THE EFFECT OF SIGMA-PHASE FORMATION ON LONG-TERM DURABILITY OF SUPER 304H STEEL

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Abstract

This work presents results of the analysis of phases formed in a SUPER 304H steel during a medium-term static isothermal ageing (675 °C/15000 h). The investigations of the precipitates were especially focused on the occurrence of sigma-phase because its formation leads to the serious embrittlement.

The evaluation and distribution of brittle sigma-phase were determined on macroscopic level by using light microscopy/colour etching. The microstructure was also investigated on microscopic level by scanning electron microscopes Tescan Lyra 3 and JEOL JSM 5410 equipped by electron backscatter diffraction unit and by transmission electron microscope Jeol 2100F. This work also investigates the effect of sigma-phase formation on the impact strength of an aged state of SUPER 304H steel. For comparison reasons the microstructure and the mechanical properties of the initial as-received) state were also investigated. It was found that the formation of brittle sigma-phase in the aged and therefore degraded microstructure led to the significant decrease of the impact strength. The influence of brittle sigma-phase on long-term durability of the degraded steel regarding its insufficient impact strength is discussed.

Keywords: Austenitic steel, medium-term ageing, SUPER 304H, sigma-phase, impact strength

1. INTRODUCTION

1.1. Description of material and application of material

SUPER 304H is fully austenitic steel used for construction of super heaters of ultra-supercritical power plants [1]. Ratio of base alloying elements 18/9 (Cr Ni) is used. For an improving of creep resistant properties nitrogen, niobium and copper are used up to 0.12 (N) 0.6 (Nb) 3.5 (Cu) mass percent [2]. It should be note that average in-service conditions of steam are temperature of 650 °C and pressure of about 25 MPa.

2. EXPERIMENTAL PART

2.1. Initial (as-received) state

Austenitic structure of initial state without PWHT (post welding heat treatment) is shown at the first figure in **Fig. 1**. There are no particles at grain boundaries. In line formation with the same orientation as tube axis the niobium carbonitrides precipitated. Some of niobium precipitates have dimension about 20 μm (**Fig. 1**). In initial state is no particles which can be identified as sigma-phase were observed.

