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Specification of IHX Test Programme & Material selection

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RAPHAEL ***(ReActor for Process heat, Hydrogen And ELectricity generation)***

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Specification of IHX Test Programme & Material selection

Abstract

This report provides a review of available materials and their limits for the key high temperature components (internals, hot gas duct, heat exchangers) of the VHTR together with a short list of materials for evaluation. From this review the most promising available candidate materials have been selected and recommendations are given for future development of some new alloys more adaptable to the VHTR upper temperature limit requirements.

A test program has been proposed for the period 24-48 months in order to improve the knowledge of high temperature mechanical properties and microstructure of the selected high temperature metallic alloys. The requirement is to advance the understanding and evaluation of high temperature long-term properties through a series of tests including creep, thermal aging, and effects cold work on mechanical properties (important for manufacture) in the temperature range [700°C-1000°C].

Revisions

Rev.	Date	Short description	Author	WP Leader	SP Leader	Coordinator
00	dd/mm/yyyy	First issue	Name, Organisation	Name, Organisation *Signature*	Name, Organisation *Signature*	Name, Organisation *Signature*
01	30/04/2006	First issue	Jean-Marie Gentzbittel CEA	Jean-Marie Gentzbittel CEA	Derek Buckthorpe NNC	

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1 Introduction

The Very High Temperature Reactor (VHTR) gas cooled system ican be used for future co-generation plants for sustainable production of electric energy and heat for hydrogen production or other high temperature processes. Such a system can require high gas outlet temperatures close to 1000°C for certain applications and to achieve high levels of efficiency. Materials for long-term structural applications in such plants must be explored to allow efficient safe and reliable operation of such advanced plants. The thermal, environmental, and service life conditions of the VHTR makes the selection and qualification of some high-temperature materials a significant challenge, and new materials and approaches may be required.

These investigations mainly concern three classes of materials: metallic materials, graphite, ceramics and composites. The high temperature metallic materials work investigated within Raphael-IP WP2 includes the selection and confirmation of materials for the internals, hot gas duct and heat exchangers for VHTR operation. A review of available materials for the key high temperature components (internals, hot gas duct, heat exchangers) of the VHTR plus a short list of most promising materials for evaluation has been made in the previous report DML2.2 [Ref. 1]. An initial recommendation on a generic test programme (short term plus ageing tests) has also been established.

This was a preliminary investigation and used to initiate discussion with the Sub project SP-CP of RAPHAEL on possible ways forward. Since then joint exchange meetings have taken place that have given further indications on the requirements for High Temperature Material components and some specific design requirements [Ref. 2, 3]. From this work candidate materials are to be selected for testing and further investigation.

2 Objectives

The purpose of this report is to review material limits for the key high temperature components (internals, hot gas duct, heat exchangers) and provide a short list of potential materials for evaluation for the VHTR. From this, the most promising available candidate materials will be selected and recommendations made for development of some new alloys more adapted to VHTR upper limit requirements. In addition the test programme to be performed within SP ML WP2 on currently available industrial options (covering issues not currently addressed in present National Programmes) will be specified.

3 Limits of current Materials

The selection of materials for developing advanced high temperature components for VHTRs for the heat exchangers, hot gas duct, internals, is dependent on the potential of such materials to meet design and service requirements and to be fabricated and assembled according to design and performance specifications. The capability of the selected material to meet these requirements is determined by mechanical, physical and corrosion properties as well as susceptibility to forming, shaping and joining by feasible means. The selection and qualification of metallic materials for high temperature VHTR components involves

1. the determination of materials data
2. influence of specific VHTR service conditions
3. development to component level, especially the transfer of uniaxially loaded data from laboratory specimen to more complex geometries and the availability of more complex thermo mechanical treatment .

Different high temperature metallic materials have been selected in the previous report [Ref. 1] for advanced high temperature gas cooled reactor components and are mainly : Alloy 617, Alloy 230, Alloy X, Alloy 800, ODS alloys, TiAl....

The properties of metallic alloys are highly dependent on the chemical composition and thermal treatment. A short review of some limitations of currents materials has been carried out taking account general requirements for corrosion, mechanical properties, thermal stability, shape and manufacturing availability, joining and the resultant metallurgical microstructures.

3.1 Limits of Nickel alloys – Alloy 617, Alloy 230, Alloy X

Nickel based alloys have been selected because of their relatively high strength at high temperature and good corrosion resistance. The material for the primary circuit must exhibit very good thermal stability for long operating times, moderate creep strength and must be capable of being used with well established metal forming and welding techniques.

3.1.1 Mechanical behaviour

In the past, exhaustive work has been performed on the alloy 617 [Ref. 4, 5, 6, 7], which was the candidate material for German team and on alloy X and the modified version alloy XR which was the chosen material for the Japanese project (HTTR). The determination of a precise temperature limit and stress limit is difficult. The very long service life and the safety assurance required for VHTR components such as the IHX (intermediate heat exchanger) take the application of high temperature alloy beyond established technological areas.

From the creep rupture point of view allowable stresses estimated following the procedures of American society of mechanical engineers (ASME) Code Case N47 for alloy 617, alloy X and alloy 800H at temperatures in the range of 800°C to 1000°C are shown below in Figure 1 [Ref.6].

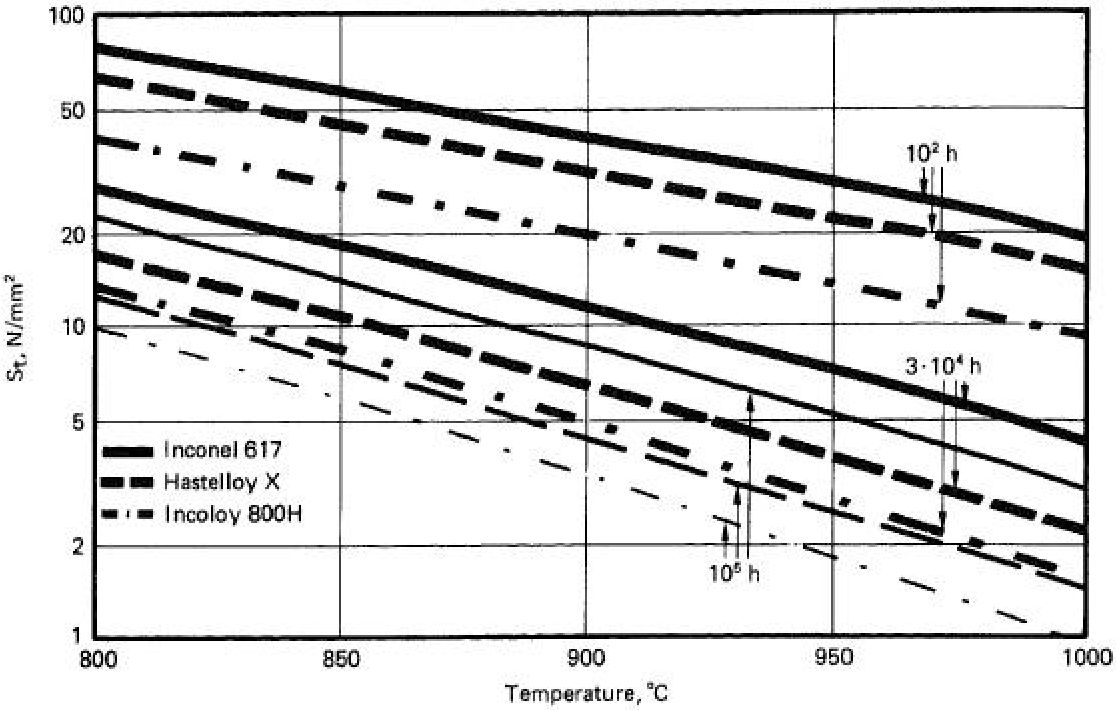

Fig. 4. Preliminary design stresses (S_t) for three high temperature alloys.

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Figure 1 Design stress for three nickel alloys – taken from Ref [6]

For the assessment of the influence of thermal cycling during start-up, and shut down, during power adjustment or during some incidental transients conditions, strain controlled fatigue (low cycle fatigue (LCF)) tests results are required. The LCF properties are as important for the determination of the remaining life of the component as the creep rupture. Results of fatigue properties at different temperature of Alloy 617 are given in Figure 2.

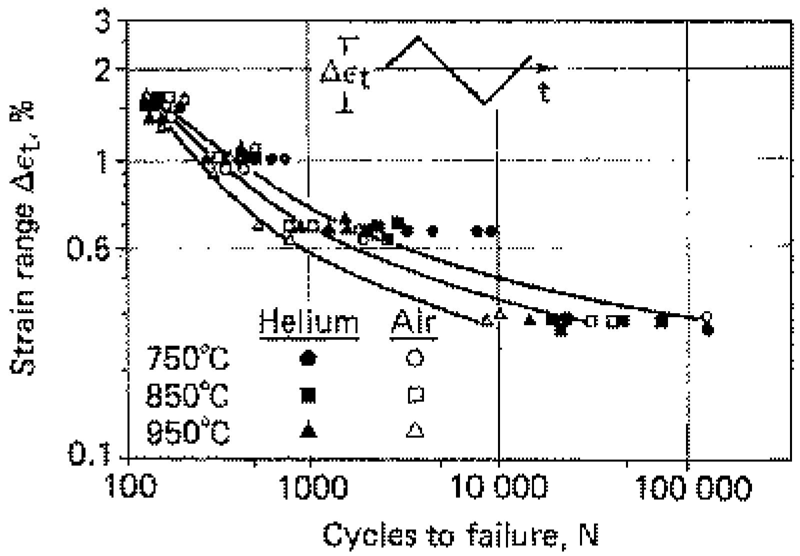


Fig. 6. Results of LCF tests on Inconel 617 (Ref. 8).

Figure 2: LCF results of Inconel 617 – taken from Ref [6]

The creep rupture strength is determined by specimens under constant load (tensile or compression). However components in service are subjected to complex load cycles which can lead to a combination of fatigue and creep effects. The expected loading history must be defined if estimations of the service life of a component are required. According to simplified damage rules, for each stress level that arises during service, the damage fraction can be calculated according a damage accumulation rule (linear, etc). An example of service life evaluation taking account some upset conditions is given for German HTR intermediate heat exchanger tubes as illustrated in figure 3.

The temperature of the tube under upset conditions is assumed to be 950°C, with a stress of 27MPa (pressure difference of 41bars) and a typical assumed duration of 10 or 20hours. Normal service conditions are set at 950°C with a stress level of 5 MPa. With these assumptions, the service life limits for tubes made from Inconel 617 and Hastelloy X are shown in figure 3. The calculations are based on allowable stresses for the two alloys following the procedure of the ASME Code N47 and using available creep rupture data. At 950°C with no upset condition, Inconel 617 has a rupture life of >10^5h and Hastelloy X of over 10^4h. If there is a pressure loss upset event during the 20hours, the maximum service life for Hastelloy X is reduced to only 7hours and for Inconel 617 to 95hours. Under the same upset condition but with a temperature increase to 1000°C, Hastellloy X tubes would fail after 20h upset duration and Inconel 617 would still have a service life of 20hours. This example from German work [Ref. 6] clearly suggests that for high temperature service conditions, a temperature increase above the normal operational temperature due to upset conditions can significantly reduce the service life of the components.

