Analysis of the relationship between changes in mechanical properties and precipitation in SUPER 304H steel during its exposure

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Abstract. Aim of the article is to provide properties comparison between initial state and two thermally exposed states of creep resistant steel SUPER 304H by usage of conventional and miniaturised tensile test specimens. Tests were performed at room temperature. Thermally exposed material was aged by 15 and 30 thousand hours at 675°C. This exposition which simulated accelerated operation exposition caused precipitation of intermetallic phases which affect mechanical properties like ultimate strength and elongation. The performed tests showed a decrease in elongation and ultimate strength between the first exposed state and initial state followed by partial increase of both tested values for the second exposed state. Sigma phase precipitation was confirmed for the exposed samples. The presence of the sigma phase also led to a change in the fracture morphology from full ductile (initial state) to combined ductile with the presence of brittle particle cleavage (exposed states). A comparison of the tests performed on classical and miniaturized test samples proved the possibilities of using miniaturized samples both for the basic material and for the exposed ones.

1 Introduction
One of the main efforts of the world's coal energy sector is to improve its efficiency. A possible way to reach this goal, which also means a reduction in the ecological burden of nature, is to increase the working parameters of steam. However, together with this increase, the application of appropriate materials is necessary. SUPER 304H steel is one of the suitable steels for heat exchange surfaces of supercritical blocks [1].

SUPER 304H steel, as shown for example in articles [2-4], shows significant microstructural changes during its temperature exposure, which affect its mechanical properties. It affects the ultimate strength and yield strength limits and the decrease in absorbed energy values. Current methods for testing mechanical properties using a minimum amount of material are increasingly being developed, where these changes could lead to skewed results. This paper evaluates mechanical and microstructural parameters of thermally exposed steel SUPER 304H by performed tensile tests at conventional and miniaturized tensile samples in combination with microscopy evaluations.
2 Methodology

The methodology chapter give to possibility of tests and examination repetition. Methodology is divided into two separated subchapters based on laboratory testing methods.

The experimental material used for evaluation in this paper is austenitic creep-resistant complex alloy steel SUPER 304H. The used states of this steel were the initial state and then the temperature-exposed states at a temperature of 675 °C for 15 and 30 thousand hours in laboratory furnaces.

2.1 Tensile testing and hardness measurement

Two types of test specimens were used for testing, namely classic short tensile specimens of cylindrical cross-section with a diameter of 5 mm clamped in threaded heads and miniaturized tensile specimens of rectangular cross-section. Drawing of miniaturized specimen is evident in the Figure 1. The miniaturized specimens were clamped pneumatically over flat jaws. In both cases, a constant crosshead feed rate of 0.5 mm / min was used for testing. The measured length was 4 mm for miniaturized tensile samples and 25 mm for conventional tensile samples. At least three samples were measured for each measured group of samples.

![Figure 1. Dimension of used miniaturized tensile test sample.](image)

Hardness maps were measured on samples prepared for microstructure observation. The load HV1 was used for conventional tensile samples and HV0.1 for miniaturized specimens due to their thickness. In all cases, three rows were measured with the smallest possible step from the fracture surface to the clamping head of the tensile specimen.

2.2 Microstructure analysis

Light and electron microscopy was used for microstructural evaluation. Samples for microstructural evaluation were hot-pressed and subsequently ground and polished. Two methods of etching were used for observation, namely selective color etching electrolytically in 10% NaOH solution (3V DC, 6s) and etching of a surface mixture of acids called glyceregia [5].

Optical microscopy was focused on the evaluation of the microstructure in the area of the final refraction of tensile samples with a focus on precipitates such as sigma phase. Furthermore, the development of fracture with respect to particles and grain of the material was evaluated. Scanning electron microscopy was focused on the observation of fracture surfaces on tensile samples in combination with the detection of backscattered electrons together with the performance of chemical composition analyzes using energy dispersive spectroscopy (EDS). The images used for this paper are a combination of the observed fracture surface and the chemical composition map, where chrome is shown in green, iron in red and niobium in darker blue.

