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Qualification of Ni-Based Alloys for Advanced Ultra Supercritical Plants

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Abstract

For the realization of advanced ultra-supercritical plant operating at service temperatures of up to 720°C plants Ni-based alloys are indispensable. This paper describes the on-going investigations on the qualification of several Ni-based alloys such as Alloy 617, Alloy 263 and Alloy 740 within the framework of the German state funded R&D initiative COORETEC. For safe design and reliable operation of components the requirements of the European Pressure Equipment Directive (PED) have to be fulfilled. Experimental work was done in order to determine the relevant material characteristics, such as long-term creep strength values for the design of critical components. Also new design methods based on numerical calculation of the creep behaviour by using a constitutive creep equation including a damage parameter are required to make full use of the strength potential but also taking into account their specific stress-strain relaxation behaviour. Investigation of the microstructure by optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of the as delivered and crept state show the changes in precipitation depending on time and temperature.

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Keywords: Ultra-supercritical power plant; Ni-based alloy; microstructure; damage mechanism; creep behaviour

1. Introduction

In Germany in the future coal will supply a significant contribution to the production of energy. The demand for resource conservation and the reduction of CO₂ means that only power plants with the highest possible efficiencies can be constructed. This could be achieved by a significant increase of the steam parameters, pressure and temperature. Especially the rise in temperature poses considerable demands on the proving of long-term creep stability and the resistance concerning corrosion (oxidation), the strength and deformation ability of the structural materials to be used. These requirements will not be fulfilled by the standard steels already used. Therefore the realization of the future high-efficiency coal-fired 700°C power plants is based on the use of qualified Ni-based alloys. However in comparison with standard steel grades only little experience has been made especially considering the long-term creep behaviour and the use of thick-walled components.

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In order to establish a reliable database of the relevant design characteristics, R&D activities have been commenced in Germany sponsored by industry and government.

2. German research COORETEC programs

The German Federal Ministry of Economics and Technology (BMWi) promotes the development of a power plant fired with fossil fuels with prospects for the future by starting the COORETEC initiative in 2002 [1]. The abbreviation COORETEC stands for CO₂ reduction technologies for coal-fired power plants. Under this heading, two strategic approaches are taken in joint projects involving industry and research: Technologies for improving power plant efficiency, Technologies for the separation and transport of CO₂ with the aim of safe long-term storage in geological formations.

With this focus, COORETEC is integrated into the German Federal Government’s 5th Energy Research Programme on “Innovation and New Energy Technologies”. The aim is to promote the transition to a reliable, economic and environmentally safe energy supply. Thus COORETEC makes a significant contribution towards implementing the Federal Government’s energy and climate policies.

With regard to material qualification the following projects were started in 2004, coordinated by the COORETEC working group AG, Table 1.

Table 1. COORETEC-R&D projects focused on material qualification for 700°C power plants.

| Boiler application | Turbine application | Turbine and pipe work application |
|--------------------|---------------------|----------------------------------|
| MARCK0 700         | MARCK0 700          | TD-1                             |
| DE-1 Fireside corrosion and steam side oxidation behaviour of materials for the 700°C power plant | DT-3 Qualification of dissimilar welds between 10%Cr-steels and Ni-based alloys | Optimization of non-destructive testing methods for thick walled components made of Ni-base alloys |
| DE-2 Characterization of superheater materials after cold deformation | DT-4 Procedures and Fracture mechanics approaches for life assessment of components operating in high temperature regime | |
| FDBR02 Qualification of pipes with longitudinal welds made of Alloy 617 | 725HWT Investigation of the long term service behaviour of tubes for the future high-efficiency power plant | |
| DE-4 Characterization of strength and deformation of pipes and forgings made of Ni-based alloys | 725HWT II Investigation of the long term service behaviour of thick walled pipes for the future high-efficiency power plant with specific consideration of flexible operation (start-up – shut down) | |
| 725HWT | | |

Guideline for the material qualification work in the projects cited in Table 1 is the European Equipment Directive (PED), which requires (amongst other things):
- Mechanical behaviour / ductility incl. ageing
- Creep rupture for the evaluation of the long term design characteristics
- Characterization of the behaviour of welded joints (HAZ) incl. creep
- Demonstration of the practicability of production (fabricability) of a component (manufacturing concept, component qualification) especially when toughness is taken into consideration.

