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1. PURPOSE AND SCOPE

The purpose of this document is to provide a summary of the studies, results and discussions on turbine materials accumulated over the first thirty months of HTR-M project.

This document therefore constitutes Deliverable 6 of Work Package 1 *Turbine* of the HTR-E project.

The scope of this document was modified to include, in addition, a summary of the preliminary results of HTR-E- WP6 on HTR Helium Environment.

2. INTRODUCTION

The objectives of the HTR-M project are as follows:

- Investigation of HTR vessel materials and data in the areas of design analysis, structural integrity and material properties under irradiated and non-irradiated conditions, including testing on welds
- Materials for the high temperature region of the HTR under simulated environments both for reactor internals and for the turbine (discs and blades)
- Program of work on graphite material data identifying new graphites suitable for HTR and performing important tests
- Graphite oxidation and consequences of severe air ingress with core burning including development of HTR models and data, protective coatings and innovative C-based materials

The project therefore considers two main areas of investigation: to review past experience and assemble available properties, and to perform tests on key materials where necessary information is lacking or scarce.

Regarding turbine materials, over the first thirty months of the HTR-M project, a technical synthesis has been carried out of the existing high temperature materials and material data for the turbine discs and blades. This collection and analysis of material information from published papers and other sources and databases led to the selection of candidate materials for the turbine disc and blades. Moreover, it has supported the decisions made on material selection for the evaluation and testing phases of the project, currently under way.

3. MATERIAL SELECTION CRITERIA

For the HTR turbine components, especially discs and blades, the criteria for material selection are based on the following main aspects:

- A safe operation period of sixty thousand (60,000) hours
- Upper operating helium temperature limits in the range of 850ºC to 950ºC
- Helium environment

Therefore, the main material considerations are those concerned with creep and environment and the combined effect. As long term service is needed, so we must aim for long term stability of the material properties.

For turbine discs it is necessary to limit the permanent growth and distortion to within typical design life targets. This is usually achieved by maintaining the greater part of the disc cross section within elastic limits. Critical regions for the disc from the point of view of potential creep and fatigue failure are invariably the hottest parts. These are at the disc neck because of unrelieved high localised stresses giving rise to undetected growth, and at the disc rim due to the additional geometric effects of the blade root slots and possible cooling holes. Careful material selection or control of localised stress and temperature conditions can avoid creep-fatigue interaction problems in these areas.

Regarding turbine blades, the main concern is the high temperature properties of the material. The gas radial temperature variation often peaks typically in the middle third of the blade with steep temperature gradients across the blade section which vary according to the transient and steady state conditions. All regions of the blade profile therefore undergo complex stress-strain cycling with reversed plasticity in some areas. For material selection an in-depth understanding of some important parameters such as creep rupture, creep ductility and creep rate are needed.

For the turbine discs and blades possible corrosion effects of environment is also an important selection criterion. The helium coolant gas used in HTR will likely contain small levels of impurities, such us H_2, H_2O, CO, CO_2 and CH_4, at low partial pressures that can interact with the metallic components and cause some loss of their properties or damage to them. Depending on the partial pressure of the impurities and the temperature, the resulting atmosphere can lead to oxidation, carburisation or decarburisation. Damage may either be at the surface (formation of surface films involving oxides or carbides) or diffuse to significant depths into the metallic matrices (internal oxidation, carburisation or decarburisation) resulting in loss of mechanical properties over a significant thickness of the material. This may lead to

either loss of strength or local embrittlement and an increase in the likelihood of initiation of cracks.

For a complete assessment of the structural integrity of turbine discs and blades, consideration must be given to the combined effect of the different possible failure modes, and particularly to the following:

- Creep-fatigue: it is generally considered that the amount of fatigue endurance reduction by creep or relaxation is increased when the material has low creep strength. Creep ductility can also be considered as a limiting parameter in creep-fatigue

- Fatigue and environment effect: initiation of cracks, particularly in the case of thermal fatigue, takes place at the surface of the material and can be influenced by the effects of the environment on the material surface

- Creep-fatigue and environment effect: the effect of environment can be important in creep-fatigue and in thermal fatigue. Experiments have shown that the reduction of fatigue life by hold times in relaxation can be quite different in a vacuum from what is observed in air, and therefore should be quantified for helium environment

Finally, the manufacturing route and capability has to be considered since it has a direct bearing on the material selection and strength.

