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Degradation of metallic materials in HTR helium coolant

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Summary

This document contains information on candidate materials for V/HTR systems. Further mechanism of degradation of these materials in V/HTR helium coolant is described. Results of tests of high temperature alloys within previous HTR programs are summarized and properties of selected alloys (e.g.800H, Hastelloy X, Alloy 617, Haynes 230) are specified in details.

Approval

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1 Metallic materials for V/HTR systems

Helium coolant in previous HTR (HTGR) systems reached temperatures up to 900℃ [1]. In Generation IV VHTR systems at higher temperatures (about 1000℃) have been considered [2]. The materials in the systems are subjected to relative high pressure and in the core of the reactor also to the neutron flux. These conditions are demanding and require good resistance and reliability from the structural materials. The key properties of candidate alloys that are important are:

- basic mechanical strength properties especially at higher temperatures
- effect of helium coolant chemistry on material degradation and changes in mechanical properties
- corrosion mechanism of the alloys
- effect of coolant and alloy composition on corrosion resistance
- Corrosion-erosion due to particulate-laden gas flow
- Effect of irradiation on the material degradation

For qualification of materials for nuclear systems the prediction of properties of material for long-time service life (typically more than 100 000 hours) is needed [3]. Material temperatures and design codes for metallic components in nuclear applications can be seen in fig. 1 [3].

Candidate alloys for V/HTR systems and their material compositions are listed in the table 1 [1] and discussed below.

Further sections focus on the corrosion of selected metallic alloys in V/HTR helium coolant, the effect of degradation of the alloys on mechanical properties and the results achieved within previous HTR programs.

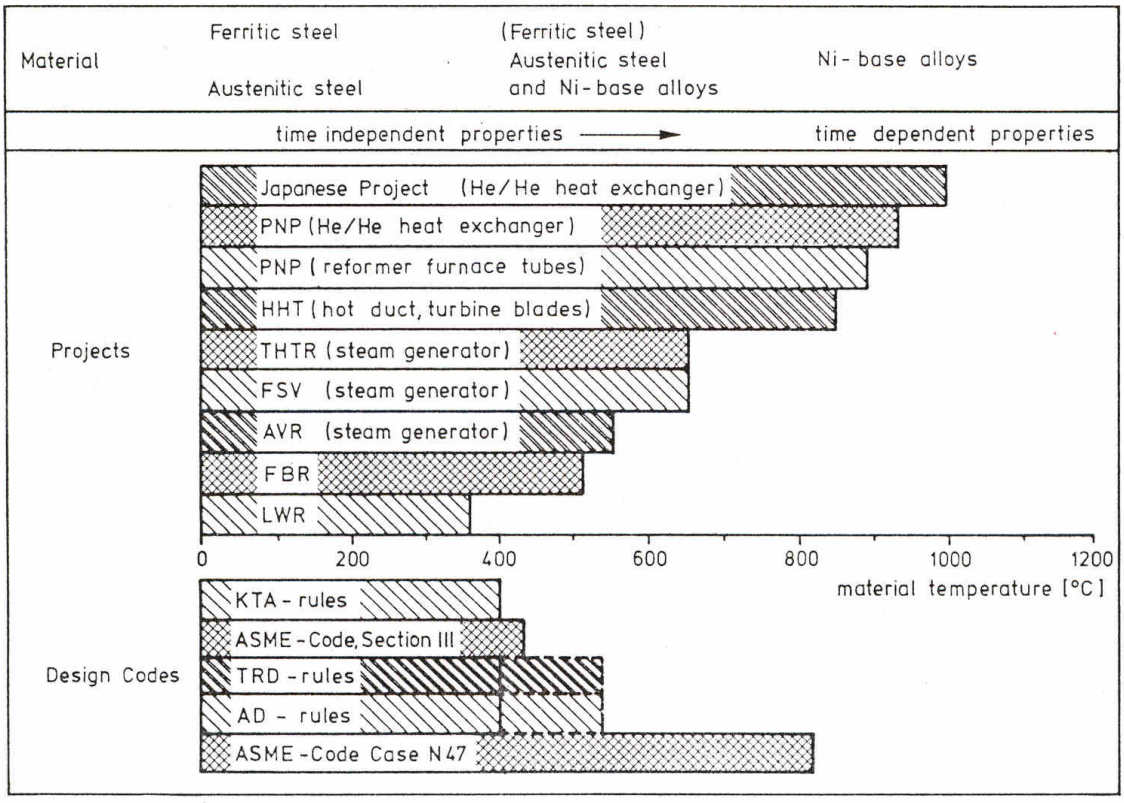

Fig. 1: Material temperatures and design codes for metallic components in nuclear applications [3]

2 V/HTR helium coolant properties

Helium is used as a coolant in HTR systems and is also proposed as a coolant for future VHTR and also GFR [2]. Helium itself is an inert gas which does not react with other materials. In reactor systems it will however contain small amounts of impurities, which may react with metals especially at higher temperatures. Typical HTR impurities are: CO, CO_2, CH_4, H_2, H_2O, O_2, N_2, simple organics and dust particles. The sources of impurities are e.g. ingress of water from boilers, small ingress of air and lubricants, desorption of elements from graphite and other structural materials, subsequent reaction of oxygen and water with fuel elements and graphite moderator, fission reactions, etc. The concentrations of impurities under steady operation of prototypes of nuclear reactor are listed in table 2. Typically the total impurity levels were not found to be

higher than 10 vppm, except under special events. On the basis of operation experience H_2:CO:H_2O rates are estimated to range from 5:5:1 to 50:50:1.

Table 2: Steady state impurity levels in helium cooled prototype reactors [4, 5]

Impurities vppm	H_2O	CO_2	H_2	CO	CH_4	N_2	O_2
Peach Bottom	<0.5	-	9	0.5	0.6	0.5	-
AVR	3	10	30	30	-	-	-
Dragon	0.05	<0.02	1.0	0.6	0.15	0.15	0.1
Fort St. Vrain	1	1	7	3	0.1	-	-
THTR	<0.01	0.2	0.8	0.4	0.1	0.1	-

Table 1: V/HTR candidate alloys and specifications

Material	C	Cr	Ni	Co	Mo	Ti	Al	Fe	Others	Application
2.25Cr-1Mo	0.20	2.3	-	-	1.0	-	-	Bal	-	Pressure vessel
9Cr-1Mo (T91)	0.08	8.6	-	-	1.0	-	-	Bal	V 0.2, Nb 0.07	Pressure vessel
HT 9	0.2	12	0.3	-	1	-	-	Bal	V 0.25, W 0.5	Pressure vessel
316 SS	0.05	18	14	-	2,2	-	-	Bal	-	Recuperator
800H	0.08	20.1	31.7	-	0.3	0.4	0.4	Bal	-	Piping, internals
Hastelloy X	0.1	21.5	Bal	2.0	9.0	-	-	18.5	W 0.6	Piping, internals
Inconel 617	0.06	21.6	53.6	12.5	9.5	0.3	1.2	0.9	-	Piping, internals
Hastelloy-XR	0.07	22	Bal	2.0	9.0	-	-	18.2	W 0.5, Mn 0.9	Piping, internals
Nimonic-86	0.07	25	Bal	-	10	0.1	-	1.7	-	Piping, internals
Hastelloy S	0.02	15.5	Bal	-	14.5	-	0.2		-	Piping, internals
Manaurute	0.4	25	35	-	-	-	-	Bal	Nb 1	Piping, internals
Inconel 519	0.3	24	24	-	-	-	-	Bal	Nb1	Piping, internals
713LC	0.07	12	Bal	-	5	0.7	6	-	Nb 2, Zr 0.1	Turbine blades
Mar-M 004	0.07	12	Bal	-	4.5	-	6	-	Hf 1.3, Nb 1.6, Ta 0.3	Turbine blades
M21	0.1	6	Bal	-	2	-	6	-	W 10.5, Nb 1.5, Zr 0.1	Turbine blades
738	0.11	16	Bal	9.0	2	-	3.4	-	W 2.6, Ta 2, Nb 0.9	Turbine blades
Udimet 520	0.05	19	Bal	12.0	6	3.0	2	-	W 1	Turbine blades
Mo-TZM	0.02	-	-	-	Bal	0.5	-	-	Zr 0.8	Turbine blades
A286	0.05	15	26.0	-	1.3	2.5	0.2	Bal	B 0.015	Turbine discs
706	0.03	16	42.0	-	0.5	1.0	0.2	Bal	Nb 2.9	Turbine discs
718	0.1	19	Bal	-	3	0.8	0.6	19	Nb 5.2	Turbine discs
Waspaloy	0.08	20	Bal	13.5	4.3	3.0	1.3	-	Zr 0.06	Turbine discs
Udimet 720	0.03	18	Bal	14.5	3	5.0	2.5	-	W 1.3	Turbine discs
MA 6000	0.05	15	Bal	-	2	2.5	4.5	-	W 4, Ta 2, Y_2O_3 1.1	Turbine discs

3 Corrosion in HTR helium and its effect on the high temperature properties of metallic alloys

Generally speaking, high temperature corrosion in HTR systems is can result in mechanisms of carburization, decarburization and oxidation (where A is a metal alloy) [1]:

$A + 1/2O_2 = AO$ (1)

$A + C = AC$ (2)

$AC+1/2O_2=AO+C$ (3)

Under equilibrium, the partial pressures of oxygen and carbon activity are defined by the following equations:

$(a_O)_{eq}=pO_2^{1/2}=\exp(\Delta G_{AO}/RT)$ (4)

$(a_C)_{eq}=\exp(\Delta G_{AC}/RT)$ (5)

$(a_C/a_O)_{eq}=\exp[(\Delta G_{AC}- \Delta G_{AO})/RT)]a_{AC}/a_{AO}$ (6)

If the activity of AC and AO are assumed to be unity, the last equation could be simplified to:

$(a_C/a_O)_{eq}=\exp[(\Delta G_{AC}- \Delta G_{AO})/RT)$ (7)

Where ΔG_{AO} and ΔG_{AO} are standard free energies for the formation of oxides and carbides, respectively, at temperature T. Note that R is the universal gas constant (8.314472 $J\cdot K^{-1}\cdot mol^{-1}$).

If then $(a_O)_{gas}>(a_O)_{eq}$ a $(a_c)_{gas}<(a_C)_{eq}$; only AO on the surface of the metal is stable.
Also if $(a_O)_{gas}<(a_O)_{eq}$ a $(a_c)_{gas}>(a_C)_{eq}$, only carbides on the metal surface are stable.

If $(a_O)_{gas}>(a_O)_{eq}$ a $(a_c)_{gas}>(a_C)_{eq}$ and if $(a_c/a_O)_{gas}>(a_c/a_O)_{eq}$; AC will be the stable phase on the boundary of the metal-gas. If $(a_c/a_O)_{gas}<(a_c/a_O)_{eq}$, AO will be a stable.

Carbon activity can be calculated from these equations in the gas phase:

$CO + H_2 = C + H_2O$ (8)

$2CO = C + CO_2$ (9)

$CH_4 = C + 2H_2$ (10)

$CH_4 + CO = 2C + H_2O + H_2$ 11)

$CO = C + 1/2O_2$ (12)

$a_c= K_1(p_{CO}.p_{H2})/pH_2O$ for reaction (8) (13)

$a_c=K_2(p_{CO})^2/p_{CO2}$ for reaction (9) (14)

$a_c= K_3p_{CH4}/(p_{H2})^2$ for reaction (10) (15)

$a_c=(K_4)^{1/2}.(p_{CH4}.p_{CO}/p_{H2O}.p_{H2})^{1/2}$ for reaction (11) (16)

$a_c=K_5p_{CO}/(p_{O2})^{1/2}$ for reaction (12) (17)

Where K is an equilibrium constant and p_x the partial pressure of the given component.

Reactions determining the oxygen partial pressure in the gas phase are:

$H_2O = 1/2O_2 + H_2$ (18)

$CO_2 = 1/2O_2 + CO$ (19)

$p_{O2}=(K_5.p_{CO}/a_C)^2$ for reaction (12) (20)

$p_{O2}=(K_6.p_{H2O}/p_{H2})^2$ for reaction (18) (21)

$p_{O2}=(K_7.p_{CO2}/pCO)^2$ for reaction (13) (22)

With increasing system pressure, the carbon activity and the partial pressure of oxygen (even if the concentration is the same) the reactions of carbon and oxygen with metal are expected to be more intensive.

According to the equations cited above the carbon activity and oxygen partial pressure in the equilibrium state can be calculated, but the HTR helium coolant is a typical non-equilibrium system. Therefore the kinetics of the reaction will also play a role [1].
From the thermodynamic data on metal-oxygen equilibrium [4] iron and nickel are calculated as not to be oxidized in a typical HTR helium coolant, while the mayor alloying elements Cr, Mn, Si, Ti and Al will be oxidized [4].
The presence of CO also offers the possibility of carbon production on the metal surfaces:

$2CO=CO_2+C$ (23)

According to the thermodynamic data [4] the reaction (22) will proceed in HTR helium coolant at lower temperatures, but the reaction rate will be low.

One way of expressing the dependence of corrosion of metallic alloys in HTR helium on the partial pressure of oxygen and carbon activity is the modified Ellingham Diagram (fig. 2) [5]. Five conditions are represented within the diagram as follows:

I-strongly reducing,
II-highly oxidizing,
III-stable external oxide with stable internal carbides,
IV-strongly carburizing internally and externally, and
IVa – strong external carburization with stable oxide layer.

Zone III was determined to be the area of highest stability (protective corrosion scales are formed), an environment oxidizing yet slightly carburizing.