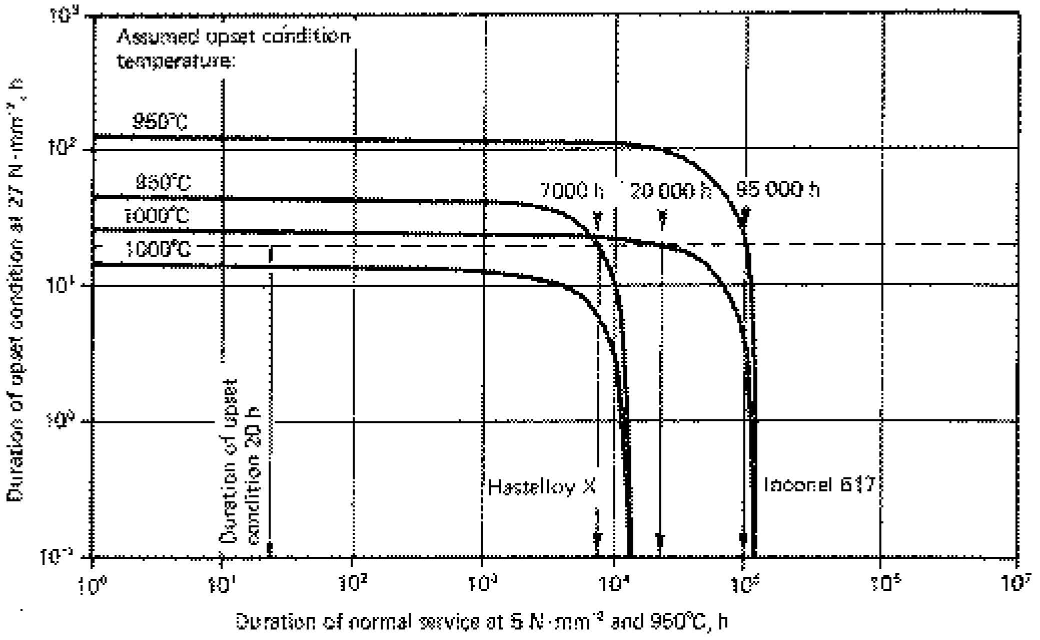


Fig. 14. Allowable service life of two nickel-based alloys, estimated from linear damage accumulation rule.

Figure 3: Example of allowable service life – taken from Ref [6].

In the previous case structural changes in the material and corrosion have not been taken into account. Exposure at high temperature for long times alters the structure of all high temperature alloys. The low and intermediate temperature mechanical properties are the most affected, especially the ductility. Figures 4 and 5 below illustrate the room temperature ductility and impact toughness evolution with ageing duration for Hastelloy X and Inconel 617 respectively. The loss of ductility after isothermal exposure can become more severe if internal oxidation or carburization occurs at high temperature

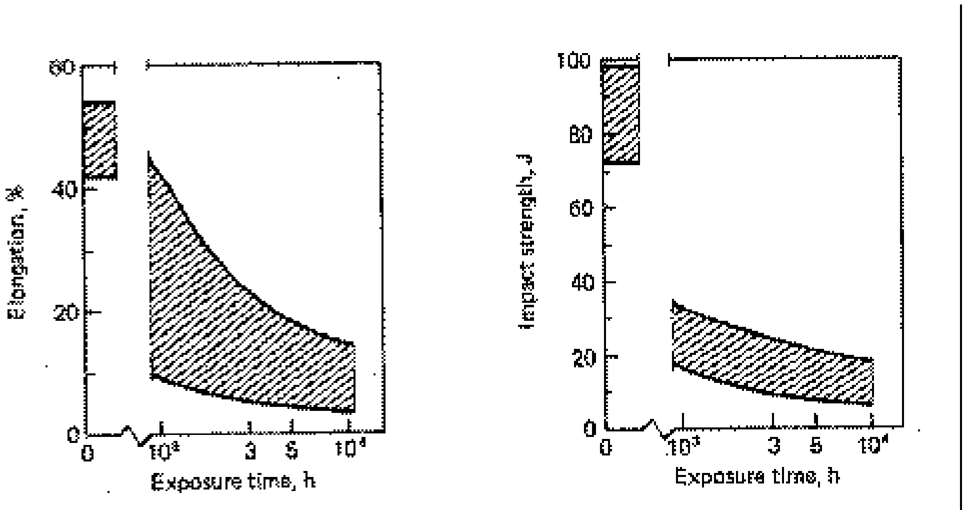


Fig. 10. Room temperature ductility of Hastelloy X after aging at 800 to 850°C in air.

Figure 4: Ageing effect on room temperature properties – taken from Ref [6].

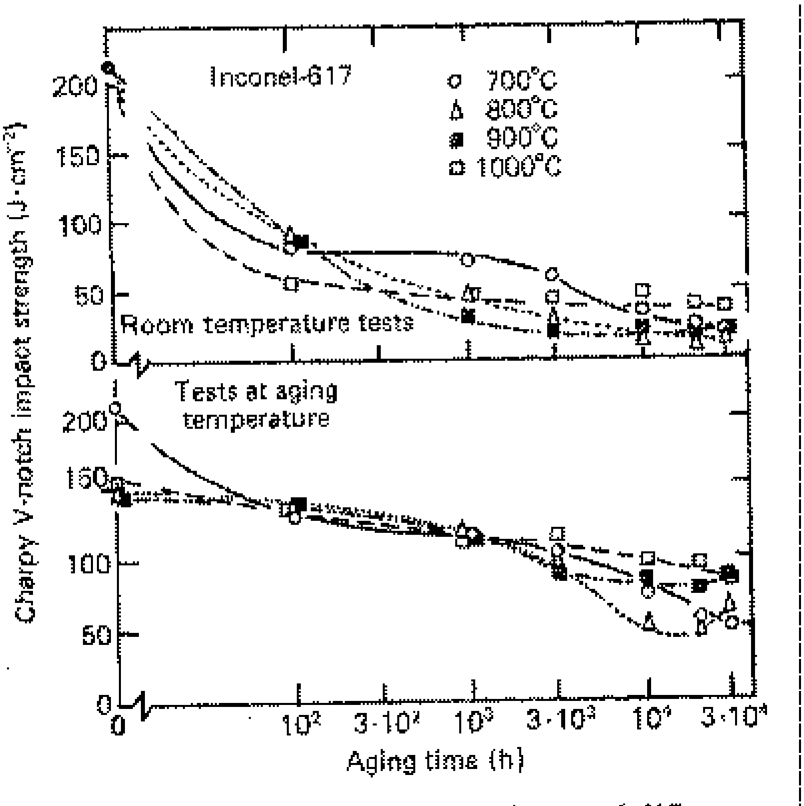


Fig. 7. Impact strength of aged Inconel-617.

Figure 5: Ageing effect on room temperature properties of Inconel 617 – taken from Ref [3]

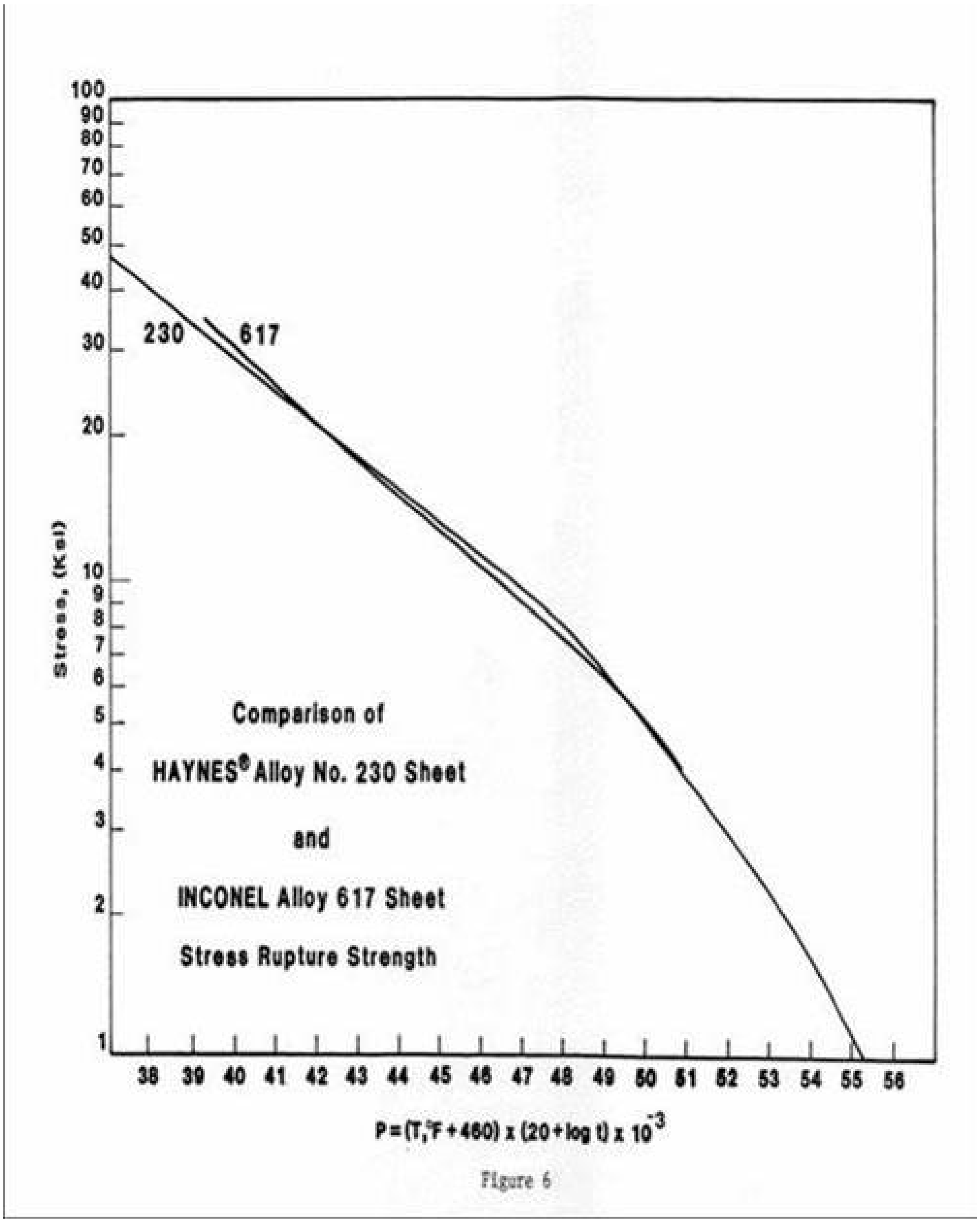


Figure 6: Comparison of creep behaviour of Haynes 230 and Inconel 617 – taken from [9]

Fewer mechanical tests have been performed on Alloy 230 compared to Alloy 617 and there is no allowable stresses estimation available following the procedures of American Society of Mechanical Engineers (ASME) Code Case N47 properties analysis. As shown in Figure 6, the mechanical tests results performed on Alloy 230 however show similar creep behaviour to Alloy 617 (see also Appendix A).

For long life estimation extrapolation procedures will be needed since long term experiments can operate at most for up to 10,000-30,00 hours duration (some long-term dada is available for Alloy 617). An approach using a simple fit formula developed at ABB for high temperature Alloys was compared with an ECCC evaluation and with some recent evaluations at CEA for Haynes 230 and IN617 and a good agreement was found. Extrapolations of long-term creep behaviour are needed for these and other high temperature alloys.

3.1.2 VHTR Corrosion induced temperature limits

The GCR primary helium coolant is actually polluted by low level of oxidizing gases as well as carbon-bearing impurities that can interact with structural metallic materials at high temperature. Surface scale growth, bulk carburization and/or decarburization can occur, in relation to the atmosphere characteristics, the temperature and the alloy chemical composition. As structural transformations affecting the surface (fatigue) or the bulk (creep, toughness…) can notably influence the mechanical properties, they often are determining in respect of the component service life.