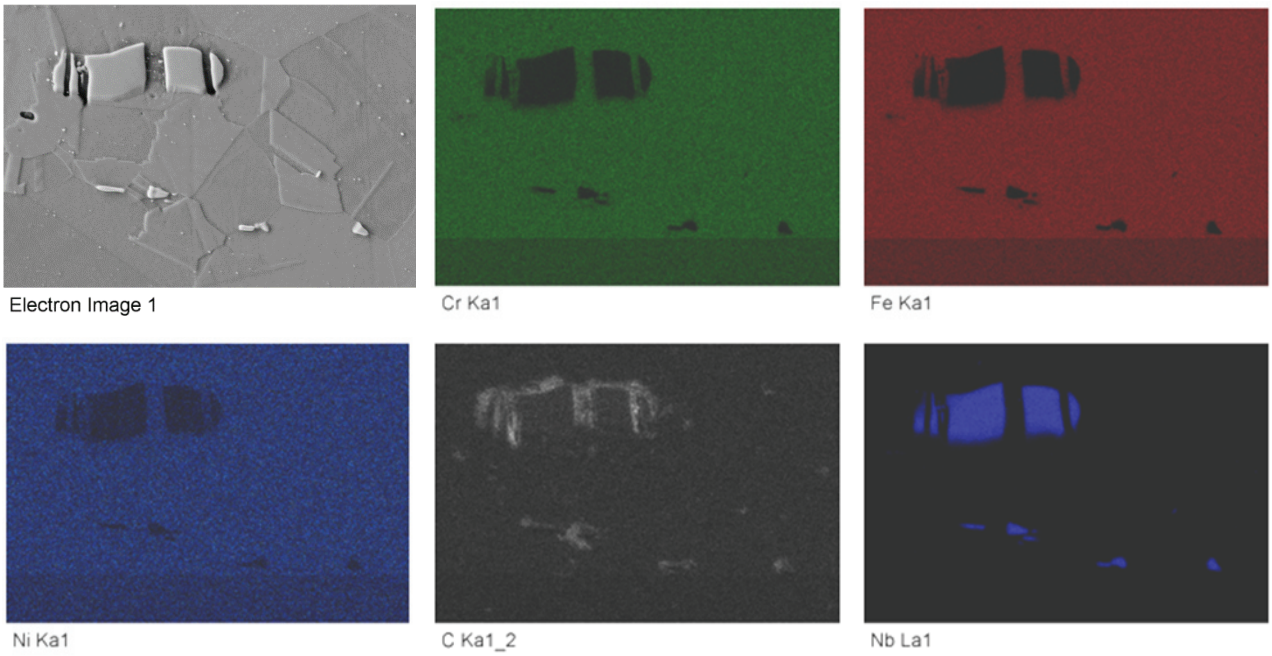

Fig. 1 Maps of chemical composition SEM/EDS - initial state

2.2. State after 15 000 hours of ageing at 675°C

After 15 000 hours of isothermal ageing (675 °C) significant changes in microstructure occur. As shown in **Fig. 2** there are several new types of precipitates. At the grain boundaries the chromium carbides and niobium carbonitrides precipitated. The niobium carbonitrides which have dimensions up to 3 μm precipitated inside the grains. The last group of precipitates can be identifying like sigma-phase with maximal dimension of about 6.5 μm.

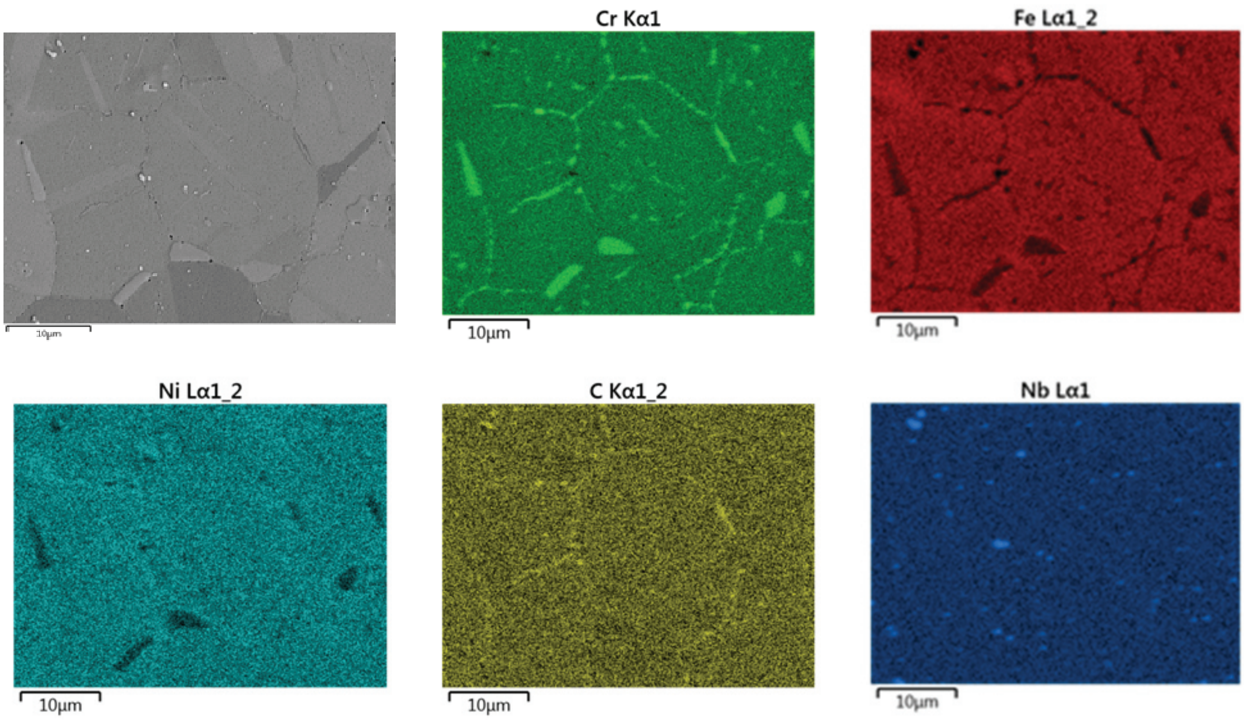

Fig. 2 Maps of chemical composition SEM/EDS - state after 15 000 h of ageing [3]

For identification of sigma-phase particles transmission electron microscopy was used. **Fig. 3** shows chemical composition maps made by EDS-detector at thin foil. There (**Fig. 3**) are three elliptic particles which can be possible sigma-phase. The length of these particles is around 2.5 μm.