The modified Ellingham diagram is based on the reactions of the most relevant compounds involved in the corrosion process – especially Cr. Depending on the partial pressures of the impurities in helium, the temperature and kinetic parameters of environment, Cr forms carbides, oxides or metallic Cr (see [5] for details). The important features of the diagram are the critical carbon activation (a_c^*), the critical partial pressure of oxygen (P_{O2}^*), and the critical partial pressure of carbon monoxide (P_{CO}^*). These parameters are calculated from the following thermodynamic reactions:

a_c^*:	$23Cr + 6C = Cr_{23}C_6$	metal-carbide equilibrium activity (24)
P_{O2}^*:	$Cr_2O_3 = 2Cr + 1.5O_2$	disassociation pressure of chromium (25)
P_{CO}^*:	$3CO + 2Cr = Cr_2O_3 + 3C$	CO pressure for this equilibrium (26)

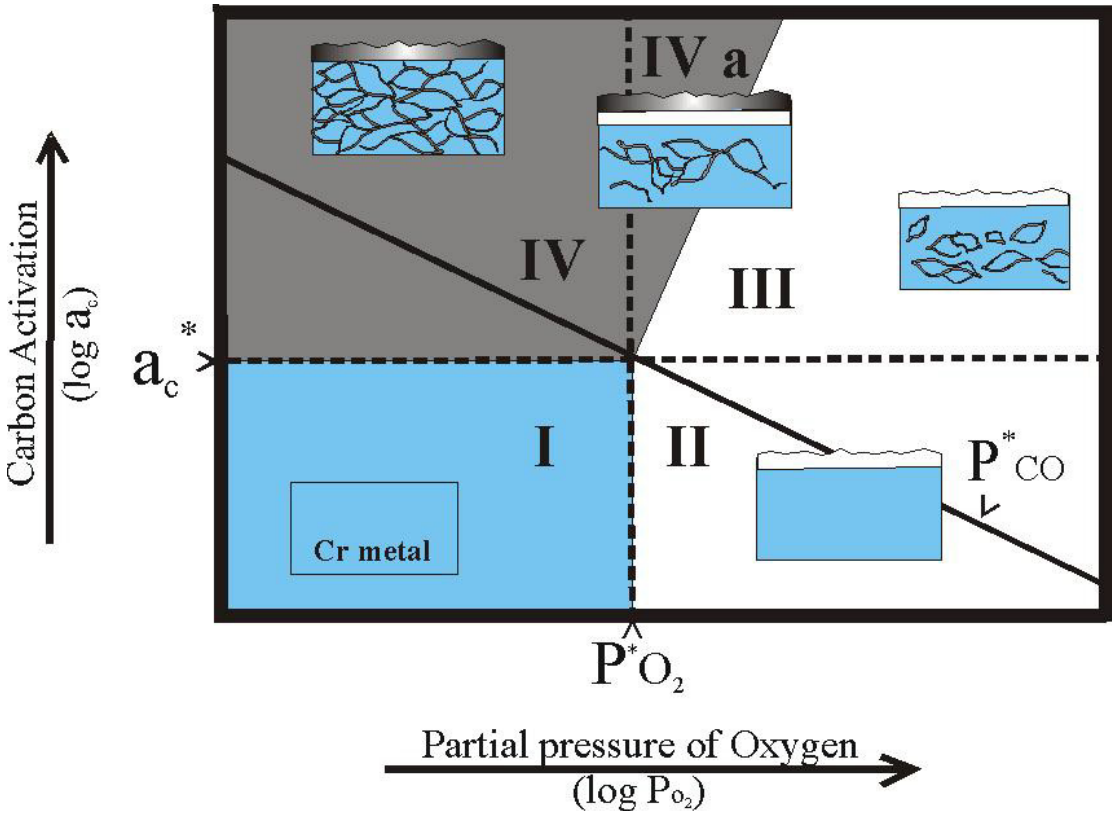

Fig. 2: Quadakkers modified Ellingham diagram [5]

The local chromium activity is associated with the reaction:

$$2Cr_2O_3 + Cr_{23}C_6 = 6CO + 27Cr \qquad (27)$$

Above the so-called critical temperature T_a the CO concentration is no longer sufficient to drive the reaction and the result is an eventual total loss of either chromium oxide or carbide, depending on the concentration, followed by complete carburization or decarburization of the alloy, depending on the gas composition. The value of Ta is estimated to range from approximately 950 – 980°C according to alloy composition and partial pressures of impurities in the helium. This degradation mechanism was not considered in the construction of the modified Ellingham diagram, also another issue not considered was the volatility of Cr_2O_3 above approx. 950°C [5].

Another expression used to describe the corrosion processes in HTR helium is the so-called Ternary Environmental Attack (TEA) diagram used for the corrosion of Alloy 617 [6] or other alloys [7]. Chromium is

considered to be the most reactive element in the alloy and on the metal surface the following reactions take place [6]:

Oxidation of chromium by water:

$$3H_2O + 2Cr = Cr_2O_3 + 3H_2 \quad (28)$$

Decomposition of methane on alloy surface:

$$CH_4 \xrightarrow{alloy} C_{solution} + 2H_2 \quad (29)$$

Reaction of water with carbon in alloy:

$$H_2O + C_{solution} \rightarrow CO + H_2 \quad (30)$$

Carbon monoxide splitting

$$3CO + 2Cr \xrightarrow{T<Ta} Cr_2O_3 + 3C_{solution} \quad (31)$$

At higher temperatures (above the critical temperature T_a) the "microclimate reaction" takes place: It is formally the reverse reaction of (31).

$$Cr_2O_3 + 3C_{solution} \xrightarrow{T>T_a} 3CO + 2Cr \quad (32)$$

At temperatures above T_a the internal carbon cannot coexist and the reaction (32) continues until all the carbon or all the oxide is removed.

The ratio P_{CH4}/P_{H2O} is also said to play a key role:
At low ratios (typically 20:1 for Inconel 617), the metal originated form reaction (33):

$$Cr_7C_3 = 3C_{solution} + 7Cr \quad (33)$$

will react with the water vapor according to reaction (28). The oxide layer is regenerated and the alloy decarburized. Due to the escape of carbon monoxide the surface layer may be porous and therefore cannot provide any protection.
At high ratio of P_{CH4}/P_{H2O} (typically 200:1 for Inconel 617), the produced metal cannot be oxidized, and the reaction (29) occurs leading to an extensive carburization.

On the basis of assumption mentioned above Brenner proposed the mapping corrosion behavior of Inconel 617 – the so called Ternary Environmental Attack (TEA) diagram illustrated in Fig. 3 [6].

The temperature of the system is assumed to be constant. TEA is in the shape of triangle with axes P_{H2O}/S, P_{CO}/S a P_{CH4}/S, where S is the sum: $P_{H2O} + P_{CO} + P_{CH4}$. The six boundary lines in the diagram are related to the thermodynamic and/or kinetic behavior of the reactions (28) to (33) and delineate areas with respect to chromium behavior occur:

- a and A: severe decarburization due to carbon removal as CO under porous oxide layers
- b: growth of a chromium oxide layer
- c: formation of mixed carbide/oxide layers and carburization (meaning carbon enrichment)
- d and D: severe carburization (meaning carbon deposition).

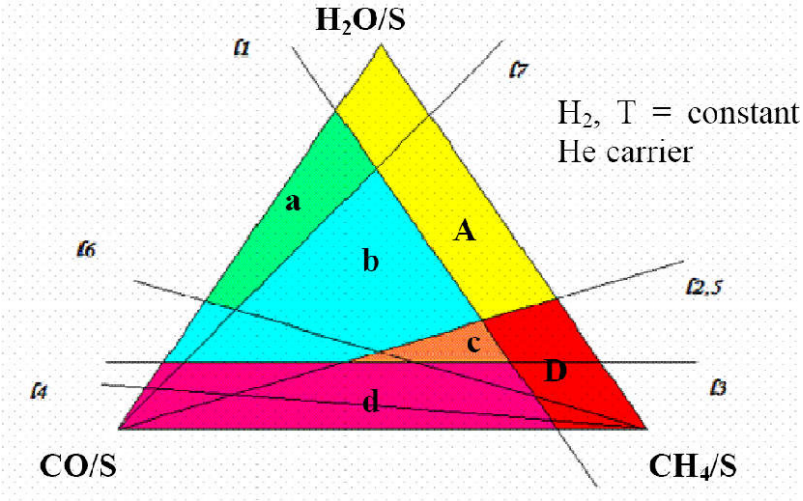

Fig. 3: TEA diagram

The high temperature corrosion resistance of Ni-Cr alloys (e.g. Inconel 617) is based on growing a compact, dense chromium-rich oxide layer, which prevents access of the corrosive species to (or from) the metal. Thus for long term metal integrity the composition of the HTR helium should allow the oxidation and correspond to the area “b” in the TEA diagram. Carburization or decarburization of the alloy could cause in-depth changes in the alloy microstructure and consequent changes in the mechanical properties. See [6] and [7] for details.

4 Effect of corrosion in HTR helium on mechanical properties

The main mechanical properties important for the V/HTR structural materials are creep, stress rupture and fatigue. Thye effect of temperature and helium coolant on these properties were studied and published in earlier investigations (some results are summarized for e.g. in [1]). The mechanical properties obtained in the simulated V/HTR helium were often compared to those obtained in other environments such as for e.g. air or in a vacuum. High temperature components are designed to operate for the major part of their life in the secondary creep range, therefore the effects of corrosion on the secondary creep behavior is considered to be important [4].

The effects of the environment on the mechanical properties can be divided into surface effects and bulk effects [4]. Surface effects such as mechanical strengthening of the bulk by the oxide film and the locking of the dislocation source or changes in surface energy are not considered to have a marked effect on mechanical properties. The bulk properties can however be affected by the gaseous environment due to the adsorption or desorption of the gaseous species or due to the production of compounds at the corroding surface which diffuse into the bulk metal. Examples of such effects are internal oxidation, carburization or decarburization. The depth of the penetration of such effects depends on the solubility of the elements in metal, the diffusion rate of the species and their availability at the surface, which will depend upon the effectiveness of the surface oxide layer as a barrier and/or the rate of production of the compounds bat the surface. The effect of the solute species in the metal can be as follows [4]:

- solid solution strengthening
- dispersion strengthening
- formation of a brittle phase with loss of ductility
- depletion of alloying elements

Diffusion processes are often more rapid at grain boundaries, therefore the effects are often more evident at the grain boundaries than in the metal matrix.

5 Experiments carried out in HTR helium and similar environments

Relatively large amounts of experimental investigations and analysis concerned with material research for the HTR were carried out in the 1960s to 1980s. The aim of the programs was to develop a database on materials for application to the steam-cycle and process-nuclear-heat based HTRs [1]. Experiments were mostly aimed at testing corrosion resistance and evaluating the changes in mechanical properties of the

metallic alloys in simulated HTR environments. The gas characteristics of some of the helium atmospheres used for some of the experiments are listed in the Table 3. Compared with Table 2 the concentrations of some impurities were higher than those for steady operation of HTR reactors especially for H_2. It is not clear, why specific compositions of gas atmospheres were chosen for some experiments but its possible that it may be associated with the HTR application (e.g. coal gasification) where the hydrogen was assumed to diffuse from the process plant into the primary coolant circuit [5]. Most studies of the gas chemistry simulation were performed at a total gas pressure close to atmospheric pressure (1-2 bar), whereas the gas pressure in the reactor is higher (3 – 7 MPa) [1]. Most laboratory experiments were carried out at low flow rates, at which the gas chemistry is close to thermodynamic equilibrium. These conditions are not representative of reactor systems, where high gas velocities are (e.g. 50 – 75 m/s). One exception is the tests on high temperature alloys (e.g. Incoloy 800H, Hastelloy X, Inconel 617 and some austenitic steels) performed in the French AIDA loop [8]. The pressure in the loop was 50 bar, the gas velocity in the AIDA loop was 2 – 5 m/s, the gas flow in the autoclaves near the loop ranged from 5 to 15 cm/s. The results from these experiments were compared with those obtained after test in helium with similar concentrations of impurities at a pressure of 2 bar. Corrosion kinetics was found to be higher at higher pressure (see Fig. 4, although the authors were doubtful that the parameters of the experiment were measured accurately).

Other tests at a pressure close to real reactor operating situation were carried out in the 10 MW loop built within the scope of THTHR development. The loop operated at a pressure at 40 bar with helium with the PNP gas composition, and at temperatures between 700°C to 950°C, the gas flow rate was also relatively high. On the tested specimens of Inconel 617 only surface oxidation was found. From these results it was concluded that higher velocities and the high pressure do not substantially change the corrosion behavior [5].

As stated above, relatively large numbers of tests on the behavior of metallic alloys in V/HTR helium were carried out in different institutions throughout the world, e.g. in USA (The Battelle national laboratories, Oak Ridge National Laboratory, General Atomics), Japan, Germany, Northland, Netherlands, France etc. Some investigations were aimed at corrosion behavior only, others studied the influence of mechanical properties using long-time exposure in impure helium at high temperatures. Most tested alloys were Incolloy 800 or 800 H, Hastelloy X and XR, Inconel 617 or other Inconels (625, 600, 702, 728),Haynes 230 and in some cases ferritic and austenitic steels (tested usually at lower temperatures) and other special alloys.

