HIGH TEMPERATURE ALLOYS FOR THE PRIMARY CIRCUIT OF A PROTOTYPE NUCLEAR PROCESS HEAT PLANT

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Summary

As part of a comprehensive materials test programme for the High Temperature Reactor Project "Prototype Plant for Nuclear Process Heat" (PNP), high temperature alloys are being investigated for primary circuit components operating at temperatures above 750 °C. On the basis of important material parameters, in particular corrosion behaviour and mechanical properties in primary coolant helium, the potential of candidate alloys is discussed. By comparing specific PNP materials data with the requirements of PNP and those of conventional plant, the implications for the materials programme and component design are given.

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dealing with the development of processes for the conversion of solid fossil fuels with heat from high temperature reactors, with the assistance of the Federal Minister for Research and Technology and the State of Nordrhein-Westfalen.

Introduction

The successful development of nuclear process heat plant depends critically on the selection and qualification of the alloys to be used in the construction of components operating at the highest temperatures within the primary circuit of the reactor. The tubes which transfer the heat from the primary circuit helium coolant either to the secondary circuit helium or to the methane reforming process gas mixture are typical examples of such components. The critical interfaces between the primary and secondary gas circuits for the present design of the German "Prototype Plant for Nuclear Process Heat" Project (PNP) are shown schematically in Fig. 1, and the thicknesses and expected nominal temperatures of the tube walls are indicated. Maximum temperatures under normal service conditions and the required minimum operation times for two essential PNP components are listed in Table I.

Comparison of the PNP service conditions with those of conventional chemical plant shows that:

1. The PNP components are not exposed to temperatures higher than those found in conventional plant. Nevertheless, the safety and reliability requirements of a nuclear plant increase the amount of data necessary to qualify the behaviour of the constructional materials. It should also be noted that the temperatures required by the PNP are above the range for which internationally agreed nuclear design codes are established. For example, ASME Code Case N-47 (formerly 1592) covers the use of four alloys in nuclear applications only up to a maximum temperature of approx. 800 ^{o}C.

2. The PNP high temperature tube components are so designed that the primary stresses remain very low under long term, normal service conditions (e.g. below 3 N.mm^{-2}). This is achieved by limiting the pressure difference between the outside and inside of the tubes to about 2 bar.

3. The PNP components are required to operate for longer service times than similar components in conventional plants, in order to reduce the expensive, time-consuming replacement of components to only once in the lifetime of the plant.

4. At temperatures above about 800 ^{o}C, corrosion effects specific to the HTR primary circuit are caused by reactions between the metallic surfaces and impurities present in the helium coolant.

The maximum normal service conditions for various PNP components and conventional chemical plant components are related to the time-dependent rupture strength of a PNP candidate alloy, INCONEL alloy 617, in Fig. 2. The long term values ($>$10.000 h) have been linearly extrapolated from log σ_R - log t_R - plots. The mean rupture strength of the alloy is shown as a three-dimensional surface, beneath which the normal operating conditions for the components are shown as columns. The figure shows that, in spite of the large differences in required service lives, the relationships between primary stress in the component and the rupture stress of INCONEL 617 for PNP and for conventional components are similar.

2. Alloy selection

As a first step in the choice of alloys for specific components, eight alloys have been selected from the currently available commercial alloys for intensive study. These "reference alloys" are listed in Table II.

A basic test programme comprising 18 tasks, each of which is concerned with the evaluation of a specific alloy property, is being carried out. The results obtained will be used as the guide lines for the first design of the PNP components. In addition to this basic programme, a broadly-based investigation of another 40 commercial alloys has been undertaken to provide a reserve list of candidate alloys, in case any of the reference alloys are shown to be unacceptable. A programme to develop alloys specifically for HTR service has also started, with the aim of producing a strong alloy resistant to the PNP service environments.

In the following sections, the currently available information on the corrosion and creep resistance of the reference alloys will be discussed with particular emphasis on the strongest wrought alloy in the list, INCONEL alloy 617.

3. Corrosion

The metallic surfaces of the primary circuit components operate in contact with primary coolant helium and either the helium of the secondary circuit or the gases of the methane reforming process. At KFA, the principle concern is with the primary coolant helium. The reactions of the metallic surfaces with the other two environments also requires investigation. For the secondary helium there is, however, the possibility of doping the gas to increase the oxidation potential allowing the formation of protective oxide films. For the process gases, PNP-orientated corrosion programmes are being carried out and existing information from conventional chemical plant can be drawn upon.

For the simulation of the primary coolant gas in the environmental testing of alloys, a helium gas mixture ("PNP-Standard helium") has been specified with the following analysis:

500 μbar H_2, 1,5 μbar H_2O, 15 μbar CO, 20 μbar CH_4, and equilibrium pressure CO_2.

