 20. 40%) for example, a 2D braided layer, instead of a He seal. This solution increases the pellet-cladding play without thermal penalties, favouring heat exchange. It allows the fuel to expand without stressing the cladding (experimental tests showed that a 10 MPa compressive stress is sufficient to achieve near-complete densification of the initial structure). It minimizes fuel pellet off-centring problems. Finally, it prevents chemical interaction between the fuel and the SiC/SiC cladding, by obtaining a source of free carbon that prevents the decarburization of the fuel (a phenomenon recognized during tests performed at 2000°C for 15 minutes that did not show degradation of the fuel pellet with a buffer seal). Nonetheless, the problem of the tightness of damaged SiC/SiC composites was a key technological issue that needed to be solved in order to use them as a GFR cladding material. CEA thus proposed a new innovative design called the sandwich design illustrated in Figure 1. This design proposes to integrate a thin ductile refractory metal liner between two layers of SiC/SiC composites. The liner confined between

two thicker, more rigid composite layers is subject to little stress during mechanical loading of the cladding and uniquely ensures the tightness of the cladding. Moreover, its high ductility should ensure hat its integrity is maintained, even under significant mechanical stress. Nonetheless, there are still a lot of unknowns, including the behaviour of the liner under irradiation conditions (excessive fragilization for example) with very high doses (100 dpa). Studies are also being performed to check the thermochemical compatibility of the envisaged liners with the SiC/SiC composite at high temperatures (1000°C) and over long periods of time (>1 year) even if estimations based on the data are encouraging.

Figure 1 SiCf/SiC cladding – sandwich developed by CEA

Within the SafeG project a partner Kyoto University developed a novel SiC composite. The Boron nitride (BN) particle dispersion composite claddings were fabricated by the liquid phase sintering (LPS) using Al2O3 sintering additive. Hi-Nicalon type-S fibers were used without fiber coating. Carbon fiber coating is applied by chemical vapor deposition (CVD) for conventional SiC composites for nuclear application. However, the coating is the weakest link in terms of oxidation. Productivity can be limited by scattering of the coating with a few hundred nm in thickness. The BN particles were dispersed in matrix instead of the fiber coating. The composites show the excellent oxidation resistance without SiC over coating on the composites. The prepreg sheet was prepared from satin woven SiC fibers and matrix slurry containing SiC, BN and Al2O3. The prepreg sheet was wrapped on a graphite fixture and sintered by hot pressing. The fabrication procedure, the fabricated SiC claddings and comparison of the particle dispersion SiC composites and conventional SiC composites are shown in Figure 2.
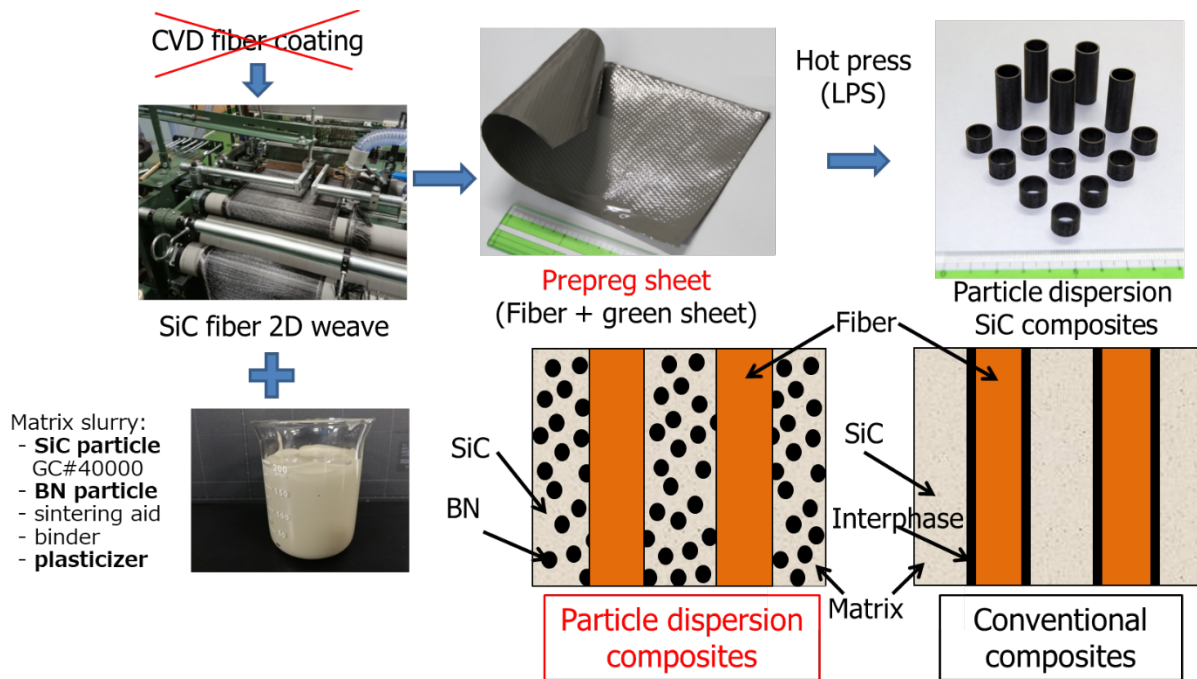
Figure 2 Fabrication procedure of BN particle dispersion SiC composite claddings, the fabricated claddings and comparison of the particle dispersion SiC composites and conventional SiC composites.

Fabrication procedure of BN particle dispersion SiC composite claddings, the fabricated claddings and comparison of the particle dispersion SiC composites and conventional SiC composites.

Graphite: can be used as a neutron moderator or reflector material in GFRs. It is stable at high temperatures and has excellent radiation resistance, though it may require protective measures to prevent oxidation.

2.1.5 Refractory Metals

Refractory metals like **tungsten (W)**, **molybdenum (Mo)**, and their alloys have high melting points and excellent mechanical strength at extreme temperatures, making them potential candidates for GFR applications.

Applications: Refractory metals could be used in high-temperature components such as control rods or other core internals that experience extreme thermal stress.

2.1.6 Advanced manufactured Ni-based alloy; AM IN 617

Different AM technologies were investigated by the SafeG project partner USFD to determine the feasibility of these advanced manufacturing processes for enabling the manufacturing IN617 and the feasibility of manufacturing the selected DHR HX component. AM IN617 samples were additively manufactured (AM) using arc-wire (AW), laser-powder (LP) and laser-wire (LW) directed energy deposition (DED) capabilities, and the powder bed fusion (PBF) process. The LPBF equipment, which was used to fabricate representative samples for ongoing material characterization studies, was specially selected for the fabrication DHR heat exchanger. The full HX component in reduced scale has been fabricated by using an advanced manufacturing process, given in Figure 3. In addition, the machinability of the resulting alloy 617 material samples was also evaluated using different cooling strategies, and the results are promising, with low roughness and a small deformation zone observed after machining.

Figure 3 Heat exchanger produced by advanced manufacturing process – material IN617

Advanced Manufacturing Techniques for IN 617

Recent advances in manufacturing technologies have enhanced the performance of IN 617. These advanced techniques offer greater control over microstructural properties, increase precision, reduce waste, and enable the fabrication of complex geometries, which are highly beneficial for nuclear applications.

Additive Manufacturing (AM) / 3D Printing:

Additive manufacturing technologies, such as Selective Laser Melting (SLM) or Electron Beam Melting (EBM), allow the production of complex geometries that are difficult to achieve using traditional methods. Layer-by-layer deposition of IN 617 powder using laser or electron beam provides better control over microstructural grain size, resulting in improved mechanical properties. The ability to optimize the internal structure of components (like lattice structures for heat exchangers) enhances the performance of IN 617 in nuclear reactor components, where weight, thermal efficiency, and mechanical stability are critical.

AM enables rapid prototyping of custom components, minimizing lead time and allowing for the optimization of nuclear reactor designs, particularly for advanced nuclear technologies.

Powder Metallurgy (PM):

In powder metallurgy, IN 617 is produced in powder form and then consolidated using techniques such as Hot Isostatic Pressing (HIP) or Spark Plasma Sintering (SPS). This method leads to fine-grained microstructures, which enhance the alloy's high-temperature strength and creep resistance. Powder metallurgy is particularly beneficial for producing complex parts, like turbine blades or internal reactor components, that must withstand both thermal cycling and radiation damage. HIP is especially effective in minimizing porosity, resulting in a fully dense material that can withstand extreme pressures and temperatures typical of nuclear reactors.

Laser Cladding:

Laser cladding is used to deposit thin, wear-resistant coatings of IN 617 onto components exposed to high temperature and corrosive environments in nuclear reactors, such as heat

exchangers and control rod drive mechanisms. The precise deposition process reduces the amount of material required, minimizing waste and enabling selective reinforcement of critical areas. This method enhances the oxidation and corrosion resistance of existing components without the need to manufacture entirely new parts.

Advanced Welding Techniques:

Electron Beam Welding (EBW) and Laser Beam Welding (LBW) techniques have been employed to join IN 617 components with minimal heat-affected zones. These welding processes result in better microstructural control, reducing the risk of cracking and distortion that can arise from thermal stresses during nuclear reactor operations.

These techniques are especially useful for joining complex geometries in nuclear systems, where leak-proof integrity is essential (e.g., pressure vessels or piping systems).

Directed Energy Deposition (DED):

DED is another advanced manufacturing process used for repair or modification of existing IN 617 components. In nuclear applications, DED can repair parts that have been subjected to radiation damage or thermal wear, thereby extending their operational life.

This method provides localized deposition and remanufacturing, making it an effective and cost-efficient solution for maintaining nuclear reactor components.

Applications of Advanced Manufactured IN 617:

IN 617 is used for heat exchangers in advanced nuclear reactors (e.g. High-Temperature Gas-Cooled Reactors (HTGRs), MSR) due to its ability to maintain mechanical strength and resist oxidation at extreme temperatures. IN 617 can be used in turbine components in nuclear power plants, particularly in the secondary loop of high-temperature reactors, where temperatures exceed 850°C. Additive manufacturing allows for the precise fabrication of turbine blades with optimized cooling channels, improving efficiency and extending component life under high-temperature operations.

Advantages of Advanced Manufacturing for IN 617:

- Enhanced Mechanical Properties: Additive manufacturing and powder metallurgy processes provide better control over grain size, leading to improved creep strength and fatigue resistance at high temperatures.

- Complex Geometries: Advanced manufacturing techniques enable the production of complex shapes that would be impossible or costly to create with traditional manufacturing methods. This allows for more efficient designs, especially in heat exchangers and reactor core components.

- Improved Material Efficiency: 3D printing and laser cladding reduce material waste, making the manufacturing process more cost-effective, which is particularly important for expensive materials like IN 617.

- Repair and Maintenance: Directed Energy Deposition (DED) enables the repair of worn or damaged components, reducing the need to completely replace expensive parts in nuclear reactors. This extends the operational life of critical components.