Table 3: Model impurity chemistries used in various experimental programs [1, 5]

Gas	Partial pressures of impurities (in Pa)						Reference
	H_2	CO	CH_4	CO_2	H_2O	N_2	
A	150	45	5	<0.05	5	-	Johnson and Lai 1981 [1]
B	20	10	2	0.5	5	-	Johnson and Lai 1981 [1]
C	50	5	5	<0.05	<0.05	-	Johnson and Lai 1981 [1]
D	50	5	5	<0.05	0.15	-	Johnson and Lai 1981 [1]
HTR	50	5	2	-	0.1	-	Graham et al. 1981 [1]
Decarb.	50	0.5	0.5	-	0.1	-	Graham 1990 [1]
JAERI-B	20	0.15	0.2	-	0.01	-	Kondo 1981 [1]
ERANS#2	30	10	0.4	0.1	0.3	<0.5	Kondo 1981 [1]
PNP	50	2	2	0.1	<0.2	0.5	Kondo 1981, Quadakkers and Schuster 1984, Bates 1984 [1]
GE	40	4	2	0.02	0.2	0.6	McKee and Frank 1981 [1]
LAB I	150	45	5	-	5	-	Cappellaere et.al. 1984 [1]
AIDA	150	45	5	-	5	-	Cappellaere et.al. 1984 [1]
LAB II	50	1.5	2	-	0.15	0.5	Huchtemann 1989 [1]
HHT	25	2	2.5	-	0.075	0.5	[5]
AGCNR	10	5	0.25	0.1	0.1	<0.25	[5]

ERANS: Engineering Research Association of Nuclear Steelmaking, Japan
JAERI: Japanese Atomic Energy Research Institute
PNP: Prototype Nuclear Process
GE: General Electric Company
Lab I and Lab II: Environment and laboratory tests
At total pressure 1 bar partial pressure 1 Pa = approx. 10 vppm

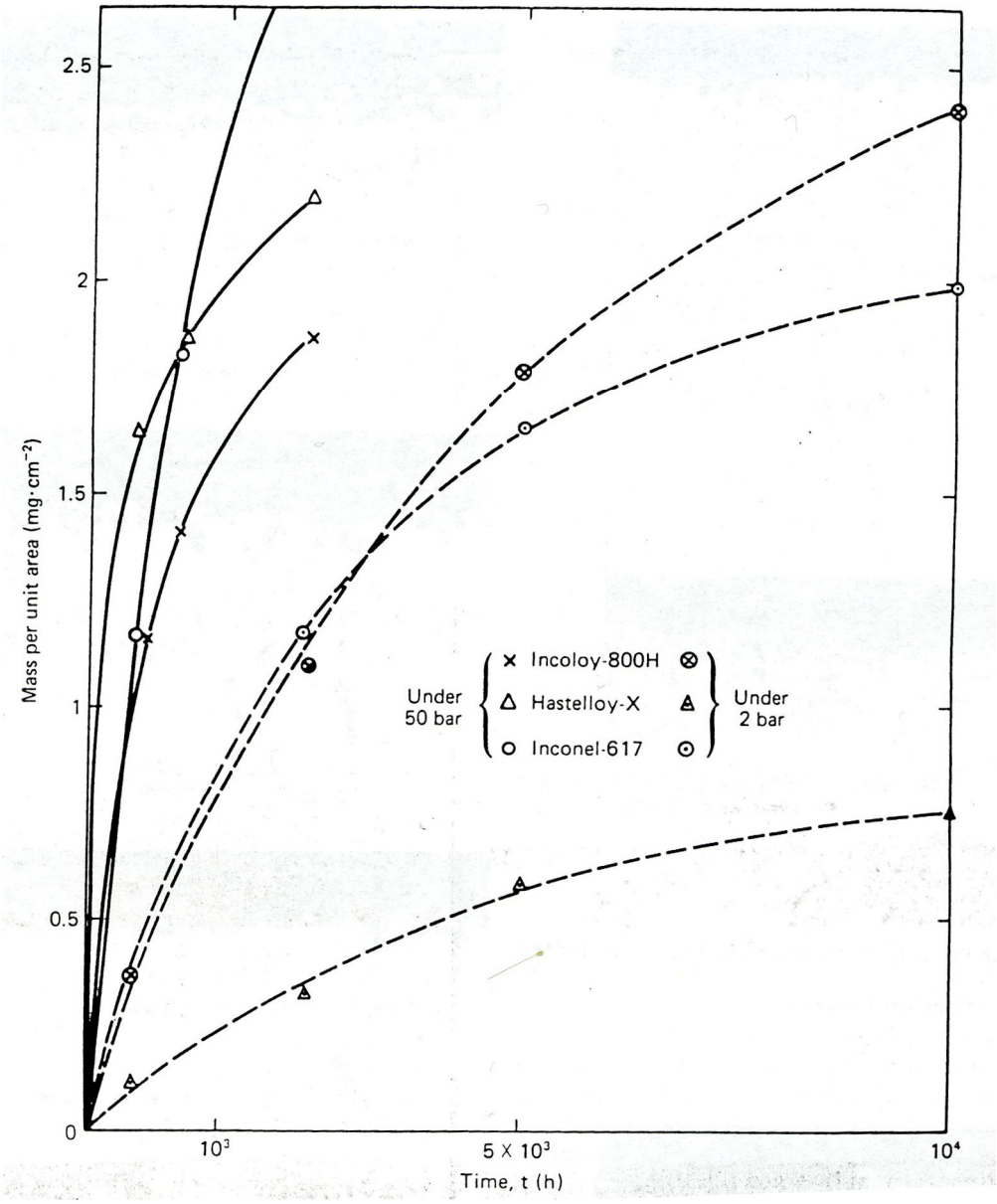

Fig. 4: Corrosion kinetics at 870°C under 2 and 50 bar in impure helium [8]

For example, within the DRAGON project, the sponsored work at CIIR, Oslo, included the exposure of a range of steels at 500 and 600°C in mixtures of CO, H_2 and H_2O in the ratios 1:1:1, 10:10:1 and 100:100:1 for periods up to 7300 hours. The results for the 1:1:1 mixture shows that there were oxide layer formations with a minor tendency to decarburization. For the 10:10:1 mixture there was oxide formation and decarburization, and for the 100:100:1 mixture carbon deposition occurred [4]. A study of the catalytic decomposition of CO in pure iron, mild steels and alloy steels was also sponsored within the DRAGON project. The tests were carried out in argon containing low concentration of CO, H_2 and H_2O in the ratios of 10:10:1 to 100:100:1. The results were that: for mild steel and low alloy steel no oxide films were formed in any of the gas mixtures; for steels with 8% or more chromium oxide films were formed. The carbon deposition on mild steel did not occur for the 500 µBar CO and 10:1 ratio but did occur for the case of 5.10^4 µBar of CO [4].

Another example was the work carried out in Atomic Power Constructions (APC), where a 3000 h test involving exposure of alloys at 700°C to helium containing 2.5 vppm H_2O,12.5 vppm H_2 and 12.5 vppm CO. The results are summarized in the Table 4.

Table 4: Results of corrosion tests at 700°C in high pressure helium carried out in APC [4]

	Weight gain (mg/cm^2)		Metallography after 1000 h
	1000 h	3000 h	
Esshete 1250	0.06	0.16	Very thin oxide. Shallow feathery oxide penetration
Type 316	0.05	0.20	Extent of thin oxide film. No evidence of penetration
Type 310	0.13	0.22	Thin oxide film with grain boundary penetration in the case of annealed material
Incoloy 800	0.13	0.31	Thin oxide film with metal particles included in the film. Subsurface penetration
Inconel 600	0.11	0.47	Irregular oxide scale. No evidence of intergranular penetration
Hastelloy X	0.10	0.25	Thin surface oxide. Some evidence of spalling: occasional penetration associated with molybdenum carbide particles
Hastelloy C	0.015	0.15	Interference film. No subsurface penetration

The subject of some studies has been to study experimental material and investigate how the content of different alloying elements can influence the corrosion behavior in V/HTR helium. Johnson [11] exposed the high temperature experimental Ni-Cr-Mo-W-Al-Ti-Zr-C alloys at 800°C, 900°C and 1000°C in helium containing 50 Pa H_2, <0.05 Pa H_2O, 5 Pa CO and 5 Pa CH_4 for up to 10000 hours. The results showed carburization and oxidation of the alloys. On the surface of the specimens, carbide and mixed oxide-carbide layers were identified. Further near-surface internal oxides, underlying alloy-depleted regions and internal carbides also occurred. After exposure of the alloys at 800°C only slight weight gains and no significant carbon uptake was observed. The weight gains reflected the development of a thin aluminum-rich surface oxide. After exposure at 900°C larger weight gains and significant carbon pickups were observed. With Aluminum-rich surface oxides of varying thickness, internal oxidation and internal carbides occurring. Carburization resistance was best for alloys containing about 2 wt % of Al and Ti. After exposure at 1000°C (above the critical temperature T_a, (see earlier) very large weight gains and increases in carbon content were observed. The alloys exhibited three-layer (carbide/oxide/carbide) or two-layer (oxide/carbide) surface scales with thickness up to around 20 µm. Surface carbide layers were rich in Cr (outer layer) or rich in Ti and Mo or W (inner layers). Surface oxide layers were rich in Al.

Similar studies were published by McKee [12]. Within this work experimental alloys with different content of Al, Ti, Si, Nb and Y were exposed in simulated HTR helium containing 40 Pa H_2, 0.2 Pa H_2O, 4 Pa CO, 0.02 Pa CO_2, 2 Pa CH_4, 0.6 Pa N_2 and <0.01 Pa O_2 at 750 – 1050°C for the period 1000 – 6000 hours. At 750 – 850°C the dominant corrosion mechanism was internal oxidation rather than carburization. Alloys containing Al were also susceptible to the formation of internal oxides and the presence of Ti inhibited the subsurface growth of Al_2O_3 particles. At these temperatures the content of Si, Nb and Y supported the growth of thin dense and protective surface scales for periods up to 6000 hours. At 950°C and above all the alloys showed carbide precipitation. The alloys most resistant to carburization were Ni-20Cr and Ni-20Cr-2Nb. Alloys containing Al were very susceptible to internal oxidation and the addition of Ti was less beneficial than at lower temperatures. Ni-Cr alloys containing Si and Ti were corrosion resistant but showed a tendency to form spalling scales and Y showed a detrimental effect to corrosion properties at higher temperatures.

Several studies have been aimed at investigating the effect of V/HTR helium on mechanical properties of candidate alloys. The investigations concerned the influence of creep, creep rupture, low- and high cycle fatigue, creep fatigue and fracture toughness. The conclusions from these tests appeared none conclusive, For example the influence corrosion form the helium environment on the mechanical properties (especially creep) of alloy 800 H is not significant up to 760℃ [1, 9] but it was concluded that further work was needed to characterize the behavior at higher temperatures and longer times.

Few of the studies were concerned with the creep rupture properties of Alloy 617. The rupture life in decarburizing V/HTR helium significantly decreased at 1000℃ compared to its rupture life in air. This decrease in rupture strength could be caused by Alloy 617 not developing a protective oxide scale, allowing significant internal oxidation and carbon loss to take place. Another study showed that the dependence on time to 1% strain and time to rupture of alloy 617 at temperatures 800 – 1000℃ is very similar in air and in HTR helium with nominal impurity levels [1]. Further studies showed a lower ductility and a different creep curve shape for Alloy 617 in helium compared with tests in air [1].

Nakamishi and Kawakami [10] performed tests on the creep properties of Hastelloy X in carburizing helium and in air at 900℃. The carburizing helium was found to slightly increase the creep strength up to the onset of the tertiary creep. The ratio of rupture stress in helium to that in air was approx. 0.9 [10]. Creep curves from this work have been reproduced in Fig. 5.

Some fatigue tests on high temperature alloys in simulated helium have been made that mostly concluded that the helium environment did not impair the fatigue properties, however further investigations under different cyclic loading scenarios are needed to confirm this (see [1] for details).

The findings from this section show that a relative large number of tests aimed at determining the behavior of alloys in V/HTR helium has been carried out However the combination of parameters, such as gas atmosphere composition, exposure time, temperature, pressure, gas flow rate, aim of the experiment (mechanical properties, corrosion) and tested material, is high and because the experiments involve long exposure times, a systematic investigation would be very demanding and time consuming. Most of the tests have been carried out at low pressure and low gas flow, and there is a need for additional tests at real reactor conditions (representative gas flow rates and pressures).

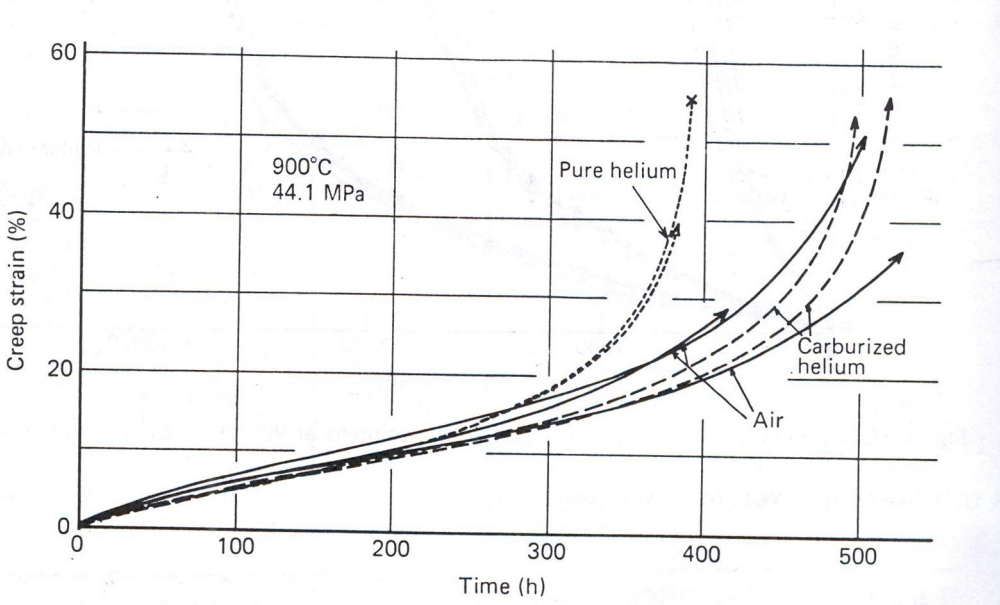

Fig. 5: Creep curves of as-machined specimens of Hastelloy X in air and helium [10]

6 Current programs for V/HTR material testing

Currently programmes dealing with corrosion issues on V/HTR materials investigation are in the USA and France [5].For example Idaho National Laboratory (INL) and Oak Ridge National Laboratory take part in projects aimed at investigating corrosion behavior of Inconel 617 and Haynes 230. The main focus of their investigations is to determine the influence of changes in the H_2O and CO concentrations on the corrosion mechanism at temperatures up to 1000℃. A computer program for prediction of corrosion mechanism has been developed [5]. The institutions are equipped with test loops for corrosion testing of coupons or specimens which are mechanically tested in a controlled helium atmosphere at the temperature up to

1000℃ with low gas flow rates and low (atmospheric) pressure. As an example see Fig. 6 which shows the scheme of the French corrosion loop [5]. Interesting aspects in the French Loop are the use of hygrometers for moisture control which can reportedly detect water concentration lower than 1 vppm, which is not common in case of hygrometers used in industry.