3.1.2.1 Characteristics of the VHTR helium

Due to the high gas flow rates into a primary circuit of a VHTR, a dynamic balance is set up between the contamination rates, the reactions of the pollutants with the core graphite or other hot materials, and the purification efficiency. The GCR primary helium coolant is actually polluted by low level of oxidizing gases as well as carbon-bearing impurities that can interact with structural metallic materials at high temperature. Many corrosion mechanisms such as surface scale growth, internal oxidation, bulk carburization and/or decarburization can occur, in relation to the atmosphere characteristics, the temperature and the alloy chemical composition.

As observed in past GCR(s), it is expected that the VHTR's cooling gas will be polluted by out-gassing of adsorbed species out of the large amount of graphite or form air ingress. The helium gas will therefore contain some traces of permanent gases, such as hydrogen, methane or carbon oxide, and water vapour. Table I gives the steady state chemical composition of the coolant in the main experimental GCR(s). The partial pressures of H_2, CO, CO_2, CH_4 and N_2 ranged from tens to hundreds of microbars, while the water vapour content was around few microbars.

Table I Impurity contents in 10^{-6} bar in the coolant helium of experimental GCRs

HTR facilities	Temp. (°C)	Total pressure (bar)	He composition (µbar)							Ref.
			H_2	H_2O	CO	CO_2	CH_4	N_2	O_2	
Dragon	750*	20*	10	1	8	0.5	1	12		III
AVR	750…950**	10**	500	1	2000	5	2		-	III
PNP			**500 ± 50**	1,5 ± 1	**15 ± 5**		**20 ± 5**	<5		II
KVK			200	**6**		240		**300**		IV
HTR-Module (1988)	700	60	< 330	< 6	< 120		< 60	< 60		I
KVK = PNP-Standard (1981)	950	40	**200**	**0.8**	**40**		**2**	**< 50**		I
HTTR	850...950	39	120	8	120	24	205	8	0.8	I
HTR-10	700...900	30	90	6	90	-	30	30	-	I
PBMR (2003)	900	72		1440	360	720	360	2700		I

[Ref. I: Deliverable 45 in HTR-E WP6 (with Waldemar Tischler - Areva GmbH - complements)]
[Ref II: .J. Quadakkers, H. Schuster, Thermodynamic and kinetic aspects of the corrosion of high temperature alloys in high temperature gas – cooled reactor helium, Nuclear Technology Vol. 66 p. 383 – 391, august 1984]
[Ref III: J.P. Ennis, H. Schuster, The effects of high temperature reactor service environments on the mechanical properties of constructional alloys, Proc. Conf. Gas-Cooled Reactors Today, Bristol, BNES – 1982]
[Ref. IV: H. Cook and L.W Graham, Chemical Behaviour and Mechanical Performance in HTR-Helium at high temperatures, Proc. International Conference on Alloy 800, Petten – 1978]

* R. A. Simon, P. D. Capp, Operating Experience with the Dragon High Temperature Reactor Experiment, Proceedings of the Conference on High Temperature Reactors, Petten, NL-April 22-24, 2002 Organized by HTR-TN in cooperation with the European Nucler Society (ENS) and the IAEA - International Atomic Energy Agency, Vienna (Austria)

**J.C. Cleveland, ORNL analyses of AVR performance and safety, Specialists' meeting on safety and accident analysis for gas-cooled reactors. Oak Ridge, TN (USA). 13-15 May 1985
IAEA-TECDOC--358, pp:73-84

There is a valuable theoretical as well as practical knowledge on the corrosion of nickel base alloys [Ref. 14, 18], mainly Inconel 617 and Hastelloy X, in impure helium but this past experience is not sufficient to qualify every material in an innovative VHTR.

The material environment could therefore be significantly different from the experiences of the former GCRs, especially with regard to higher temperatures and longer life times. The available results for effects of corrosion do not provide for a valuable extrapolation of the corrosion effects to complex service conditions and long durations for a VHTR primary circuit component mainly because the corrosion results are very sensitive to many factors:

- slight changes in the impurities concentrations in helium
- temperature
- minor alloying elements such as aluminium, titanium, manganese and silicon
- surface conditions of the specimens and material
- heat treatment and strain deformation.

The main corrosion processes in VHTR helium are:

- oxides are formed by reaction of the metal surface with the helium impurities H_2O and CO
- some oxides (Al_2O_3 , $TiO_{, ...)}$ are stable over the temperature range of interest otherwise Cr_2O_3 is not always formed at the highest temperatures
- Carburization and de-carburization may happen
- The presence of aluminium produces susceptibility to internal oxidation
- some oxide can form an effective barrier at high temperature

3.1.2.2 *Surface reactivity of Intone 617 in impure helium*

Some authors, especially Brenner [Ref **18**], examined the possible gas/metal reactions between helium impurities and alloy 617 surface. Accordingly, numerous sets of reactions can be established, considering the growth of chromia and the deposition of $C_{solution}$ (carbon dissolved in the alloy): oxidation of chromium by water, reduction of oxide by hydrogen, A specific process, called "microclimate reaction" described by Brenner takes place at the highest temperatures.

$$Cr_2O_3 + 3\ C_{solution} \xrightarrow{T>T_a} 3\ CO + 2\ Cr \qquad (1)$$

From the experimental point of view, it is as if the above equation (1) reverses at a critical temperature T_A for given surface activities of the dissolved carbon and the reactive metal, at the carbon monoxide partial pressure prevailing in the helium.

At temperatures above T_A, protective surface oxide Cr_2O_3 can no longer co-exist with internal carbon and, provided that all other parameters remain constant, reaction (1) continues until either all the carbon or all the oxide is removed. The temperature of microclimate reaction has been measured between 920°C and 960°C for both 617 alloy and Haynes 230 alloy.

3.1.3 Conclusion of Nickel alloys limits.

The recent mechanical properties and corrosion results and the previous experimental and analysis work performed of Nickel alloys (Alloy 617, Alloy X and Alloy 230) shows clearly that there is much less knowledge's on ageing and corrosion behaviour and less margin for use of these materials at the upper temperatures defined in the initial VHTR requirements. The operating temperature limit of solid solution nickel alloys (Alloy 617 or Alloy 230) when used as a heat exchanger material (with life duration over 100.000hours) is estimated at this time to be close to 850°C. Some indicative values of limits of different materials is given below in Table 2.

Table 2: Heat Exchanger material development

Material	Temp Limit °C	Limiting Factor	Further Development	Issues for VHTR/ RAPHAEL
Mod 9Cr 1Mo steel	**Operating: 550°C**	Long term Creep strength	ODS version capable of 100°C Higher temperatures - Fusion development – to be tested in future framework.	Established material for sodium and Gas cooled systems —moderate temperatures
	Max: 650°C			
Austenitic Stainless Steel	**Operating: 550°C**	Long term Creep strength		Established material for sodium and Gas cooled systems —moderate temperatures
	Max: 750°C			
Alloy 800 Alloy 800H	**Operating: 650-750°C**	Long term Creep strength		Used in gas cooled and Sodium cooled systems.
	Max: 920-980°C	Corrosion		
Alloy 617	**Operating: 750-850°C**	Long term Creep strength <10Mpa @ 100,000h	ODS version possible for Higher temperatures Effect of cold work (forming) on creep strength - limit of 5%	Established in German HTR Programme - KTA Rules developed For ODS version Micro - structural development required as a first step -
	Max: 920-980°C	Corrosion; Cr_2O_3 evaporation		
Alloy 230	**Operating: 750-850°C**	Long term Creep strength <10Mpa @ 100,000h	ODS version possible for Higher temperatures Effect of cold work	Selected as industrially developed alternative to IN 617 – for corrosion resistance

	Max: 920-980°C	Corrosion; Cr_2O_3 evaporation	(forming) on creep strength absent from National Programmes	For ODS version Micro-structural development required – Investigation of cold work on creep strength & ageing Developments to be included in next stage of RAPHAEL programme
Alloy XR	**Operating: 750-850°C**	Long term Creep strength <10Mpa @ 100,000h	Effect of cold work (manufacturing) on creep strength - limit of up to 10% Tests @800-1000°C	Established for HTTR Operation at 750°C
	Max: 920-980°C	Corrosion; Cr_2O_3 evaporation		
ODS - Ferritic	**Operating: 550°C**		Manufacturing development required Investigated in EXTREMAT	Not developed for heat exchanger application – significant programme required on joining/forming involving manufacturer
	Max: 650°C			
ODS - Austenitic	**Operating: >550°C**		Manufacturing development required Investigated in EXTREMAT	Not developed for heat exchanger application – significant programme required on joining/forming involving manufacturer
	Max: >650°C			

3.2 Work on ODS and TiAl materials

Interim assessment has been made for ODS and TiAl materials (Appendix A) covering effects of thermal and irradiation creep. The alloys were assessed at temperatures exceeding 950°C using 200µm thick specimens. The results have been compared with information on Ni based alloys and found to give an increased creep strength compared with Alloy 617. For the comparison an established ABB parametric interpretation of the stress to rupture curves was used, previously compared with Alloy 617 data (see section 3.1.1. and Appendix A). The assessment showed the TiAl material to be a factor of 2 stronger in terms of creep rupture stress. Although this is a promising conclusion a number of issues remain to be addressed including micro-structural stability, longer term data and data scatter, possible production routes, environment, low temperature brittleness and potential for bonding.

For the ODS material, the thermal and irradiation creep behaviour of ferritic PM2000 was investigated. Experiments were performed on thin specimens (100µm) in the annealed condition. Results at 850°C and 1100°C for the 104h creep rupture strength, showed an increased value compared with Alloy 617 at higher temperatures but at temperatures below 700°C, the creep rupture strength is lower. For this material, despite its potential for increased strength, there are many additional investigations required particularly with respect to its manufacturing capabilities (see Table 2). The material is shown however to behave well with respect to irradiation creep. Issues concerning the interaction of helium produced during long-term operation also require investigation. Creep processes can create voids at grain boundaries and helium from the atmosphere can also diffuse into the grain boundaries forming additional voids. Such actions may contribute to the growth of existing cavities and a reduction in creep strength. With respect to safe prediction of long-term creep strength this needs further investigation in the future.

4 Material selection

A short analysis of the available data base and information on the knowledge missing areas (bibliographic data and on going tests) on these alloys and following the discussion at a recent SP ML joint meeting with SP CP and a further SP ML WP2 specialist meeting on this subject [Ref. 20, 21] further discussions took place involving WP2 partners to precise the likely temperature limit for which the currently available materials such as Alloy 617 and Alloy 230 might be used for. Defining a cliff edge is important for these materials even in an initial rough form as this provides a first step to aid selection. Recommendations and specifications from IHX designers (link with SP-CT) have been taken into account, also to define limiting factors with respect to the manufacturing process directly linked with the IHX design.

It is of high importance to improve the knowledge base of the high temperature mechanical properties and microstructure of the Alloy 230 because a large database already exists on alloy 617.

The selection of a material for further near term development within the RAPHAEL SP ML WP2 programme is expected to be one of the currently proposed materials such as Alloy 230 or alloy 617 since ODS (nickel or iron based) is likely to require much longer timescales and be required for future applications (e.g. hydrogen generation using the IS process).

In order to evaluate the long term property benefits of ODS nickel alloys compared to Alloy 230; ageing and tensile tests could also be performed on few samples for two temperatures in the range 850°C-1000°C and in the exact same conditions as performed for the nickel alloys.