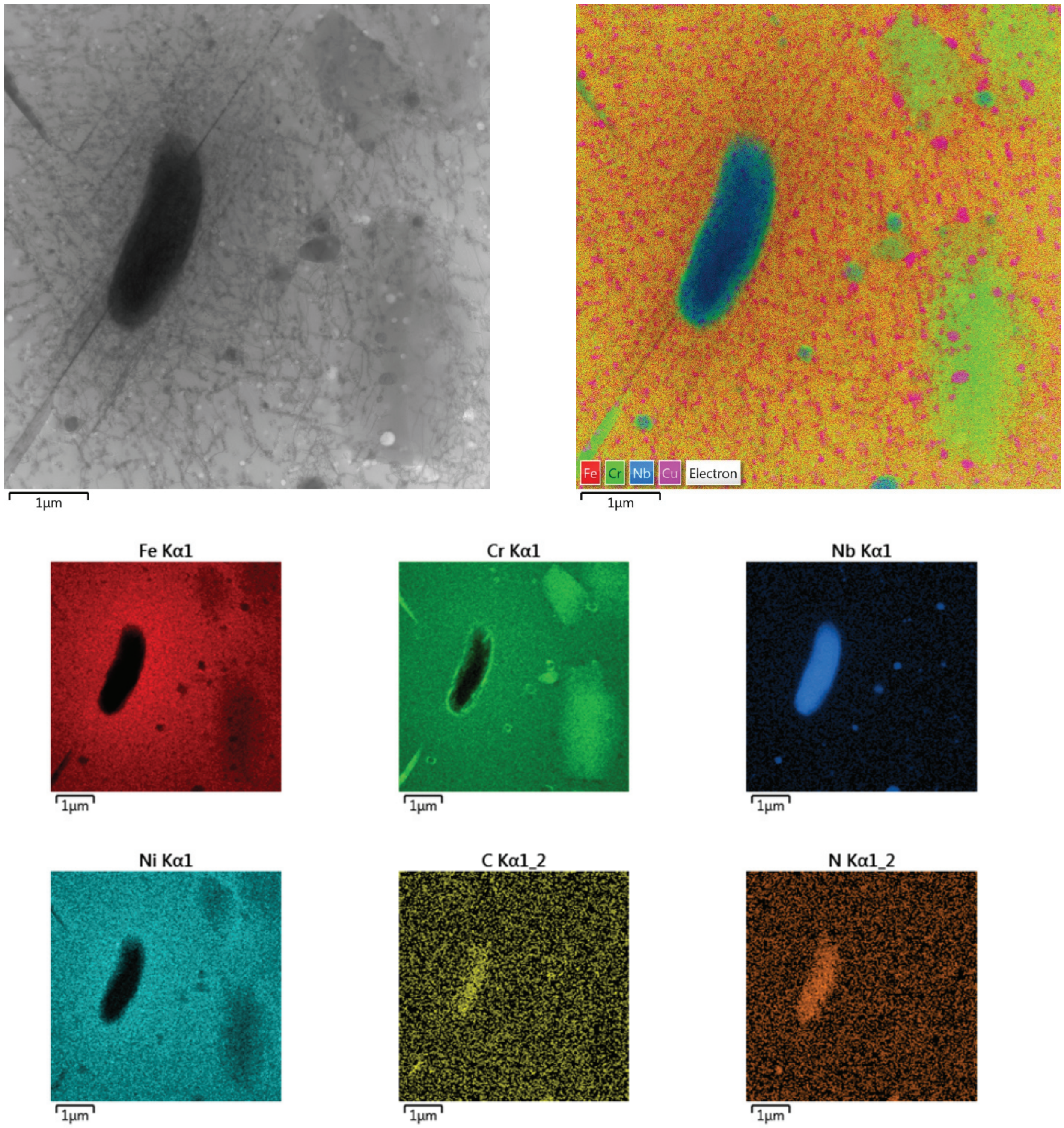

Fig. 3 Maps of chemical composition TEM/EDS - state after 15 000 h of ageing [4]

Identification of particles by using chemical composition is shown in **Fig. 4**. In the case of sigma-phase the nominal chemical composition is shown at **Fig. 4**, too.

Lines obtained from transmission diffraction were compared whit theoretical model for sigma-phase. Conformity with the theoretical model is at **Fig. 5b**.

