The influence of the temperature on the mechanical properties of Sanicro 25 steel

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Abstract. Austenitic steel 22Cr25NiWCoCu (Sanicro 25) is one of the newest and most promising steels for use in supercritical and ultra-supercritical power units. High resistance of Sanicro 25 steel to corrosion and oxidation in the steam atmosphere at up to 700 °C is ensured by chromium content at 21.5-23.5 wt%. Also, higher chromium content provides less mass decrement during high-temperature corrosion at 700 °C. Currently, the Sanicro 25 steel is characterised by the highest creep strength among the commercially used creep-resistant stainless steels. In this work, the study of precipitation processes and microstructure stability in the delivery state and after the ageing process in time up to 20,000 h at 750 °C was performed. Identification of secondary phases was performed using electron diffraction on thin films using transmission electron microscopy and X-ray phase composition analysis. Long-term ageing depending on time and temperature showed that there are four secondary phases in Sanicro 25: M23C6, MX, NbCrN, σ-phase and Cu-rich. The precipitation and increase in the size of secondary phase particles during ageing results in a decrease in matrix saturation with alloying elements, which leads to a reduction in hardening by solid solution mechanism. These processes and effects result in changes in mechanical properties. The alloy overaging effect observed for the ageing temperature of 750 °C results in obtaining strength properties similar to those of the steel in the as-received condition.

1 Introduction
In the analysis of the operation of the national power system within the next several years, the following factors should be taken into account: European Union law, world and national climate policies, Poland’s energy security, ability to improve technical and economic indicators, development and availability of materials and operating technology. These factors and significant depreciation of the national power generation infrastructure must be taken into account in the development of the method for achieving the technical and economic objectives and meeting the increasingly stringent EU requirements focused on the implementation of the so-called Climate and Energy package concerning, but not limited to, the maximum greenhouse gas emission limits [1-4].

Despite the increase in harmful gas emission prices, which were to curb the development of the conventional power generation, there are no signs that the proportion of electricity generation sources could significantly change in the coming years. The electricity production in Poland is still based on coal and lignite. Due to having the national coal and lignite reserves, they are the primary source of energy. This results in adverse emission of significant amounts of pollutants into the atmosphere, such as carbon dioxide (CO2), sulphur dioxide (SO2), nitrogen oxide (NOx) and different types of dusts. These pollutants can be reduced, for example, by increasing steam parameters which affect the increase in boiler operation efficiency and reducing coal consumption.
The other important aspects are the optimisation of processes and system modules, strict control of the operation, an increase in thermal flexibility and introduction of the carbon capture technology [5-9].

The economic and environmental considerations and continuous improvement in the thermal efficiency of power units force the introduction of newer and newer materials for use in modern conventional power industry which includes, but are not limited to, the newly developed austenitic steels [10-12].

The 22Cr25NiWCoCu (Sanicro 25) steel was developed by AB Sandvik Material Technology in Sweden. This steel was produced under the European Therme AD700 program aimed at the development of a new type of power unit, and thereby the structural materials with a stable microstructure, high mechanical properties and significant resistance to corrosion and steam oxidation during the operation at 700 °C [13].

2 Materials and methods

The subject of the research was \( \phi 38 \times 8.8 \text{mm} \) samples taken from the superheater coils made of creep-resistant austenitic steel 22Cr25NiWCoCu (Sanicro 25). The chemical composition of the investigated steam superheater sample is presented in Table 1. The scope of the research included the investigations of both the microstructure and mechanical properties of Sanicro 25 after long-term ageing at 750 °C. The microstructure of the Sanicro 25 steel was observed with Inspect F scanning electron microscope (SEM) on conventionally prepared electrolytically, etching in the Mi19Fe reagent, metallographic microsections.

The identification of precipitates was carried out using the selected area electron diffraction through a transmission electron microscope Titan 80-300 (TEM) with thin foils, which were electrolytically thinned to perforation using a solution of 20% perchloric acid in ethanol at a temperature of approx. -30 °C and voltage of approx. 20 V. Long-term ageing is one of the most appropriate methods to simulate the operating conditions of materials used in the power sector. The investigations were carried out for material in the as-received state and aged for up to 20,000 h. Ageing at high-temperature levels for up to 20,000 h was to simulate changes in the microstructure and mechanical properties at a temperature similar to the long-term service temperature. The application of ageing temperature higher than the maximum expected service temperature was to accelerate the degradation processes in the test steel without changing the nature of the phenomenon.

| 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 discussion

In the as-received condition (figure 1), the Sanicro 25 steel had an austenitic matrix with a grain size of 7 according to the scale of ASTM E112-13 standards (which corresponds to the average diameter of 31.2 μm). Fine-grain structure of austenitic steels contributes to an increase in their strength and plastic properties and impact energy, but also have a positive impact on an increase in oxidation resistance compared to the coarse-grained steels. The improved oxidation resistance of fine-grained austenitic steel results from numerous and easy ways of diffusion, such as grain boundaries. However, during ageing/operation, grain boundaries as defects which allow faster diffusion compared to the grain interior affect the reduction in \( \sigma \)-phase precipitation incubation time. In the microstructure of the test steel in the solution-treated condition, primary NbX and NbCrN precipitates (Z phase) are observed.