The microstructure of INCONEL alloy 617 after exposure for 1500 hours at 850 °C in a similar atmosphere is shown in Figure 3. Of significance for the PNP design are the following four observations:

1. Oxidation of the most reactive elements present in the alloy (e.g. Cr, Ti, Al, Mn, Si) results in the formation of a porous oxide scale. An increase in the wall thickness should be considered to allow for the loss of material in oxide formation, but for alloys having acceptable corrosion behaviour the allowance will probably be insignificant for the long term stress-bearing capability calculations.

2. Internal oxidation occurs with the formation of oxides principally along grain-boundaries. Such oxides reduce the grain-boundary cohesion and may facilitate crack nucleation at the surface during stressed exposure.

3. An alloy depleted zone is formed below the oxide layer. The formation of surface and internal oxides depletes the matrix of important solid solution strengthening elements as well as strengthening precipitates formed during heat-treatment of the alloy. Providing the ductility is not reduced in this zone, an assumption shown by microhardness measurements to be reasonable, a straightforward thickness allowance would probably suffice for the design.

4. Inward diffusion of carbon occurs and carbide precipitates are formed. In the absence of a dense, compact surface oxide, carbon originating from the CH_4 and/or CO impurities in the helium can rapidly diffuse into the bulk material and precipitate carbides at grain-boundaries and within the grains. Heavy carbide precipitation may reduce mechanical ductility, and lead to premature failure, especially at temperatures below about 600 ^{o}C under conditions of cyclic loading.

It is the carburisation which poses the most difficult problem from the design point of view. Available data suggests that carbide precipitation in the absence of a protective oxide will occur to depths of around 10 mm for 140.000 hours exposure at 900 ^{o}C, following a parabolic rate law (i.e. depth of carburisation is proportional to square root of exposure time).

To tackle this problem, two approaches are being investigated. Firstly, attempts are being made to provide a dense surface barrier layer, produced, for example, by coating or modifying the alloy composition. Carbon penetration can then be expected to follow a linear rate law, determined by the barrier effectiveness. To be effective, the rate of carbon ingress must always be well below the parabolic curve which applies when there is no protective surface layer. The intersection of the two curves should be displaced to more than 100 times the service life by the barrier layer.

Secondly it may be possible to design components taking into consideration the time-dependent property gradients in the critical areas, as suggested by Walther 1 . To provide the basic information for such a design, experiments relating the amount and morphology of the carbide precipitation to mechanical and physical properties will be carried out, the important properties being

- creep strength and creep ductility
- low temperature ductility (important for shut-down and re-start operations)
- thermal conductivity
- specific volume (it must be ascertained whether the volume changes resulting from carbide precipitation contribute to the total strain in the components).

preliminary results, which consider room-temperature ductility after carburisation, are shown in Fig. 4. Such data will help to define maximum service temperatures and maximum operating time between inspections provided that a minimum ductility is specified.

4. Creep behaviour

The determination of the time-dependent stress-bearing capability of materials forms a major part of any high temperature design. Methods of measurement, interpretation and extrapolation of creep-rupture properties are well developed up to temperatures of 800 °C. To take into account the different creep responses of materials, the ASME Code Case N-47 for nuclear components requires that the design stress is based on the lowest of

1. 67 % of the minimum rupture stress,
2. the minimum stress for 1 % strain,
3. 80 % of the minimum stress for the onset of tertiary creep,

all the stresses above relating to design lifetime.

The practical significance of this analysis in respect to the high temperature behaviour of the reference alloys is illustrated in Fig. 5 which shows a classical creep curve and some typical creep curves for three of the reference alloys. These show similar times to 1 % strain but very different rupture lives, ranging from 1000 to 6500 hours. Creep curves for alloys having similar rupture lives but widely different times to 1 % creep strain have also been obtained. These observations point to a problem with the high rupture strength alloys, such as INCONEL alloy 617, which achieve long lifetimes by virtue of their resistance to fracture rather than creep resistance, exhibiting very high rupture ductilities. It can be seen that if the ASME rules are applied, no advantage can be taken of the high rupture resistance of such alloys. Kitagawa et al. 2 have made some proposals for designs to be based on a proportion of the rupture ductility (e.g. 5 or 10 % of creep rupture strain) rather than on a strain limit of 1 %, but it is not clear whether a design based on a strain limit higher than 1 % in the component lifetime would be practicable or acceptable.

A complicating factor in the assessment of creep-rupture strength of the candidate alloys is the effect of the service environment described in the previous section. The carburisation which can occur may significantly affect the stress-bearing capability of the components. In the short term, some strengthening due to carbide precipitation could occur but in the long term, the loss of important strengthening elements to the carbides may reduce the strength. The present test programmes are aimed at determining the balance between these two possible effects, to test times of 30.000 hours.