5 Test program and recommendations on future test programme

A test program is proposed for the period 18-48 months in order to improve the knowledge of high temperature mechanical properties and microstructure of the selected high temperature metallic alloys. The requirement is to advance the understanding and evaluation of high temperature long-term properties through a series of tests including creep, thermal aging, and cold work effect on mechanical properties in the temperature range of 700°C-1000°C.

The corresponding investigations on weld metal, heat affected zone of the base metals and also at alternative joining techniques (e.g. diffusion bonding, brazing) and the related materials shall be performed in the next program step in a future Framework Programme) since requirements by environmental condition are the same as for base materials and the current interaction of material scientists and designers (through link meetings between SP-ML and SP-CP) is needed in order to drive an optimization process.

5.1 CEA test program

The initial proposal for the CEA test program was based to improve the understanding and data from different heats or products forms in order to fulfil the requirements of developing technical rules.

The selected IHX PFHE design requires channel forming. A revised CEA's proposal has therefore been developed that is more focused on the IHX design and manufacturing (forming) effect on high temperature properties. The investigation of the effect of cold work on tensile and creep properties at high temperature is proposed, to be performed on Alloy 230. Several cold work levels (e.g. up to 20% deformation level) are to be applied to specimens to investigate this effect. Creep tests at 850°C and 950°C will be performed on specimens with and without pre-deformation. Microstructural observations (SEM, TEM) of the initial material and after creep tests will be performed in order to analyse the microstructure changes and damage mechanisms (see below – Tables 3 & 4).

Table 3 Test program on alloy 230

(a) period 18-36

State	Microstructure examination	Interrupted Tensile tests at 20°C	Rupture tensile tests
As Received	SEM + EDS		Tensile tests at 20°C, 850°C, 950°C
Cold work level 1		Interrupted tensile test to deformation level 1	Tensile tests at 20°C, 850°C, 950°C
Cold work level 2		Interrupted tensile test to deformation level 2	Tensile tests at 20°C, 850°C, 950°C

Period	18-36month-

(b) period 24 -48

State	Microstructure examination	Creep test at 850°C	Creep test at 950°C
As Received	SEM + EDS	Creep tests at 850°C /SEM + EDS	Creep tests at 950°C /SEM + EDS
Cold work level 1		Creep tests at 850°C /SEM + EDS	Creep tests at 950°C /SEM + EDS
Cold work level 2		Creep tests at 850°C /SEM + EDS	Creep tests at 950°C /SEM + EDS
Period	24month-42 month		30-48

5.2 EdF test program

The EdF programme is devoted to the investigation of ageing of industrial products for the heat exchanger. The tests considered currently are to investigate thermal ageing of Alloy 230 for durations of 1000h and 5000h at temperatures of 850^{o}C and 950^{o}C. Short time tests (1.000 h) at very high temperature (1000 °C) will also be performed, to study the behaviour of the material in accidental conditions. Short-term ageing (1.000hours) will also be performed on pre-deformed samples. These tests will provide information about the ageing effect of cold worked material where the effect is measured by the mechanical properties and the microstructure evolutions.

Mechanical tests will be performed (tensile tests, impact toughness tests), as well as microstructural examinations (SEM + TEM), according to the test matrix presented in Table 4.

Additional data will also be provided from the VHTR-CORBA project (Grant for Cooperating with Third Country from EURATOM for Dr. Arkadiusz Dyjakon). These additional data are not funded by RAPHAEL. Corresponding data are presented in Table 4.

Table 4 : EDF tests and examination matrix

<table>
<tr><th>Alloy</th><th>State / Thermal aging duration</th><th>100 h [1]</th><th>300 h [1]</th><th>500 h [1]</th><th>1000 h</th><th>5000 h</th></tr>
<tr><td rowspan="4">Alloy 230</td><td>As Received</td><td rowspan="4">SEM + EDS</td><td rowspan="4">SEM + EDS</td><td rowspan="4">SEM + EDS</td><td rowspan="4">Charpy tests
Tensile tests
SEM + TEM</td><td rowspan="3">Charpy tests
Tensile tests
SEM + TEM</td></tr>
<tr><td>Aged at 850 °C</td></tr>
<tr><td>Aged at 950 °C</td></tr>
<tr><td>Aged at 1000 °C</td><td>-</td></tr>
<tr><td>Alloy 230 Pre-deformed</td><td>Aged at 850°C
Aged at 950°C</td><td></td><td></td><td></td><td>Tensile tests +SEM</td><td></td></tr>
</table>

6 Material Information Base

Following on from the work and proposals of deliverable D-ML2.2 [Ref. 1], this section reviews the present situation on material's data and available standards for the above materials. As far as possible the data are compiled and attached.

Information for Alloys 617 and 230 are presented in sections 6.1 and 6.2.

6.1 Alloy 617

AMERICAN STANDARDS		
Designation	**Reference Standard(s)**	
UNS N06617	ASME SB 166 ASME SB 168 ASME SB 564 ASME SB 167	Rod, Bar and Wire Plate, Sheet and Strip Forgings Seamless Pipe and Tube
UNS N06617	ASME Section II-D, 2004, Requirements integrated in Section VIII Division 1 *Properties up to 525°C*	
ERNiCrCoMo-1 UNS N06617	SFA-5.14 - Weld Metal	

[1] Additional data coming from the VHTR-CORBA project (not funded by RAPHAEL)

ENiCrCoMo-1 UNS W86117	SFA-5.11 - Weld Metal
GERMAN STANDARDS	
Designation	**Reference Standard(s)**
Alloy 617 (NiCr 23 Co 12 Mo)	KTA 3221.1, Draft 1992 All semi-finished products *Properties up to 1050°C*
NiCr 23 Co 12 Mo Mat.-No. 2.4663	VdTUEV-Werkstoffblatt 485, (Ed. 2001) *Properties up to 1050°C*
EL-NiCr 21 Co 12 Mo Mat.-Nr. 2.4628	Weld Metal - DIN 1736, Ed. 1985 (recommended in VdTUEV WBl. 485)
SG-NiCr 22 Co 12 Mo UP-NiCr 22 Co 12 Mo Mat.-Nr. 2.4627	Weld Metal - DIN 1736, Ed. 985 (recommended in VdTUEV WBl. 485)
EUROPEAN STANDARDS	
Designation	**Reference Standard(s)**
NiCr 23 Co 12 Mo Mat.-No. 2.4663	EN 10302, Ed. 2002 Bar, Wire, Sheet, Strip *Properties up to 750°C (short term), 1200°C (long term)*
E Ni 6617 NiCr22Co12Mo9	Weld Metal - EN ISO 14172, Ed. 2004
S Ni 6617 NiCr22Co12Mo9	EN ISO 18274, Ed. 2004

6.2 Alloy 230

AMERICAN STANDARDS		
Designation	**Reference Standard(s)**	
UNS N06230	ASME SB 572 ASME SB 435 ASME SB 564 ASME SB 622	Rod, Bar and Wire Plate, Sheet and Strip Forgings Seamless Pipe and Tube
UNS N06230	ASME Section II-D, 2004, Requirements integrated in Section VIII Division 1	

	Properties up to 525°C
ERNiCrWMo-1 UNS N06231	SFA-5.14 - Weld Metal
ENiCrWMo-1 UNS W86231	SFA-5.11 - Weld Metal
GERMAN STANDARDS	
Designation	**Reference Standard(s)**
NiCr 22 W14 Mo Mat.-Nr. 2.4733	DIN 17744 Ed. 2002 - Wrought Nickel Alloys with Molybdenum and Chromium - Chemical Composition
EUROPEAN STANDARDS	
Designation	**Reference Standard(s)**
E Ni 6231 NiCr 22 W14 Mo	Weld Metal - EN ISO 14172, Ed. 2004
S Ni 6230 NiCr 22 W14 Mo 2	Weld Metal - EN ISO 18274, Ed. 2004

REMARKS:

- The material data in KTA 3221.1, Draft 1992, is based on the results of the German R&D project performed in 1980 to 1992. Since this project was related to High Temperature Reactors, in KTA 3221.1 compiles data most related to HTR issues.

  For further information see [19]

- German VdTUEV Material sheet 484 was generated since year 1985 and contains also data gained within the German R&D on HTRs.

- European standard EN 10302 compiles information on most high temperature steels and nickel-base alloys and also contain data for Alloy 617, Alloy 800 H and Alloy X.

- American Standards are under development considering the upper temperature range and the data base.

7 Conclusions

A review of available materials and their limits for the key high temperature components (internals, hot gas duct, heat exchangers) of the VHTR has been made together with a short list of materials for evaluation. From this the most promising available candidate materials have been selected and recommendations made for future development of some new alloys more adaptable to the VHTR upper temperature limit requirements.

The future test program of work to be performed within Rapahel SP-ML Workpackage 2 has been proposed for the period 24-48 months. This involves evaluation of high temperature mechanical properties of Haynes 230 and microstructure evaluation for further development of future high temperature metallic alloys. The requirement is to advance the understanding and evaluation of high temperature long-term properties through a series of tests including creep, thermal aging, and effects cold work on mechanical properties (important for manufacture) in the temperature range [700°C-1000°C].

8 References

1 Materials for Internals and Heat Exchangers and test programme
RAPHAEL Contract Number: 516508 (FI6O)
RAPAHEL Deliverable (D-ML2.2)

2 Components specifications for IHX , isolation valves and coolers RAPHAEL Contract Number: 516508 (FI6O)
RAPHAEL Deliverable (D-CT1.1) C. MAUGET, D.VANVOR, G. BRINKMANN

3 U. BRUCH, D. SCHUHMACHER , PJ. ENNIS, .E. HESEN -Tensile and impact properties of candidate alloys for high temperature gas cooled reactor applications- Nuclear Technology, vol 66, 357-362, 1984.

4 COOK, R. H.-Creep Properties of Inconel-617 in Air and Helium at 800 to 1000 deg C- Nuclear Technology 84 vol66 p.283

5 F. SCHUBERT, U. BRUCH, R. COOK, H. DIEHL, P.J. ENNIS, W. JAKOBEIT, H.J. PENKALLA, E. te HEESEN, G. ULLRICH, Creep rupture behavior of candidate materials for nuclear process heat application, Nuclear Technology, 66, 227-240, 1984.

6 H. NICKEL, P.J.ENNIS,F. SCHUBERT, Qualification of metallic materials for application in adavanced high temperature gas cooled reactors, Nucl. Techn. Vol 58, P 90-109, 1982

7 HP MEUER, H. BREITLING, ED GROSSER Fatigue and creep properties of alloys, IAEA Specialist Meeting, Vienna, May 1981N° 4086, U1-U12

8 Y. KURATA, H. UTSUMI, K. KIKUCHI, T. SUZUKI, T. MIURA, *Microstructural evolution during creep of Ni-base solid solution alloys and in-situ observations at high temperature*, 4th International Conference on Recrystallization and Related Phenomena, Japan Institute of Metals, 1999.

9 HAYNES® 230™ ALLOY, 1993, Haynes International, Inc.

10 Sicherheitstechnische Regel des KTA, KTA 3221.1, Metallische HTR-Komponenten, Teil 1: Herstellung von Werkstoffen und Erzeugnisformen, Entwurfsvorschlag Dezember 1992

11 Draft alloy 617 code Case (prepared by Task Force Very High Temperature Design) Corum, J. M., and J. J. Blass 1991. "Rules for Design of Alloy 617 Nuclear Components to Very High Temperatures," Fatigue, Fracture, and Risk, PVP-Vol. 215, American Society of Mechanical Engineers, New York.