For the turbine discs there is a requirement to produce large ingots without porosity and segregation. Such a process requires the production of around ten tons of ingots with subsequent forging. For aero-engines the manufacturing route includes re-melting technology (vacuum induction melting, vacuum arc remelting, electroslag remelting) in order to produce large diameters. However, with current alloys, discs produced in this way have reached the limit of their performance. The possibility of producing near-shaped large diameter discs using hot isostatic pressing (HIP) seems more promising, following the availability of large diameter HIP furnaces. The future possibility of a bonded disc produced in this way should also not be discounted. HIP produces materials with design properties different from those of the corresponding forged or cast alloy.

With respect to the manufacture of the turbine blades, single crystals (SC) offer the highest creep properties but their cost is high, properties can be anisotropic and they cannot be easily repaired if damaged. Directionally solidified blades (DS) are good candidates for non-cooled blades. They offer improved creep properties compared with conventionally cast versions and better repair possibilities, and their use in industrial land-based gas turbines is more extensive. Conventionally cast grades are easy to procure and have extensive industrial experience and the fabrication of HTR

blades should be possible. However, the major limitation is the modest creep strength at 850ºC.

4. CANDIDATE MATERIALS FOR DISCS AND BLADES

4.1 CANDIDATE MATERIALS FOR DISCS

The following candidate materials for HTR turbine discs have been identified:

Grade	Description
A286	Fe Ni Cr precipitation hardened grade. It was proposed in the frame of the Dragon Project for the turbine disc production. It has medium high temperature properties. This grade can only be envisaged in the case of cooled turbine discs. Sufficient forgeability for large disc production.
IN 706	Fe Ni Cr precipitation hardened grade alloy. It was also proposed in the frame of the Dragon Project for the turbine disc production. As for A286, this grade has medium high temperature properties and can only be envisaged in the case of cooled turbine discs. It also has sufficient forgeability for large disc production. IN 706 with additional Mo and Nb allows for the manufacture of large discs but the process is very complex.
IN 100	Strengthened Ni-based super-alloy. Originally proposed for PBMR turbine discs and blades. It has good carburisation resistance. The material forms a thin protective Al oxide surface scale on exposure to HTGR helium. As with other similar Ni-based super-alloys, low cycle fatigue cracking is appreciably enhanced by oxidation both in terms of numbers of cracks and cycles. It can be easily forged or cast. Possible using powder metallurgy and HIP process.
Waspaloy	Age-hardenable nickel based alloy. It was extensively used in the past for turbines. Excellent strength at elevated temperatures often used for critical turbine engine components. Now being replaced by IN 718 and Udimet 720.

Grade	Description
IN 718	Ni-based precipitation strengthened super-alloy with additions of Cr, Fe, Co, Mo, Ti and Al. Extensively used for gas turbine discs, it was selected for the HTGR turbine discs. It has good oxidation and creep resistance at temperatures up to 650ºC. With a turbine inlet temperature of 850ºC it will require active cooling to lower the temperature of the disc to around 650ºC and ensure the necessary strength, short-term creep and corrosion resistance. Segregation problems during casting can occur. Also because of low castability, the production of large ingots has not been possible so far.
Udimet 720	Ni-based alloy with cobalt. It may be better in terms of high temperature strength than IN 718. It achieves this high strength due to its γ' Ni3 (Al, Ti) precipitate duplex mircrostructure (coarse and fine) obtained by heat treatment. It is considered the most promising of the Ni-based super-alloys for turbine disc application. Billets of up to 250 mm diameter have been produced by forging. Also the material can be processed by powder metallurgy and hot isostatic pressing (HIP) which is expected to be required to produce large diameter discs. Only the oxide dispersion strengthened (ODS) material offers greater potential strength at higher temperatures. However the manufacturing route of Udimet 720 is significantly more mature than ODS material.
IN MA 6000	Oxide dispersion strengthened (ODS) Ni-based super-alloy. It is one of the proposals for GT-MHR. It offers very high strength and microstructural stability. It has excellent corrosion / oxidation resistance. Its cyclic life is comparable or better than IN 738 LC. The creep strength of this grade could reach values higher than 185 MPa for 60,000 hours at 850ºC. It is considered to be the only existing super-alloy that could be envisaged for a non-cooled first stage disc. This grade is produced by mechanical alloying of powders and subsequent HIP or hot extrusion. The main difficulties with using ODS grades are that the process route is not mature and that much work is needed to produce large ingots with homogeneous mechanical properties.