3. Materials for future 700°C power plants

The critical components of boilers for the 700 °C technology are the membrane and furnace walls, the final superheater and reheater stages, boiler tubes (hot sections), in- and outlet headers (hot sections) as well as the
thick-walled components, mainly the high-pressure outlet headers and the piping to the turbine. The realization is linked to the development of stronger high-temperature materials capable of operating under high stresses at high temperatures. The use of ferritic steels is actually limited to 620°C steam temperature. Even if the development of new alloys for temperatures up to 650°C were successful, the major limiting factor in using these materials is their susceptibility to oxidation on the steam side. Therefore the candidate materials for the boiler components, which are being investigated intensively at the moment, are Alloy 617, Alloy 263 and Alloy 740. The chemical composition of the materials investigated is listed in Table 2.

Table 2. Chemical composition of the investigated Ni-alloys (wt-%).

|          | Cr  | Mo  | Co  | Al  | Ti  | Nb  | B   | Fe  | others |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|--------|
| Alloy 617|     |     |     |     |     |     |     |     |        |
| pipe     | 0.06| 21.7| 8.6 | 11.3| 1.21| 0.39|     |     |        |
| tube     | 0.06| 22.0| 8.85| 11.6| 1.17| 0.42|     |     |        |
| Alloy 617 mod |     |     |     |     |     |     |     |     |        |
| min      | 0.050| 21.0| 8.0 | 11.0| 0.80| 0.30|     |     |        |
| max      | 0.080| 23.0| 10.0| 13.0| 1.30| 0.50|     |     | 1.50   |
| Alloy 263| 0.08| 21.0| 6.1 | 21.0| 0.6 | 2.4 | 2.2 | 0.005|        |
| Alloy 740| 0.03| 25.0| 0.5 | 20.0| 0.9 | 1.8 | 2.0 | 0.70 |        |

4. Mechanical and physical properties

There are significant differences in the mechanical and physical properties of the austenitic Ni-alloys and ferritic steels, commonly used in coal-fired power plants for pressurized components. These differences have an impact on the manufacturing (e.g. welding), but also on the component behaviour as deformation, stress state development and thus on the design i.e. on the critical wall thickness. Ni-based alloys show lower thermal conductivity and a higher thermal expansion coefficient in comparison to ferritic steels. Due to the substitution of nuclear power plants by renewal energy (solar, wind) a high operational flexibility of the new 700°C power plants is required. During start-up and shut-down of the plant thermal stresses caused by temperature gradients especially in thick walled parts will appear. The above mentioned differences in thermal conductivity as well as in thermal expansion will lead to higher cyclic stresses in Ni-based alloys. Therefore the component design has to cater for the specific characteristics of these materials.

4.1. Creep behaviour of base metal

A comparison of the 10^5h creep strength between ferritic steels and Ni-based alloys is given in Figure 1. Obviously the Ni-based alloys show significant higher creep strength. The creep rupture curves for Alloy 263 and Alloy 740 however have to be confirmed by on-going long term creep tests within the scope of the above mentioned R&D projects.

In Figure 2 the creep rupture curves of the martensitic steel P92 is compared with that of the Alloy 617. At the standard operation temperature of both materials (600°C and 700°C) they show a comparable strength. The Alloy 617mod developed within a nationally funded project [2] with a limitation of the span of specific elements, Table 2, shows a better creep strength than the standard Alloy 617.
The influence of chemical composition on creep rupture behaviour of Alloy 617 was studied taking boron and titanium into consideration. The results at 700°C for boron and titanium are shown in Figure 3. Melts with a moderate content of boron and those with a higher content of titanium tend to have better creep resistance. However, at this point it must be noted that the significance of consideration of single elements is limited [7].
4.2. Creep behaviour of welded joints

The strength of welded structures under creep load is an important characteristic for the safe operation of components. In ferritic steels the heat affected zone (HAZ) consists of different, overlapping structure zones, as a result of the heat input by the welding. Their properties, especially the creep behaviour, are different from those of base material (BM) and weld metal (WM). The welding of the ferritic steels – especially of the high alloy martensitic steels – can cause major problems in operation as the HAZ has to be considered as a zone with low creep resistance. It represents the weakest link in weldments and can lead to premature failure of the component. There are two major factors: first, the outer fine grained or intercritical heat affected zone shows poor creep resistance due to its microstructure and precipitates’ characteristics. On the other hand, a severe multiaxial stress state can be observed in that region of welded components [8], which also cause lower creep strength.

