INCREASED TEMPERATURE AND LONG-TERM IMPACT OF THE AGEING PROCESS ON CHANGES IN THE MICROSTRUCTURE OF THE HR6W ALLOY

The study was carried out to determine the effect of long-term ageing (1,000 and 10,000 hours) at 700°C and 750°C on the microstructure of the HR6W alloy. The study indicates that the long-term effect of high temperature causes significant changes in the microstructure of the examined alloy:

1. After ageing for 1,000 hours at 700°C, in addition to primary MX and M23C6 precipitations, an increase in the size and number of precipitates was observed both inside and along austenite grain boundaries, and the occurrence of the Laves phase was also observed.

2. After 10,000 hours at 700°C, a significant increase in M23C6 precipitates was observed, especially inside and along grain boundaries. An increase in the Laves phase in the microstructure was also observed.

The effect of the increase in the ageing temperature to 750°C:

1. It significantly accelerated the precipitation process after just 1,000 hours.

2. In addition to a network of M23C6 precipitates along austenite grain boundaries, their coagulation and an increase in the size of the Laves phase precipitates inside the austenite grains was observed.

3. The extension of the ageing time to 10,000 hours at 750°C contributed to a significant increase in the size of Laves phase precipitates inside austenite grains.

Keywords: HR6W, microstructure, ageing, precipitates

1. INTRODUCTION

In recent years, there has been a demand for higher efficiency of fossil-fuel power stations from the point of view of reducing environmental burden represented by the reduction of carbon dioxide emissions. The term supercritical parameters refers to power blocks operated in steam conditions at 565–620°C and pressure up to 30 MPa and ultra-supercritical (USC) conditions, i.e. 650–720°C/30–35 MPa with an efficiency of 45–50%.

Advanced ultra-supercritical (A-USC) power stations operating at steam temperatures of 700–760°C are the most promising technology to improve the efficiency of fossil-fuel power stations to reduce CO2 emissions.
3. TESTING METHODOLOGY

The observation of the microstructure of the tested material was performed on metallographic microsections on tubes’ cross-sections for the following states:
- as-delivered (after solution heat treatment),
- after ageing at 700°C and 1,000 hours,
- after ageing at 700°C and 10,000 hours,
- after ageing at 750°C and 1,000 hours,
- after ageing at 750°C and 10,000 hours.

The microsections were obtained by grinding and polishing followed by electrolytic etching using a 50% HNO₃ solution.

The microstructure was observed using a NEOPHOT 2 light microscope (LM) at magnifications up to 1000× and using an Inspet F scanning electron microscope (SEM) at magnifications up to 5000×. The chemical composition of the inclusions and precipitates present in the microstructure of the material was analysed using a scanning electron microscope, which is equipped with an EDS detector for the analysis of chemical composition in micro-areas. The chemical composition of the precipitates and their identification was confirmed using a TITAN transmission electron microscope (TEM).

4. TEST RESULTS

4.1. MICROSTRUCTURE OF THE AS-DELIVERED HR6W ALLOY

The as-delivered HR6W alloy after solution heat treatment has an austenitic microstructure with a small content of primary carbides (Nb,Ti)C. Figure 2a shows the alloy’s microstructure observed using a light microscope (LM). Figure 2b shows the microstructure observed using a scanning microscope (SEM).

4.2. MICROSTRUCTURE OF THE HR6W ALLOY AFTER THE AGEING PROCESS

The image of the observed microstructure of the HR6W alloy after ageing (time \( t = 1,000 \) and \( 10,000 \) hours, temperature \( T = 700°C \)) differs from the as-delivered microstructure (Fig. 3).

It was shown that the ageing process of the HR6W alloy intensifies the processes of precipitation of secondary phases. In the microstructure along grain boundaries, an increase in the number of and size of \( \text{M}_2\text{C}_6 \) precipitates and intermetallic phase – \( \text{Fe}_2\text{W} \) Laves rich in tungsten was observed. Evenly distributed fine precipitates of \( \text{M}_2\text{C}_6 \) and MX carbides were observed inside the HR6W alloy grains. The beginnings of Laves phase precipitations were observed inside the grains in the form of elongated particles (1,000 hours), while after a longer time (10,000 hours) a significant increase in the Laves phase inside the grains in the form of elongated particles of irregular shape was observed.

Table 1. Chemical composition of the investigated superheater coil material with reference to the requirements of VdTÜV 559/2 09.2011

| Source of analysis | Alloying element [wt %] |
|-------------------|------------------------|
|                   | C | Si | Mn | P | S | Cr | W | Ti | Nb | Fe |
| Standard VdTÜV 559/2 09.2011 | 0.09 | 0.95 | 1.32 | 0.005 | 0.003 | 24.15 | 7.95 | 0.18 | 0.28 | rest |
| Follow-up         | 0.10 | 1.0 | 1.50 | 0.030 | 0.015 | 21.5–24.5 | 6–8 | 0.20 | 0.35 | 20–30 |
The increase of the ageing temperature to 750°C caused a significant acceleration of the precipitation process after just 1,000 hours. In addition to a network of $\text{M}_2\text{C}_6$ precipitates along austenite grain boundaries, their coagulation and an increase in the size of the Laves phase precipitates inside the austenite grains was observed. The extension of the ageing time to 10,000 hours at 750°C contributed to a significant increase in the size of Laves phase precipitates inside austenite grains (Fig. 4).

After the ageing of the tested material, the microstructure was investigated using light microscopy (LM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as shown in Fig. 5–8.