- Reduced Lead Time: Additive manufacturing allows for rapid prototyping and shorter production cycles, which is crucial for developing and implementing new reactor designs in the nuclear industry.

2.1.7 Advanced Ferritic and Oxide-Dispersion Strengthened (ODS) Steels

Oxide-dispersion strengthened (ODS) steels are advanced materials that combine the strength of ferritic steels with improved high-temperature performance due to the dispersion of oxide particles within the metal matrix. Among the many promising materials for nuclear power applications are ferritic FeCrAl alloys with different Cr and Al contents. FeCrAl alloys are increasingly interested in applications such as accident-resistant fuel cladding, structural components for fast fission reactors, and first wall and jacket structures for fusion reactors. Additionally, traditional stainless steels like 310S or 316L are unsuitable for use because they are prone to forming volatile chromium compounds at high temperatures. Alternatively, an iron-based alloy that forms aluminum oxide, called FeCrAl, can be used. These alloys exhibit improved oxidation and corrosion resistance than FeCr alloys, partly due to their high mechanical strength at high temperatures, and the formation and growth of passive chromium-aluminum oxide (α-Al2O3) layers on the surface during high-temperature operation. Ti and V additions improve the strength and ductility of these alloys, ensuring better performance at extreme temperatures. Thus, it is essential to develop novel advanced materials suitable for nuclear power generation.

Characteristics:

- High resistance to radiation damage and creep at elevated temperatures.
- Enhanced oxidation resistance and mechanical strength due to the dispersion of oxide particles like yttria (Y_2O_3).
- Radiation tolerance, essential for long-term performance under neutron irradiation.

Example Alloys:

ODS-Eurofer: An ODS version of Eurofer steel, specifically developed for high-temperature applications in fusion.

MA957: An ODS ferritic steel with excellent resistance to high-temperature corrosion and radiation damage.

FeCrAl-ODS alloys with Ti and V additions:
In this project, a partner NCBJ developed, manufactured, and tested the FeCrAl-based alloys with Ti and V (maximum 1 and 0.5 wt.%) and Y2O3 oxide particles. Ti and V are known to be responsible for the reinforcement and improvement of their corrosion resistance in the microstructure of ODS/F-M (ferritic-martensitic) steels i.e. EUROFER-ODS etc. Detailed description is given in Deliverable 2.6. This report will focus on their performance in the high-temperature helium environment. Advantages of Ti and V Additions:

- **Enhanced Creep Strength:** The oxide dispersion, along with Ti and V, helps to pin grain boundaries, thereby improving the material's resistance to creep deformation at high temperatures.
- **Improved Oxidation Resistance:** Ti and V additions further enhance the formation of a protective oxide layer on the alloy surface, helping it resist oxidation in harsh environments.

- **Microstructural Stability:** These additions help refine the grain structure and stabilize oxide dispersoids, leading to improved strength retention and resistance to radiation-induced swelling.

Applications: ODS steels are being investigated for use in the reactor core, cladding, and other critical components where radiation and temperature resistance are paramount. Advanced Nuclear Reactor Cladding: FeCrAl-ODS alloys with Ti and V are being explored for use in accident-tolerant fuels (ATF) in nuclear reactors. Fuel Cladding in Fast Breeder Reactors (FBRs): The alloys are used as cladding materials for fuel rods in FBRs, where the combination of high temperature, radiation, and corrosive liquid metal coolants (such as sodium or lead) demand materials. High-temperature components such as turbine blades, where resistance to oxidation and creep at elevated temperatures is essential.

2.1.8   Alumina-forming austenitic (AFA) stainless steels

Alumina-forming austenitic (AFA) stainless steels are a class of high-temperature, corrosion-resistant steels that have been specifically designed to form a stable and protective alumina (Al_2O_3) scale. This class of steels combines the favourable mechanical properties of austenitic stainless steels with enhanced oxidation and corrosion resistance due to the formation of an alumina layer rather than the more common chromia (Cr_2O_3) layer seen in traditional stainless steels.

Characteristics:

- Alumina Scale Formation: AFA steels are alloyed with aluminium (Al) to promote the formation of a protective Al_2O_3 scale when exposed to high temperatures. This alumina layer offers:
- Superior oxidation resistance compared to chromium-forming stainless steels, especially in high-temperature and corrosive environments.
- Thermal stability at elevated temperatures, typically up to 1000–1200°C, which is significantly higher than traditional austenitic steels.
- Austenitic Microstructure: These steels maintain a stable austenitic (face-centred cubic) microstructure, which provides:
    - Good ductility and toughness, even at low temperatures.
    - High creep resistance at elevated temperatures.
    - Enhanced weldability compared to ferritic alloys.

Addition of Alloying Elements:

Aluminium (Al): Typically 2-4% aluminium is added to form the alumina scale.

Chromium (Cr): High chromium content (18-20%) to maintain base corrosion resistance.

Niobium (Nb), Molybdenum (Mo), and Nickel (Ni): Added to improve strength, especially at high temperatures, and increase corrosion resistance.

Titanium (Ti), Tungsten (W), and Carbon (C): These elements may be added to strengthen the matrix and prevent grain growth, enhancing the creep strength.

Applications: AFA stainless steels have gained interest for use in advanced nuclear reactors due to their ability to withstand harsh operating conditions, such as high temperatures, oxidative atmospheres, and radiation exposure. Below are key areas where AFA steels can be

applied in the nuclear industry. Accident-Tolerant Fuel (ATF) cladding is a major application for AFA steels. The primary advantage of AFA cladding is the formation of a stable alumina scale that provides enhanced oxidation resistance, particularly during loss-of-coolant accidents (LOCA) in nuclear reactors. The ability of alumina to withstand high temperatures and provide corrosion protection is crucial in preventing fuel rod failure in such scenarios. AFA steels could replace zirconium alloys, which are more prone to high-temperature oxidation in steam environments, producing hydrogen—a safety risk in severe accidents. In Generation IV reactors (e.g., sodium-cooled fast reactors, gas-cooled reactors), AFA steels offer excellent oxidation resistance even in oxygen-poor environments, which helps maintain the integrity of core components, heat exchangers, and steam generators during extended reactor lifespans. The alumina scale in AFA steels significantly reduces the potential for corrosion and cracking, extending the operational life of the reactor pressure vessel and reducing maintenance requirements.

2.2 Challenges in Material Selection for GFRs

Despite the potential benefits of various materials, there are several challenges in selecting structural materials for GFRs:

Radiation Damage: Fast neutrons in GFRs can cause embrittlement, swelling, and cracking in materials, particularly in the core. Ongoing research is needed to improve radiation resistance.

Material Degradation: Prolonged exposure to high temperatures and radiation can degrade materials over time, leading to embrittlement, creep, or cracking.

Thermal Stresses: The wide range of operating temperatures can lead to thermal expansion and contraction, causing fatigue or cracking in certain materials. Materials with low thermal expansion coefficients, such as ferritic steels, are preferable in this regard.

Cost: Nickel-based superalloys and advanced metallic and ceramic materials are expensive and difficult to fabricate, leading to higher costs for reactor components.

Compatibility with Helium Coolant: In helium-cooled reactors, even small impurities (oxygen, water vapor, carbon monoxide) can react with materials, necessitating high-purity helium and corrosion-resistant materials.

3   OPERATING ENVIRONMENT OF GAS FAST REACTOR

The Gas-Cooled Fast Reactor (GFR) is a Generation IV nuclear reactor concept designed to operate in an extreme environment, with the goal of achieving high efficiency and sustainability. Its operating environment is characterized by high temperatures, fast neutron flux, and the use of helium gas as the primary coolant. These reactors are part of the fast reactor family, which means they operate with fast neutrons, enabling them to use fuel more efficiently and produce less long-lived radioactive waste.

GFRs operate in harsh environments, characterized by:

- High Temperatures: The reactors operate at temperatures up to 850°C, potentially reaching even higher temperatures in advanced designs.
- Fast Neutron Spectrum: GFRs use fast neutrons (energetic neutrons) to sustain the fission chain reaction. Fast neutrons cause more significant material damage compared to thermal reactors (e.g., cracking, swelling, embrittlement).
- Helium Coolant: While helium is chemically inert, impurities in the gas (e.g., oxygen, carbon monoxide, or water vapor) can lead to high-temperature corrosion of structural materials.

3.1 High-Temperature Corrosion of Metals in Helium Gas

High-temperature corrosion refers to the degradation of metals and alloys when exposed to high-temperature environments, often accompanied by gases or other reactive species. In the case of helium gas, corrosion can still occur, particularly under extreme temperatures, despite helium being chemically inert. The corrosion mechanisms depend on impurities present in the gas, metal types, operating temperatures, and the reaction kinetics.

3.1.1 GFR coolant chemistry

Helium itself is an inert noble gas and does not chemically interact with metals under normal conditions. However, helium used in industrial or research applications, such as in nuclear reactors, is rarely pure. Chemical compatibility in reactor environments is highly dependent on the thermodynamic stability of structural materials of the components in the coolants and in contact with the possible impurities contained therein. For example, helium coolant may contain small amounts of gas impurities such as CO_2, CO, H_2, O, H_2, CH_4, O_2, as well as solid particles coming from a variety of sources throughout the reactor system. The key oxidizing impurities to consider in the He coolant will be oxygen and water vapour. Material testing in mixtures of He and N_2 gasses at different temperatures, durations and with appropriate gas impurity control will be performed to evaluate the compatibility of baseline materials, welds, and corrosion-resistant advanced materials with the coolant, simulating operation and accident conditions. Next to that attention should be paid to the mechanical properties of the candidate materials. The interaction of irradiation with mechanical damage including the potential impact of cracks and surface damage e.g. clad to spacer grid fretting are also important issues that remain to be addressed.

To understand the corrosion behaviour of structural materials in a GFR environment, it will be important to understand the likely coolant chemistry. However, since no GFR has ever been built, no data exists on the chemistry resulting from an actual GFR helium purification system. Therefore, the GFR coolant chemistry considered by this review is taken from the reported experience of the modern helium purification system of the Chinese HTR-10 prototype high-

temperature reactor (HTR) which is of similar scale to the proposed ALLEGRO GFR demonstrator and currently operating HTR-PM. It is necessary to focus on ALLEGRO as it is a nearer-term prospect and because there is no modern data available for larger-scale helium-cooled reactors, given that the most recent.

The concentration and partial pressure data are presented in Table 1.

Table 1 He gas composition

Gas mixture	HTF (atm.p) Vppm	GFR (70bar) vppm	GFR specific %
H_2	210	3 ± 0.2	-
CH_4	70	1 ± 0.1	-
CO	210	3 ± 0.2	-
He	Bal.	Bal.	20
H2O	70	0.9 ± 0.1	-
CO_2	70	1 ± 0.1	-
N_2	140	2 ± 0.1	80
O2	70	1 ± 0.1	-

3.1.2 Temperature's Effect on Corrosion

At high temperatures, corrosion reactions are accelerated due to increased atomic mobility and reaction kinetics. The behavior of metals in helium gas can be categorized as follows:

Below 300°C: Corrosion in helium gas is minimal at low temperatures, as reaction kinetics are slow and impurities in the gas do not have sufficient energy to engage in significant reactions with the metal surfaces.