Grade	Description
Zh56F	Ni-based precision investment cast alloy. Contains Cr, Co, Mo, tungsten, Ti, Al, Ni, vanadium and hafnium. It is the Russian proposal for GT-MHR. It contains more tungsten and niobium than the other Russian proposal for GT-MHR (V2HL12U). Cast parts are not used for large discs in aero-engines and consideration must be given to the viability of manufacturing a large disc in this way.
V2HL12U	Ni-based precision investment cast alloy. It is the other Russian proposal for GT-MHR. Contains more chromium, cobalt, molybdenum and titanium than Zh56F but less tungsten and no hafnium. Consideration must also be given to the viability of manufacturing a large disc by casting.

4.2 CANDIDATE MATERIALS FOR BLADES

The following candidate materials for HTR turbine blades have been identified:

Grade	Description
IN 713 LC	Ni-based precipitation hardened alloy with low cobalt content. There is wide industrial experience in conventional gas turbines (turbine housings, case and stator). It was one of the reference alloys selected for testing within the Dragon metal program. Used for HHV Project turbine blades and during the short high temperature lifetime experience (350 hours at 850ºC) no material problems appeared. It has high creep resistance. In HTGR, helium can be susceptible to carburisation and sulphidation problems and coatings have to be envisaged. The DS or SC versions overcome this but contain more cobalt (10%). It can also suffer from over-temperature damage which can blister the coating and substantially alter the creep behaviour (removal of tertiary creep phase). Creep rupture strength decreases sharply with temperature and the rupture ductility drops to just a few percent between 500-700ºC.

Grade	Description
	A test duration in impure helium of about 37,000 hours was achieved. It is well suited for turbine blades except for the first stage blades where cooling would be necessary to achieve the required lifetime. It has superior castability.
IN 100	Strengthened Ni-based super-alloy. It is an aluminium oxide former material. It is the original PBMR reference alloy for power turbine cooled blades and for the discs. The material forms a thin protective Al oxide surface scale on exposure to impure helium. It has good carburisation resistance. As with other similar Ni-based super-alloys, low cycle fatigue cracking is appreciably enhanced by oxidation both in terms of numbers of cracks and cycles. It can be easily forged or cast. Possible using powder metallurgy and HIP process.
IN 738 LC	Cr Co Mo W Ti Al Ta super-alloy. IN 738 LC is presumably a low carbon variant of IN 738. It has been widely used for large land-based gas turbine blade applications. The effect of environment on creep and fatigue behaviour plus crack growth rates have been studied through tests in air, vacuum and hot corrosive environments. Test in impure helium suggested fatigue results should not differ markedly from those for a vacuum. Conventionally cast.
IN 792 DS	Its chemical analysis similar to IN 738, with higher contents of niobium, tantalum, cobalt, tungsten and titanium, slightly lower chromium content and additions of hafnium. Developed for higher strength at the expense of corrosion. IN 792 may have an advantage of 30ºC in high temperature strength with respect to IN 738 and of 10ºC with respect to IN 100. The directionally solidified (DS) IN 792 produces a further improvement in high temperature strength of around 25ºC. Crack growth resistance in impure helium of IN 792 is similar to IN 738. Conventionally cast or, as proposed, directionally solidified.

Grade	Description
M21	Low chromium Ni-based alloy that combines precipitation hardening and solid solution hardening (~10% tungsten addition). It has good corrosion resistance in impure helium but not as good as IN 713 LC or IN 738. Conventionally cast.
MAR-M 004	Ni-based alloy derived from IN 713 LC. It is a cobalt free aluminium oxide former material. It has a similar creep rupture strength to IN 713 LC and is claimed to have better toughness because of hafnium addition. It has a good resistance to corrosion in impure helium environment. Conventionally cast.
TZM	Molybdenum based alloy. The investigation of TZM material was carried out within HHT materials program. It exhibits completely different creep-resistance behaviour as compared to the Ni-based alloys, mainly due to its high melting point (2607ºC). It has excellent creep strength at high temperatures. Almost flat creep curves make this material a potential candidate for service periods of 60,000 hours for a non cooled blade. TZM alloy reaches a higher lifetime then IN 713 LC under similar conditions. It has not been used in industrial gas turbines because of its poor oxidation resistance in air (due to the volatility of molybdenum). However, R&D efforts carried out in German HTGR programmes have demonstrated a promising application for helium turbine blades. Precision forged blades were fabricated, starting from vacuum-arc-melted or power metallurgy ingots. However, due to the fact that it is brittle at temperatures up to 360-440ºC, that the notch sensitivity remains high at elevated temperatures and that in the event of air ingress the blade will suffer massive oxidation, and because of microstructure heterogeneity due to the fabrication difficulties, this alternative was abandoned in the past.