After ageing the HR6W alloy at $T = 750°C$ and for $t = 10,000$ hours, the microstructure was investigated using scanning electron microscopy (SEM) (Fig. 9–10).

### 4.3 HARDNESS MEASUREMENT

The ageing of the HR6W alloy caused an increase in its hardness. The as-delivered alloy’s hardness was approx. 181 HV10. After performing individual heat treatment variants, the hardness of the alloy was:

- $t = 1,000$ hours at $T = 700°C$ – hardness: 193 HV10
- $t = 10,000$ hours at $T = 700°C$ – hardness: 205 HV10
- $t = 1,000$ hours at $T = 750°C$ – hardness: 202 HV10
- $t = 10,000$ hours at $T = 750°C$ – hardness: 236 HV10.

The increase in hardness of the examined alloy is associated with the precipitation of secondary phases in its structure. Figure 11 presents a graph showing a summary of the average hardness value of the HR6W alloy from measurements (median calculated from 5 unit measurements).
Fig. 4. Comparison of the microstructure of the HR6W alloy as delivered and after ageing at 750°C
Rys. 4. Porównanie mikrostruktury stopu HR6W w stanie dostawy i po starzeniu w temperaturze 750°C

Fig. 5. Analysis of the chemical composition of the $\text{M}_{23}\text{C}_6((\text{Cr,Fe,W})_{23}\text{C}_6)$ precipitate in the HR6W alloy after ageing for 1,000 hours at 700°C
Rys. 5. Analiza składu chemicznego wydzielenia typu $\text{M}_{23}\text{C}_6((\text{Cr,Fe,W})_{23}\text{C}_6)$ w stopie HR6W po starzeniu przez 1000 godzin w temperaturze 700°C

| Item | Wt % | At % |
|------|------|------|
| $\text{Cr}K$ | 51.15 | 51.48 |
| $\text{Fe}K$ | 6.36 | 5.96 |
| $\text{Ni}K$ | 6.30 | 5.62 |
| $\text{WM}$ | 29.49 | 8.39 |
| $\text{SK}$ | 0.23 | 0.38 |
| $\text{CK}$ | 6.47 | 28.17 |

Fig. 6. Distribution of chromium and tungsten concentration in the microstructure of the HR6W alloy after ageing at 700°C for 1,000 hours. SEM observation (map of precipitates)
Rys. 6. Rozkład stężenia chromu i wolframu w mikrostrukturze stopu HR6W po starzeniu w temperaturze 700°C przez 1000 godzin. Obserwacja SEM (mapa wydzieleń)
Fig. 7. Identification of the M$_{23}$C$_6$ precipitate in the HR6W alloy after ageing for 1,000 hours at 700°C (TEM)
Rys. 7. Identyfikacja wydzielenia typu M$_{23}$C$_6$ w stopie HR6W po starzeniu przez 1000 godzin w temperaturze 700°C (TEM)

Fig. 8. Identification of the Laves phase precipitate in the HR6W alloy after ageing for 1,000 hours at 700°C (TEM)
Rys. 8. Identyfikacja wydzielenia typu faza Lavesa w stopie HR6W po starzeniu przez 1000 godzin w temperaturze 700°C (TEM)

| Item | Wt % | At % |
|------|------|------|
| W    | 68.39| 39.16|
| Co   | 0.00 | 0.00 |
| Cr   | 13.58| 27.50|
| Fe   | 10.90| 20.55|
| Ni   | 7.13 | 12.78|

Fig. 9. Analysis of the chemical composition of the Laves phase precipitate in the HR6W alloy after ageing for 10,000 hours at 750°C
Rys. 9. Analiza składu chemicznego wydzielenia typu faza Lavesa w stopie HR6W po starzeniu przez 10 000 godzin w temperaturze 750°C

Fig. 10. Distribution of chromium and tungsten concentration in the microstructure of the HR6W alloy after ageing at 750°C for 10,000 hours. SEM observation (map of precipitates)
Rys. 10. Rozkład stężenia chromu i wolframu w mikrostrukturze stopu HR6W po starzeniu w temperaturze 750°C przez 10 000 godzin. Obserwacja SEM (mapa wydzieleni)
5. CONCLUSIONS

Based on the carried out research and analysis, the following conclusions can be drawn:

In the state after solution heat treatment, the HR6W alloy has a coarse-grained structure with small primary MX precipitates and M$_{23}$C$_6$ carbides.

The increase of the ageing temperature to 750°C caused a significant acceleration of the precipitation process after just 1,000 hours. The extension of the ageing time to 10,000 hours at 750°C contributed to a significant increase in the size of Laves phase precipitates inside austenite grains.

The use of transmission electron microscopy (TEM) after ageing for 1,000 hours at 750°C enabled the identification of M$_{23}$C$_6$ precipitates in the HR6W alloy, as well as the Fe$_2$W Laves phase inside austenite grains.

The measured hardness of the as-delivered HR6W alloy was at the level of 181 HV10. It increased to 193 and 205 HV10 after the ageing rate of 1,000 and 10,000 hours respectively at 700°C. Similarly, an increase in hardness was observed after ageing at 750°C – it was, respectively, for 1,000 and 10,000 hours: 202 and 236 HV10.

The observed increase in hardness depending on the temperature and ageing time indicates the rate of changes in the microstructure of the HR6W alloy as a result of the precipitation of secondary phases. This, in turn, will probably have an impact on the decrease in its plasticity, deteriorating its performance.

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