3 Measurement and observations results

3.1 Tensile testing

Tensile tests were performed in order to compare the behavior of the material in tests of both conventional and miniaturized tensile samples. A comparison of representative tensile diagrams for each group of tested samples is shown in Figure 2, where MTT denotes miniaturized tensile samples and TT conventional tensile samples. Marking 0 corresponds to the initial material, 1 to the exposed state for 15,000 hours and marking 2 to the exposed state for 30,000 hours.
From the comparison of the measurements, it is evident that with the increasing thermal exposure of the material, its ductility decreases, which is in accordance with the ongoing precipitation processes inside the material. For miniaturized samples, the ductility decreases from 52.4% for the initial state over 41.3% to 38.7% for the exposed state after 30,000 hours. A similar trend can be observed for conventional tensile samples where the ductility decreases from 54.5% for the initial state to 32.6% for the material exposed for 30,000 hours. Furthermore, it is possible to observe a decrease for the ultimate strength from the initial state for the exposed state after 15,000 hours which is followed by a gradual increase for the exposed material after 30,000 hours. For miniaturized samples, this change is from an initial value of 615 MPa through 599 MPa to a final value of 607 MPa. In the case of conventional tensile samples, the trend is the same, from 761 MPa through 707 MPa to the value of 736 MPa. The overall trend of changes documented by means of conventional and miniaturized specimens is in both cases the same with an offset of approximately 130 MPa.

**Figure 2.** Comparison of SUPER 304H TT and MTT tensile diagrams for base and exposed state. The performed measurements of hardness maps, both for classical samples and for miniaturized samples, are summarized in Figures 3a to 3d. In all cases, it is demonstrable that the deformation of the specimen body and thus its strengthening occurs evenly over the test part. Furthermore, it can be stated that the reinforcement of the material is corresponding both for the initial state between the classical sample (from 375 to 186 HV1) and miniaturized samples (from 396 to 169 HV0.1). The exposed material after 15,000 hours also shows the same hardening manifested on the hardness which has a measured range for conventional samples from 417 to 202 HV1 and for miniaturized samples from 416 to 197 HV0.1.

**Figure 3a.** Hardness measurement map of base material, conventional tensile test sample.

**Figure 3b.** Microhardness measurement map of base material, miniaturised tensile test sample.

**Figure 3c.** Hardness measurement map of exposed material, conventional tensile test sample.

**Figure 3d.** Microhardness measurement map of exposed material, miniaturised tensile test sample.
3.2 Microstructure analysis

To verify the presence of the sigma phase on the fracture surfaces, the chemical composition was measured by point analysis using EDS. The marked sites of analysis were selected based on the assumption that the sigma phase is a brittle intermetallic phase [6]. The measurement sites are shown in Figure 4 and the results of the weight percentages are given in Table 1. The measured chemical composition corresponds to the sigma phase composition in this steel type and the results given in [2,3,4,6].

Table 1. Measured chemical composition (wt. %).

|       | Spectrum 2 | Spectrum 3 |
|-------|------------|------------|
| Si    | 0.57       | -          |
| P     | 0.57       | -          |
| Cr    | 37.61      | 39.38      |
| Fe    | 55.92      | 53.48      |
| Ni    | 3.69       | 1.89       |
| Cu    | -          | 5.25       |
| Mo    | 1.64       | -          |

Figure 4. EDS measurement position for sigma phase confirmation.

The following two figures (Figures 5a and 5b) document the fracture surfaces prepared as a metallographic sample using subsequent surface etching and color etching to highlight the sigma phase. In both cases, grain deformation and the presence of the sigma phase in the microstructure are evident. For both types of samples (exposed for 15,000 hours), a gradual development of failure is observable, combined with the predominant transcrystalline propagation of the fracture using weakened sigma phase sites.

Figure 5a. Microstructure of fracture surface, conventional tensile sample, expose state.

Figure 5b. Microstructure of fracture surface, miniaturized tensile sample, expose state.

