The Influence of Long-term Ageing on the Microstructure of Sanicro 25 Steel

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Abstract. Sanicro 25 (22Cr25NiWCoCu) is a newly developed austenitic stainless steel used in the boiler pressure superheaters and reheaters with ultra-supercritical high-efficient parameters. The paper presents the results of microstructure testing and secondary phase separation processes after 20,000 h ageing at 700 and 750 °C. In the initial stage of ageing, the precipitation of numerous very small M\textsubscript{23}C\textsubscript{6} chromium carbides and Laves phase were observed. The long-term ageing related to temperature revealed the existence of secondary phases: M\textsubscript{23}C\textsubscript{6}, MX, NbCrN, Laves phase and \sigma phase. The test results presented in the paper are part of the developed material characteristics to be used for predicting the service life of the material of components operated under creep conditions.

1 Introduction

In spite of the extensive promotion of renewable energy sources (solar, wind or water) for years and the expected increase in the share of nuclear technologies in the energy balance, not only in Europe but also in the world power industry, the global energy sector is still mostly based on fossil fuels.

Despite the significant rise in prices of harmful gas emissions into the air, which is to curb the development of the conventional power generation, there are no signs that the proportion of sources of electricity generation could significantly change in the coming years [1-3]. The electricity generation in Poland is still based on coal and lignite. Due to their considerable reserves, they are the basic and at the same time the cheapest source of energy [1-3]. Therefore, to reduce the costs of electricity generation, the obsolete power units (mostly with a capacity of 200 MW, built a few decades ago) have been modernised and the modern supercritical power units have been built for several years in Poland. It is inextricably linked to the development of the materials technology and the need to use materials with increased performance. Other important aspects are the optimisation of processes and installation modules, strict control of the operation, the increase in thermal flexibility and the introduction of the carbon capture technology [4-7].

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One of the most modern currently used materials is Sanicro 25 (X7NiCrWCuCoNbNB25-23-3-3-3-2) steel, which was developed by AB Sandvick Material Technology. This steel is characterised by high nickel (24%), chromium (22%) and tungsten (3%) contents and the addition of elements such as niobium, cobalt and copper. It is primarily intended for components of boiler pressure superheaters and reheaters to be operated at up to 700 °C [8].

The Sanicro 25 has higher creep strength compared to other austenitic structural steels, i.e. HR3C and Super 304H. Creep strength of Sanicro 25 steel determined at 700 °C for up to 100,000 h is 95 MPa, and it is similar to that of the much more expensive HR6W nickel-base alloy [1, 8, 9]. The high performance of Sanicro 25 steel justifies the increasingly higher demand for it and its more and more widespread use in ultra-supercritical and advanced ultra-supercritical power units [1, 9].

2 Material for investigations

The material used in the investigations was Sanicro 25 steel delivered in the form of a coil sample of Ø38x8.8mm. The chemical composition of the investigated steam superheater sample is presented in Table 1. The microstructure of the Sanicro 25 steel was observed with Inspect F scanning electron microscope (SEM) on conventionally prepared electrolytically etched metallographic microsections. The metallographic examinations were carried out on the material in the as-received condition and after long-term ageing at 700 and 750 °C for 10,000 and 20,000 h.

| Chemical composition, wt.% |
|-----------------------------|
| C  | Si  | Mn  | P  | S  | Cu | Cr | Ni | W  | Co | Nb | B  | N  |
| 0.06 | 0.25 | 0.50 | 0.01 | <0.01 | 2.9 | 23.0 | 24.1 | 3.2 | 1.4 | 0.4 | 0.005 | 0.17 |

3 Results and discussions

The microstructure of Sanicro 25 steel in the as-received condition, observed with the scanning electron microscope, is shown in Fig. 1. The investigated steel is characterised by the austenitic matrix with the grain size of 7 according to the scale of models with annealing twins and numerous primary precipitates of varying size arranged in bands both within the grains and at the grain boundary. The structure of Sanicro 25 steel is typical of the niobium-stabilised heat-resistant austenitic steels.