Grade	Description
CM 247 LC DS	Derived from MAR M 247, an aluminium oxide former with low values of Ti/Al ratio. It was designed for blades and vanes of aero-turbines. The material has been successfully used in industrial turbines with ductile high chromium coating for resistance to hot corrosion attack. It has reduced carbon content (approximately one half), improved stability and alloy ductility plus reductions of Zr and Ti to improve grain boundary cracking without sacrificing strength. The W and Mo levels are reduced to minimise the formation of undesirable effects resulting from carbide degeneration. It has higher strength and improved oxidation resistance than IN 738 or IN 792. In terms of metal temperature capability. the DS CM 247 LC is expected to provide a 50ºC greater temperature at stress levels of 138-207 MPa compared with IN 738. It offers better castability and greater process flexibility than IN 738 or IN 792.
Nimonic 80A	It has relatively lower creep rupture strength than, for example, IN 713 LC and is only suitable for lower service temperature operation but could be considered for blades of the last turbine stage.
FIS 145	Alloy combining precipitation hardening and solid solution hardening (~13.5% tungsten addition). It was developed in Germany for HTGR applications. It has high castability.
Ch120M	Ni-based alloy. It is the Russian proposal for GT-MHR turbine blades. CMSX2 grade is the US equivalent of Ch120M SC. Cast as a single crystal (SC).
EI929, EI893, EP800	Ni-based alloys with chromium, molybdenum, tungsten and aluminium. Proposed for GT-MHR as a backup alternative if Ch120M is proved to be unacceptable. EI893 is cobalt free and EP800 has niobium instead of titanium.

Grade	Description
SC16	It is a cobalt free γ' hardened high chromium alloy. Its Ti/Al ratio is close to unity making it a chromium oxide former material in HTGR helium. Proposed as a single crystal (SC) alloy, it is expected to provide an increase in temperature of up to 60ºC compared with IN 738, potentially a similar temperature capability (in terms of creep rupture strength over 10,000 hours) to DS CM 247 LC Single crystal.

5. SELECTED MATERIALS FOR TESTING

The work of collecting and analysing material information from published papers and other sources and databases carried out over the first thirty months of the HTR-M project has to be considered as the first step towards selecting materials for the disc and blades of future HTRs.

The review has considered nine potential materials for the turbine disc and thirteen for the blade (including the Russian backup options). Creep resistance and high temperature strength are important requirements and are expected to be the main selection criteria. The manufacturing route and capability also has to be considered since it has a direct bearing on the material selection and strength.

Discussions with the turbine materials manufacturer Aubert & Duval, together with the results from a review of published information, identified Udimet 720 as the best available candidate for the turbine disc. Udimet 720 is still under development and the current view is that it may not be usefully applicable for discs above 700ºC. This suggests that a cooled disc may be necessary.

Udimet 720 can be processed by powder metallurgy and hot isostatic pressing (HIP), and this is considered necessary to produce larger diameter discs. The literature search produced very few published data on this material. This shortage of data will clearly be addressed during the testing phases of HTR-M project, since this material has been chosen for short term testing within the HTR-M programme. Of the several materials examined, only the oxide dispersion strengthened (ODS) material (MA 6000) looked capable of providing greater strength at higher temperatures, but its manufacturing route still requires significant work.

Of the blade materials investigated, the best potential long-term creep strength was provided by the molybdenum based alloy TZM. This has seen a significant amount of testing within the German HTR programme but its high ductile brittle transition temperature appears to make it a less practical option compared with Ni-based alloys. This material is however to be included in the database and its suitability for future application will be assessed as further information is gathered.

Of the Ni-based super alloys, the most promising in terms of creep strength are the single crystal alloy SC CMSX-4, the direction solidified CM 247LC DS (plus MAR M247), and IN 100. From published data, these are expected to have a creep rupture strength of the order of 150-200 MPa at 850^{o}C after 60,000 h. IN 792 DS is also included in this group since it is expected to have a 35ºC advantage over IN 100. A cobalt-free option to these materials would be SC 16, which is similar in strength to CM247 LC DS. The Russian alloy Ch120M is comparable to the single crystal CSMX-2 grade and therefore also offers potential. It should be noted however that an

additional design margin of around 2.0 on stress would normally be required for nuclear components important to safety. The need for such a factor for the turbine would have to be reviewed. Alloys IN 713 LC and IN 738 LC -although well established as turbine blade materials- are expected to have much lower strengths (<100 MPa).