5. Conclusion

Two material parameters, corrosion resistance and creep strength, both of which are important in the design of high temperature components, have been discussed. Available results show that microstructural changes occur in the simulated reactor environment due to carburisation which can affect the mechanical behaviour of the components.

Although operating temperatures required by the PNP project remain within the range of conventional technology, the increased standards of safety and reliability required for nuclear plant do not allow direct transfer of the experience from conventional plant to the nuclear side. A detailed description of the mechanisms of corrosion and creep processes has to be established and the designs must find new methods for dealing with the problems of high temperature materials behaviour specific to HTR service.

References

/1/ WALTHER, H. "On the Future Development of Experimental and Theoretical Techniques in the Dragon Project Metals Programme at CRL, Fiat", OECD Dragon Project Report 935 (July 1975)

/2/ KITAGAWA, M. et al. "Some Problems in Developing the High Temperature Design Code for a 1,5 MW Helium Heat Exchanger" Elevated Temperature Design Symposium 1976, ASME, Mexico City (Sept. 1976)

Table I: Typical Service Conditions for PNP Components

Component	Maximum nominal operating temperature (mid-wall) /°C/	Environment	Required service life /h/	Characteristic dimensions (internal diameter x wall thickness) /mm/
Steam reformer tube	875	primary circuit He$^{1)}$ steam reforming gas$^{2)}$	140.000	100 x 15
Intermediate heat exchanger tube	930	primary circuit He$^{1)}$ doped He$^{3)}$	140.000	20 x 2,3

(1) $H_2/H_2O/CO/CH_4$: 500/1,5/15/20 μbar
(2) $H_2/H_2O/CO/CO_2/CH_4$: 35/50/5/5/5 vol. percent
(3) containing additions to increase the oxidation potential

Table II: Chemical Compositions of PNP Reference Alloys (significant values)

Alloy type	Alloy	Carbon	Nickel	Chromium	Molybdenum	Iron	Cobalt	Others
wrought, nickel-base	HASTELLOY S	0,02	balance	15,5	14,5	-	-	La
	HASTELLOY X	0,1	balance	22 - 25	9 - 10	18	1,5	W
	NIMONIC 86					-	-	Ce
	INCONEL 617					-	12,5	Al
wrought, iron-base	INCOLOY 800 H	0,1	32	20	-	balance	-	Ti, Al
	INCOLOY 802	0,35						
cast iron-base	IN-519	0,3-0,4	24	24 - 25	-	balance	-	Nb
	Manaurite 36 X		32					

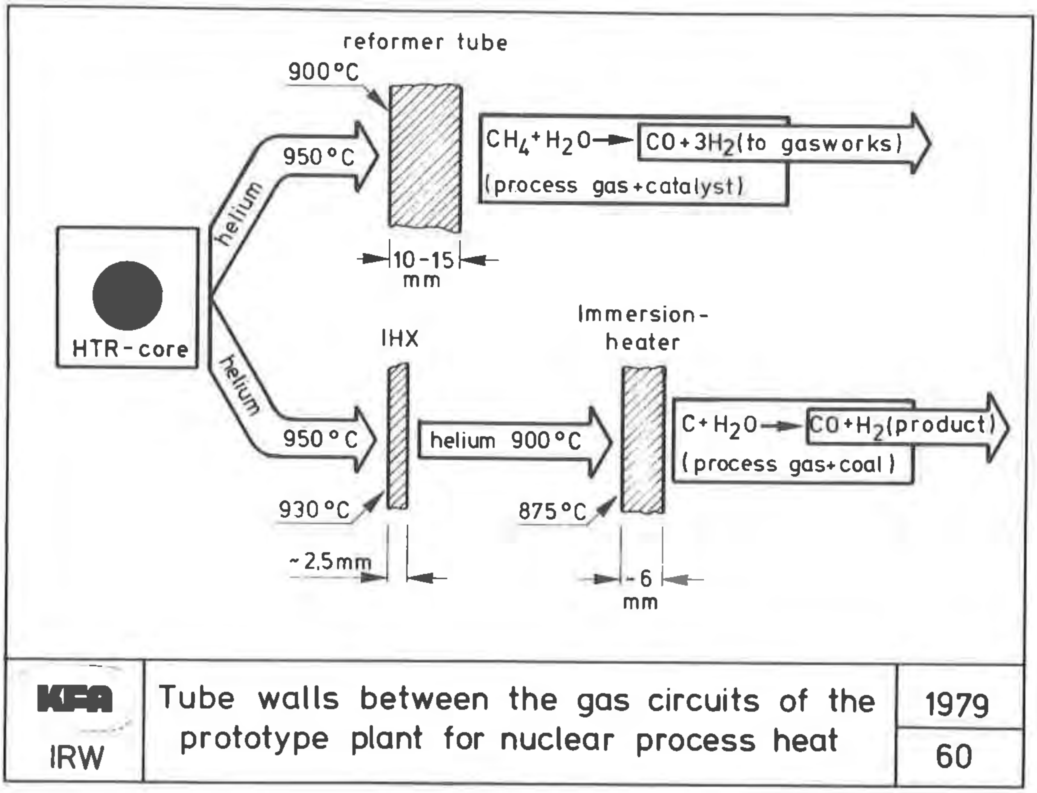
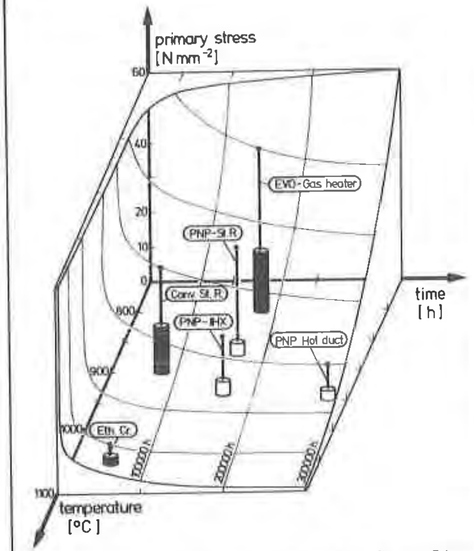