Ni-based alloys do not show a HAZ comparable to that in ferritic steels, as no phase transformation during the heat input of the welding process and the subsequent cooling down takes place. Therefore only a limited influence of the welding on the creep strength of crossweld specimens could be expected. For Alloy 617mod a reasonably good long-term database for base material and welded joints of tubes and pipes obtained by crossweld tests already exist. Results obtained with crossweld specimens from SMAW-girth and TIG-girth welds of tubes and pipes for temperatures of 700°C and 750°C are within the base material scatter band. Long-term tests longer than 10,000 h testing time show a tendency towards the base material mean values.

A comparison of the creep strength of different materials commonly used in power plants is shown on the basis of the weld creep strength factor WSF in Figure 4 [8].

![Diagram showing weld strength factors for 100,000 h creep rupture strength](image)

Fig.4. Weld strength factors for 100,000 h creep rupture strength [9] [10] [11] and comparison with recent results from research projects and literature on the basis of creep tests (rupture times 10,000 h to 50,000 h).

The weld strength factor is defined by:

$$WSF(t, \vartheta) = \frac{R_{u/(w/t)/\vartheta}}{R_{u/t/\vartheta}}$$  \hspace{1cm} (1)

with:

- $R_{u/(w/t)/\vartheta}$ = Creep rupture strength of the welded joint
- $R_{u/t/\vartheta}$ = Creep rupture strength of the parent material.

For Alloy 617 mod a WSF of 0.85 could be stated, which is rather high in comparison to the WSF of martensitic steels.
Despite good creep strength properties it has to be taken into account that nickel based materials tend to generate hot cracking during or immediately after welding in the weld metal and/or in the base metal near the fusion line. Also intercrystalline cracking was observed in areas near the fusion line. Thus, in order to reduce the sensitivity to intercrystalline cracking in welds of Alloy 617 it is recommended to perform a stabilization annealing after welding.

4.3. LCF behaviour of base metal

To investigate the fatigue behaviour, LCF tests have been performed by using round bar specimens machined out of the wall superheater tubes, Figure 5. The comparison show, that Alloy 263 and Alloy 740 yield a higher number of cycles to crack initiation than the Alloy 617.

Fig. 5. LCF behaviour at 700°C (R=-1; da/ds=6%/min).

5. Microstructural characterisation

Alloy 263 as well as the Alloy 740 is a gamma prime hardened and solid solution strengthened material and both are used in the age hardened condition. Alloy 617 is a solid-solution strengthened and carbide-hardened material. The changes in the microstructure in these materials caused by heat treatment or ageing due to service will have a strong impact on the material behaviour as well as failure of components.

The effect of age hardening and creep loading on the microstructure in comparison to the initial solution annealed state is exemplarily shown for the Alloy 740 in Figure 6. The effect if short time hardening (800°C, 4h) is applied, could be described by an increasing number and size of $\text{M}_2\text{C}_6$ particles at the grain boundaries in comparison to that in the grain. With longer ageing time size and number of the $\text{M}_2\text{C}_6$ particles increases. With longer ageing time the number of $\gamma'$-particles in the grain decreases slightly, whereas the size increases. After creep loading no $\text{M}_2\text{C}_6$ particles in the grain could be observed and the particles at the grain boundaries coarsened. The MC particles disappeared and the number of $\gamma'$-particles in the grain became lower to that after age hardening. The $\gamma'$-particles still present after creep loading, show larger sizes.
6. Summary

For the realization of the 700°C technology for coal-fired power plants Ni-based alloys are required. Extensive experimental qualification work within the scope of a nationally funded R&D initiative COORETEC is underway. Microstructural analysis was performed in order to understand mechanisms of microstructural changes, which have a decisive influence on the long-term properties. For Alloy 740 the influence of duration of age hardening and effects of creep load on the microstructure was investigated by using optical and transmission electron microscopy. For this material but also for the Alloy 263 further investigations and long-term experiments are necessary to gain a better knowledge of microstructural processes and their influence on creep behaviour.

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