300°C to 800°C: In this temperature range, oxidation becomes more pronounced if oxygen is present as an impurity. The metal surfaces form protective oxide layers, which can reduce the rate of further corrosion.

Above 800°C: At these extreme temperatures, even small amounts of impurities can lead to rapid oxidation, carburization, or other types of high-temperature degradation. Diffusion rates of reactive species into metals are significantly enhanced, leading to accelerated corrosion.

3.1.3 Metals and Alloys in Helium Environments

Different metals and alloys exhibit varying corrosion behavior when exposed to high-temperature helium environments, often depending on their protective oxide layers or intrinsic resistance to carburization.

Stainless Steels: Stainless steels form a protective chromium oxide (Cr_2O_3) layer that can mitigate oxidation at high temperatures. However, under helium with carbon impurities, stainless steels can be susceptible to carburization, especially at temperatures above 600°C.

Nickel-Based Alloys: These alloys are commonly used in high-temperature helium environments because of their excellent resistance to oxidation and carburization. The formation of nickel oxide (NiO) or mixed oxide layers helps protect the metal from further degradation.

Ferritic and Austenitic Alloys: Both classes of alloys are often used in high-temperature helium environments, such as in nuclear reactors. Ferritic alloys may suffer from carburization, but they can perform well if the chromium content is high enough to form a stable oxide layer.

3.1.4 Mitigating High-Temperature Corrosion in Helium

To minimize high-temperature corrosion in helium environments, several strategies are employed:

- Protective Coatings: Coating metal surfaces with oxidation- or carburization-resistant materials can extend the lifetime of components. Ceramic coatings or specialized metallic layers are often applied to reactor materials.

- Alloy Selection: Using alloys that form stable, protective oxide layers (like those rich in chromium or nickel) can provide natural resistance to high-temperature corrosion in helium environments.

3.2 Challenges of the GFR Operating Environment

Material Durability: The combination of high temperatures, fast neutrons, and helium coolant poses a significant challenge for material selection. Structural components, fuel cladding, and heat exchangers must be able to endure thermal creep, neutron irradiation damage, and helium-induced embrittlement over long operational periods.

Helium Leakage: As a small, inert molecule, helium can easily permeate through materials, leading to potential coolant loss. Special attention is required to seal systems effectively and maintain high helium pressure.

High Neutron Flux: The fast neutron environment increases the rate of radiation damage to reactor materials, requiring advanced materials with high resistance to swelling, embrittlement, and irradiation creep.

Complex Heat Transfer and Flow Dynamics: Efficient heat removal in the core is essential to prevent hot spots and ensure thermal stability. The high-temperature gas must be efficiently circulated through the reactor, often involving complex heat exchange systems.

Specifically research and development activities in the WP2 of the project were focused on enhancing performance (and thus consequently safety in case of an accident) of various components within the primary circuit, which have been identified as the weak points in the reference design, namely:

- ALLEGRO Core support plate

- the hot part of the DHR heat exchanger

- the main heat exchanger (for the gas-gas version)

- Innovative fuel cladding

4   HIGH TEMPERATURE MATERIALS TESTING

The main requirements for the structural materials to be used in advanced nuclear reactor systems are dimensional stability under irradiation, acceptable evolution under aging of the mechanical properties, and a good behaviour in corrosive environments. These requirements must be met not only under normal operating conditions, but also in off normal and accident conditions. Material testing in the High-Temperature Facilities has been carried out. Degradation of previously mentioned materials (chapter 2) under conditions (impure helium at elevated pressures and temperatures up to 900°C) simulating helium coolant in V/HTR&GFR systems has been evaluated. Subsequently, the mean weight changes of the specimens were determined, and the specimens were examined and analysed by scanning electron microscopy (SEM/EDX).

4.1   Experimental facilities

4.1.1   High Temperature Furnace (HTF)

HTF (Figure 4) is the horizontal furnace for the high temperature corrosion testing of samples. The inner tube-retort is made of quartz for corrosion test in gaseous atmosphere at elevated pressure, a gas flow of up to 1l/min, and a maximum temperature of 900°C. The oven temperature can be programmed for the duration of the experiments up to several thousands of hours. The space with constant temperature has a length of approx. 20cm and it is sufficient for testing of several samples in once. Gas cylinders of helium with a given level of impurities and bottles of pure helium have been used to control the low concentration of gas mixture. The gas cylinders are connected to the oven with flexible tubes. Before the test, all circuits were evacuated below 0.13 kPa. High-purity helium was injected and then evacuated repeatedly three times. A slight positive pressure was applied to prevent air ingress into the HTF. Finally, the HTF has been filled with the given test gas mixture. The resulting impure helium flow passes through a test section, retort heated through a furnace up to 900°C. After the test section and humidity monitoring, gas is released into the specific gas ventilation system (one–through). For experiments in pure helium, the residual oxygen was further removed from the gas by placing the titanium foam before the test section. Samples were placed on the specific holder (Figure 4b) and inserted into the HTF. The composition of gas mixtures used as corrosion atmosphere for the exposure is listed in Table 4. The duration of the exposure took up to 1000 hours and the gas flow was approx. 0.1 l.min-1. The oven temperature during the experiment was held at 900°C, heating and cooling rate was 1°C.min^{-1}. An additional humidity in the gas was controlled by an optical hygrometer BARTEC.
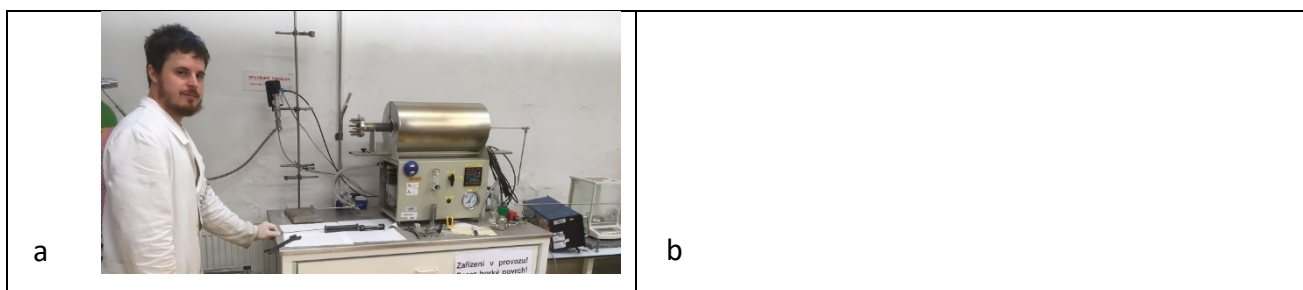

Figure 4 a) High temperature helium furnace (HTF) used for high temperature corrosion tests in gas environments; b) ceramic sample holder for metallic samples

4.2 HT corrosion test in N2 gas

Summary of tests:

Tested material: Alloy 625; IN 617; Hayness 230; Hayness HR 160

Duration: 1000h

Temperature: 900°C

Gas composition: bal. N2 at low oxygen pressure

All these materials showed a very good gravimetric evaluation, i.e. their mass changes in this environment were minimal. The formation of the oxide layer is due to the presence of residual oxygen in the apparatus, and it will be always present in the GFR reactor system.

The development of the microstructure of the individual test materials is illustrated in Figure 5 to Figure 8, where the microstructures of the materials at different exposure times are captured - from top to bottom 0, 200, 500 and 1000 hours of exposure in nitrogen at 900 ° C. It is clear from the figures that the microstructure of the tested materials did not change significantly during the thousand hours of exposure. Since these are highly alloyed alloys, only the growth of phases in the structure of the material was observed - carbides, intermetallic phases.

Table 2 Chemical composition in phases of materials after exposure 1000 h, nitrogen, 900 °C

Alloy 617B				Alloy 625		
Element	Oxidation layer	Phase grain boundaries		Element	Oxidation layer	Phase grain boundaries
C	1,11	5,94		C	0,35	1,11
N	0,31	1,16		N	0,16	0,24
O	34,2	0,00		O	41,29	0,03
Al	0,05	0,03		Al	2,50	0,03
Si	0,42	0,26		Si	2,21	0,21
Ca	0,17	0,00		Ca	0,00	0,00
Ti	0,24	0,67		Ti	0,16	0,19
Cr	32,08	58,74		Cr	46,15	35,68
Mn	0,28	0,43		Mn	0,25	0,13
Fe	0,52	2,75		Fe	0,02	0,02
Co	0,23	9,92		Co	0,00	0,00
Ni	25,79	4,34		Ni	2,92	45,61
Cu	0,09	0,01		Nb	0,02	6,23
Mo	3,79	14,01		Mo	1,92	9,28

Haynes HR-160				Haynes 230		
Element	Oxidation layer	Phase grain boundaries		Element	Oxidation layer	Phase grain boundaries
C	0,30	7,84		C	0,17	7,78
N	0,19	1,44		N	0,19	0,34
O	32,91	0,00		O	36,62	0,00

Al	0,02	0,05		Al	0,11	0,11
Si	0,77	0,22		Si	0,10	0,10
Ti	0,16	0,36		Ti	0,00	0,00
Cr	36,44	61,37		Cr	35,57	35,79
Mn	0,24	0,29		Mn	0,00	0,00
Co	5,20	10,11		Co	2,36	5,42
Ni	21,99	2,01		Ni	4,70	2,24
Mo	0,40	13,72		Mo	0,25	3,40
W	0,00	0,00		W	17,86	42,96

The composition of the oxide layers on surface of the individual samples as well as the chemical composition of the phases along the grain boundaries are shown in Table 2. The analysis was performed with a wave dispersion spectrometer, whose accuracy is an order of magnitude better than EDS / EDX - The results show that on the surface of the samples there were layers consisting mainly of oxides, mainly oxides of chromium and nickel. In the case of Haynes 230, tungsten is also an important component. The chemical composition of the phases at the grain boundaries showed that these are mainly carbides and intermetallic with different compositions according to the alloying elements, especially molybdenum, niobium, cobalt and tungsten.