**Figure 1.** Microstructure of Sanicro 25 steel in the as-received condition, hardness 184 HV10

Long-term ageing of Sanicro 25 steel contributes to the secondary phase precipitation strengthening (Figs. 2, 3, 4). In the initial stage of ageing, there is an intensive precipitation process during which numerous excellent copper particles coherent with the matrix are precipitated within the grains. The copper-rich precipitates (called ε_Cu precipitates) in austenitic steels are observed just
after one hour of ageing at 650 °C [10]. Due to their nanometric dimensions, they strengthen the alloy very intensively [10, 11]. The second precipitate that occurs in the structure of the investigated steel is M_{23}C_6 carbides. The M_{23}C_6 carbides precipitate mainly at the grain boundaries, and in contrast to the ε_{Cu} precipitates, they are characterised by lower thermodynamic stability, which results in their high tendency to coagulate and create the so-called continuous network of precipitates at the grain boundaries [12, 13].

![Figure 2. Microstructure of Sanicro 25 steel after 1000 h ageing at 700°C, hardness 215HV10](image)

![Figure 3. Microstructure of Sanicro 25 steel after 1000 h ageing at 750 °C, hardness 226HV10](image)

After 1000 h ageing at both 700 and 750 °C, the fine Laves-phase precipitates (Fe_{2}W) were revealed in the matrix of the investigated steel (Fig. 2). The Laves-phase precipitates were observed both within the grains and at the grain boundaries. The fine particles of M_{23}C_6 carbides and Laves phase precipitated at the grain boundaries have a positive effect on the increase in creep strength by inhibiting the slip at the grain boundaries [12, 13]. After 10,000 h ageing, the increase in the size of precipitates of this phase was observed (Fig. 4,5). Longer ageing times of approx. 20,000 h contribute only to the slight growth of the Laves phase particles (Figs. 6, 7). The impact of the Laves phase precipitated within the grains on steel properties depends on its size and volume fraction. The finely dispersed Laves phase particles precipitated within the grains have a positive effect on creep and fatigue strength. The Laves phase coagulation during service results in the gradual disappearance of this positive effect [9, 14].
Figure 4. Microstructure of Sanicro 25 steel after 10,000 h ageing at 700 °C, hardness 234 HV10

Figure 5. Microstructure of Sanicro 25 steel after 10,000 h ageing at 750 °C, hardness 247 HV10

Figure 6. Microstructure of Sanicro 25 steel after 20,000 h ageing at 700 °C, hardness 249 HV10

Figure 7. Microstructure of Sanicro 25 steel after 20,000 h ageing at 750 °C, hardness 239 HV10
Long-term ageing also contributed to the precipitation of unfavourable \( \sigma \) phase at the austenite grain boundaries. The privileged place was the meeting point of the three-grain boundaries (Figs. 6, 7). The precipitation of the \( \sigma \) phase results in a significant reduction in plastic properties and ductility of austenitic steels [9, 12, 13].

4 Summary

The metallographic examinations carried out for Sanicro 25 steel in the as-received condition and after ageing at 700 and 750 °C have shown that:

• in the as-received condition, Sanicro 25 steel is characterised by the austenitic microstructure with numerous primary MX and Z-phase (NbCrN) precipitates;
• ageing leads to the precipitation of copper-rich (\( \varepsilon_{\text{Cu}} \)) particles, Laves phase and secondary Z-phase precipitates in the matrix, while at the grain boundaries, the occurrence of \( \text{M}_{23}\text{C}_6 \) carbides and the Laves- and \( \sigma \)-phase precipitates were observed.
• the extension of the ageing time up to 20,000 h at the test temperature results in an increase in the number and size of precipitates both within the grains and at the grain boundaries, and it is particularly visible in relation to the \( \text{M}_{23}\text{C}_6 \) carbides and \( \sigma \) phase.

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