Finally published papers on the corrosion behavior of Inconel 617 and Haynes 230 in impure helium [13, 14] and tests concerning carburization test of W- and Re-rich alloys in simulated V/HTR helium at 1000℃ [15] have also been cited. Mention should also be made of the Czech V/HTR material research program and the new experimental device – High Temperature Helium Loop (HTHL) which has been built (fig. 7) [16] for corrosion and irradiation experiments. This facility with projected maximum parameters of 900°C temperature and 7MPa pressure in the test section with a gas flow rate of 38 kg/hours – should approach the representative reactor conditions. In the future the HTHL is planned to enable in-pile tests (after movement of the test section to the core of experimental reactor) to be performed. Currently the HTHL is in the status of the experimental operation with the projected maximum parameters not yet reached.

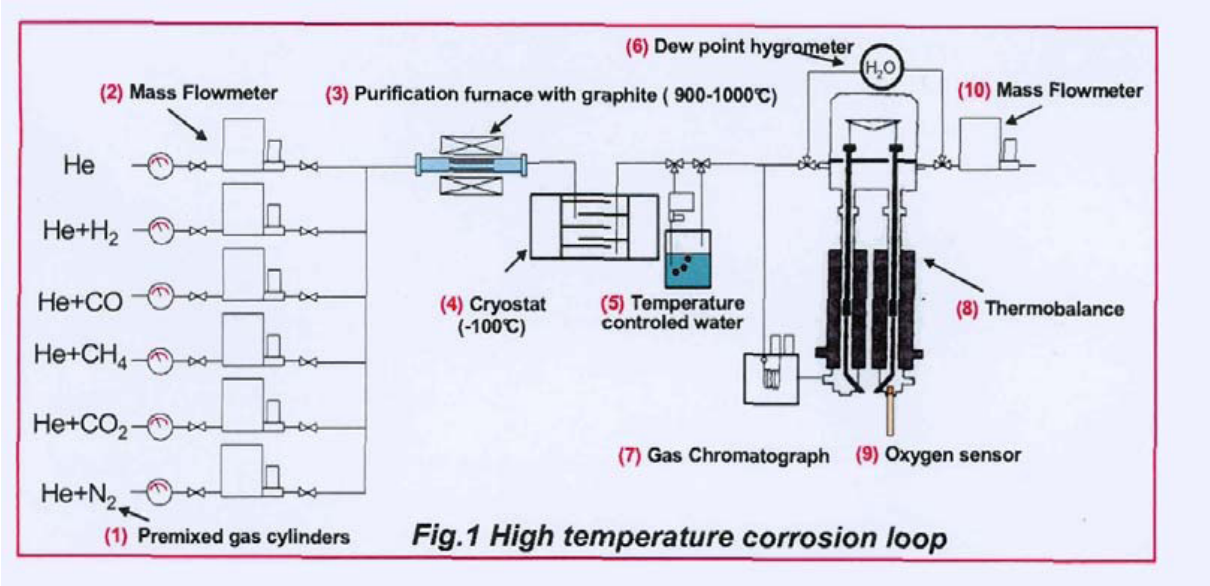

Fig. 6: Scheme of the French corrosion loop [5]

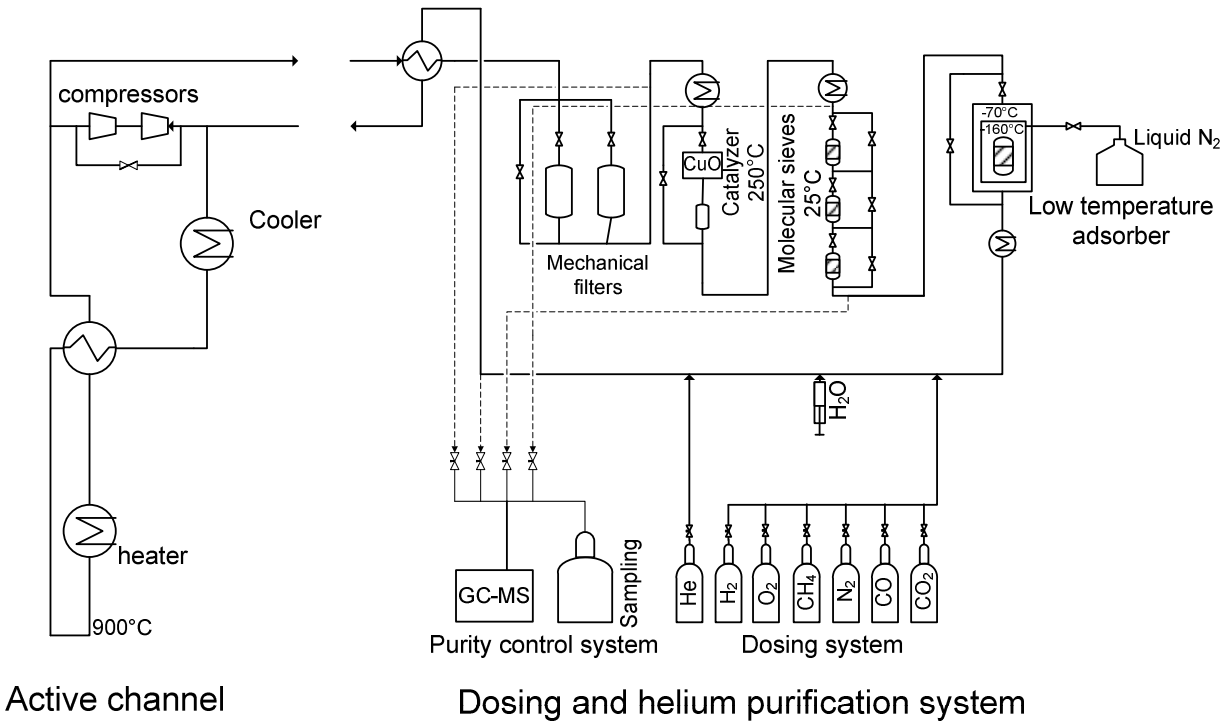

Fig. 7: The design of the High Temperature Helium Loop in Rez, Czech Republic

7 Properties of selected candidate V/HTR alloys and their degradation in impure helium

Inconel 617, Haynes 230, Alloy 800 H, Hastelloy X and XR and austenitic steels (such as 316) and ferritic steels (9Cr-1Mo) are the most investigated metallic materials within the previous and present V/HTR research programs. In the following chapters some results for these materials will be summarized.

7.1 Inconel 617 and Haynes 230

These alloys are proposed for similar usage and therefore their properties and behavior in V/HTR helium are often compared. The chemical composition of the alloys is shown in Table 5.

Table 5: Chemical composition of Inconel 617 and Haynes 230 [18]

	Ni	Cr	W	Co	Mo	Fe	Al	Mn	Ti	Si	Cu	C	B
Inconel 617	base	21.6	*	12.0	9.2	1.0	1.0	0.1	0.4	0.2	0.1	0.06	0.002
Haynes 230	base	22.0	14.7	0.2	1.3	1.3	0.4	0.5	0.1	0.4	*	0.11	0.002

Inconel 617 is proposed for piping, and heat exchangers of the V/HTR. Such components have to withstand temperatures of up to 1000°C (for the VHTR case) and stresses arising from temperature differences (e.g. heat exchanger). Due to the content of Co and Mo this alloy is strain-resistant at temperatures above 870°C. Inconel 617 is also resistant to oxidation and carburization. The material's thermal expansion behavior is also lower than that of austenitic steels. Alloy Haynes 230 is characterized by high corrosion resistance and due to the content of tungsten also high mechanical resistance.
Creep curves of In 617 measured in simulated V/HTR helium at 950°C are shown in Fig. 8. These curves have a reduced secondary creep zones. The influence of helium on creep properties was found to be minimal up to 760°C. The rupture life obtained from tests in helium at 950°C compared with corresponding tests in air are shown in Fig. 9 [1].

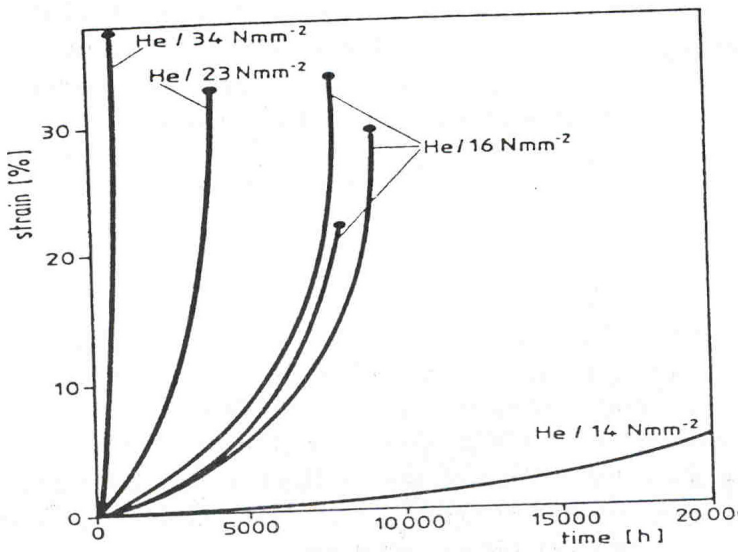

Fig. 8: Creep curves of Inconel 617 at 950°C in helium [1]

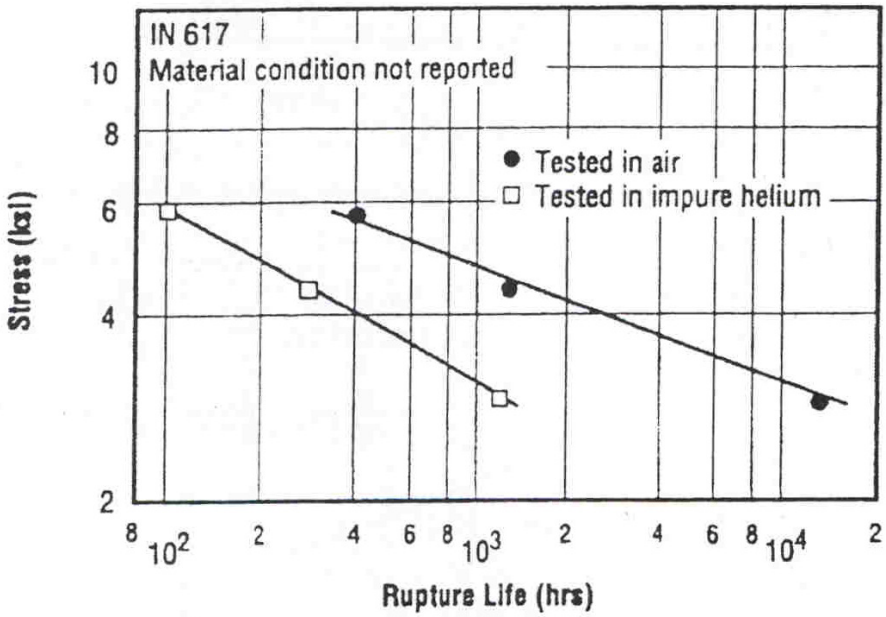

Fig. 9: Creep rupture of In 617 at 950℃ in helium compared to that in air [1]

Inconel 617 has been found to have a much lower ductility in simulated V/HTR helium compared with that in air [1]. This behavior corresponds to differences in the metallography – see Fig. 10 [1]. The time to rupture at 900℃ was found to decrease in the three different environments vacuum>air>helium – Fig. 11 [17].