Longer ageing times result in the occurrence of the particle with different morphology, i.e. \( \sigma \)-phase, at the grain boundary. The amount and size of precipitates of this phase increase with the extension of the ageing time, which results from high susceptibility of the \( \sigma \)-phase to coagulation. At a higher ageing temperature, 750 °C, the relative amount and size of the \( \sigma \)-phase precipitates (figure 2) at
the grain boundaries are greater than those in the material aged at 700 °C. Like M$_2$C$_6$ carbides, the σ-phase is precipitated at the grain boundaries, and the privileged site is the interface of three-grain boundaries.

Figure 1. The microstructure of Sanicro 25 in the as-received condition, SEM

In addition to ε-Cu precipitates, the presence of finely-dispersed secondary Z-phase precipitates at 750 °C was revealed too. The finely-dispersed, or worm-shaped, the form of these precipitates and their relatively high stability make both single particles and clusters of these precipitates effectively inhibit and limit the dislocation movement, and thus contribute to precipitation hardening of the alloy. The interaction between a precipitate and dislocation may take place by the Orowan mechanism or cutting through a particle. The precipitation hardening is assumed to be mainly related to interaction by the Orowan mechanism because secondary precipitates in austenitic steels are too hard to be cut by dislocations [14,15].

Figure 2. σ-phase precipitate in Sanicro 25 steel after 20,000 h ageing at 750 °C: a) bright field, b) resolved diffraction pattern from the area in figure a, c) EDS spectrum
In addition to the $\varepsilon_\text{Cu}$ phase, Laves phase and secondary Z-phase particle precipitates, the existence of composite complexes of precipitates: primary Z-phase precipitates – Laves phase – $\text{M}_2\text{C}_6$ carbide precipitates, where the $\text{M}_2\text{C}_6$ particles and the Laves phase nucleate heterogeneously on the primary Z-phase precipitate, were revealed within the grains in the test alloy after 20,000 h ageing at 750 °C (figure 3).

Figure 3. The microstructure of Sanicro 25 steel after ageing at 750 °C for 20,000 h, SEM

Changes in microstructure of the steel affected the reduction in its mechanical properties. In the initial period of ageing at 750 °C, the strength properties are increased, and plastic properties are decreased.

The effect of ageing time at 750 °C on the tensile strength, yield strength and elongation determined at room temperature is shown in figures 4-6. The increase in tensile strength after 5,000 h ageing can be seen, which was about 9% of the properties as-received. After this time, a slight decrease in tensile strength was observed, which is about 5% after ageing of 20,000 h. A similar tendency was observed for the yield strength, which initially increases by approx. 11% for 5,000 h of ageing, and then slightly decreases (by about 6%) for the material aged 20,000 h. This trend is very similar to the determined hardness values and takes place as a result of the appearance of a large number of precipitates of different morphology. The elongation, on the other hand, decreased by about 60% after the 20,000 h ageing compared to the elongation of the material as-received. This decrease is due to the coagulation and spheroidization of the precipitates and the processes of twins decay. After 20,000 h of ageing, the tensile strength, yield strength values are still above the minimum [16], while the plasticity of the tested steel has dropped by half.

The precipitation and increase in the size of secondary phase particles during ageing results in a decrease in matrix saturation with alloying elements, which points to a reduction in hardening by solid solution mechanism. Also, changes in the dislocation substructure, i.e. dynamic recovery and recrystallisation processes, loss of twins and formation and increase in width of the precipitation-free zone, were visible in the test steel. These processes and effects result in changes in mechanical properties. The rate of the changes in the microstructure of the test steel depends on the ageing temperature. At a higher temperature, the steel microstructure degradation was more advanced, which resulted in a gradual reduction in proof stress and tensile strength determined at room temperature.
Figure 4. Change in tensile strength of Sanicro 25 steel after long-term ageing at 750 °C

Figure 5. Change in yield strength of Sanicro 25 steel after long-term ageing at 750 °C

Figure 6. Change in elongation of Sanicro 25 steel after long-term ageing at 750 °C

4 Conclusion
Due to its good mechanical properties, including high creep strength with simultaneously high resistance to high-temperature corrosion and economically well-balanced chemical composition, the Sanicro 25 steel is an alternative to creep- and heat-resistant nickel alloys which are currently used in the power industry for components of the pressure equipment designed to work at elevated temperature.
The alloy overageing effect observed for the ageing temperature of 750 °C results in obtaining strength properties similar to those of the steel in the as-received condition.

The metallographic examinations carried out for Sanicro 25 steel in the as-received condition and after ageing have shown that ageing of up to 20,000 h at 750 °C leads to the precipitation of copper-rich (ε_Cu) particles, Laves phase, σ-phase and secondary Z phase precipitates in the matrix, while at the grain boundaries the occurrence of M23C6 and Laves phases.

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