The choice of materials for the short and medium experiments of HTR-M project are as follows:

- Turbine disc: Udimet 720
- Turbine blade: IN 792 DS

  CM 247 LC DS

The test information gained during the HTR-M project will be included in the database. For the turbine blade tests, direction solidified chromium former and aluminium former materials have been selected. The current view is to avoid single crystal materials if possible at this stage in the development.

6. COATINGS

Coatings have been used to protect gas turbine hot section components from oxidation and hot corrosion. In particular, aluminide coatings were successfully developed for resistance to oxidation. Improvements for corrosion resistance were obtained by the development of metal, chromium, aluminium and yttrium coatings (MCrAlY, metal M being nickel, cobalt or iron) which are currently used for protection from hot corrosion.

More recently, a thermal barrier coating (TBC) was developed for turbine blades. It consists of a second porous coating layer which can give an additional gas operating temperature advantage of up to 100 C. The composition of TBC is zirconia + yttrium (around 7%).

Deposition of such coatings is done using electron beam physical vapour deposition (EB-PVD) or plasma spray: the first being better but more expensive.

In general, coatings are necessary when aiming for long-life turbine blades. In spite of the use of coatings, a base material with adequate corrosion resistance is regarded as essential. The choice of coating remains to be made and tested and its durability assessed for the HTR helium environment.

The coating must be of the same type (chromium oxide former or aluminium oxide former) as the base alloy.

The cobalt and tantalum content of the alloy is not important with respect to potential contamination whenever coatings are used, but it is important in the coating itself.

As already mentioned, chromium oxide former and aluminium oxide former blade materials have been selected for the HTR-M testing programme.

7. HELIUM ENVIRONMENT

The helium coolant gas used in HTRs will likely contain low levels of impurities that can interact with the component materials and cause some loss of their properties or damage to them (corrosion effects at high temperatures, 850-900 ºC).

In view of this, a specific working group (WP6) was set up within the HTR-E project to analyse in detail the possible effect of the helium environment on the materials and to provide recommendations on helium purification system specifications. For two years, the activities of WP6 have focused on the documentation and analysis of available know-how from former HTR projects and on the identification of input data for the system design. The main findings of WP6 that could have an impact on material selection and the design of the HTR Turbine are summarised below.

The impurities that one could normally expect to find in the HTR helium coolant are those which are desorbed from the reactor primary circuit components, or those which result from refuelling operations (residual air, water, etc), air ingress, fission products that migrate from the fuel, moisture and contaminants from new helium supply. These impurities in the helium will mainly be H_2, H_2O, CO, CO_2 and CH_4, at low partial pressures (in the 1-100 µbar range). Erosion effects due to the graphite particle content (dust) and which is said to be significant in the direct cycle concept will also have to be considered.

The basic mechanisms of the interaction between the anticipated impure Helium environment and the metallic materials of the HTR components have been studied. Special attention was focused on the reactions stemming from the interaction of impure helium and nickel-based alloys, since the latter have been identified as the leading candidate materials for the HTR Turbine discs and blades.

Corrosion in a helium environment is therefore caused by the reaction of the metal with helium impurities. The influent parameters are temperature, the partial pressures of the impurity concentrations, and the composition of the alloy.

The main corrosion mechanisms that may arise are oxidation, carburisation or decarburisation. The corresponding damage can be either superficial or internal. The consequences are the following:

- Oxidation: The formation of an oxide layer on the alloy surface. If this layer is porous or cracked, internal oxidation is possible and will depend on the diffusion rate of oxidising elements toward the outside and oxygen towards the inside. The consequences are loss of thickness (superficial) or a loss of ductility and crack formation (internal)

- Carburisation: The formation of carbides. Carburisation occurs when the carbon potential in the material is lower than in the gas or when carbon transfer takes place. Different carbides can be formed, depending on the alloy composition and the carbon solubility. The formation of a superficial non-protective layer of carbides could interfere with the oxidation process and inhibit the formation of a protective oxide layer. This results in a porous layer which may allow both severe oxidation and carbon access to the bulk material and carbide formation when the solubility limit is reached. Internal carburisation (granular or inter granular) of the alloy by carbon diffusion into the matrix could also occur and could be very fast if there is no protective oxide layer. The internal carburisation rate is determined by the diffusion of carbon into the material. The consequences are non-protection against oxidation (external layers) or ductility loss and crack formation (internal)

- Decarburisation: The reaction between carbon and water. This reaction can disturb the formation of the oxide layer because of gas bubble production, and can lower the carbon content of the alloy matrix so low that the carbides become unstable and can be dissolved. Furthermore, some very high temperature alloys take their good mechanical behaviour from solid solution effects and carbide precipitates. These mechanical properties will decrease if decarburisation occurs. The consequences are a loss of creep resistance and strength associated with the dissolution of carbides.