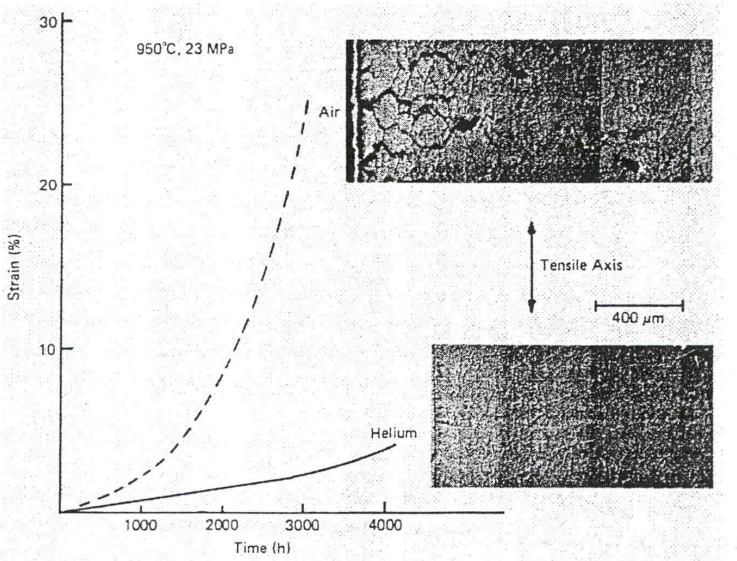

Fig. 10: Examples of creep curves and cracking behavior for Alloy 617 tested in simulated V/HTR helium and in air at 950℃ [1]

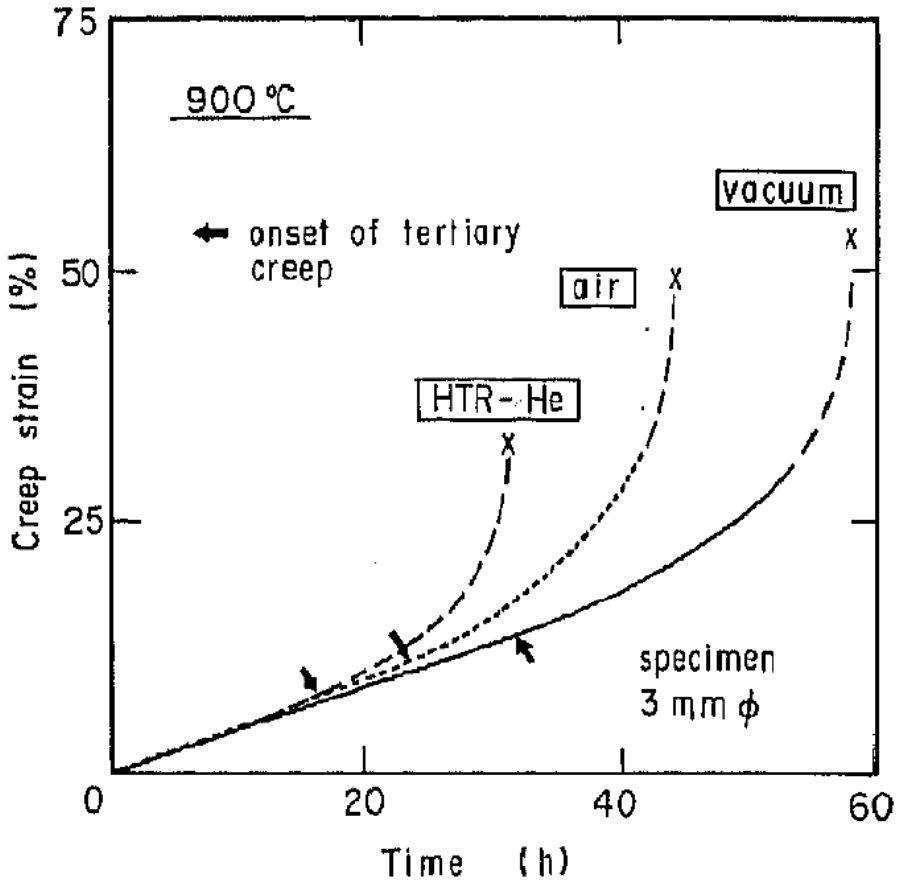

Fig. 11: Creep properties of Inconel 617 in HTR Helium, air and vacuum at 900℃ [17]

Fatigue tests (at 4.10^{-3} s^{-1} loading rate) have also been carried out in impure helium (H_2:CO:CH_4:H_2O with a ratio of 30:2:3:0.2) at temperatures up to 870℃. Several tests investigating the corrosion behavior of Inconel 617 in impure helium have also been published. As an example tests were carried out in four different helium environments [1] at temperatures of 649 – 1000℃ for up to 10000 hours. The results showed that carburization occurred in environments with low and high oxygen partial pressure. The rate of carburization was higher in the environment with the low oxygen partial pressure. The test with high oxygen partial pressure showed that the outer corrosion scale contained oxides of Mn and Cr, and for low oxygen partial pressure the outer corrosion scale also contained carbides. Other experiments suggested that corrosion in impure helium at temperatures under 475℃ is minimal, largely because of a protective thin chromium oxide scale. The protective scale is developed at temperatures up to 900℃,and also internal oxidation of the aluminum takes place. Above 900℃ fast carburization or decarburization takes place. The critical temperature (depending on the alloy and the gaseous atmosphere composition) was estimated to be between 900℃ to 975℃ [1, 19]. At 900 to 970℃ carburization takes place and above 990℃ decarburization occurs. For temperatures, at which carburization take place, the carburized layer is observed at the surface with Cr and Mo carbides precipitated in the grain boundaries. At temperatures, at which decarburization take place, these carbides disappear and carbide depleted zone near the surface of approximately 2000 µm thickness after 500 hours at 1040℃ are observed. After exposure in the air at the same temperatures a thick compact protective oxide scale is observed, while after exposure in simulated V/HTR helium the scale becomes porous.

Investigations [20] on the effect of relatively small changes of H_2O levels on the corrosion of Inconel 617 have been carried out. The moisture level changed mainly at the startup period of the experiment (after approx. 100 hours). The results are summarized in Fig. 12 and are grouped according to the water levels observed during the startup period:

1. 0.5 – 0.8 µBar (1 µBar = 0.1 Pa)
2. 0.3 – 0.5 µBar
3. < 0.3 µBar
4. << 0.3 µBar

With H_2O levels of 0.5 – 0.8 µbar, Cr-Ti oxide scale with complete surface coverage were formed. With lower moisture level (0.3 – 0.5 µBar) the carburization rate was doubled and the oxide scale was thinner and less

complete. With < 0.3 µBar H_2O, a threefold increase in carburization rate occurred, but when the water level dropped to under 0.1 µBar during a startup period, a completely protective thin alumina scale was formed.

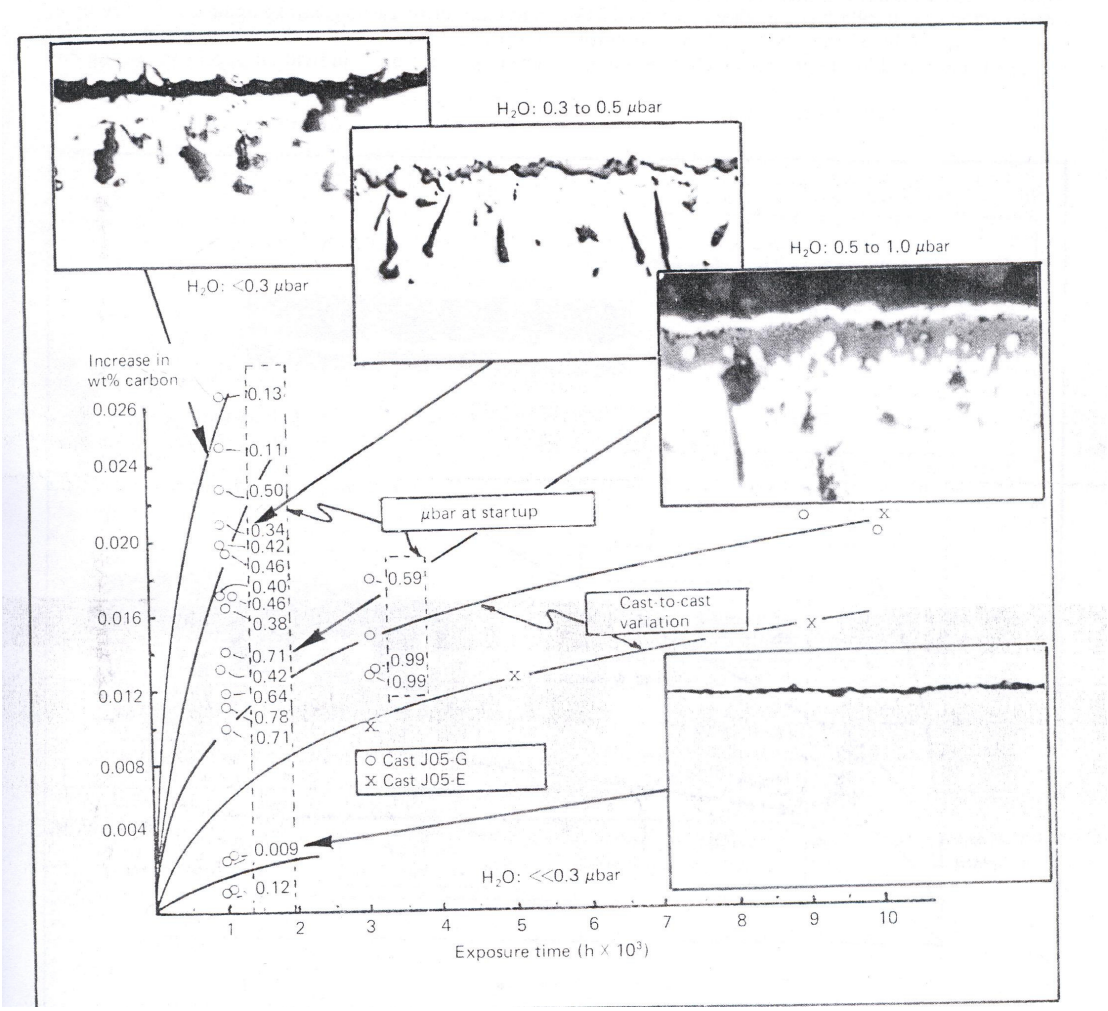

Fig. 12: The effect of H_2O level at startup on scale formation and the carburization of Inconel 617 [20]

Alloys 617 and Haynes 230 (and other alloys) were tested within the frame of French V/HTR program in 2 loops (AREVA, CEA) [21]. The critical temperatures T_a for both alloys were found to be similar depending on gas atmosphere composition, especially CO partial pressure. At temperatures below T_a Inconel 617 formed Cr_2O_3 scale with Ti content, while Haynes 230 formed an outer scale composed of Cr and Mn oxides mixture. Both alloys showed internal oxidation of the Al, but Hayness 230 was less intensive. Above T_a oxides were reduced according to the reaction: $Cr_2O_3 + 3C(s) = 3CO + 2Cr$ in all atmosphere compositions.
The Corrosion of Inconel 617 and Haynes 230 has been investigated in different gas atmospheres as shown in the Table 6 [18]. Mixtures from He-1 to He-8 were used to test the surface reactivity, He-10 – He-12 were used for corrosion tests. The tests on surface reactivity showed that the critical temperature T_a depends on the gas atmosphere composition and was found to be in the range 895 to 969°C (1168 K 1242 K ±5 K) for atmosphere He-1 – He-5. The corrosion tests were carried out for testing periods lasting up to 5000 hours in oxidizing atmosphere (He-9) and decarburizing atmosphere, and for reducing and carburizing atmosphere (He-10 – He-12).

After exposure in He-9 an oxide scale rich in chromium oxides was formed. Further slight increases of carbon content, internal aluminum oxidation, slight increases of carbon content in the alloy and occurrence of carbide depleted zone near the surface were observed. For Haynes 230 the internal aluminum oxidation was observed in the grain boundaries, while for Inconel 617 it was seen in the grains and between them. The oxide scale on the surface was found to prevent internal carburization of the alloy during exposure. The cross-section of the surface of Haynes 230 and Inconel 617 after 813 hours exposure in He-9 can be seen in Fig. 13 [18].

Table 6: Helium environments for testing of Inconel 617 and Haynes 230 within the French program [18]

	H_2 (Pa)	H_2O (Pa)	CO (Pa)	CH_4 (Pa)	T_A (K)
He-1	20.5+-0.4	0.50+-0.24	0.61+-0.01	2.00+-0.04	1168+-5
He-2	49.6+-0.9	0.20+-0.09	1.74+-0.04	31.0+-0.6	1198+-5
He-3	19.8+-0.4	0.08+-0.04	2.24+-0.04	2.11+-0.04	1211+-5
He-4	19.3+-0.4	0.16+-0.08	4.90+-0.10	1.90+-0.04	1236+-5
He-5	19.5+-0.4	0.40+-0.19	4.90+-0.10	2.10+-0.04	1234+-5
He-6	18.8+-0.4	0.15+-0.07	5.03+-0.10	2.02+-0.04	1236+-5
He-7	19.6+-0.4	0.05+-0.02	5.25+-0.10	2.11+-0.04	1242+-5
He-8	18.9+-0.4	0.06+-0.03	5.44+-0.10		1247+-5
He-9	20	0.05-1	5	2	
He-10	20	0.05-1.2	0.5		
He-11	20	0.05	0.5	2	
He-12	50	0.05	1.5	30	

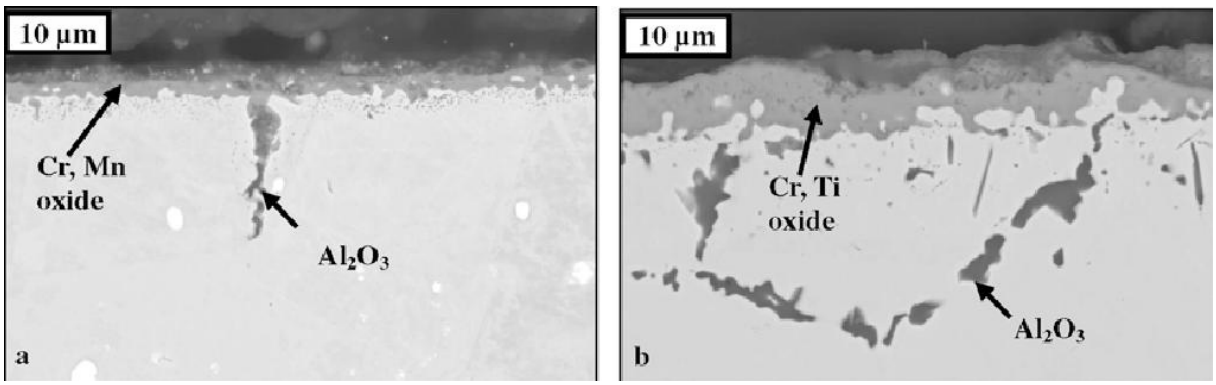

Fig. 13: SEM images – Cross section of the surface of Alloy 230 (a) and Alloy 617 (b) after 813 hours at 1223 K in He-9 [18].