Doba expozice: 0h   200 µm

Doba expozice: 200h   200 µm

Doba expozice: 500h   200 µm

Doba expozice: 1000h   200 µm

Doba expozice: 0h   200 µm

Doba expozice: 200h   200 µm

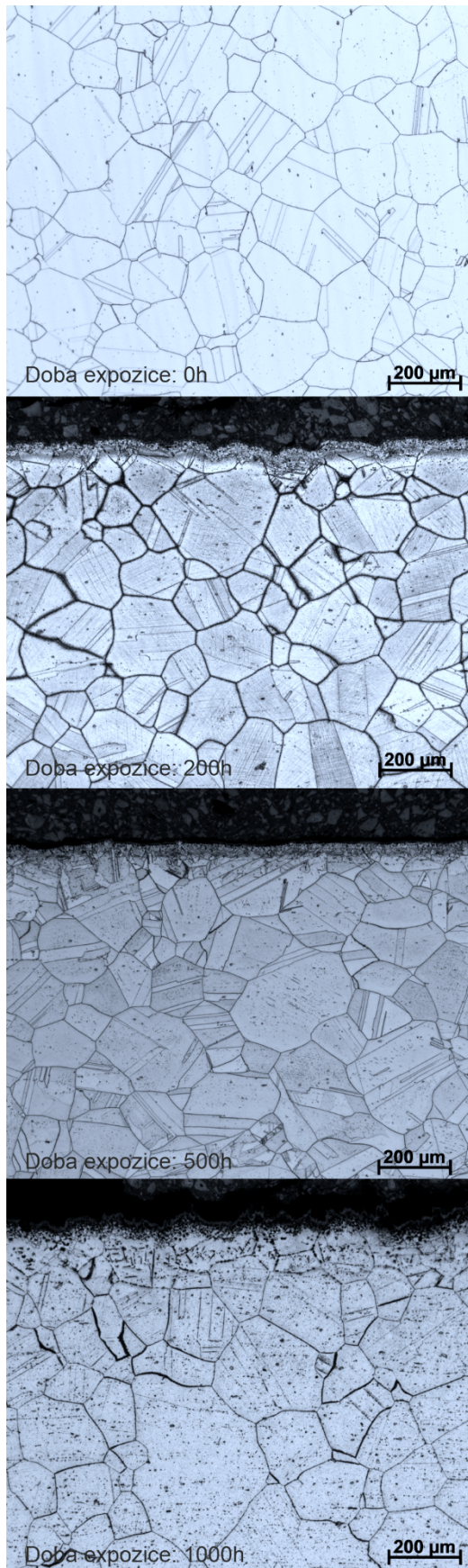Doba expozice: 500h   200 µm

Doba expozice: 1000h   100 µm

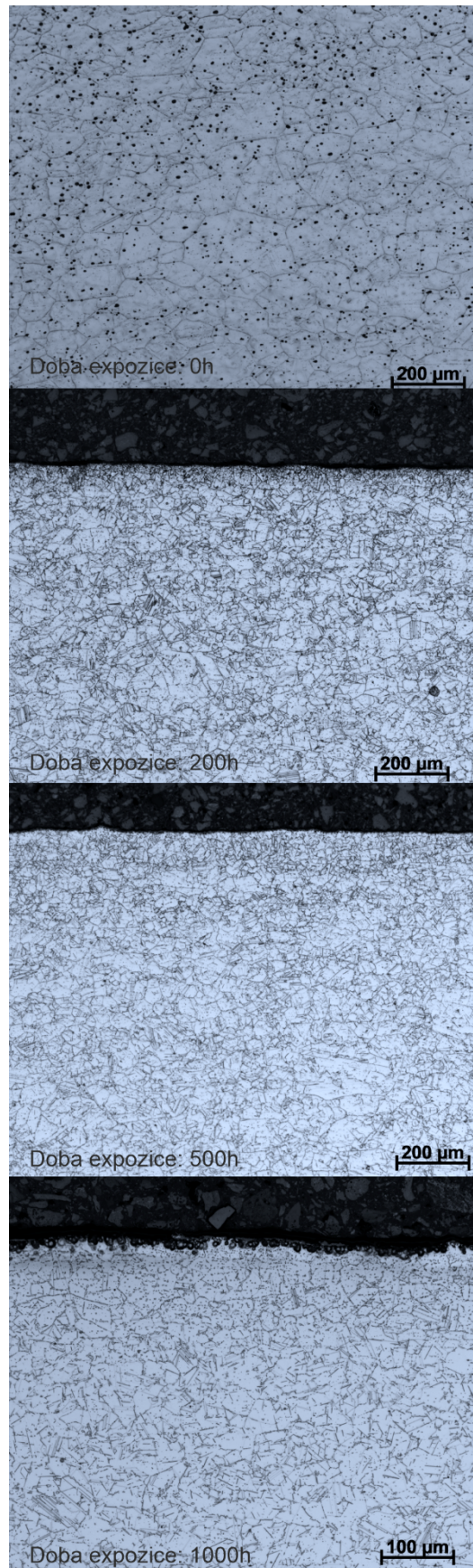**Figure 5 Alloy 617B after exposure in N2 at 900 °C; 0, 200, 500, 1000h**

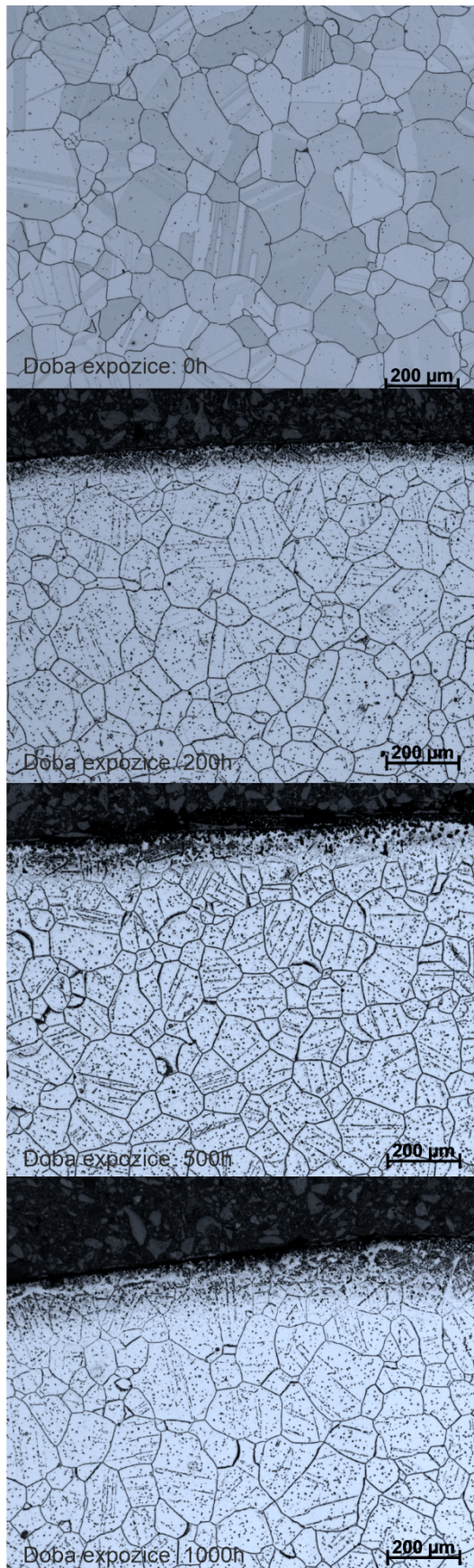**Figure 6 Alloy 625 after exposure in N2 at 900 °C; 0, 200, 500, 1000h**

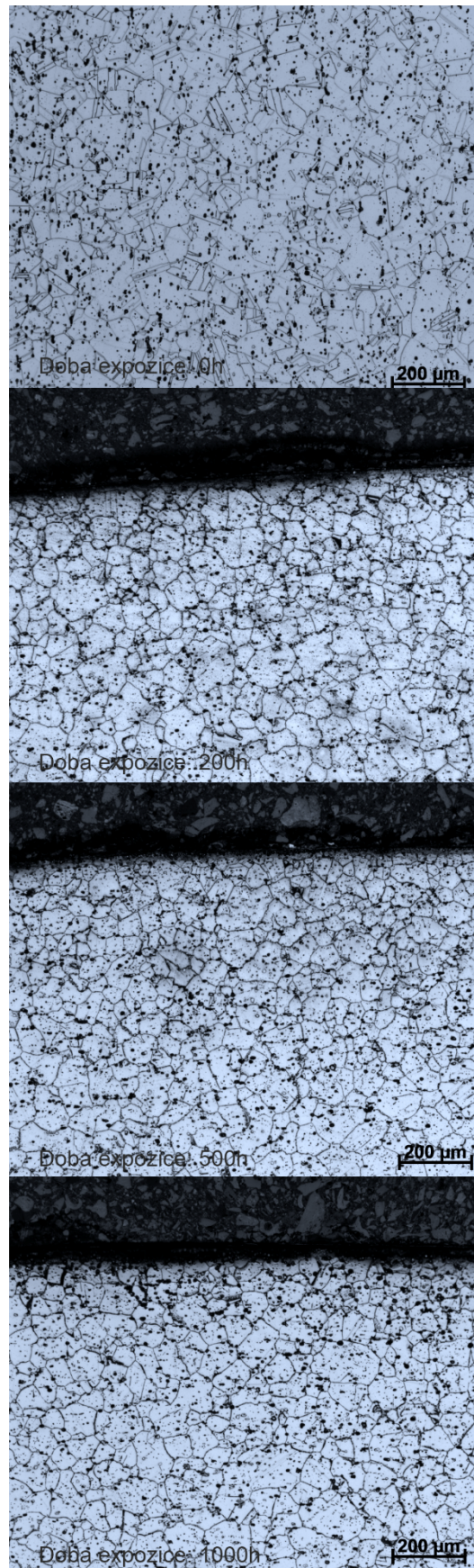**Figure 7 Haynes HR-160 after exposure in N2 at 900 °C; 0, 200, 500, 1000h**

Figure 8 Haynes 230 after exposure in N2 at 900 °C; 0, 200, 500, 1000h

4.3 HT corrosion tests in He gas

The reference test in pure helium has been performed with the same set of metallic samples. The input gas was 99.9%He, at 5×105 Pa pressure and a flow velocity of 1-10 ml/min (static conditions). The furnace was sealed by steel-carbon sealing (Spiratem, Temac). Temperature was kept at 900°C. Titanium foam was inserted in the furnace to absorb residual oxygen impurities; however, residual O impurities were estimated to be equivalent to PO2=10-30 Pa. It has been extremely difficult to obtain pure helium conditions due to elevated oxygen diffusion. A pure helium coolant should not be of concern, but in reality, the coolant may have a slight oxidizing character either because traces of O2, CO2, or H2O, that are expected to be always present.

Summary of test 1:

Tested material: SS 316, Alloy 800H, IN 617, IN 625, HEA alloys, AFA steel 15-15Ti alloy

Duration: 1000h
Temperature: 900°C
Pressure: 5 bar
Flow of He through the sample section: 1l/min
Gas composition: bal. He at low oxygen pressure and high temperatures

The gravimetric analyses of all materials, respectively, after oxidation at 900 °C, in He mix, for 1000 hours reveals that oxidation rate below 0,15 mg/cm2. It is worth noting that for the stabilized Al2O3 coating onto 15-15 Ti the oxidation rate at 900 °C is greater than for the pure Al2O3 coating. The lowest oxidation rate based on gravimetry exhibited AFA steel and IN 617. When the oxide growth follows a parabolic law, the oxidation kinetics is controlled by oxygen and/or cation diffusion through the oxide scale. Gravimetric measurements show that the kinetics of oxidation exhibits more sub-parabolic behaviour where the gross weight change is proportional to the square root of the exposure time in the range 900°C. The sub-parabolic to parabolic regime of oxidation can result from the occurrence of growth stress within the oxide scale large enough to provoke the formation of cracks offering an easy path to oxygen that results in an enhancement of the oxidation process at the interface substrate/oxide. The related increase of weight gain is the signature of such a mechanism. The differences in behaviour between studied samples is due both to the difference in the stress generated within the oxide scale upon cooling and the difference in the extent of stress relief afforded by the plastic deformation of the alloy substrate (specifically observed for the coated 15-15 Ti). Since the weight changes include also eventual spallation or mass loss during the cooling to room temperature, further analyses for the oxidation evaluation are needed. Morphology of the oxide is similar, the thin oxide grown at the surface of the coupons lies along the machining grooves of the substrate.