12 F. SCHUBERT, Evaluation of Materials for Heat Exchanging Components in Advanced Helium-Cooled Reactors, *Proc. of a symposium on heat exchanging components of gas cooled reactors*, Dusseldorf (1984), IWGGCR-9, 309

13 H. BREITLING et al., Evaluation of Mechanical Properties of the Alloy NiCr22Co12Mo (Alloy 617) for Heat Exchanging Components of HTGRs *Proc. Of a symposium on high temperature metallic materials for gas-cooled reactors,* Cracow (1988) , IWGGCR-18, 91

14 W.J. QUADAKKERS, *Werkstoffe und Korrosion*, 36, (1985) 141-150 and 335-347

15 C. CABET *et al.*, *Proc. HTR 2006 Conf.*, Sandton, SA, Oct. 1-4 (2006) E00000143

16 F. ROUILLARD *et al.*, *Proc. EUROCORR 2005*, Lisbon, Portugal, Sept. 4-8 (2005) 358

17 C. CABET *et al.*, *Mat. Corr.*, 57 n°2 (2006) 147

18 K. G. E BRENNER and L. W. Graham, “Development and application of a unified corrosion model for high-temperature gas-cooled reactor systems”, *Nuclear Technology*, 66, 2, 404 (1984)

19 Schubert, F., Breitbach, G., Nickel, H.
German Structural Design Rule KTA 3221 for Metallic HTR-Components
PVP-Vol. 262,
High-Temperature Service and Time-Dependent Failure
ASME 1993, p 9-18

20 D. Buckthorpe. Minutes of 3rd progress Meeting on Materials Development – Vessel and High Temperature Materials. RAPHAEL-0611-M-ML1-3

21 D. Buckthorpe. Brief notes of a 2nd specialist meeting on VHTR IHX materials. RAPHAEL-0703 M-ML2.4

Appendix A

1) **Stress to Rupture ssessments of Alloy 617 using a digitized parametric assessment.**

2) **Contribution on ODS and TiAl materials: Thermal amnd Irradiation Creep of High Temperature Materials**

Stress rupture assessments for IN-617 using a digitized old data set and an „Isostress" based parametrization

(Paper for discussion by Wolfgang Hoffelner, Senior Lecturer at Swiss Federal Institute of Technology Zürich/Switzerland, May 9th, 2006)

Introduction:

This is a very first attempt to discuss the use of digitized old literature data in future GENIV related databases. Starting from a set of data produced by Jülich and published already in 1984 [1] an attempt was made to correlate the data with current state of the art evaluations by comparing the results with CEA, Haynes [4] and an extensive data assessment performed within the European Creep Collaborative Working Group (ECCC) [2]. Parametrization of the digitized data was performed according to a formula which we developed at ABB about 25 years ago. It is based on the fact that (for physically unknown reasons) the "Isostress" extrapolation of stress rupture data gives surprizingly good results. The formula and some background has been published in [3].

Procedure:

The stress rupture data from Jülich which were the basis for the evaluation are shown in Figure 1:

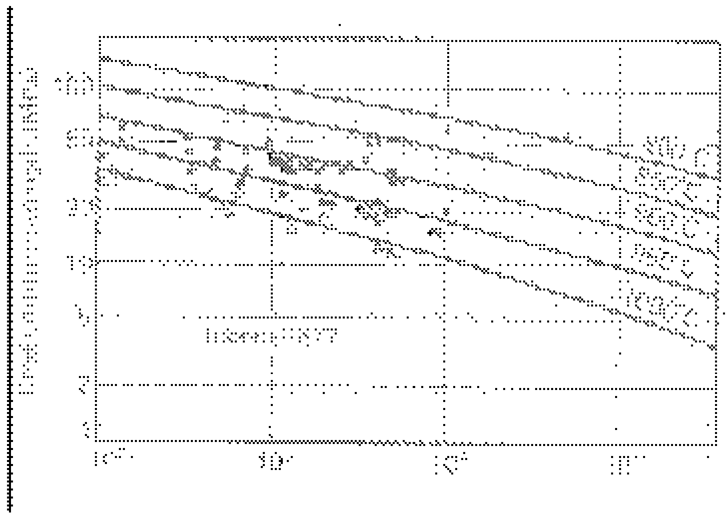


Figure 1: Copy of the Jülich stress rupture data published in 1984 [1]

This set of more than 80 data was digitized and converted into an Excel-table. With a commercially available simple fitting program the formula developed by ABB at about 1983 was applied:

$$\log10(tF) = T.(A.\log10 (sigma)+B.sigma+C) + D \quad (1)$$

(tF…time to fracture, T…Temperature (in C), sigma…applied stress)

leading to the coefficients A,B,C,D

In a next step the results of this parametrization were compared with literature:

<u>Comparison with the original Jülich data (Figure 2):</u>

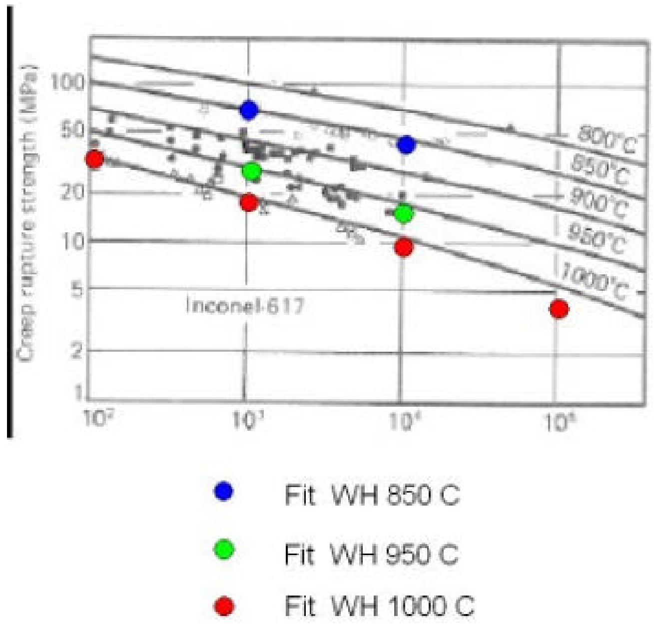
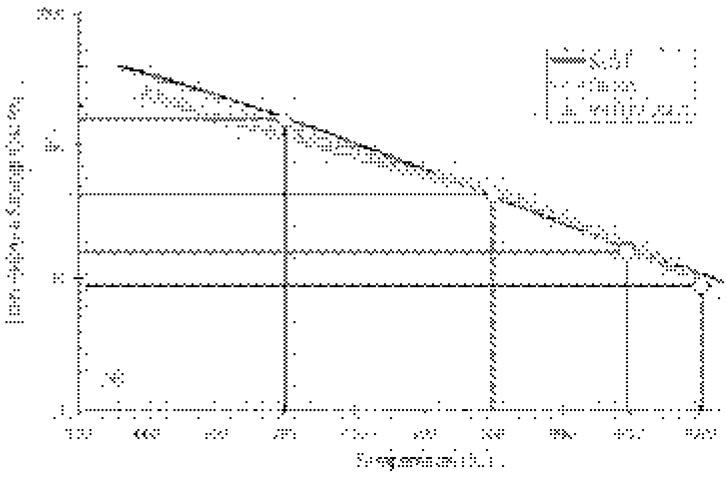


Figure 2: Comparison of the current curve fit with the original Jülich data

It is obvious that in the regime where data exist the agreement is very good. In the extrapolation regime, however, our approach is more conservative than the extrapolation of Jülich. In order to get a better feeling about the extrapolation capabilities a comparison with the most recent creep rupture data assessments of alloy 617, published in 2005 was made.

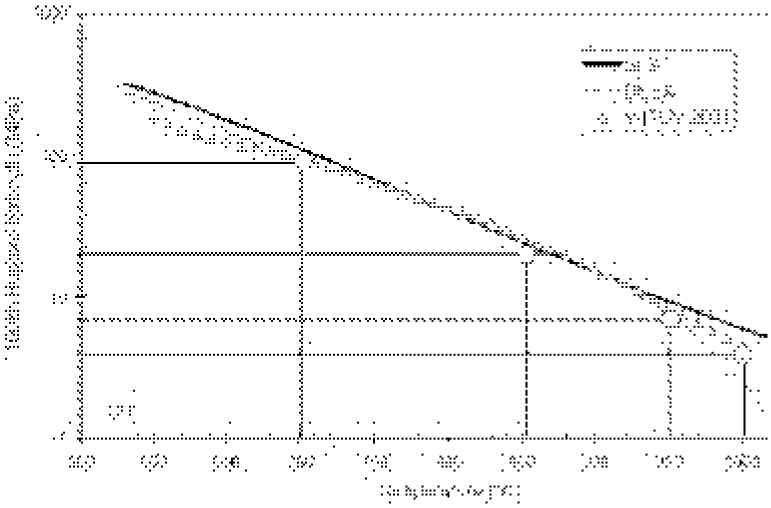
<u>Comparison with the ECCC evaluation [2]:</u>

The ECCC group made a very extensive evaluation of the available IN-617 data sets. In their comparisons three mean value fitting techniques were given for 10000 hour and for 100000 hours. Figures 3 and 4 just compare our "80-data-digitized-fit" with the results of a huge collaborative action:



-◇- Calculated according to WH-fit

Figure 3: Comparison of existing 10'000 h stress rupture curves with the fit described in this notice

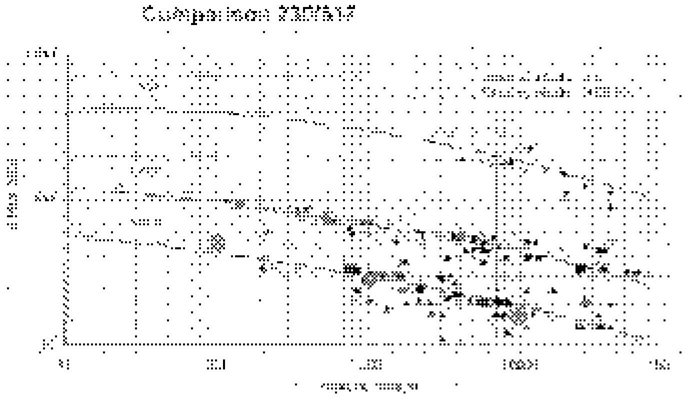


-◇- Calculated according to WH-fit

Figure 4: Comparison of existing 10'000 h stress rupture curves with the fit described in this notice

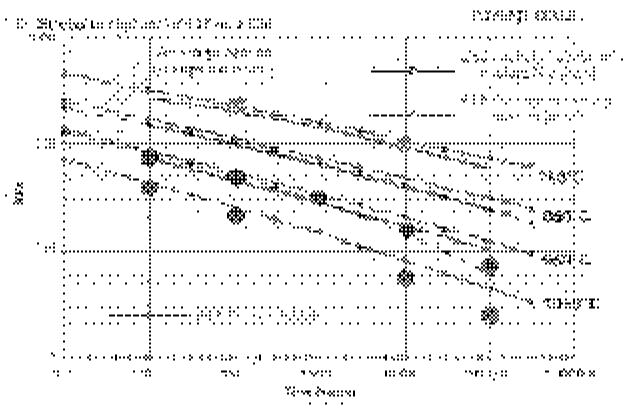
I was really surprised by these results. In order to compare with more raw data available I also tried to fit them into a set of CEA and Haynes data which is shown in Figures 5 and 6.

<u>Comparisons with CEA/Haynes Data:</u>



ATTENTION: red and blue data refer to Haynes 230
They belong to the graph as published by CEA [4]

Figure 5: Comparison with data published by CEA. Our predictions are more conservative.