Other corrosion mechanisms that could occur are nitriding, evaporation, spallation and chromium depletion (on the alloy surface).

For a given temperature, the proper behaviour of an alloy is associated with the formation of a protective oxide layer and low carburisation of the alloy. The formation of a stable oxide layer results from the presence of water in sufficient proportion (P_{H2O}/P_{H2}> critical value) and the balance between oxidation and carburisation reactions which are a function of both thermodynamics and kinetics factors. In an impure HTR helium environment, oxygen activity is determined by H_2O and H_2 content, and carbon activity is determined by CO content (thermodynamically) and CH_4 content (kinetically).

For nickel-based alloys in the HTR helium environment, chromium is the main element governing the corrosion mechanisms (*chromium activity*). For these alloys, a high Cr content will increase the stability domains of oxide and carbide. The presence in the alloy of aluminium, or of any other element that can also form an oxide layer, will modify the chromium activity and therefore the alloy behaviour with regard to corrosion.

These possible interactions between impure helium and alloys are described by the *stability diagrams,* which relate the material properties and the conditions of the

environment. These stability diagrams are very useful and allow estimating, for a given temperature and material defined by its chromium activity a_{Cr}, whether the helium environment composition (described by the oxygen partial pressure and the carbon activity) leads to the formation of a protective oxide layer or not.

The stability diagram for chromium oxide former Ni-based alloys in an HTR helium environment at a given temperature is given in Figure 1. A significant presence of other oxide former elements in the alloy composition (Al, Ti, Mn and Si) will modify this stability diagram.

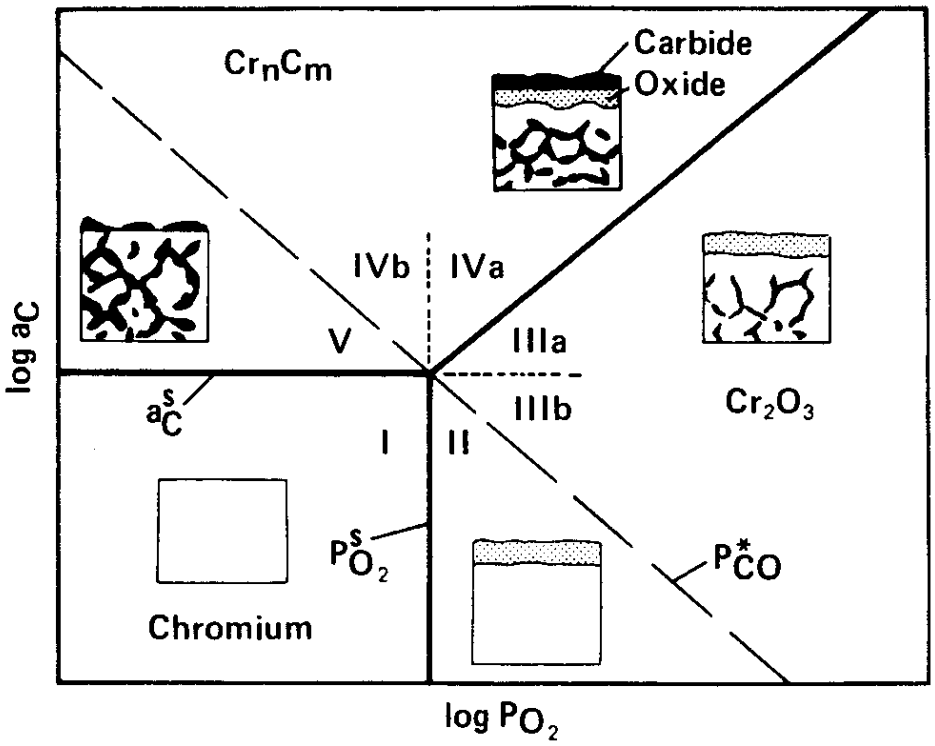

Figure 1: Stability diagram (Ni-Cr alloys)