15-15 Ti
The top surface is a flat scale of pure chromium oxide Cr2O3 on which, if the temperature and/or the exposure time are sufficiently high, nodules of spinel MnCr2O4 and even manganese oxides are located (Figure 9). The formation of the spinel results from the concurrent fast diffusion of Mn through the chromia scale as the chromium reservoir in the near surface region gradually depletes.
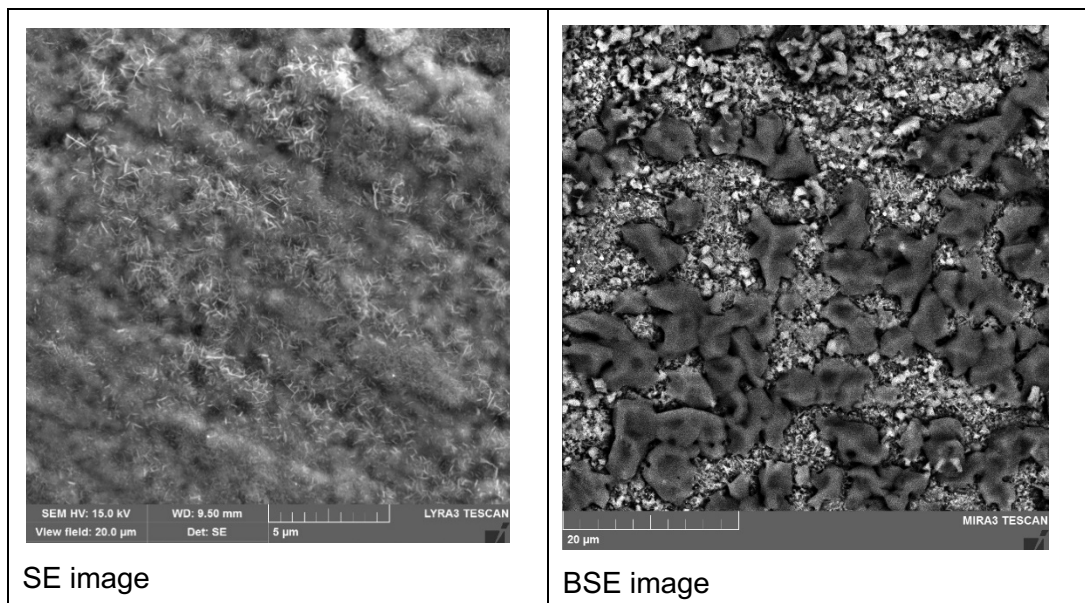
Figure 9 Surface of 15-15Ti after exposure HTF He, 900°C, 1000h

When the exposure time and/or the thermal activation are sufficient, the spinel layer grows laterally and forms, in the shape of highly faceted Mn containing crystallites, on the whole surface of the specimen (Figure 9). Cross-sectional investigation confirms the multi-layer structure of the scale. The overall composition of the oxide layer of 15-15Ti @900°C and specific areas – surface oxides are given in Table 3.

Table 3 Surface oxides composition 1515 Ti after exposure HTF 900°C

Wt %	O	Si	Ti	Cr	Mn	Fe	Ni
Surface composition	27.45	0.14	1.1	34.18	30.4	6.19	0.54
Cr based oxides	28.53	0.07	0.98	42.82	22.68	4.37	0.5
Mn containing crystallites	23.17		0.21	4.36	66.2	6.07	

Stainless steel 316
After corrosion tests in He (1000h, 900°C), a layer of chromium oxides with a thickness of tens of microns was analyzed on the surface of the 316 steel samples (Figure 10 a). Analysis of cross-sections showed that there was a coarsening of the microstructure (Figure 10 b), and exclusion of carbides and other particles often along grain boundaries after exposure to 900°C in a helium gas atmosphere. This is a common phenomenon for these steels, if they are slowly cooled after heat treatment or welding, in the critical temperature range of approximately 600 to 800°C, carbides are precipitated along the grain boundaries. This causes the formation of intergranular corrosion. However, there are ways to prevent this by changing the chemical composition (low C content, Ti or Nb additives), solution annealing (annealing at temperatures above 1000°C) followed by rapid cooling to normal temperature. Figure 6 shows the microstructure of steel 316 after corrosion test in high-temperature helium.
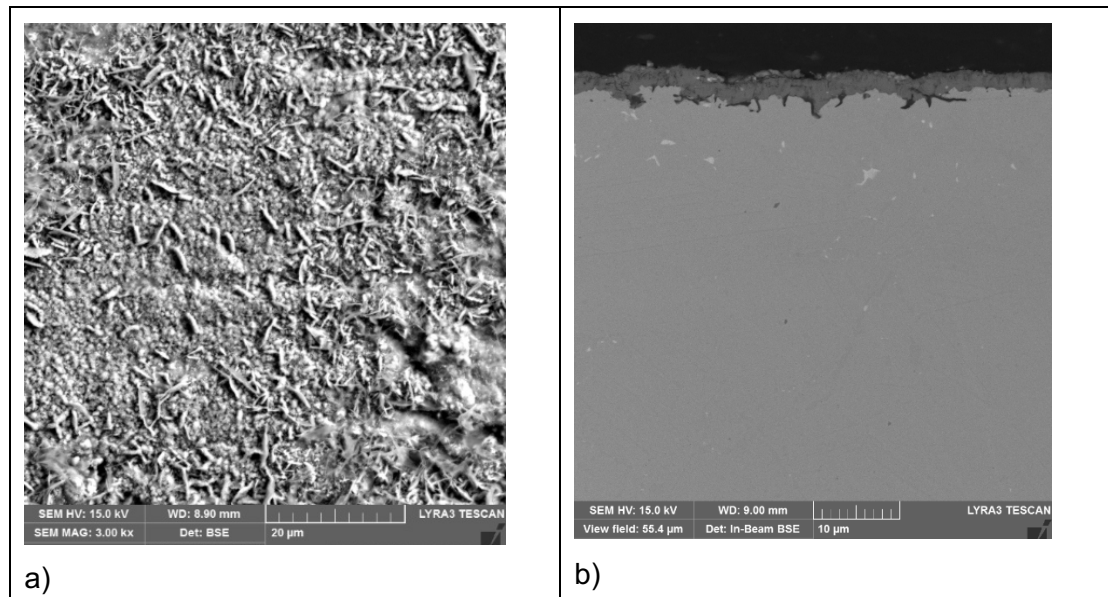
Figure 10 Steel 316 after exposure to 1000h, 900C, He, HTF, a) surface b) microstructure on a cross-section of a 316 steel sample.

Typical oxygen and water impurities result in the formation of an oxide film, including the oxide in the outer layer (**Chyba! Nenašiel sa žiaden zdroj odkazov.**) rich in Cr, Mn and Si oxide on the surface of SS 316, Mn occurs in the possible form of the Mn-Cr-O chromite spinel. The concentration of the Cr is increasing towards the surface intensity of chromic oxide Cr_2O_3 significantly increases because of the higher oxidation kinetics and the spallation of oxide films.

The oxide film is nonhomogeneous, about 5 microns thick with visible cracks under the higher magnification. Therefore, it cannot be considered as protective layer against further high temperature oxidation. Furthermore, chromium and Mo segregation has been observed in structure of the base material after the HT exposure. It is well known that the thermodynamics of chemical reactions determines the formation of different types of oxides, and oxidation kinetics determines the nucleation and growth of the oxides. Both the thermodynamics and kinetics of the formation of oxides are determined by temperatures, exposure periods, oxygen partial pressure and chemical composition of the alloy.

IN 625

The next investigated material was Ni based alloy IN 625. the grain structure of the nickel-base superalloy 625 has a significant impact on its mechanical properties. Predictability of the grain structure evolution in this material is particularly pertinent because it is prone to inter-metallic precipitate formation both during manufacture and long-term or high temperature service. Intermetallic intragranular precipitates in the governance of the mechanical properties of the material with grain coarsening being accompanied by a significant increase in hardness. Carbides are the controlling precipitate phase concerning the grain size of the alloy (Figure 11). The experiment confirmed the grain coarsening behaviour of both austenitic materials SS 316 and the Ni- based IN 625 in temperatures up to 900°C.
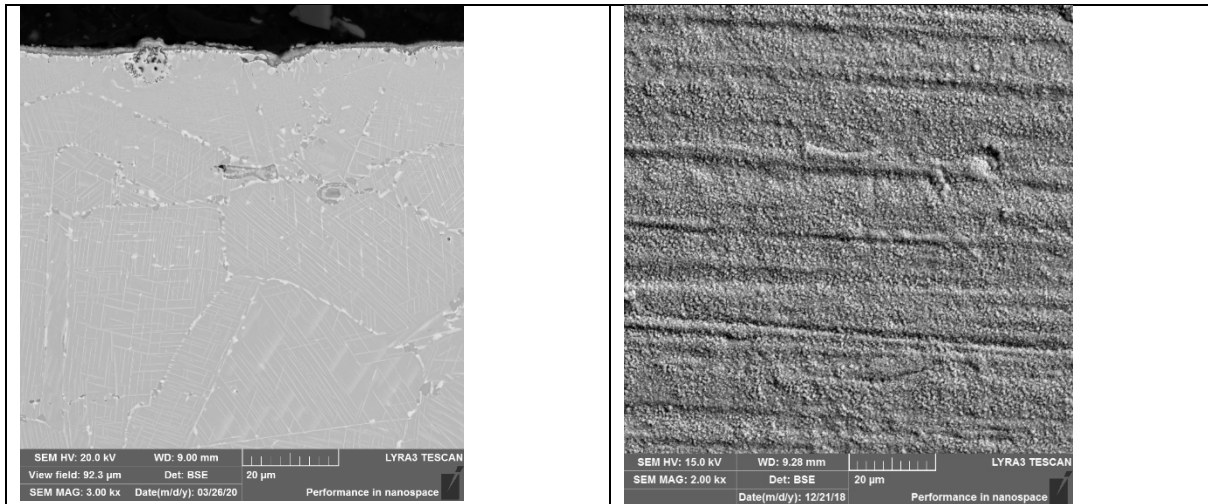
Figure 11 IN 625 after experiment cross section; oxidized surface