Fit YH 1050 C

Fit YH 850 C

Fit YH 750 C

Figure 6. comparison with Haynes data. Source [4]

The trend which was already recognized when comparing with the Jülich data was seen also here. Our evaluation leads to more conservative extrapolations at high temperatures and long exposure times. There is even an indication that the drop of the HAYNES 230 data would be present also for 617.

Conclusions:

A digitized set of old IN-617 data produced in Jülich evaluated with a purly empirical parametrization led to surprisingly good coincidence with most recent stress rupture assessments. Although this is only a very first evaluation it seems to prove that digitized data can have some value for design limit assessments.

Literature:

[1] H-J. Penkalla, H-H Over, F. Schubert, Constitutive Equations for the Description of Creep and Creep Rupture Behaviour of Metallic Components above 800 C, Nuclear Technology, vol 66, Sept 1984 685-692

[2] S. Chandra et al., Creep Rupture Data Assessments of Alloy 617, Creep and Fracture in High Temperature Components, ECCC Creep Conference London Sept 2005, Conf Proc. Pp. 178-188

[3] W. Hoffelner, Creep Dominated Processes, ,"High Temperature Alloys for Gas Turbines and other Applications 1986". Eds.:W.Betz et al.,D.Reidel Publ.Comp. Dordrecht 1986, p.413

[4] Ph. Billot et al
http://nstg.nevada.edu/heatpresentations/HTHX%20QR%20UNLV%20Dec%202005/Dec%205/Billot%20CEA%20HX%20Technical%20program.pdf

Proceedings HTR2006:
3rd International Topical Meeting on High Temperature Reactor Technology
October 1-4, 2006, Johannesburg, South Africa

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THERMAL AND IRRADIATION CREEP OF ADVANCED HIGH TEMPERATURE MATERIALS

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ABSTRACT

Gas temperatures of future advanced gas cooled reactors will exceed 900 °C with the aim to even reach 1000 °C and more. This also needs structural materials with high creep resistance not only for piping and heat exchangers but also for in-core or close to core supports or fixations. Therefore not only thermal creep but also irradiation creep is important. The paper will present recent creep results for an intermetallic TiAl-alloy and the ferritic oxide dispersion strengthened (ODS) steel PM2000 (Plansee). Tests were performed at different temperatures and also under He-implantation. Although at high temperatures only negligible displacement damage was found this type of damage can become important during transients when relatively low temperatures combined with stresses occur. The paper summarizes the results and discusses them with respect to damage evolution and damage interaction.

INTRODUCTION

Advanced high temperature gas cooled reactors called very high temperature reactors (VHTR) according to their very high coolant temperatures are a key technology for the international Generation IV initiative [1]. VHTRs are considered as a core element in future cogeneration plants for electricity and process heat. An intensively studied option is the production of hydrogen with a thermo-chemical reaction which, however, requires gas outlet temperatures of 950°C or higher to meet the efficiency goals. Future VHTRs are expected to operate at gas outlet temperatures exceeding 950°C and at gas inlet temperatures up to 500°C. These demands provide a real challenge for the materials. The reactor pressure vessel (RPV), in current LWRs a carbon steel, must be replaced by a highly creep resistant steel to accommodate the 400 to 500°C in the negligible creep regime. Reactor internals like core barrel, core support and control rod must also operate at temperatures well above the current experience. Besides the reactor itself also the balance of plant components like piping and intermediate heat exchanger need materials which can safely operate under VHTR exposure conditions. Properties of carbon steels and nickelbase alloys were reviewed with respect to their capabilites as HTR in-core structural materials (restraints, seals, thermal barriers, control/power rods) in [2]. Nickelbase alloys were analyzed as structural materials for nuclear process heat applications in [3]. Both investigations were performed with respect to the German HTR project already more than 20 years ago. Higher gas temperatures for the VHTR and availability of new materials need a re-assessment. Our paper will focus on advanced candidate materials for structural components outside and inside the reactor core allowing material temperatures in excess of 950 °C. Creep resistance, behavior under irradiation and resistance against impure helium are the most important material properties for such applications. We will limit our considerations to creep strength at temperatures up to 1100° C and irradiation damage of up to 10 dpa. As potential candidates we investigated a ferritic oxide dispersion strengthened (ODS) steel and a highly creep resistant titanium aluminide. Results of extended investigations on IN-617 being performed in context with the German high temperature reactor [4] are considered as benchmark. Our considerations were limited to technical assessment of the potential of these materials only. With respect to economic aspects it can be expected that both materials investigated are more expensive than comparable superalloys like IN-617. A precise economic assessment would need data for the whole component production chain and a valuation of gains in process efficiency which is currently difficult.

MATERIALS AND EXPERIMENTAL

Investigations of the irradiation behavior r of metallic materials for Two classes of advanced materials were investigated in this study. They are considered as potential candidates for different components in a VHTR plant. A cast intermetallic α_2/γ titanium aluminide developed by ABB (now

Alstom [5], called ABB2, and an oxide dispersion strengthened (ODS) ferritic steel PM2000 from Plansee [6].

These two materials offer additional strengthening mechanisms at high temperatures. The intermetallic shows an ordered lattice structure and it gets its strength by a bimodal microstructure and the fact that the movement of dislocations through an ordered lattice is more difficult than through a disordered solid solution strengthened matrix. The ceramic dispersoids of PM2000 can pin dislocations at the high temperatures thereby increasing the creep resistance. It should be clearly stressed, that the aim of our study is to evaluate the potential of these materials for VHTR applications. Questions concerning optimization of

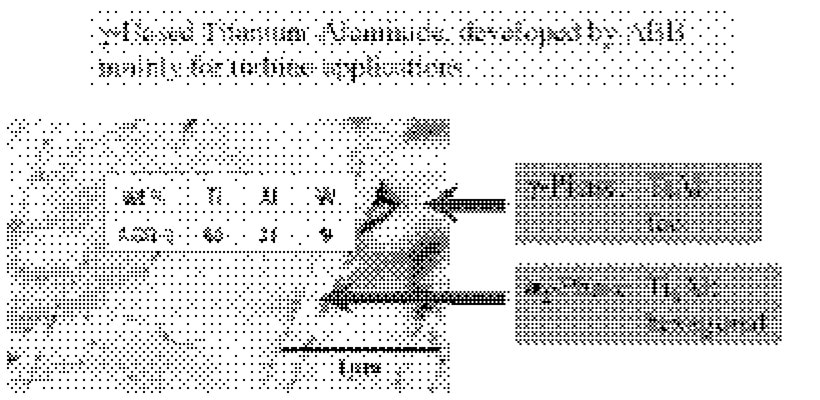

Figure 1: Microstructure (TEM-micrograph) of the titanium aluminide ABB-2 investigated. The two phases are clearly visible.

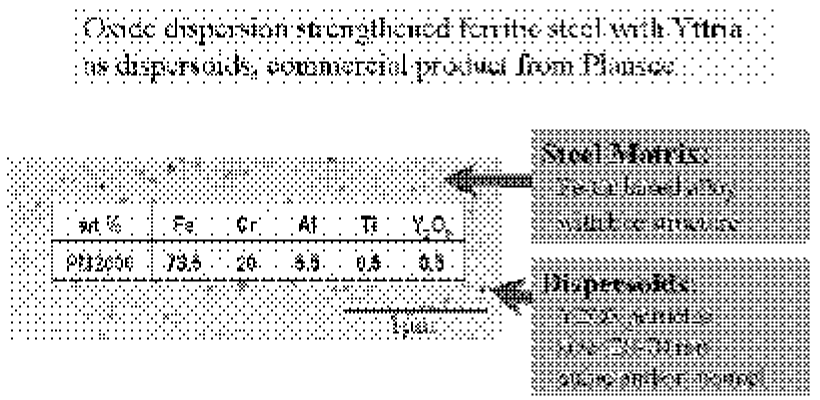

Figure 2: Microstructure (TEM-micrograph) of the ferritic oxide dispersion strengthened steel PM2000.

microstructure, production and machining of components and joining are not included.

Titanium Aluminides

Titanium aluminides are well accepted structural materials for high temperature applications though they tend to be brittle at room temperature. The current application temperature is limited to about 800°C. This temperature limit is not a result of insufficient strength. It is a result of inferior oxidation resistance which cannot be tolerated in oxygen containing combustion gases. As the atmosphere of a VHTR consists of impure helium this limitation is most probably not valid there. First results from exposure experiments carried out in a He/CO mixture with small amounts of oxygen impurities at 950°C for up to 500 hours support this assumption [7]. The microstructure of ABB-2 can be seen from Figure 1. The two intermetallic phases, the hexagonal Ti_3Al and the face centered cubic TiAl are clearly visible. ABB-2 was designed as cast material. It was optimized with respect to creep properties. Similar titanium aluminides are produced powder metallurgically. For a more detailed information about this material, its microstructure and its mechanical properties we refer to the literature [8].

Oxide Dispersion Strengthened (ODS) materials

The good high temperature strength of ODS materials is due to the finely dispersed oxide particles which hinder the dislocation movement. Several matrices austenitic, ferritic, and ferritic/martensitic can be reinforced by dispersoids. Currently this class of materials is intensively investigated as a potential candidate for nuclear applications: fusion, fast reactors and VHTRs. We have chosen for our feasibility investigations the commercially available ferritic alloy PM2000 because of its good very high temperature strength [6]. The matrix is reinforced by fine Y_2O_3 particles. The microstructure of this material is shown in Figure 2 as a TEM micrograph. As the dispersoids cannot be mixed into the molten material ODS alloys are powder metallurgically produced. The process starts with mechanical alloying, consolidation by extrusion and an annealing heat treatment. This process leads to very large grains which are elongated parallel to the extrusion direction. For more detailed information we have to refer to the literature [9].

Creep Tests

Conventional creep test and creep tests under irradiation were performed with both materials. The irradiation source was the 28 MeV compact cyclotron of the Research Center Jülich [10,11]. Ion irradiation with He and protons was used. To get through irradiation of the samples during the creep tests only a limited thickness (200 micrometer for TiAl, 100 for ODS) could be used. Dog bone thin strip samples were prepared and creep tested in the irradiation facility at 300°C, 400°C and 500°C. The testing procedure and the testing parameters for the TiAl are reported in [12]. The testing parameters for PM2000 were presented at the EMRS 2006 Conference in Nice, they will be published elsewhere.

A point worth discussing is the influence of sample thickness on the results gained. Figure 3 compares creep rates determined with thin strip samples (tested without irradiation) with results from conventional creep tests and a good agreement was found. This does not mean that we propose to use thin strip tests for the determination of design curves, but it proves that thin samples are well suited for basic damage considerations.

RESULTS

For thermal creep the steady state creep rate and the applied stress are usually related by a power law where the temperature dependence enters as an Arrhenius term.

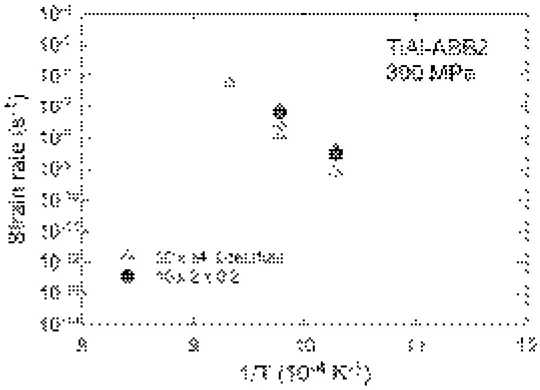

Figure 3: Comparison of creep rates determined with thin strip tests with conventional sample geometries. A good agreement was found demonstrating the validity of the results

Formally this well know Norton law can be written as follows:

$$\dot{\varepsilon} = B\sigma^{n} e^{-\frac{Q}{RT}}$$

As long as there are no significant changes in the creep mechanism there should be a linear dependence between $\log(\dot{\varepsilon})$ and 1/T.