The stability diagram is divided in different domains. These domains are delimited by the following environment characteristics depending on the temperature and the chromium activity in the alloy:

- Oxygen activity, given by the partial pressure of oxygen (P_{O2}) and by H_2O and H_2 content (PH_2O/PH_2) in the helium environment. If the oxygen activity is greater than the critical value (P_{O2}^S) the chromium oxide layer is stable
- Carbon activity (a_C). If carbon activity is in excess of the critical value (a_C^S) chromium carbides will form

- Partial pressure of CO (P_{CO}). If the partial pressure of CO is less than a critical value (P_{CO}*) no protective layer can be formed and the alloy will show severe damage either by carburisation or by oxidation and decarburisation

Seven different domains can be identified in the stability diagram. The possible behaviours in the HTR helium environment of chromium oxide former Ni-based alloys are the following:

- In domain I, metallic chromium is stable, no protective oxide layer can be formed ($P_{O2} < P_{O2}^S$) and strong decarburisation may occur if the carbon activity (a_C) is too low

- In domain II, chromium oxide is stable ($P_{O2} > P_{O2}^S$), but a low carbon activity (a_C) will result in alloy decarburisation. The decomposition of the carbides will lead to gas production that will damage the oxide layer

- In domain III-a, chromium oxide is stable ($P_{O2} > P_{O2}^S$) and the formation of a protective layer on the alloy is possible. In addition, the carbon activity is in excess of the critical value ($a_C > a_C^S$) and chromium carbides can be formed under the oxide layer. Provided that the oxide layer is protective, this domain of the stability diagram is a safe region as far as Ni-based alloy degradation is concerned, with slight chromium carbide formation below the oxide layer.

- In domain III-b, chromium oxide is still stable ($P_{O2} > P_{O2}^S$) but the carbon activity is too low for the chromium carbides to be stable ($a_C < a_C^S$). However, since the pores of the protective oxide layer are not too large, the depletion of water in these pores causes a local increase of the carbon activity. As a consequence, the environment is slightly carburising in the pores. This domain of the stability diagram is considered to be the safest.

- In domain IV-a, chromium carbides are stable ($a_C > a_C^S$) and a non-protective surface layer of chromium carbides may be formed. This layer will alloy internal carburisation of the material even if an oxide layer is formed ($P_{O2} > P_{O2}^S$) under this carbide surface layer, since the latter will not be very protective. This domain is not safe for Ni-Cr alloys.

- In domain IV-b, carbon activity is also high and carburisation will occur. A non-protective chromium carbide surface layer is formed and if the porosity of this layer is not too high, an oxide layer may be formed under the carbide layer due to local decrease on carbon and local increase of oxygen activities in the pores. The behaviour of the alloy is therefore similar to domain IV-a.

- In domain V, chromium carbides are stable ($a_C > a_C^S$) and the alloy will undergo severe carburisation since no protective layer can be formed ($P_{CO} < P_{CO}$*).

For aluminium oxide former nickel-based alloys, that is, alloys of low chromium content and high titanium/aluminium content, safe behaviour as regards corrosion in the HTR helium environment requires the formation of a continuous protective alumina layer. The formation of this alumina layer will only be possible if it is not impaired by the oxidation of chromium, that is, if the Cr content in the alloy is not too high and the environment is not too oxidising ($P_{O2} < P_{O2}^{S}$).

The definition of the stability diagrams requires determining the chromium activity of the alloy, which is dependent on both the other alloying elements and the metallurgical condition of the material. In addition, the surface reaction may cause a surface depletion of oxidisable elements that could modify the Cr activity in that area and thus the critical values of P_{O2} and P_{CO}.

It is therefore difficult to define the real Cr activity of Ni-based alloys in the HTR helium environment. Moreover, there is a significant lack of experimental data for high temperature metallic materials in impure Helium environments. Complementary studies are still required on those materials to establish their maximum temperature of use, including surface film evaporation at high temperatures, and possible break away leading to oxide spallation.

However, some parametric studies have been carried out for chromium oxide former Ni-based alloys in an HTR helium environment. Two different helium temperatures have been considered, 950ºC and 1000ºC, and two different chromium activities of the alloy, 0.6 and 0.3, the latter in order to consider a reduced chromium activity due to the possible surface chromium depletion.