Alloy 800 H

Figure 12 show images from the SEM of the surface and a cross-section of Alloy 800H specimens, after the exposure in the HT He. In pictures, a corrosive layer formed on the surface of the specimens, and damage to the specimen under this layer is noticeable. The thickness of the corrosive layer on the base metal is around 3 µm. According to EDS analyses, the surface layer consists of chromium and manganese oxides; in the minority, there are other elements. Alloy 800H contains 0.40% titanium and 0.02% carbon and hence tends to form titanium carbide and titanium nitride or carbonitride during high-temperatures exposure. Precipitates in the form of carbides were found in the austenitic matrix (40 microns from the gas-metal interface) and along the grain boundaries,
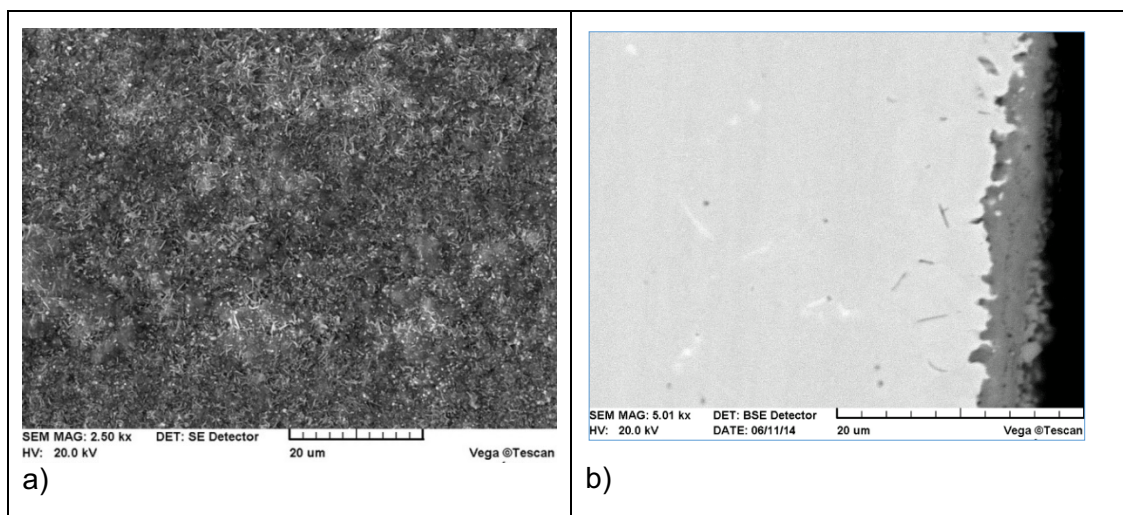

Figure 12 Alloy 800H after exposure to 1000h, He, HTF, a) surface b) microstructure on a cross-section

AFA steel

Next to the Al2O3-containing coating, another innovative high-temperature resistant material is alumina forming austenitic steels (AFA).

After thorough selection accompanied by corrosion experiments, the most promising AFA steel composition was chosen. Taking into consideration the balance between the austenite stability and the corrosion resistance, the chemical composition of AFA steels, for applications implying oxygen at high temperatures has been optimized, Fe-(2.5-4) Al-(14.5-16.5) Cr-(20-29) Ni [wt.%]. In which small amounts of elements targeting beneficial mechanical properties and improved adherence to the oxide scale could be added.
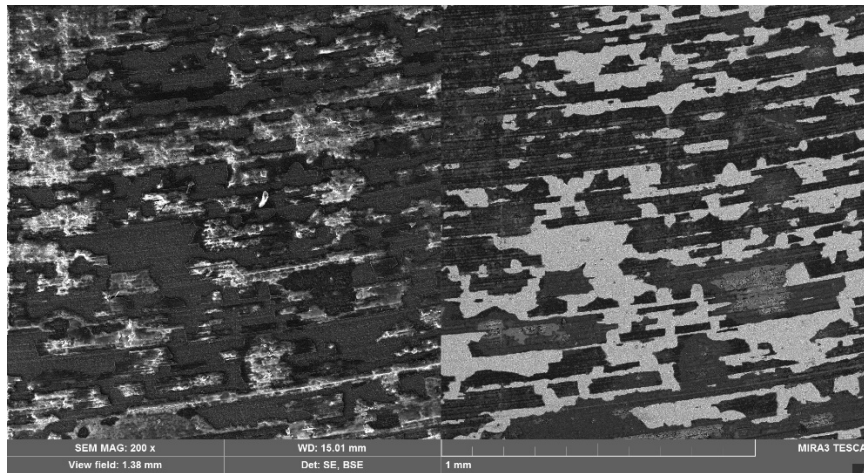
Figure 13 AFA after HTF experiment @900°C; He; Overview surface SEM image SE (left) and BSE (right)

Figure 13 shows the surface of AFA steel after the test in HTF (He mix @900°C). Again, as for the 15-15Ti material the oxidation of the surface is following the machining grooves of the substrate. Large bright are correspond to Fe, Cr, Ni, Mn oxides, while the chemical composition of the dark areas corresponds to Al_2O_3 enriched phase. Composition of both phases is given in **Chyba! Nenašiel sa žiaden zdroj odkazov.**. Even from the secondary image on the **Chyba! Nenašiel sa žiaden zdroj odkazov.** it is not clear what phase is spalling off or overgrowing the initial substrate. Nb has been detected in form of precipitates along the grain boundaries (Figure 14**Chyba! Nenašiel sa žiaden zdroj odkazov.**).
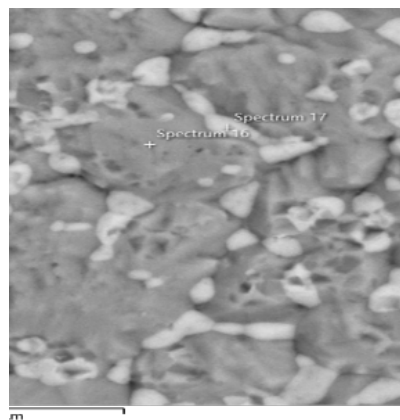

Figure 14: Nb precipitates on grain boundaries, AFA steel after experiment @900°C, HTF

Table 4 Results of EDX analysis on the points indicated in Figure 15

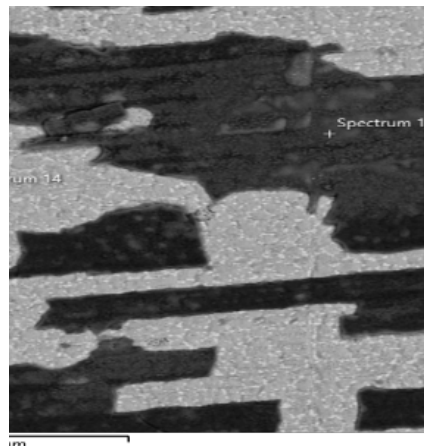| Wt. %	O	Al	Si	Cr	Mn	Fe	Ni	Nb
Spectrum 14	0.49	1.15	0.13	15.66	2.45	65.4	14.12	0.6
Spectrum 15	25.76	19.8		22.48	26.51	5.45		

Figure 15 Detail out of Chyba! Nenašiel sa žiaden zdroj odkazov. **with selected areas analysed with EDX.**

Alloy617 (IN 617)

Alloy 617 (UNS N06617) 52Ni-22Cr-13Co-9Mo is the leading candidate material for the intermediate heat exchanger in high-temperature gas-cooled reactors, because of its superior creep and corrosion resistance. Alloy 617 Is an austenitic alloy based on nickel-chromium with further alloying additions of cobalt, molybdenum, and aluminium. The alloy has also exceptional creep strength at temperatures above 870°C, enhanced by solution strengthening from the molybdenum and cobalt additions. It has good cyclic oxidation and carburization resistance, imparted by the chromium and aluminium additions.

Getting a new material into the code is a lengthy process and requires significant amounts of data. The US national labs spent years testing the material properties of Alloy 617 to qualify the metal for commercial use. Alloy 617 was added to the code in the fall of 2019 and is the first high-temperature material cleared for commercial use since the 1990s.
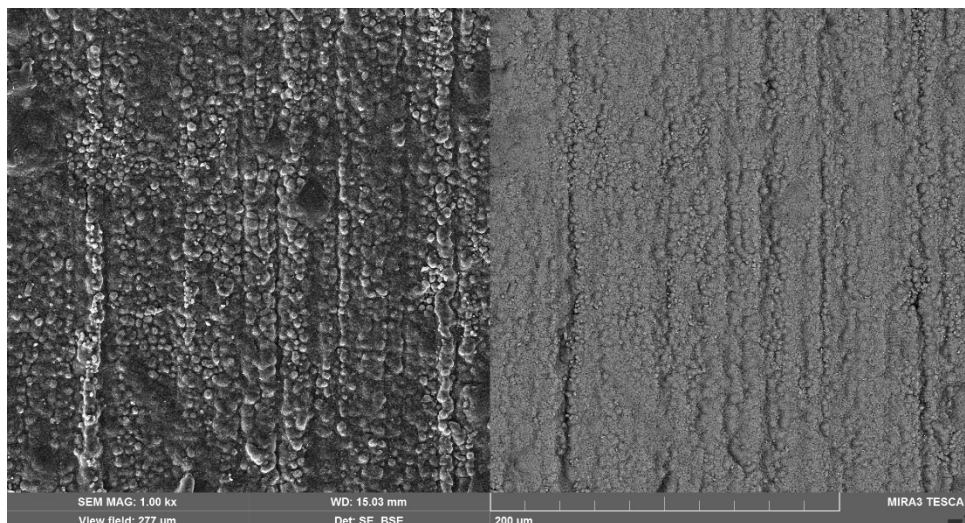

Figure 16 Overview surface SEM image SE and BSE Alloy 617 after the experiment @900°C, HTF

Alloy 617 is strengthened by solid solution hardening provided by the alloy elements chromium, cobalt and molybdenum as well as by intra- and inter-granular carbide precipitates. The high temperature oxidation resistance is derived from the high nickel and chromium content.
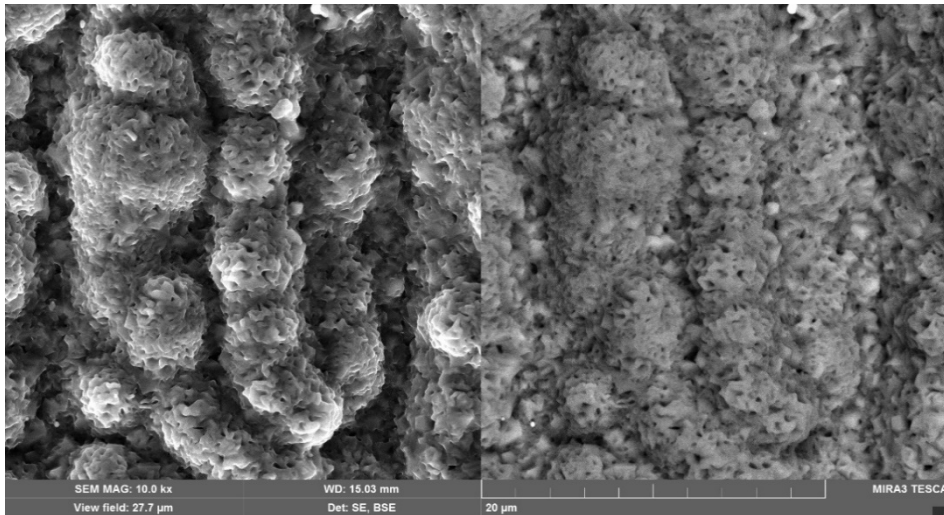
Figure 17 Deatiled imagies of the oxidized surface IN 617 @900°C, HTF; SEM image SE (left) and BSE (right)

Oxidation of the IN 617 showed parabolic oxidation behaviour at 900°C where protective chromium oxide was formed. A detail of the crystalline oxide structure is visible on Figure 17 Also, the EDX analyses confirmed the BSE image that the chemical composition of the sample surface remains constant. Chromium oxide is accompanied by a small amount of Ti and Mn. Corrosion data of the alloy 617 have been already published elsewhere. Our experiments only confirmed the excellent properties in the given cooling medium – He gas at elevated temperatures.