After exposure in atmosphere He-10 (reducing and decarburizing) the absence of the chromia scale on the surface, of internal aluminum oxidation and a decrease in carbon content and dissolution of the primary carbides plus a development of a deep carbide-depleted zone was observed. Because of the lower partial pressure of CO, the Cr_2O_3 from surface scale was reduced by carbon from the alloy (eq. 35) and at the same time the water reacts with the chromium, which causes the partial regeneration of the Cr_2O_3 surface scale (eq. 35) [18]:

$$H_2O+Cr = Cr_2O3 + H_2 \quad (34)$$

$$Cr_2O_3(s) + 3C(s) \rightarrow 3CO(g) + 2Cr(s) \quad (35)$$

The residual Cr_2O_3 scale on the surface is no longer protective and after 500 hours exposure the carbon content in Inconel 617 halved compared with that of the state before exposure. Dissolution of secondary carbides from the alloy is also supposed to have a negative effect on the mechanical properties of the alloy [18]. The Alloy 230 surface after exposure at 1223 K in He-10 is showed in Fig. 14 [18].

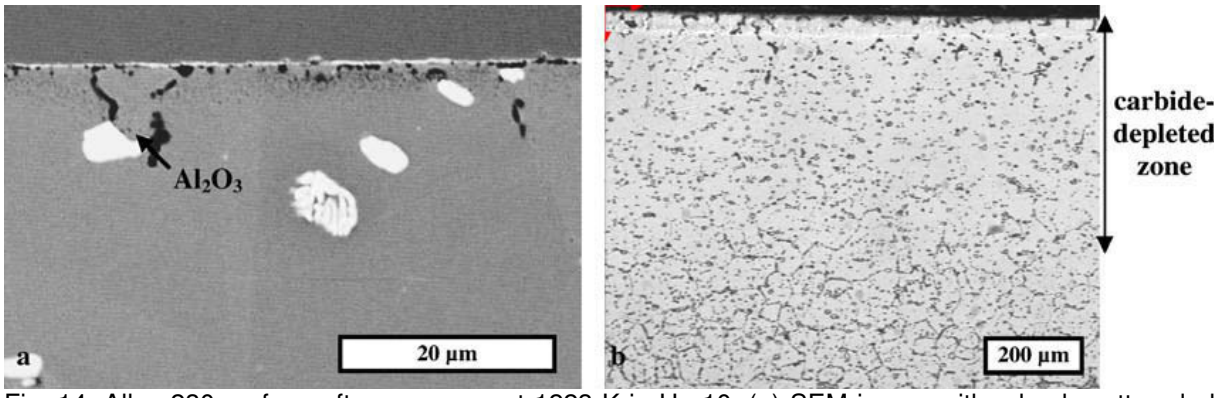

Fig. 14: Alloy 230 surface after exposure at 1223 K in He-10: (a) SEM image with a backscattered electron contrast at 20 kV after 240 h, and (b) micrograph after 1000 h [18]

Exposure in He-11 and He-12 atmospheres (reducing and carburizing [18]) resulted in an absence of chromium oxide scale on the surface, in internal oxidation of Al, the growth of carbon content in the alloy, surface and internal precipitation of carbides. Precipitation of rough carbides is supposed to result in embrittlement of the alloy at lower temperatures with an Increase of carbon content of 0.4 % causing total embrittlement of the alloy.

The kinetics of the reactions (34, 35) and also the decomposition of methane: CH_4 (g) = C(s) + $2H_2$(g) influences the transport of carbon and oxygen from/to the alloy. The increased partial pressure of methane in He-11 (2 Pa) compared to He-10 (0 Pa) changes the corrosion behavior from decarburising to carburising. Further increases of CH_4 partial pressure in He-12 results in the carburization becoming more rapid. SEM images of the surface of Inconel 617 and Haynes 230 after exposure of 240 hours in He-12 can be seen in Fig. 15. After testing the carbon content in the alloy is compared to that of the as-received state in Table 7.

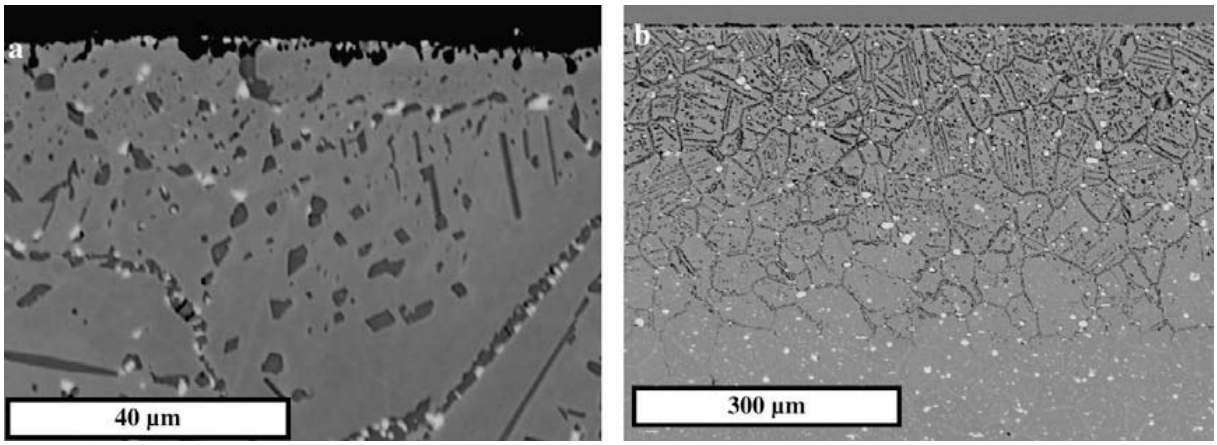

Fig. 15: SEM images with backscattered electron contrast at 20 kV of the surface of Alloy 617 (a) and Alloy 230 (b) after 240 h at 1223 K in He-12 [18].

Table 7: Carbon content (in % by weigh) in the alloys after 500 hours exposure at 1223 K compared to those in as-received state [18]

Alloy	As-received state	He-9	He-10	He-11	He-12
Haynes 230	0.101±0.05	0.075±0.03	0.075±0.03	0.170±0.08	1.78±0.90
Inconel 617	0.067±0.03	0.097±0.02	0.035±0.02		0.56±0.20

Summary for Inconel 617 and Haynes 230

Both alloys have similar mechanical properties however because of the W content the creep properties of Haynes 230 are better. The alloys are relatively resistant to corrosion in V/HTR helium up to 900 – 970°C. In both alloys internal oxidation of aluminum occurs, but for the case of Haynes 230 less intensively. Results form tests aimed at investigating the effects of corrosion on the mechanical properties of alloy 617 in V/HTR helium are not single-valued. The helium coolant atmosphere seems to have none or little negative impact on creep and fatigue properties, but further experiments are needed to confirm this.

7.2 Hastelloy X and XR

Hastelloy X and Hastelloy XR are high temperature resistant alloys proposed for piping, internals or the heat exchanger of the V/HTR. They are considered to be oxidation resistant up to 1200°C and have good mechanical properties up to 870°C. Hastelloy XR is a modified version of Hastelloy X developed in Japan.

Influence of corrosion on creep properties of Hastelloy X in V/HTR helium have been investigated in earlier Japanese and American HTR programs [10]. Tests were carried out in pure helium, helium containing impurities and in air. The results from experiments were found to be affected by the surface treatment of the samples. In carburizing helium the carburization led to an acceleration of crack growth and a shorter time-to rupture. The shape of the creep curve was slightly changed depending on the environment (see Fig. 5) and the ratio of rupture stress in helium to that in air was approx. 0.9 [10] at 900°C.

Fatigue properties of Hastelloy X in simulated V/HTR helium were also tested and compared with fatigue properties of alloys KSN and SSS113MA [22]. Fatigue properties of KSN and SSS113MA were found to be worse than Hastelloy X and XR, and the differences between Hastelloy X and XR were insignificant. Due to the presence of corrosion scale in the low-cycle fatigue tests of Hastelloy X at 1000°C a shortening of the time to rupture was observed.

The corrosion behavior of Hastelloy X was investigated at 900°C in two helium atmospheres with different compositions. Hastelloy X was found to be susceptible to intergranular corrosion and internal oxidation whereas Hastelloy XR was found to be more resistant and developed a compact surface oxide scale up to temperatures of 1000°C. The increased resistance of Hastelloy XR is probably results from the composition of the oxide scale where the outer layer consisted of $MnCr_2O_4$ and the inner layer of Cr_2O_3. Hastelloy X was also tested in the AIDA loop at 5000 kPa (with other alloys) [8] at temperatures of 550 – 870°C and the results of the tests were compared with those carried out in a 2 bar experimental circuit. The Hastelloy X showed better resistance against oxidation than Alloy 800 H and Inconel 617. The kinetics of the oxidation were higher at higher pressure and the corrosion damage after 2500 hours at 5000 kPa was higher than after 10 000 hours at 2 kPa at the same temperature.

7.3 Alloy 800H

Alloy 800 H consists of Fe-Cr-Ni with a minimum carbon content of 0.05 % by weigh [1]. Alloy 800 H must be solution annealed at 1093°C, has a stable austenitic structure and is proposed for use at temperatures higher than 590°C. Because of the to relatively high carbon content and the solution annealing at high temperature the alloy consists of large grains, which provide better creep properties. This alloy has been approved under ASME Code for nuclear service up to 760°C[1].

Corrosion tests on Alloy 800 H and other alloys within DRAGON project were carried out in the 1970's [23]. The tests were performed in simulated V/HTR helium and in air, Corrosion behavior and mechanical property tests were performed. Several types of Alloy 800 H with different compositions were investigated. The tests at 650 – 800°C lasted up to 15 000 hours. Following the tests in helium intergranular corrosion of Alloy 800H was observed also Ti and Al internal oxidation. For specimens not exposed to strain during testing, no chromium oxides were observed in the samples, but for specimens, exposed to strain, intergranular Cr and Mn oxides were found probably due to microcrack being formed during the test. Carburization was observed only on one type of Alloy 800H (800H1), which was annealed in a vacuum before exposure. When the alloy was not annealed before the test, only a thin oxide scale was observed after exposure and sub-surface carbide precipitation was not seen. (Fig.16). It was also noted that the ductility of Alloy 617 at 650°C in helium was lower than that observed in air.

Fig. 16: Oxidation of Alloy 800H1 in V/HTR helium and in air at 750℃: a) Specimen annealed in vacuum before exposure in helium (10 000 hours) without stress performed thick oxide scale and precipitation of carbides, b) specimen not annealed before exposure (10 000 hours, stress), c) specimen annealed in vacuum, tested in air (12 000 hours, strain) [23]

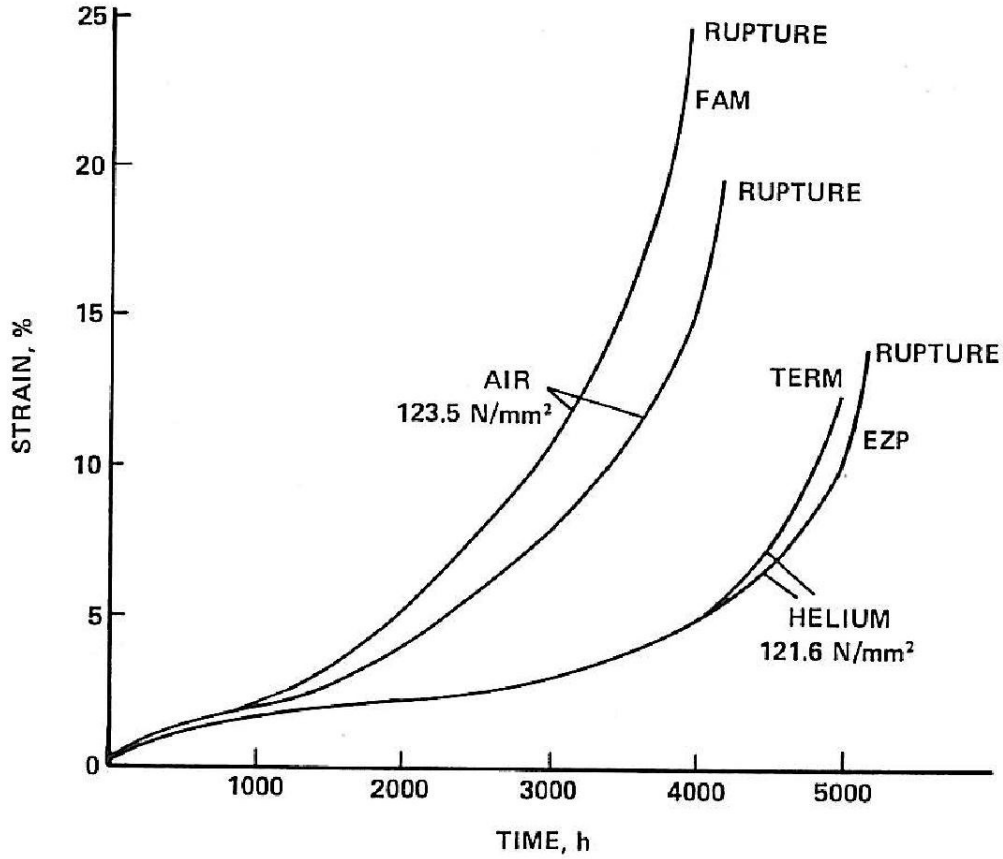

Fig. 17: Creep curves of Alloy 800H at 650°C in air and in helium [1]

Creep properties of Alloy 800H were investigated in air and in helium at 650°C (see Fig. 17). Tensile properties were obtained after 5000 hours exposure in V/HTR helium and in air at temperatures up to 1000°C. The results show that when the material is tested in air its tensile properties are considerably decreased compared with the properties of material before exposure whereas exposure in helium produces almost no changes. Compared with Hastelloy X the tensile properties of Alloy 800H were found to decrease with increasing temperatures between 650-800°C because of corrosion and the tensile strength of Alloy 800H was found to be strongly dependent on the environment. For Hastelloy X the influence of corrosion on tensile properties is relatively small.