The following figures (Figures 6a to 6d) document the fracture areas together with the chemical composition maps. Chromium-rich areas are shown in green. Iron-rich areas are shown in red. Niobium-rich areas are shown in dark blue. The areas shown only in grayscale of the original scanning electron microscopy image are places where, due to the fragmentation of the fracture surface, there was a shadow of secondary electron detection for EDS analysis. The fracture morphology for the initial state without exposure is shown in Figure 6a for the conventional sample and in Figure 6b the miniaturized sample. In both cases, the fracture surface
can be assessed as fully ductile with a pit morphology. The images also show the presence of niobium-rich regions, which represent niobium carbonitrides. The fracture surfaces of the conventional sample (Figure 6c) and the miniaturized sample (Figure 6d) for samples after temperature exposure for 15,000 hours also show the same morphology. In both cases, it is possible to observe a combination of ductile fracture of the material and brittle cracking of particles on the fracture surface, which have been identified as sigma phases. The sigma phase is highlighted in these two images due to the higher chromium content compared to the steel matrix. Furthermore, as with samples without temperature exposure, it is also possible to observe niobium-rich areas highlighted in dark blue.

![Figure 6a. Fracture surface of conventional tensile test sample of base material combined with EDS chemical maps.](image)

![Figure 6b. Fracture surface of miniaturized tensile test sample of base material combined with EDS chemical maps.](image)

![Figure 6c. Fracture surface of conventional tensile test sample of exposed material combined with EDS chemical maps.](image)

![Figure 6d. Fracture surface of miniaturized tensile test sample of exposed material combined with EDS chemical maps.](image)

4 Discussion

Laboratory exposition at a constant temperature of 675 °C for 15 and 30 thousand hours was used to accelerate the achievement of microstructural changes that take place in SUPER 304H steel during its operational exposure. Microstructural changes are described, for example, in [2-4]. In general, it can be stated that chromium carbides precipitate and subsequently the brittle sigma intermetallic phase during thermal exposition. Confirmation of these microstructural changes was performed by chemical composition EDS analysis of exposed material (Figure 4 and Table 1).

The results from the evaluation of the initial and exposed material showed a very good conformity from the point of view of the morphology of the fracture surface. For the origin material, the
ductile pit morphology of fractures on tensile samples was observed for both conventional and miniaturized samples. The exposed samples also showed the same fracture morphology by a combination of ductile disruption and cleavage facets through the sigma phase. From the point of view of measuring hardness maps, the conformity between conventional and miniaturized samples for the basic and exposed state was also proved. From the point of view of the materials parameters inside the samples, a methodical conformity is proved, which confirms the possibility of using miniaturized samples for tensile tests of the basic and exposed state of SUPER 304H steel. The trend of changes in mechanical properties is also similar for both conventional and miniaturized samples. The only documented difference was in the direct measured values obtained from the tensile tests. In the measured values summarized in Chapter 3.1, the miniaturized specimens show lower overall values, both in terms of yield strength and elongation. The reason for this difference does not stem from differences in the microstructure, at most the results could be influenced by the number of grains with respect to the fracture surface. The next possible reason can be in the difference of initial (engineering) strain rate for TT and MTT samples.

4 Conclusions
The main goal of the performed analyzes was to compare the difference in testing results using conventional and miniaturized tensile samples. It was a matter of creating data on whether it is possible to apply test methods to superheater tubes made of SUPER 304H not only in the initial state but also in the degraded or operated material, which will involve microstructural changes.

The performed tests showed a decrease in elongation and ultimate strength during first half of exposition followed by partial increase of both tested values for the second half of exposition. The presence of the sigma phase led to a change in the fracture morphology. In general documented changes are same in both case conventional and miniaturized samples. These assumptions give the possibilities of using miniaturized samples both for the initial material and for the exposed ones. Future experimental work will deal with comparison of tensile samples with same strain rate because of the initial strain rate for MTT samples with gauge length 4 mm is different in comparison with TT samples with gauge length 25 mm.

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