Irradiation induced creep can be understood as biased flow of point defects to sinks. Usually a linear dependence of stress and almost no influence of temperature is found which can in good approximation be written as follows:

$$\dot{\varepsilon} = B\sigma K$$

The dependence between $\log(\dot{\varepsilon})$ and 1/T should therefore be close to a horizontal line.

The results of our creep tests shown in Figure 4 demonstrate that both materials follow these two equations. A relative clear transition between thermal creep and irradiation induced creep was found in a temperature range of 600 to 700 °C. Based on these observations it can be concluded that parts made of these materials will not suffer from irradiation damage (displacement damage) at very high temperatures. Support elements operating at lower temperatures irradiation induced creep effects should be considered. Eventual effects from helium produced by irradiation might affect the creep rupture properties.

THERMAL CREEP

We will now compare the capabilities of the two materials with respect to possible applications in a gas cooled reactor. As reference we show the nickelbase superalloy IN-617 which is the current state of the art material for high temperature reactors. We shall base our considerations

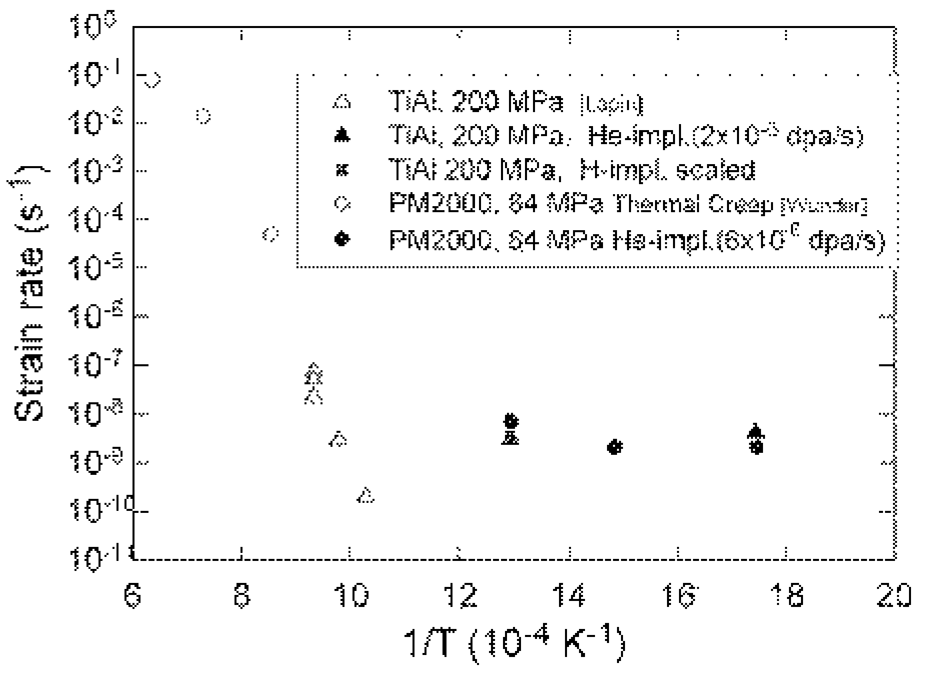

Figure 4: creep strain rates of Alch-2 and PM2000 as a function of the inverse absolute temperature at a particular stress (Lapin [8], Wunder [19])

mainly on existing creep rupture or creep data. At temperatures above 600 °C and for applications which are not exposed to irradiation during service thermal creep behaviour is most important. In contrast to the very well investigated standard alloy for the highest temperature in HTR environment i.e. IN617 [3,4] only limited creep rupture data exist for PM2000 and ABB-2. To assess creep rupture curves it is therefore necessary to construct them from the existing scarce data with a suitable parametrization. Several important extrapolation methods like Larson-Miller [13], Orr-Sherby-Dorn [14], Manson-Haferd [15] etc. are based on the fact that for metallic materials at a particular stress a linear relationship between the creep rupture time $\log(t_R)$ and the testing temperature T or the inverse testing temperature 1/T exists . A very comprehensive discussion of the different methods is given e.g. in [16]. Since for high temperature materials better correlations were found using the linear dependence from T [17], we will base our extrapolations on this fact. The other experimental evidence we use is the fact that isothermal creep rupture curves can well be parametrized by the following equation

$$\log10(t_R) = a.\log10(\sigma) + b.\sigma + c \qquad (1)$$

Where t_R means creep rupture time, σ means applied creep stress and a,b,c being constants.

Combining this formula with the linear dependence from T mentioned before we can write using the constants A, B, C, D:

$$\log10(t_R) = T.(A.\log10(\sigma) + B.\sigma + C) - D \qquad (2)$$

This procedure was successfully used for the evaluation of these rupture data at the creep laboratory of ABB Switzerland, now Alstom [13]. The current standard alloy for

4

high temperature applications is alloy IN-617 for which a large database exists. In order to prove the validity of our approach it was checked if currently available mean value curves of IN-617 could be reproduced. A dataset, published in 1984 by researchers from the research center Jülich [4] was used for this purpose. Data were extracted and parametrized according to equation (2). A very good agreement with published mean values [18] was found. Based on this observation we tried to find a well defined set of data for PM2000 and the ABB-2 TiAl. Stress rupture data for PM2000 can be found in the datasheet from Plansee. The creep behaviour of the materials was extensively investigated in [19] where, however, mainly secondary creep rates were studied. As a first approximation we determined the time to reach 1% creep strain assuming that only secondary creep was taking place. This procedure is frequently used to get an assessment of creep rupture data. A very good agreement with the Plansee data was found. Even more difficult is the situation for the TiAl ABB-2 where almost only creep strain rates exist [8,20]. ABB-2 is a cast material with very high creep rupture strength making it difficult to find comparable data from other qualities of this type of material. Because of the oxidation limitations of titanium aluminides the creep temperatures are usually limited to temperatures below 850 °C. Creep properties up to 1050 °C were investigated for another high strength titanium aluminide [21]. As the strength of this material was clearly below ABB-2 at all temperatures this set could not be fully included into our evaluation. Figure 5 shows a comparison between the measured and calculated data. The very good agreement fully justifies the use the chosen parametrization.

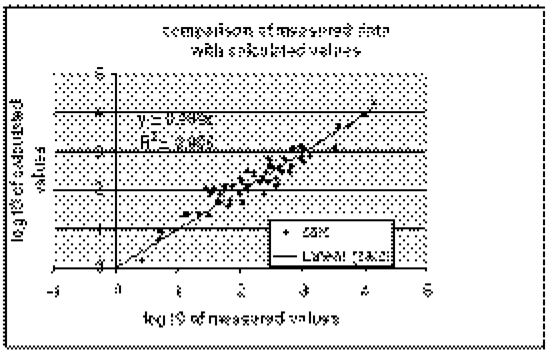

Figure 5: Comparison of measured creep data [8] with data determined according to equation 2 for ABB-2

A comparison of the 10^4 h and 10^5 h creep rupture strengths is shown in Figures 6 and 7. It can be seen that the creep rupture strength of PM2000 in the investigated (extruded and annealed) condition is by far the highest at temperatures between 850 °C and 1100 °C. The creep rupture strength of ABB-2 is higher than the one of IN-617 by about a factor of 2 in the whole temperature range. However, as long as no long term creep rupture data for ABB-2 at temperatures above 850 °C and no information about microstructural stability of this material exist the data must be considered with care. Nevertheless, the results suggest that titanium aluminides can be considered as candidate materials.

IRRADIATION INDUCED CREEP AND THERMAL CREEP-IRRADIATION INTERACTIONS

In this section we would like to discuss the role of irradiation effects. With respect to creep basically two effects must be considered: creep due to displacement damage and degradation of creep rupture properties by the formation of helium voids along the grain boundaries. Helium can occur as a by-product of nuclear reactions producing alpha particles. According to the results of our in-situ creep tests displacement damage is only expected below 650 °C. One interesting finding was that the dispersoids being responsible for the favorable high temperature creep performance of PM2000 have no influence on irradiation induced creep. The creep rates for the intermetallic measured for 380 MPa load were the same as the ones measured for PM2000 at 54 MPa. This finding is consistent with the current explanations of irradiation induced creep suggesting that it is rather based on point defect reactions than on movement of dislocations.

The possible interaction of helium produced during long term operation and thermal creep properties need still consideration. Creep processes can create voids at grain boundaries which grow and coalesce until fracture occurs. Helium can diffuse to the grain boundaries forming additional voids there or contribute to the growth of existing creep voids. This leads to reduction of creep rupture life. In case of a VHTR only limited formation of helium is expected. With respect to the long design life of VHTRs this point still needs further investigation in the future.

During operational transients of a plant other creep-irradiation damage interactions can occur which shall be demonstrated with the schematic loop shown in Figure 8. Let us assume that a point of a component can undergo displacement controlled straining during transients (e.g. as a result of thermal induced strains during start-up/shut down). Let us additionally assume that this point is designed to move along the elastic line in a way that neither plastic deformation nor thermal creep can occur. During a temperature rise combined with irradiation, irradiation induced compression creep can occur leading during steady state operation to a stress well above the design stress which might even cause thermal creep. This example shall illustrate possible damage interactions which can occur during service. Unfortunately, the conditions (time, temperature, irradiation) which would be necessary to analyse such damage interactions experimentally cannot be achieved in laboratory. Advanced material modelling methods like molecular dynamics, Kinetic Monte Carlo or dislocation dynamics can help to assess such long term damage effects [22]. A first attempt to study possible effects of irradiation induced point defects on existing grain boundary voids was recently published [23]. Based on molecular dynamics calculations no significant effect of interstitials was found. It needs now to include also vacancies using Kinetic Monte Carlo techniques.