Summary for Alloy 800H

Alloy 800 H showed good corrosion resistance at temperatures up to 650°C. Above this temperature oxidation and sub-surface carburization takes place. The creep properties were found to be better in helium than in air at 650°C. Mechanical properties are strongly dependent on the environment and Alloy 800 H would be more acceptable for lower temperatures than Hastelloy X or Alloys 617 and 230.

8 Codes and Standards

Reactor operation experience shows corrosion issues and stress corrosion cracking can lead to significant outages of plant. Although Design Codes do not normally include design procedures on corrosion and environmental issues, the designer nevertheless has to take these into account when assessing the conservative of the design. Often there is a need to include a corrosion allowance (such as in the case of steam generator tube thicknesses) to ensure that sufficient material is provided to compensate for thinning during the specified service life of the component (see RCC-MRx section RB 3191). Some standard test procedures are available to test the sensitivity of material to corrosion (as an acceptance test) and R & D programmes for design verification and qualification of material often include corrosion activities but in general the subject of corrosion when applied to the design of nuclear plant is not covered in a systematic manner.

Under normal chemistry conditions of reactors, corrosion cracking may occur after long incubation periods for specific weldment structures however, in general, corrosion cracking occurs mainly during events outside normal operating conditions. The combination of the chemistry of the system under faulted conditions, unacceptable microstructural conditions of the material and stress and temperature conditions may all contribute to corrosion cracking.

Within the UK the requirement is to select materials that are compatible with chemistry conditions during manufacture, storage, transport, assembly and service. In such cases advice from corrosion specialists should be sought. UK standards also provide for inter-crystalline corrosion testing of austenitic steels.

Current Codes & Standards contain little information for the designer on the effect of such fluids on material properties and/or component performance and often do not include property information (physical and thermal) for the individual fluids themselves. Such information added to existing appendices or included as separate annexes will help to support and maintain the consistency of design calculations and assessments which are often the first step in the component design development. A recommended set of physical and thermal properties for helium for example will help to standardise the input information for design investigations.

The use of helium gas as the coolant is expected to involve the introduction of alternative materials (such as Alloy 800H, Alloy 617, and Alloy 230, etc.) having different applicable temperature limits. These materials will operate satisfactorily within a defined temperature range: within an upper limit defined either by the level of stress with time (creep rupture) together with applicable number of cycles (fatigue) if significant or by a material corrosion limit; and above a lower limit given either by the system operating parameters or by a change in behavior of the material (brittle transition). As a guide to designers (for material choice and selection) it is suggested that for each alternative material the temperature (and other) limits of applicability are defined (possibly in the form of a table in a material Annex) with recommendations giving known upper and lower values and guidance on how to identify the limits for the particular material being investigated.

For helium cooling metal components exposed to coolant gas containing small levels of impurities (H_2, H_2O, CO, CO_2) at low partial pressures can experience degradation of properties (carburization and decarburization, oxidation) as discussed in this report. The effect of such corrosion on long term and short term strength and behavior needs to be included in any Codes & Standards defining the material behaviour. This could be in the form of a corrosion factor which could be applied to the material design curves for determining allowable stresses. Such a corrosion factor could be applied to the Sr and St values to determine design allowable limits.

9 Conclusion

Test parameters and proven properties associated with the resistance of selected materials in V/HTR helium are summarized in Table. 8.

Most of tests on the High-Temperature alloys were carried out within the previous HTR projects. Tests in impure helium were mostly carried out at parameters near the chemical equilibrium conditions – i.e. low total gas pressure and low flow rate. Under this condition the corrosion behavior of the alloys could be different compared to that at high pressure and high gas flow rate (at the same temperature and gas atmosphere composition). Therefore further tests under more representative reactor conditions are needed.

Within the previous experimental programs corrosion tests in simulated V/HTR helium coolant and tests on the influence of the corrosion on mechanical properties have been carried out. High temperature alloys experienced carburization, oxidation and/or decarburization depending on the gas atmosphere composition (to be specific carbon activity and oxygen partial pressure in gas atmosphere), exposure temperature and the alloy composition. The specific influence of helium atmospheres (in contrast to other gaseous atmospheres or vacuum) on the mechanical properties of alloys was investigated in some of the tests, but the results are not of a low order and the investigations on the effect of V/HTR helium on alloy behavior selective and not systematic, The recent French Programme has adopted a more systematic approach to the testing of Hynes 230 and Alloy 617however in general such testing materials in different gas atmospheres at different temperatures and pressures for thousands hours is time-consuming and costly.

Table 8: Comparison of properties of selected V/HTR alloys and test conditions

Alloy	Inconel 617	Haynes 230	Hastelloy X/XR	800H
Duration of mechanical tests (hours)	Up to 20 000	Up to 10 000	Up to 3 000	Up to 5 000
Duration of corrosion tests (hours)	Up to 10 000	Up to 5 000	Up to 10000	Up to 15 000
Creep resistance	Up to ca. 950°C	Up to ca. 950°C	Up to. 870°C	Up to 760°C
Oxidation stability	under T_a internal oxidation of Al	under T_a internal oxidation of Al but less intensive than in case of Inconel 617	Stable at 750°-870°C	Good resistance up to ca. 650°-700°C
Behavior in simulated V/HTR helium at 800-1000°C	Up to 900°C form Cr_2O_3 scale with content of Ti oxides, partial Al oxidation, at 900°-970°C carburization, above 990°C k decarburization takes place	Up to 900°C forms Cr_2O_3 and Mn oxides	Susceptible to carburization and oxidation, intergranular attack in case of alloy X; alloy XR more resistant due to compact oxide scale	Max. 800°C – development of Cr_2O_3 + internal Al a Ti oxidation, intergranular attack
T_A	Depends on atmosphere composition; estimated at 1240 K (970°C)	Depends on atmosphere composition; estimated at 1240 K (970°C)		
Behavior in "oxidizing He" at 950°C	Development of Cr_2O_3, internal Al oxidation (more intensive than in case of Alloy 230)	Development of Cr_2O_3, internal Al oxidation	Development of Cr_2O_3 (in case of Alloy XR development of double layer $MnCr_2O_4$ and Cr_2O_3)	
Behavior in "reducing He" at 950°C	Outer Cr_2O_3 scale is not developed, internal Al oxidation, increase content of C in alloy	Outer Cr_2O_3 scale is not developed, internal Al oxidation, increase content of C in alloy		

An important parameter is the so called critical temperature T_a. Above this temperature protective scale on the alloy surface cannot be formed and total carburization or decarburization can take place. This limit also probably also has negative impact on the mechanical properties. Therefore the value of T_a is important for determining acceptable operating conditions for the V/HTR components and for selecting the material. The

value of T_a ranges from between approximately 900 – 1000°C for high temperature alloys and depends on the alloy and the gas atmosphere composition. A more systematic evaluation of T_a has been carried out but only for Alloy 617 and Haynes 230.

Suggestions have been made on the need for including the influence of Corrosion in Design Codes. Such a provision could include the collant gas physical properties used in design calculations plus a corrosion check list or similar that designers could use when considering material selection and performing their design calculations. Within Codes and Standfards such as RCC-MRx a corrosion factor could be given for different alloys (in much the same way as weld factor) applied to the material design curves for determining allowable stresses. Such a corrosion factor could be applied to the Sr and St values to determine design allowable limits.

A future experimental program on corrosion for the V/HTR alloys could be (among others) aimed at::

- The testing of high temperature alloys in atmospheres with different compositions compared to those used in previous programs (corrosion tests and tests of changes of mechanical properties) and at different temperatures to provide a more complete picture of the behavior.
- The testing of new or improved alloys, including the resistance of welded joints, etc. to determine mechanical properties during and after exposure
- The determination of T_a for high temperature alloys and its dependence on other conditions (e.g. gas atmosphere composition, alloy composition/modification, gas flow rate, system pressure, etc.)
- Tests under more representative reactor conditions (i.e. high pressure and high flow rate) and comparison of such results with those obtained from tests carried out at low pressure and low flow rates.

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11 List of acronyms

ERANS	Engineering Research Association of Nuclear Steelmaking, Japan
GE	General Electric Company
GFR	Gas Fast Reactor
HTR	High Temperature reactor
INL	Idaho National Laboratory
JAERI	Japanese Atomic Energy Research Institute
ORNL	Oak Ridge National Laboratory
PNP	Prototype Nuclear Process
VHTR	Very High Temperature Reactor

12 Appendix - selected investigations related to previous V/HTR programs

Investigations on Hastalloy X and XR

Alloy	Test temperature	Exposure time	Overall exposure pressure	Partial pressures - mean values							Tested mechanical properties	Corrosion tests	Comments	Main results	References
				H_2	CO	CO_2	CH_4	H_2O	O_2	N_2					
	℃	hr.	Mpa	Pa	Pa	Pa	Pa	Pa	Pa	Pa					
Three types of modified Hastelloy X	heat cycles from room temperature to 1000℃, heating/cooling rate = 3℃/40℃	300 hr per each cycle	0.1	20.5	10.5	0.25	0.55	0.1	-	-	-	Oxidation kinetics and spallation of oxide film		Mn in Hastelloy X improves the adherence and protective function of oxide film formed in simulated HTR coolant The spallation itself did not affect the time dependence of the oxidation kinetics during thermal cycling	26
Hastelloy X	1000	up to 5000	0.1	21.8	11.3	0.196	0.61	1.9	0.07	0.21	Tensile properties	Microstructure	results were compared to those obtained by testing in air	small effect of exposure on strength and ductility in helium and in air	27
Hastelloy X	760, 871	16000 - 35000 (highest value for test in air)	0.13	-	-	-	-	250	-	-	Long therm creep behavior	-	results in "wet" and "dry" helium were compared to those in air	rupture life in wet helium is lower than in the air, in the helium with reduced concentration of water rupture life is much bigger, minimum creep rates are slightly decreased compared to air test, lowest rupture ductility has been observed for dry helium test An extensive thermal aging effect observed, small recrystalized grains in the matrix, spallation and oxide scale. These factors may contribute to reduction of long term creep strength at 871℃ oxidation was observed in helium with both water concentrations.	28
				-	-	-	-	up - 1	-	-	Long term creep behavior	-			

Hastelloy X	900	up to 3000		7.5-75	7.5-45	-	-	<0.03	-	-	Creep properties		Resurts were compared with those carried out in air environment	Creep behavior depends on surface finish of the specimen. In air the creep strength of as-machined specimen is higher than that of electrolytically polished specimen, because severe oxidation attack occurs on the surface of ellectrolically polished specimen due to poor protective oxide film	29
				7.5-75	45-90	<0.3	<0.6	<0.015	-	-				In helium the creep strength of electrolytically polished specimens is higher due to heavy carburization	
				<0.15	<0.6	<0.3	<0.6	<0.015	-	-				The ratio of rupture stress in helium environments to that in air is 0.9	
Hastelloy X	760, 871		0.13	20	4	1	2	250	-	-	High cycle fatigue		results were compared to those obtained by testing in air	More oxidation resistance compared with Alloy 800H. Severe oxidation (e.g. During test in air) tendency to form cracks in the thick oxide scale and small surface cracks in the chromium depleted and recrystalized region below the scale would case a loss of fatigue life.	31
Hastelloy X	1000	up to 5000	0.1	21.8	11.3	0.196	0.61	0.19	0.07	0.21	Low cycle fatigue, tensile properties	Microstructure, metallography	Tensile tests carried out at RT to 1000°C, results compared to those obtained in air	small degradation in tensile properties by exposure both to helium and air, low fatigue life reduced by thy formation of surface corroded scale	23

Hastelloy XR	800, 900, 1000	up to 10000	0.1	20-21	10 - 11	0.2-0.3	0.5-0.6	0.08-0.12	-	-	Creep rupture	metallography, carbon content		Hastelloy XR improved corrosion resistance during creep deformation in helium compared to Hastelloy X, Insignificant difference between creep-rupture results obtained in helium and in air	35
Hastelloy X	900		0.05	10	10	0.1	0.1	0.1	-	<0.01	Creep properties			Creep behavior is sensitive to surface of the specimen. The crack growth rate was enhanced by the lack of oxide film on the crack surface in helium. The ratio of rupture stress in helium to that in air is 0,9	10
				10	50	<0.1	<0.1	<0.1	-	<0.01					
				<0.1	<0.1	<0.1	<0.01	<0.1	-	<0.01					
Hastelloy X Hestelloy XR	900		0.1	20 - 21	10 - 11	0.2-0.3	0.5-0.6	0.8-1.2	-	-	Low cycle fatigue			Appreciable carburization along fatigue crack, No significant differences between Hastelloy X and XR	22
Hastelloy X J02-G	700 - 900	up to 10000		50	4	-	5	0.03	-	0.5		Corrosion, metallography, carbon uptake,	CIIR tests	Very good carburization resistance proved, slow parabolic increases in carbon level occurred	20
Hastelloy X J02-J				45 - 50	1 - 1.5	-		0.05 - 0.1	-	0.3 - 0.7			Reference PNP tests	Defects free Cr2O2 formed, resistance to spalling proved	
Hastelloy X (two heats)	650, 800, 900, 1000	3000 or more		50	2 - 4	-	3 - 5	0.1 - 0.2			Creep		CIIRC loop	Carburization has been identified as the primary corrosion phenomenon, with respect to degrading mechanical properties at temperatures above 800℃. No carburization observed at 650℃. Carburization and bulk carbon content increases dramatically at 900℃ and higher	36