As a preliminary result, assuming that chromium depletion will reduce to 0.3 the surface Cr activity of a Ni-based alloy, safe behaviour regarding corrosion will require the following levels of impurities in the helium environment:

	Temperature	
	950 ºC	1000 ºC
Po_2	> 2 x 10^{-23}	> 10^{-21}
P_{H2O} /P_{H2}	> a few 10^{-4}	> a few 10^{-4}
P_{CO} (µbar)	> 150	> 500
P_{CH4} /P_{H2O}	< 10^{-2}	(1)

(1) The critical value of the ratio P_{CH4} /P_{H2O} at 1000ºC is unavailable since it results from the relative kinetics of two reactions and no data is found, for this temperature, in the literature.

In addition, the higher the temperature, the faster the kinetics of material degradation. Thus, the higher the temperature, the more strictly above helium specifications have to be enforced.

The management of helium impurities in modern HTRs working at temperatures of around 900ºC cannot rely on the simple concept of helium purification that consists of indiscriminately decreasing all impurity content as far as possible, but should evolve towards a concept of helium impurity control.

The target values of controlled impurity levels have to take into account the theoretical critical values presented in the above Table, while additional safety margins need to be evaluated based on the variation of the operating parameters and the long term evolution of the alloy surface compositions.

Further work is required in areas such us modelling the chromium activity of the alloys and the evolution of chromium on the alloy surface over time, constraints related to the oxidation of graphite at high temperatures and the possible formation of carbon dust and CO_2 in low-temperature regions. Finally, the the need for N_2 specification should also be assessed.

8. CONCLUSIONS

This document summarises the work carried out during the first thirty months of the HTR-M project. During this first phase of the project, the material selection criteria for HTR turbine discs and blades have been discussed, those of main concern being the creep resistance, the high temperature strength, corrosion resistance and the manufacturing route.

Based on the identified selection criteria, a technical synthesis of the existing high temperature materials and material data has been carried out, collecting and analysing material information for turbine discs and blades from published papers and other sources and databases. During one of the first steps, nine potential materials for the turbine discs and thirteen for the blades (including the Russian backup options) were identified as candidate materials.

Discussions within the HTR-M project and with turbine materials manufacturer Aubert & Duval, together with the results from the material synthesis and analysis previously carried out, led to the identification of Udimet 720 as the best available candidate for the turbine disc. Udimet 720 is considered to have a potential for operation up to 700ºC. This suggests that a cooled disc may be necessary. Suitable quantities of this material are being procured and characterisation tests have started. Tests on disc materials will be carried out at 700ºC and 750ºC.

With regard to the turbine blades, Ni-based super alloy materials were considered to offer the best all round properties. The current view is to avoid single crystal materials and two directionally solidified grades have been selected for testing: CM 247 LC DS — an aluminium oxide former, and IN 792 DS — a chromium oxide former. Procurement of these turbine blade materials from recommended suppliers has been secured and they will be available before the end of this year. Tests under tensile and creep conditions will be carried out at 850ºC.

In general, coatings are necessary when aiming for low-life turbine blades. Therefore, the use of coated blades is proposed, bearing in mind that the coatings must be of the same type as the base alloy of the blade.

The test matrix and proposals for the test conditions will as far as possible bound the temperature and transient cases to those of the turbine. High temperature short-term mechanical/creep tests are planned for turbine disc and blade materials in simulated environments. The duration of the intermediate creep tests is expected to be around 3000 h and will include aged samples. Four environments will be used to fully cover carburised, decarburised, reference heat-treated and delivery conditions.

A material database is being developed and the information will be managed through a web-based system to allow remote partner access and to maintain secure transfer of information. The already collected and analysed information regarding turbine disc and blade materials is going to be included and the database will be continuously updated with information resulting from the material tests.

Regarding the HTR Helium Environment, it will likely contain small levels of impurities that could interact with the component materials and cause some loss of their properties or damage to them (corrosion effects at high temperatures).

HTR-E WP6 was specifically established to analyse the HTR Helium Environment and to provide recommendations regarding the purification system. Special attention was paid to the reactions involved in the interaction between impure helium and nickel-based alloys, the candidate materials for the HTR Turbine discs and blades.

The work has been concluded, leading to preliminary results for safe behaviour of Ni-based alloys regarding corrosion in impure helium environments at high temperatures. The level of impurities, such as O_2, H_2, H_2O, CO, CO_2 and CH_4, should be controlled to keep them within the corresponding thresholds and not simply decreased as far as possible indiscriminately.

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