Fig. 1



St R Steam Reform, Tube, IHX: Interm Heat Exch, Eth Cr Ethyl Cracking Tube

IRW

Typical Primary Stresses for Conventional and PNP Components in Relation to Average Rupture Strength (Extrapolated) of a High Temperature Alloy (INCONEL 617)

1979

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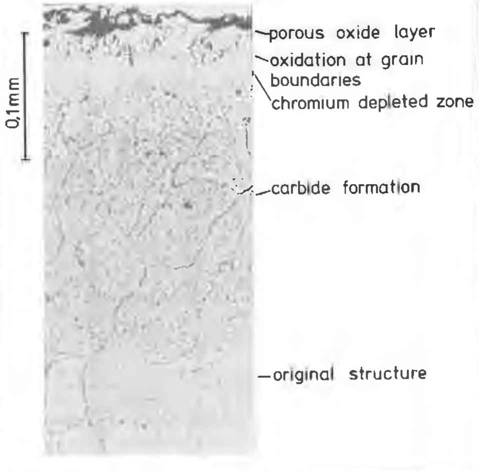
Fig. 2



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Typical corrosion in HTR-helium (Inconel 617, 1500 h at 850°C)

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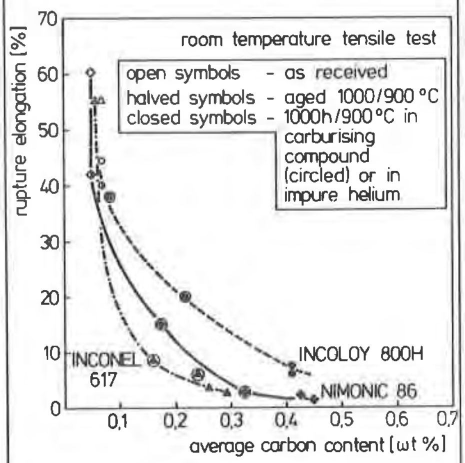
Fig. 3



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Influence of Carbon Content on Room Temperature Ductility

1979

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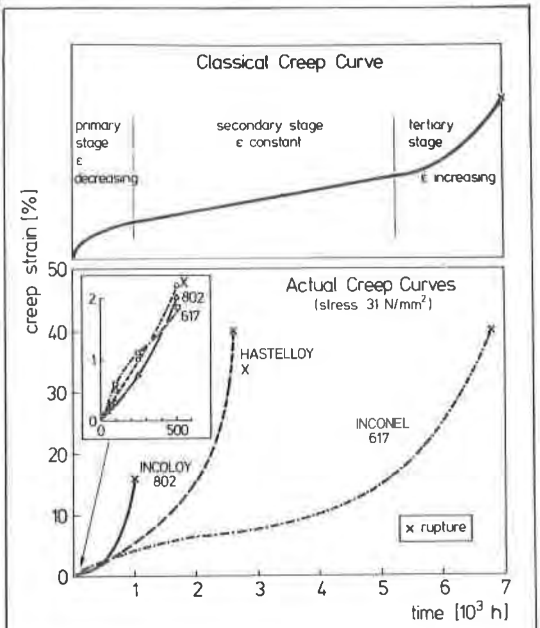
Fig. 4



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Comparison of Actual Creep Curves at 900 °C with Classical Creep Curve.

1979

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Fig. 5