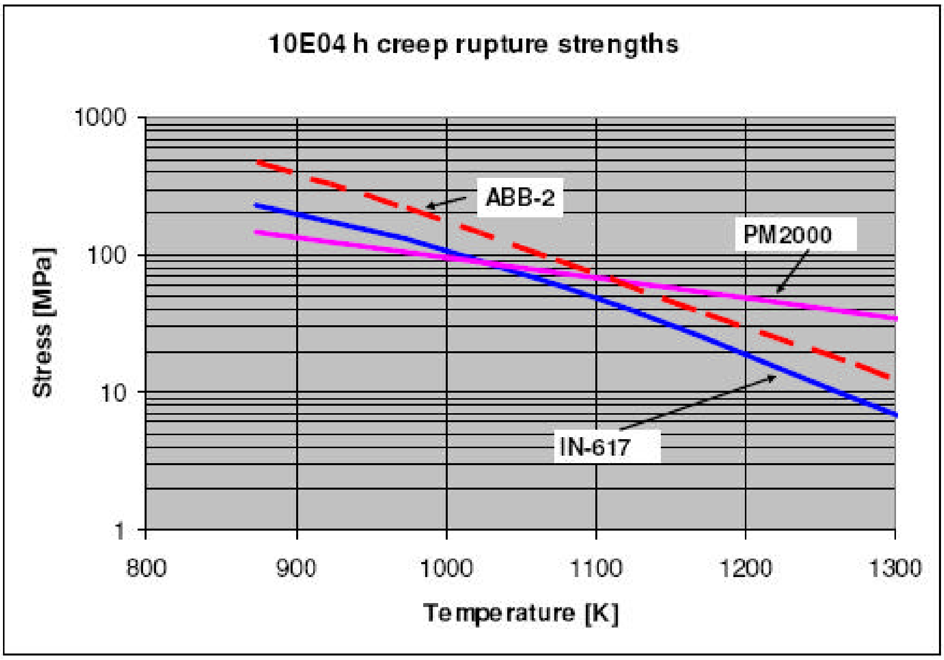

Figure 6: 10^4 hours creep rupture strength for advanced VHTR materials

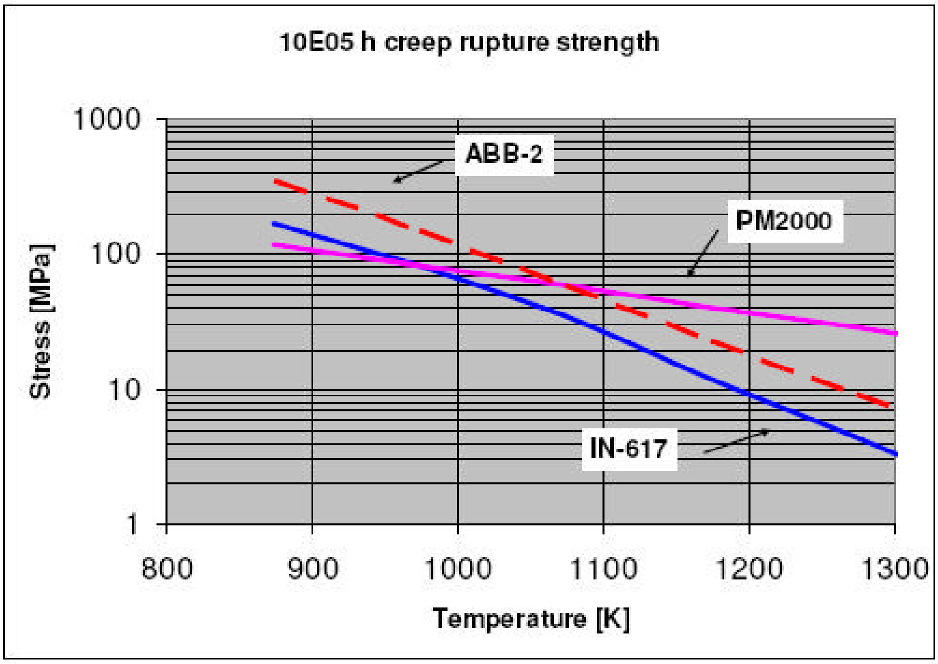

Figure 7: 10^5 hours creep rupture strength of advanced VHTR materials

CONCLUSIONS

The potential of two possible candidates (titanium aluminide, ferritic ODS) for future VHTRs with gas temperatures exceeding 950 °C was assessed on the basis of thermal and irradiation induced creep data. The results were compared with IN-617 which is today the standard metallic material for the highest temperatures in HTR plants. For thermal creep an established parametrization of stress rupture curves was used. The applicability of the parametrization was first demonstrated for IN-617 where currently available state of the art creep rupture curves could be reproduced. Creep rupture curves based on scarce existing data for the two advanced materials were assessed with the same method.

The material IN-617 has been successfully in use over decades in different high temperature applications and a huge data set with a wide range of experience exists which forms a good basis for design. It can be expected that IN-617 will remain an important material for the current generation of HTRs and temperatures below or equal 950 °C which is still not too high. It also behaves well with respect to irradiation induced creep. According to its high nickel content He-formation is expected, degrading the creep rupture properties. It is fair to say that the material has only very limited to no potential for very high temperature applications exceeding 950°C.

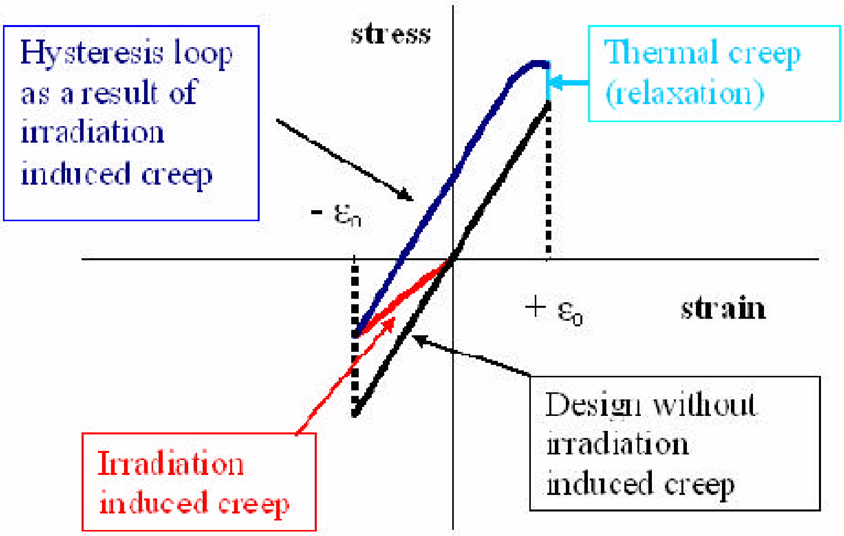

Figure 8: Possible irradiation-thermal creep interaction during thermal transients

ABB-2

The assessment showed that the titanium aluminide can be expected to take about 2 times more stresses as IN-617 at the very high temperatures. Uncertainties concerning long term microstructural stability, long term creep data and data scatter require more investigations which eventually qualify this material for future nuclear applications. Possible production routes, effects of environment, low temperature brittleness and bonding must be included in future feasibility considerations

PM2000

The ferritic ODS steel PM2000 shows by far the best thermal creep rupture behaviour. It has these reserves even up to 1100 °C. It is a real candidate for advanced VHTRs. The material was only investigated in the annealed condition. Further investigations are necessary to assess the long term stability (particularly of the dispersoids), and to improve the material towards component manufacturing including bonding. The dispersoids do not participate in the irradiation induced creep process and therefore high creep rates occur already at low stresses.

Irradiation-thermal creep damage interactions are basically possible particularly for transient conditions. They should be considered in situations where thermally induced transient strains and irradiation induced creep can occur. As long term interactions are difficult to simulate in the laboratory advanced materials modeling techniques should be employed to analyze such effects.

NOMENCLATURE

Fcc: face centered cubic lattice
GENIV: Generation IV initiative
HTR: High Temperature Reactor
IN-617, ABB-2, PM2000: alloy designations
RPV: Reactor Pressure Vessel
TEM: Transmission Electron Microscope
VHTR: Very High Temperature Reactor

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REFERENCES

[1] 2002. "A Technology Roadmap for Generation IV Nuclear Energy Systems ". Issued by the U.S. DOE Nuclear Energy Research Advisory Committee and the Generation IV International Forum. December 2002, see also following link http://www.ne.doe.gov/genIV/Generation_IV_Roadmap_1-31-03.pdf (visited June 19, 2006).

[2] 1984. "High Temperature Gas-Cooled Reactor Materials - Irradiation Behavior", Nuclear Technology, 66, Sept. 1984, pp.597-646

[3] 1984. E. Schubert et al. "Creep Rupture Behavior of Candidate Materials for Nuclear Process Heat Applications", Nuclear Technology, 66, Aug 1984, pp.227-240.

[4] 1984. Penkalla, H-J., Over, H.-H., Schubert, F., "Constitutive Equations for the Description of Creep and Creep Rupture Behavior of Metallic Materials at Temperatures above 800°C", Nuclear Technology, 66, pp. 685-692,

[5] Nazmy, M., Staubli, M., US Patent 5,207,982 & EP 45505 B1.

[6] 2003. "Dispersion-Strengthened High-Temperature Materials. Material Properties and Applications", Plansee 706 DE.04.02 (3500) RWF.

[7] 2004. Wolf, T., "Einfluss von Kohlenmonoxid auf die Oberfläche der Hochtemperatur-Titanaluminid-Legierung ABB2", Semester Thesis, ETH Zürich, Dpt. Materials.

[8] 2004. Lapin, J., Nazmy, M., "Microstructure and Creep Properties of a Cast Intermetallic Ti-46Al-2W-0.5Si Alloy for Gas Turbine Applications", Materials Science and Engineering , A 380, pp. 298–307.

[9] 2001. Capdevila, C., Chen, Y. L., Lassen, N. C. K., Jones, A. R., Bhadeshia, H. K. D. H., "Heterogeneous Deformation and Recrystallisation of Iron Base Oxide Dispersion Strengthened PM2000 Alloy" Materials Science and Technology, 17, pp. 693-699.

[10] 1985. Jung P., Schwarz, A., Sahu, H. K., Nucl. Instr. and Meth. A 234, 331.

[11] 1981. H. Schroeder, P. Batfalsky, J. Nucl. Mater. 103&104, 839.

[12] 2006. Chen, J., Jung, P., Nazmy, M., Hoffelner, W., "In Situ Creep under Helium Implantation of Titanium-Aluminium Alloy", Journal of Nuclear Materials 352 pp. 36–41

[13] 1952. Larson, F.R., Miller,E.J., "Time-temperature Relationship for Rupture and Creep Stresses", Trans ASME, v. 74, pp. 765-775, 1952.

[14] 1954, Orr, R.L., Sherby, O.D., Dorn, J.E., "Correlations of Rupture Data for Metals at Elevated Temperatures", Trans ASM, 46, pp. 113-118.

[15] 1953, Manson, S.S., Haferd, A.M., "A Linear Time-temperature Relation for Extrapolation of Creep and Stress Rupture Data", NACA TN 2890.

[16] 2005. Francisco dos Reis Sobrinho, J, Oliveira Bueno, L., "Correlation Between Creep and Hot Tensile Behaviour for 2,25Cr-1Mo Steel from 500°C to 700°C. Part 2: An Assessment According to Different Parameterization Methodologies", Revista Matéria, v. 10, n 3, pp. 463 – 471.

[17] 1986. Hoffelner, W., "Creep Dominated Processes", in High Temperature Alloys for Gas Turbines and other Applications, Proc. Eds.: W. Betz et al., D. Reidel Publ. Comp. Dordrecht, p.413

[18] 2005. Chandra, S., et al.," Creep Rupture Data Assessments of Alloy 617", ECCC Creep Conference, 12-14 September 2005, London, Conf. Proc. Paper 16.

[19] 1997, Wortler, J., "Mikrostrukturelle Beschreibung der Warmfestigkeit Ferritischer Superlegierungen", Fortschr.-Ber. VDI, Reihe 5, 510

[20] 2006, Lapin, J., "Creep Behaviour of a Cast TiAl-Based Alloy for Industrial Applications", Intermetallics, 14, pp. 115–122.
[21] 2003, Dorner, D., Roeller, K., Skrotzki, B., Bernhard Stoeckhert , B., Eggeler, G., "Creep of a TiAl Alloy: A Comparison of Indentation and Tensile Testing", Materials Science and Engineering A357, pp. 346-354.
[22] 2006, Hoffelner, W., Samaras., M., Victoria, M., "Modeling of Advanced Structural Materials" ANS Conf. 2006, Embedded Topical Meeting on Materials for Advanced Nuclear Applications, Phoenix, Submitted for Publication in Jounal of Nuclear Materials.
[23] 2006, Samaras, M., Hoffelner, W.,.Victoria, M., "Irradiation of Pre-Existing Voids in Nanocrystalline Iron", Journal of Nuclear Materials 352, pp. 50–56