Summary of test 1:

Tested material: AM IN 617, FeCrAl-ODS alloys with Ti and V, AFA steel

Duration: 1000h
Temperature: 900°C
Pressure: 5 bar
Flow of He through the sample section: 1l/min
Gas composition: GFR mix

The experiment involved exposing the samples to high temperatures, He gas mixture in the HTF for an extended period of 1000 hours (approximately 41.67 days) to observe changes in mass over time. Samples were carefully prepared (degreased) and measured for their initial mass (weight and dimensions) before placing them into the special ceramic holder.
Samples were placed in the test section in the middle of the quartz retort. The crystal retort of HTF with a diameter of 40 mm allows corrosion tests in a gaseous atmosphere at atmospheric pressure and gas flow of up to 1l/min, at a temperature of 900°C. Every 250 hours (at four intervals: 250h, 500h, 750h, and 1000h), the furnace is temporarily halted, and the samples are removed. The samples were slowly cooled down to room temperature in the He gas environment to prevent thermal expansion from affecting the mass measurements. The samples were weighed on a precise balance with an accuracy of 0,01 mg to determine any changes in mass. After 1000 hours of exposure and all measurements taken, the data is analysed to evaluate trends in mass change over time. The summary of the weight changes of the AM IN617, FeCrAl-ODS alloys with Ti and V and AFA steel are given in Figure 18.

Results

For all samples, the mass gain has been observed, probably due to the high-temperature oxidation which is a prevailing corrosion mechanism in high-temperature gas environments. This precondition has been further evaluated by studying the surface layers of the samples, using the Scanning Electron Microscope (SEM/EDX). Overall, bigger weight changes than for conventional HT materials were detected for all AM samples and the values after 250h, 500h, 750h, and 1000h exposure@900°C, He mixture are given in Figure 18.
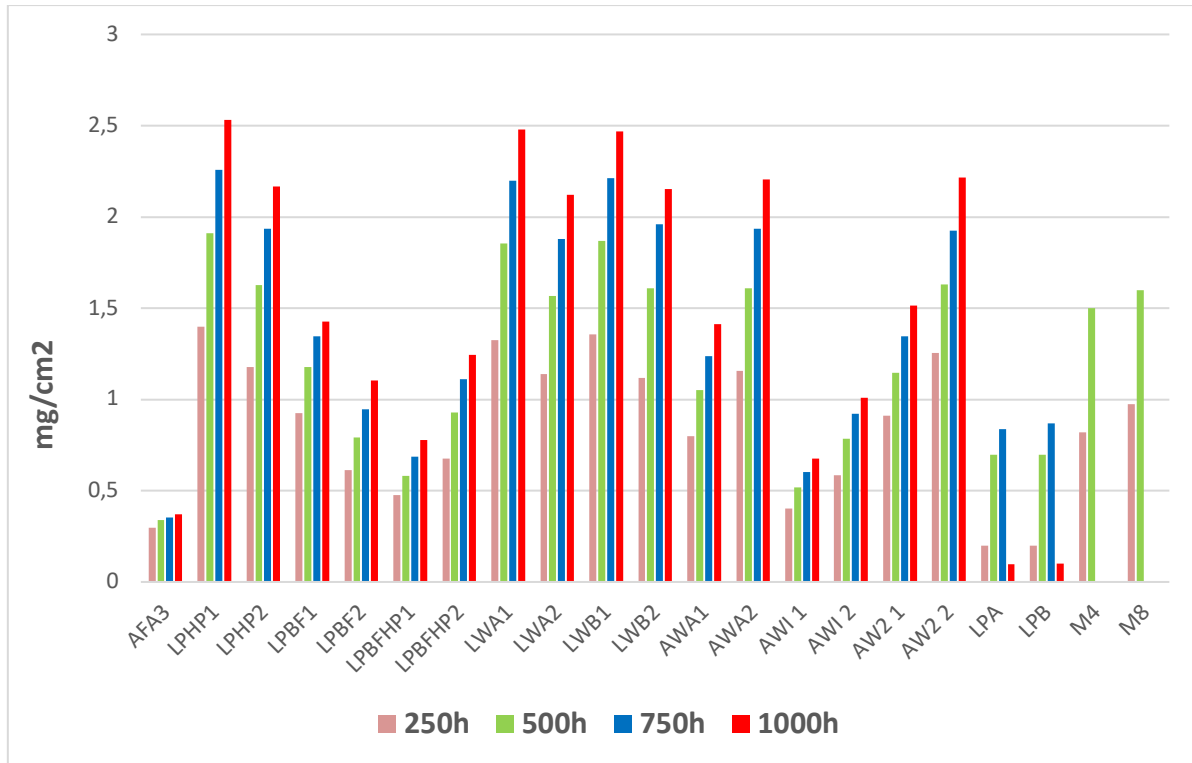
Figure 18 Weight changes of the AM IN617, FeCrAl-ODS alloys with Ti and V and AFA steel @900°C, He mix.

The initial comparison of the weight changes after exposure brought an interesting relationship between the AM manufacturing process and the weight gain of specimens.

| LP 617 (a.r.) | LPHP 617 (a.r.) | LPBF 617 (a.r.) | LPBFHP 617 (a.r.) |

| LP 617 | LPHP 617 | LPBF 617 | LPBFHP 617 |

Figure 19 Laser powder fusion bed samples as received (top raw) and after 1000 h @900°C, He mix

The lowest weight gain concerning AM samples can be observed for the samples manufactured by the laser powder fusion bed and arc welding processes. The following figures show the microstructure and chemical composition of the surface layer of samples LP, LPBF, LPBFHP and LPHP in the initial state and after exposure, Figure 19 . The surface analysis results of the sample as received and after the exposure are summarized in Table 5.

Table 5 Chemical composition of the surface area AM samples (LP) as received and after exposure @900°C, He mix

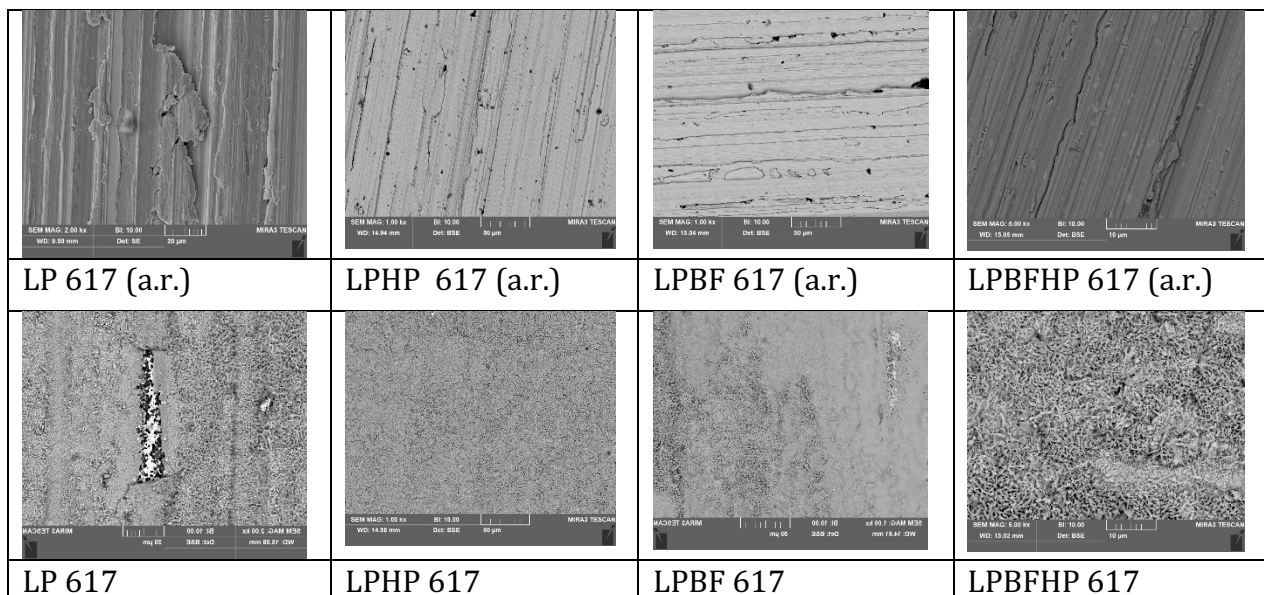| Wt %	LP (a.r.)	LP @He	LPHP (a.r.)	LPHP @He	LPBF (a.r.)	LPBF @He	LPBFHP (a.r.)	LPBFHP @He
O	0	27.5	0	30.3	0	26	0	28.3
Ni	48	1	49	0	48.9	0.8	50.5	0.9
Cr	20.9	44.4	22	21.9	20.7	24.7	21.7	45.5
Co	11.8	0	10.5	0	10.3	0	10.2	0
Mo	8.7	0	8.2	0	8.1	0	9	0
Fe	1.8	0	2	0	2.1	0	2.3	0
Mn	1	24.5	0	28.5	0.9	43.2	0	22
Al	1	0.1	1.1	0	0.9	3	1.1	0.9
Si	1	0.1	0.3	0	0.7	0	0.9	0
Ti	0	0	0.5	17.4	0	0	0	0
C	5.9	2.3	6.3	1.9	6.7	2.3	4.4	2.3

The main mechanism observed was the high-temperature oxidation, with different oxides formation, mainly Cr and Mn oxides. Chromium oxides (Cr_2O_3) are generally more protective than manganese oxides (MnO, Mn_2O_3, Mn_3O_4) when it comes to oxidation resistance in metallic materials. The Cr_2O_3 layer is very stable and has a low diffusion rate for both oxygen and metal ions. This means that it acts as an excellent barrier, preventing further oxidation. Chromium oxides can remain protective up to very high temperatures (around 800–1000°C) without spalling or cracking. Manganese oxides are less protective compared to chromium oxides. They tend to be less dense and have higher diffusion rates for oxygen, allowing oxidation to continue more readily.