	800, 900			50	5	-	5	<0.1			Tensile (unstressed), impact	Surface and microstructural changes, X-ray	GA (once - through device)	Enhanced carbide precipitation on the grain boundary , in matrix and twin boundary found	
Hastelloy X	750, 870	Up to 10000	5	150	45	-	5	5	-	-		Corrosion kinetic, microstructure , metallography	AIDA loop	Better resistance to oxidation than Inconel - 617 and Alloy 800 H, Carburization at higher temperatures occured,	8
	750, 870		0.2										2-bar, once through device	Large differences in oxidation kinetics under 2 bar and 50 bar observed	
Hastelloy XR (XR-54, XR-11)	900		0.1	30	10	0.1	1.5	0.3	-	-	Creep rupture		Testing of boron addition on creep rupture	Creep rupture properties were largely improved by addition of B, Formation of M23C6 due to B addition may be responsible for decrease of creep rate in XR-II, all tested specimens carburized	38

Investigations on Incolloy 800 H

Alloy	Test temperature	Exposure time	Overall pressure	Partial pressures - mean values							Tested mechanical properties	Corrosion tests	Comments	Main results	References
				H2	CO	CO2	CH_4	H_2O	O_2	N_2					
	℃	hr.	Mpa	Pa	Pa	Pa	Pa	Pa	Pa	Pa					
Alloy 800 H	1000	up to 5000	0.1	21.8	11.3	0.196	0.61	1.9	0.07	0.21	Tensile properties	Microstructure	results were compared to those obtained by testing in air	exposure to air was found to reduce strength and ductility remarkably compared to exposure in helium	27
Incolloy 800 H	649., 860	16000 - 35000 (test in air)	0.13	-	-	-	-	250	-	-	Long term creep behavior	-	results in "wet" and "dry" helium were compared to those in air	creep properties in wet and dry helium environment are not significantly different from those in air at 649℃. At 760℃ slight decrease in the rupture life in the wet helium appeared. Dry helium increases the rupture life compared to the air test. Minimum creep rates are slightly lowered in the dry helium. Oxidation was observed in helium with both water concentrations.	28
				-	-	-	-	up - 1	-	-	Long term creep behavior	-			
Incolloy 800 H	538, 649		0.13	20	4	1	2	250	-	-	High cycle fatigue	-	results were compared to those obtained by testing in air	Fatigue strength depends on thermal aging before the test. Thermal aging for 1500 - 2000 hrs. Lead to significant loss of strength. Longer aging restores the most of the strength loses. Tests in helium may yield the less fatigue strength than those in air. Rapid spallation of oxide scales and rapid penetration of fatigue crack along chromium depleted grain boundaries	31

Incolloy 800 H	650 - 800	up to 10 000	0.18	5 - 10	2.5 - 5	-	0.3 - 0.8	0.05 - 3	-	-	Creep tests	Microstructure. metallography. Corrosion scales depth (surface. subsurface). mechanical stability of oxide scale	Creep tests	Thin oxide layer on surface. intergranular oxidation of Al and Ti showed. Creep rupture life in helium in most cases as good as to that in air. Rupture ductility after testing at 650℃ for 5000 h. in helium compared to that after testing in air	34
Incoloy 800 Incoloy 800H	1000	up to 5000	0.1	21.8	11.3	0.196	0.61	0.19	0.07	0.21	Low cycle fatigue. tensile properties	Microstructure. metallography	Tensile tests carried out at RT to 1000℃. results compared to those obtained in air	Low fatigue life reduced by thy formation of surface corroded scale. Exposure to air reduces tensile properties remarkably. while only little effect of HTR helium to tensile properties	23
Alloy 800 H H01M1 Alloy 800 H H0NK	700 - 900	up to 10000		50 45 - 50	4 1 - 1.5	- -	5	0.03 0.05 - 0.1	- -	0.5 0.3 - 0.7		Corrosion. metalography. carbon uptake.	CIIR tests Reference PNP tests	Good carburization resistance proved. Slow parabolic increases in carbon level. subjected to severe spalling in cast containing 0.5% silicon (H01NK)	20
Alloy 800H	650., 750, 870 650, 750, 870	Up to 10000	5 0.2	150	45	-	5	5	-	-		Corrosion kinetics., microstructure. metallography	AIDA loop 2-bar. once through device	Excellent behavior at 650℃. carburization at higher temperatures. worse oxidation resistance than Hastelloy X Large differences in oxidation kinetics under 2 bar and 50 bar observed	8
Alloy 800 (different heats)	650 - 800	up to 10000	0.18	10 5 - 10	10 2.5-5	-	-	2 - 4 0.05 - 0.3	- <0.02	- 0.2-0.8	creep studies	corrosion studies	CIIR Rig	Some heats performed to have greater creep strength in helium than in air. others have the strength in helium reduced by 20%. Oxidation of reactive constituent takes place forming surface scale and sub-surface oxides. Carburization occurs at 750 - 800℃ and can penetrate to depth up to 800 µm after 5000 hours	42

Investigations on Inconel 617

Alloy	Test temperature	Exposure time	Overall pressure	Partial pressures - mean values							Tested mechanical properties	Corrosion tests	Comments	Main results	References
				H2	CO	CO2	CH4	H2O	O2	N2					
	℃	hr.	Mpa	Pa	Pa	Pa	Pa	Pa	Pa	Pa					
Inconel 617 J05-E	700 - 900	up to 10000		50	4	-	5	0,03	-	0,5		Corrosion, metallography, carbon uptake,	CIIR tests	Good carburization resistance proved, slow parabolic increases in carbon level, formation of Cr2O3, resistance of spalling good carburization resistance can be lost or reduced when water level drop below 0,5 µBar	20
Inconel 617 J05-E				45 - 50	1 - 1.5	-		0.05 - 0.1	-	0.3 - 0.7			Reference PNP tests		
Inconel 617	750. 870	Up to 10000	5	150	45	-	5	5	-	-		Corrosion kinetic. microstructure. metallography	AIDA loop	Worse resistance to oxidation than Hastelloy X. carburization at higher temperatures occured	8
	750. 870		0.2										2-bar. once through device	Large differences in oxidation kinetics under 2 bar and 50 bar observed	
Inconel 617	950		0.1	27	9	<0.1	4	<0.1	-	-	Creep rupture			Creep rupture strength and ductility were higher in order of vacuum. air and helium. Growth of surface cracks accelerated due to carburization in helium	39
Inconel 617	1000	1000	0.1	43.2-43.8	25-26.8	0.04-0.07	0.25-0.4	0.06-0.07	-	<0.5			Corrosion behavior	Little difference in corrosion behavior. Si and Mo neither oxidized nor carburized	40
				38.7-99.2	10.2-16.5	0.85-1.16	0.34-0.44	0.05-0.08	-	<0.5					
				3.3-4.1	14-16.3	0.07-0.09	0.35-0.5	0.06-0.07	-	<0.5					
				43.1-43.5	26-26.7	0.07-0.09	3.43-3.45	0.07-0.07	-	<0.5				Different results in this atmosphere than in previous cases reached. Si. Mo were carburized	
Inconel 617	900 - 1040	200-500	0.1	30	10	0.1	0.4	0.3	-	0.5				Alloy carburized at 900 - 970℃, decarburized above 990℃. T_a estimated at 975℃. Largest carbon pickup observed at 940℃. Oxide film on the surface formed in helium was porous and much less protective compared to that formed in air	41

Investigations on austenitic steels

Alloy	Test temperature	Exposure time	Overall pressure	Partial pressures - mean values							Tested mechanical properties	Corrosion tests	Comments	Main results	References
				H_2	CO	CO_2	CH_4	H_2O	O_2	N_2					
	℃	hours	Mpa	Pa	Pa	Pa	Pa	Pa	Pa	Pa					
Mild steel Type 316 SS 20% Cr/35% Ni SS 15% Cr/15%Ni SS	400 - 800	up to 10000	0.1	50	50	-	5	5	-	-	Creep rupture properties	Metallography	Creep rupture properties in HTR helium and in air were compared	No effect of environment was detected at 400℃ The rupture strengths at 650/750℃ are 10-15 % lower than in air. The creep strengths are also reduced by 10-15 % At highest temperatures (>750℃) and highest stresses severe surface cracking was observed	25
AISI 321 AISI 347 AISI 316	650-800	up to 10000	0.18	5 - 10	2.5 - 5	-	0.3 - 0.8	0.05 - 3	-	-	Creep tests	Microstructure, metallography, corrosion scales depth (surface, subsurface), mechanical stability of oxide scale	Creep tests	Steels with 9 - 17 Ni and 0,16 to 1,0% Nb formed thin continuous oxide with no visible subsurface structural changes due to environment and no intergranular oxides steels with 9 - 17% Ni and up to 1% Ti (but no Nb) showed thick scales, accompanied by intergranular oxidation and subsurface carburization Spalling was observed in most of tested alloys above 700℃, Intergranular oxidation and subsurface carburization did not impair creep properties compared to those in air	34
Type 316 Type 304	650, 750	Up to 10000	5	150	45	-	5	5	-	-		Corrosion kinetics, microstructure, metallography	AIDA loop	Excellent behavior up to 650℃	8

	650, 750	0.2									2-bar, once through device		
Ni-26%, Cr-16%	1000		30.4	10.1	0.1	1.5	0.3	-	-	Creep rupture		Both oxidation and carburization observed, The corrosion behavior in the cracks depends on the distance from the crack entrance	37

Investigations on ferritic steels

Alloy	Test temperature	Exposure time	Overall pressure	Partial pressures (mean values)							Tested mechanical properties	Corrosion tests	Comments	Main results	References
				H2	CO	CO2	CH4	H2O	O2	N2					
	℃	hours	Mpa	Pa	Pa	Pa	Pa	Pa	Pa	Pa					
1% Cr Mo 2,25% Cr Mo	400 - 800	up to 10000	0.1	50	50	-	5	5	-	-	Creep rupture properties	Metallography	Creep rupture properties in HTR helium and in air were compared	Ferritic steels tested at 400 - 550℃ showed no gross cracking when tested in helium. In case of 1 % Cr at 500℃ and 2,25 Cr at 550℃ small reduction in creep and rupture strengths were observed in helium.	25
2,25 Cr Mo	482-649	40000 and more		34	1.9	-	3.2	0.2	-	<0.5	Long-term creep tests		Results were compared with those carried out in air environment	No significant effect of environment on creep at temperatures below 600℃. Oxidation in air and decarburization in helium caused degradation of creep properties at 649℃	30
2,25 Cr Mo	400 -450	100 - 10000 for creep 3000 for corrosion	0.13	20-30	10--15	0.7-1	0.7-1	0.1	<0.1	<0.1	Creep, fatigue	carbon deposition, carburization-decarburization, internal oxidation, correlation between environmental effect and strength		Fatigue life in helium is longer than that in air, no significant difference between creep rupture strength in both helium and air, negligible internal oxidation. Carburization and internal oxidation extrapolated to 105 hrs. They are estimated to be 30 µm and 0.15 µm respectively.	32

Investigations on other alloys

Alloy	Test temperature	Exposure time	Overal pressure	Partial pressures - mean values							Tested mechanical properties	Corrosion tests	Comments	Main results	References
				H_2	CO	CO_2	CH_4	H_2O	O_2	N_2					
	℃	hours	Mpa	Pa	Pa	Pa	Pa	Pa	Pa	Pa					
HK 40 MA 754 (oxide strengthened alloy) In 713LC	900	500, 1000, 2000, 3000	0.17	50	5	- -	5	<0.05	-	-	-	Scanning electron micrograph of surface, corrosion scales, weight changes, bulk carbon concentrations		Surface finish had no important effect on corrosion behavior of alloy HK 40 and MA 754and only a minor effect upon the corrosion behavior if IN 713LC, oxide scales formed in air can inhibit carburization of alloy in simulated HTR helium Decarburization was observed for all surface condition of MA 754 Effective carburization-barrier scales appear to be based on either the Al2O3 oxides containing titanium or spinels similar to Cr2MnO4. Chromium-manganese oxide scales formed without preoxidation do not necessary inhibit carburization	24
31 different alloys (iron- and nickel-based austenitic alloys, cast nickel based alloys, ODS)	750 - 1050	up to 10000	0.2	40	4	0.02	2	0.2	-	-	creep rupture, low and high cycle fatigue, post-exposure tensile properties	oxidation, thermal aging, effect, carburization	31 alloys and coating systems and 11 weldments were studied within this extensive work	Environmental effect is significant only in the highest temperature range, thermal aging appears to be the cause of most of changes observed during lower temperature exposures. See source literature for details.	33
Nimonic 86 J06-K Nimonic 86 J06-L	700 - 900	up to 10000		50 45 - 50	4 1 - 1.5	- -	5	0.03 0.05 - 0.1	- -	0.5 0.3 - 0.7		Corrosion, metallography, carbon uptake,	CIIR tests Reference PNP tests	Good spalling resistance proved, slow parabolic increases in carbon level, formation of Cr_2O_3, resistance of spalling, good carburization resistance can be lost or reduced when water level drop below 0,5 µBar	20
A 596 carbon steel	370, 550		0.2	150	45	-	5	5	-	-		Corrosion kinetics, microstructure, metallography	2-bar, once through device		8
SA 387 steel	370, 550		0.2	150	45	-	5	5	-	-		Corrosion kinetics, microstructure, metallography	2-bar, once through device		