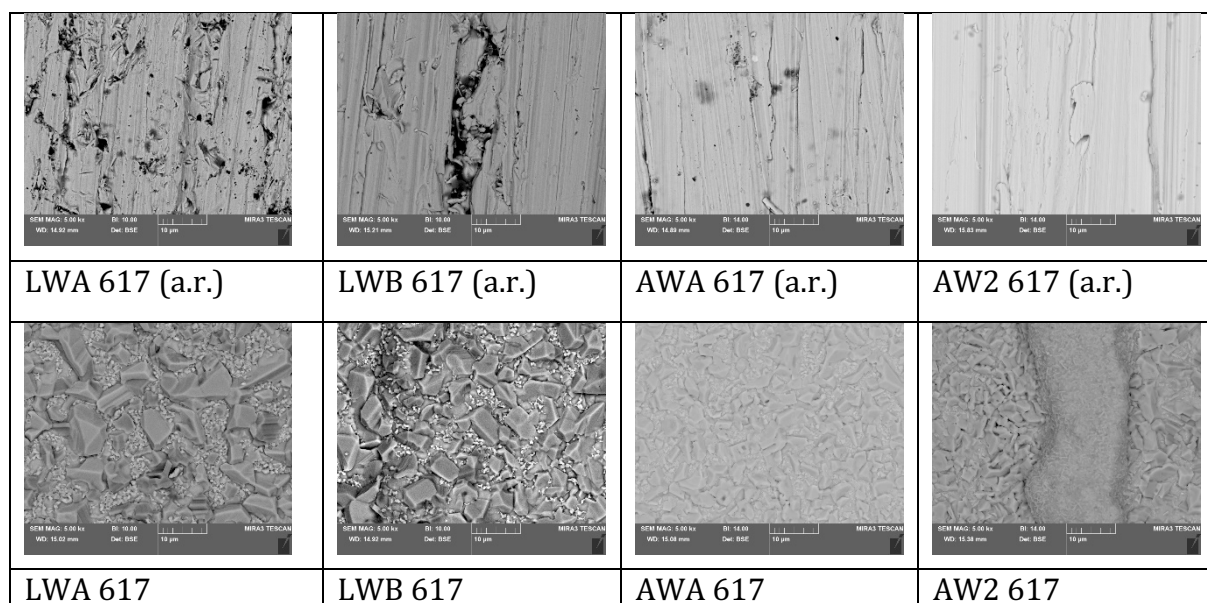|			
LWA 617 (a.r.)	LWB 617 (a.r.)	AWA 617 (a.r.)	AW2 617 (a.r.)
LWA 617	LWB 617	AWA 617	AW2 617

Figure 20 Laser wire and arc welding process samples as received (top raw) and after 1000 h @900°C, He mix

Laser and Arc welding-based additive manufactured samples as received and after exposure @900°C, He are presented in the Figure 20. A dense oxide layer has been formed on the sample surface. Even the self-healing process when chromium reformed the protective Cr_2O_3 layer, has been observed.

Table 6 Chemical composition of the surface area AM samples (LW and AW) as received and after exposure @900°C, He mix

Wt %	LWA (a.r.)	LWA @He	LWB (a.r.)	LWB @He	AWA (a.r.)	AWA @He	AW2 (a.r.)	AW2 @He
O	0	32.3	0	31.9	0	29.3	0	29.5
Ni	46	0	49.1	0	47.8	0	48.9	0
Cr	19.6	28.1	21	28.5	20.7	32.8	21.7	30.2
Co	10	0	10.8	0	10.8	0	10.9	0
Mo	8.5	0	8.9	0	8.2	0	8	0
Fe	1.9	0	2	0	1.7	0	1.8	0
Mn	0	21.9	0	20.8	0.4	24.5	0	25.8
Al	1.2	0	1.1	0	1	0	1.1	0
Si	1.6	0	0.2	0	0.2	0	0	0
Ti	0	15.8	0.5	17.1	0.5	11.7	0.4	12.6
C	9.8	1.9	5.3	1.7	7.5	1.8	6.4	1.8

Given the high levels of Chromium (Cr) and Titanium (Ti) in the composition of oxides in LW and AW samples (Table 6), these alloys is likely to form a protective oxide layer. The Cr_2O_3 and TiO_2 oxides will contribute significantly to the oxidation resistance, while the MnO will be less protective. With more than 11% Ti, a protective titanium oxide layer may form, contributing significantly to the overall corrosion resistance of the alloy.

The following SEM images compare the surfaces of the AM sample AW 617 (arc welding AM process), the AFA steel (conventional metallurgy) and ODS FeCrAl samples M4, and M8 (powder metallurgy), after the exposure @900°C, He mix. Significantly different oxide layers can be observed for two materials with the expected alumina forming a protective layer AFA and ODS FeCrAl (M4, M8) samples. The contribution of the alumina (Al2O3) on the M4 and M8 samples is irregular, accompanied by iron oxide areas. Iron oxide (Fe_2O_3) is less protective compared to Cr or Al oxides. Iron oxides tend to flake off and offer less corrosion resistance in the long term.
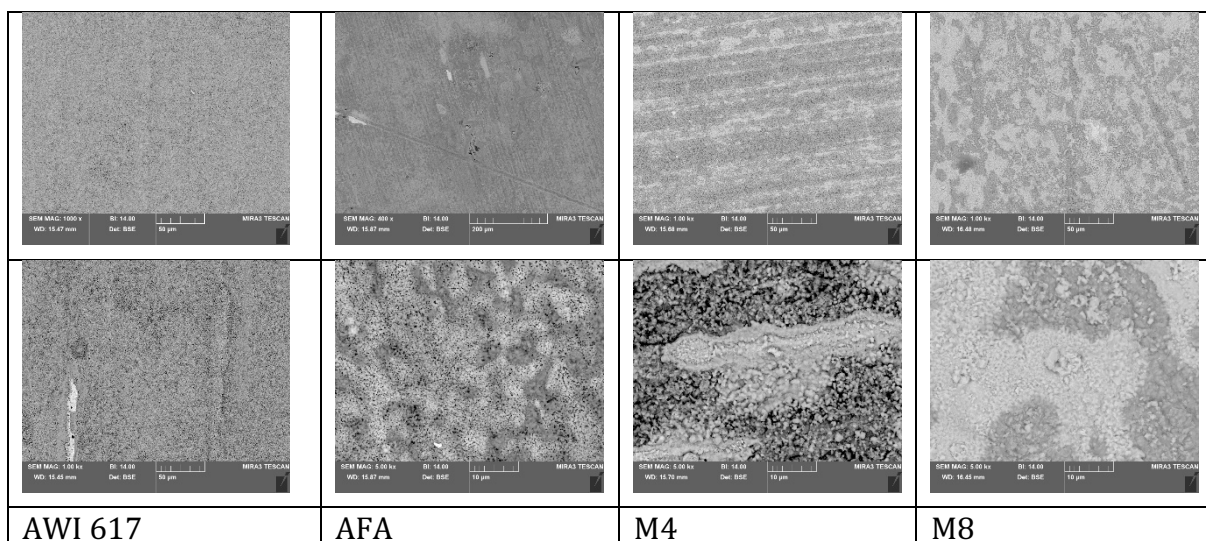

| AWI 617 | AFA | M4 | M8 |

Figure 21 arc welding process sample, AFA steel and two (M4, M8) ODS FeCrAl samples lower magnification (top raw); after exposure1000 h @900°C, He mix

Al2O3 is another highly stable and protective oxide. It is especially good at high temperatures and in oxidative environments. Results of the chemical composition of the oxide layer formed on AFA steel (Cr: 23.2%, Al: 17.7%), Table 7 and weight changes of the AFA steel sample (Figure 18) showed that the oxide layer likely offers better protection overall, especially at higher temperatures. The combination of Cr_2O_3 and Al_2O_3 oxides makes it robust against oxidation in more extreme conditions. The composition of the M8 sample (Al: 42.5%, Fe: 16.5%) has the highest Al_2O_3 content, which should provide excellent protection, particularly in high-temperature environments. However, the presence of iron specifically iron oxide-rich areas could lead to corrosion and spallation issues when the samples are exposed for a longer time and thermally cycled.

Table 7 Chemical composition of the surface area arc welding process sample, AFA steel and ODS FeCrAl samples after exposure @900°C, He mix

Wt %	AWI a.r.	AWI @He	AFA @He	M4 @He	M8 @He
O	0	27.6	32.2	41.5	38
Ni	46.7	1.3	0.6	0	0
Cr	20.4	43.9	23.2	0.6	0.4
Co	11.5	0.6	0	0	0
Mo	7.9	0	0	0	0
Fe	1.7	0	6.1	18.2	16.5
Mn	0.8	24.1	13.9	0	0
Al	0.9	0	17.7	39.5	42.5
Si	1	0	0	0	0
Ti	0	0	0	0.2	0.1
C	8	2.1	2.3	0	0
Zn	0	0	4.1	0	0

5 CONCLUSIONS

The deployment of GIV systems depends crucially on the availability of materials that can withstand the harsh conditions expected in the GFR system. The results provide insight into the durability and behaviour of selected materials under prolonged exposure to high temperatures, helping in the development or selection of materials for high-temperature applications. Several candidate structural high-temperature materials have been selected, manufactured, and tested in the simulating GFR´s gas coolant environments.

Based on the high-temperature oxidation test results, the tested materials can be ranked in the following order AFA > IN617 > Alloy 800H ~ 15-15Ti > AM IN617: LP (LPBF, LPBFHP) ~ AW > ODS FeCrAl. This ranking highlights that AFA steels are at the top of the performance spectrum, particularly in terms of oxidation resistance and mechanical integrity at high temperatures, followed closely by IN617. IN617 is a nickel-chromium-cobalt-molybdenum alloy known for its excellent oxidation resistance at high temperatures. Additive manufacturing methods such as DED and LPBF enhance control over the microstructure of IN 617. Investigated AM IN617 materials exhibit good oxidation resistance and mechanical properties, but the specific additive manufacturing process influences the HT performance. The ODS FeCrAl samples exhibit good oxidation resistance but moderate mechanical strength. Alloy 800H (a nickel-iron-chromium alloy) and 15-15Ti (austenitic stainless steel stabilized with titanium) both offer good resistance to oxidation. Alloy 800H has good high-temperature strength, while 15-15Ti provides excellent toughness and high-temperature tensile properties. However, these materials are inferior to IN617 or AFA steel.

The primary goal of evaluating these advanced materials' resistance to high-temperature environments, simulating the conditions of helium gas coolant in a Gas-cooled Fast Reactor (GFR) system, was successfully achieved. The results demonstrate the promising oxidation resistance of the newly developed AM IN617 produced via the LPBF process. However, further research and optimization of the powder manufacturing process are required to fully realize its potential.