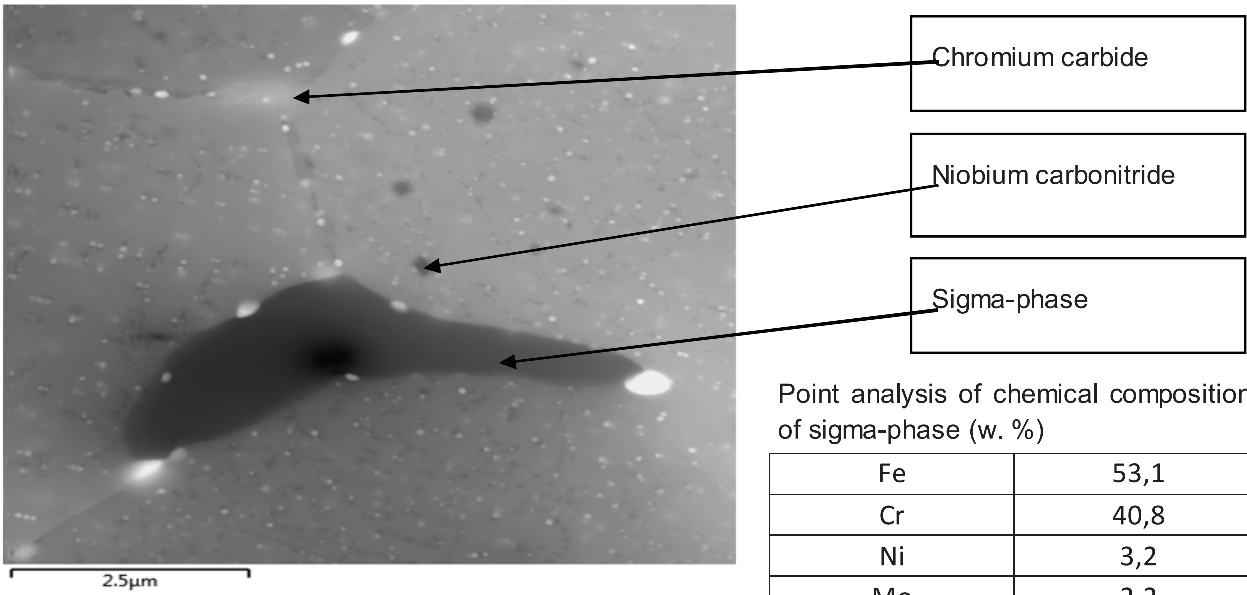

Fig. 4 Identification of particles and chemical composition of sigma-phase - state after 15 000 hours of ageing [3]

Point analysis of chemical composition of sigma-phase (w. %)

Fe	53,1
Cr	40,8
Ni	3,2
Mo	2,2
Si	0,8

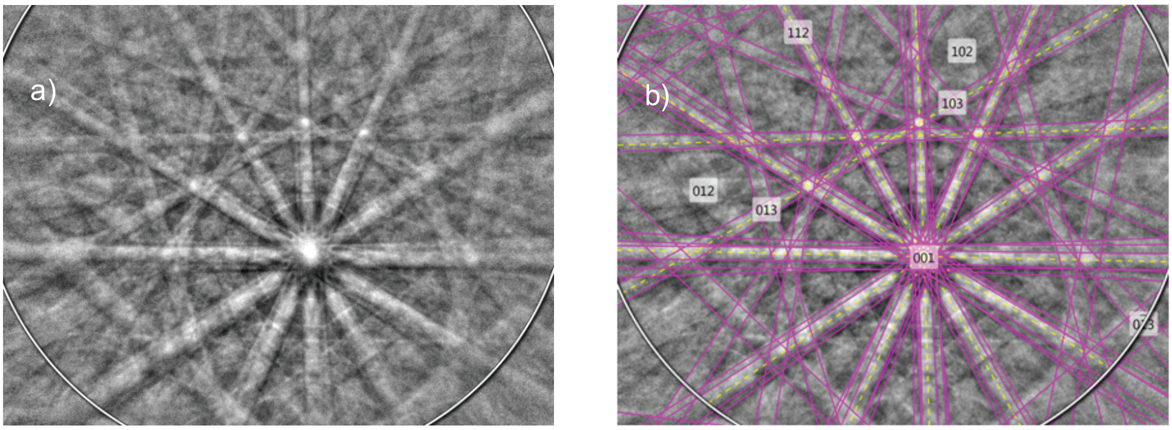

Fig. 5 EBSD lines obtained in the analysis of sigma phase in the steel Super 304H a) measured lines b) conformity with the theoretical model [3]

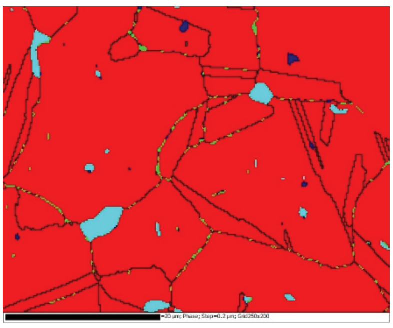

Fig. 6 EBSD analysis [3]

Phase map is shown in [1]. Identification of phases:

- Red - Austenitic matrix
- Green - Chromium carbide
- Light blue -sigma phase

Phase map shown that sigma-phase precipitates are situated at grain boundaries, respectively inside grain.

2.3. State after 20 000 hours of ageing

Changes between states after 15 000 and 20 000 hours of ageing include an increase of size of sigma-phase. Sigma-phase has dimension about 10 µm (**Fig. 7**) which can lead to significant decreasing of the impact strength.

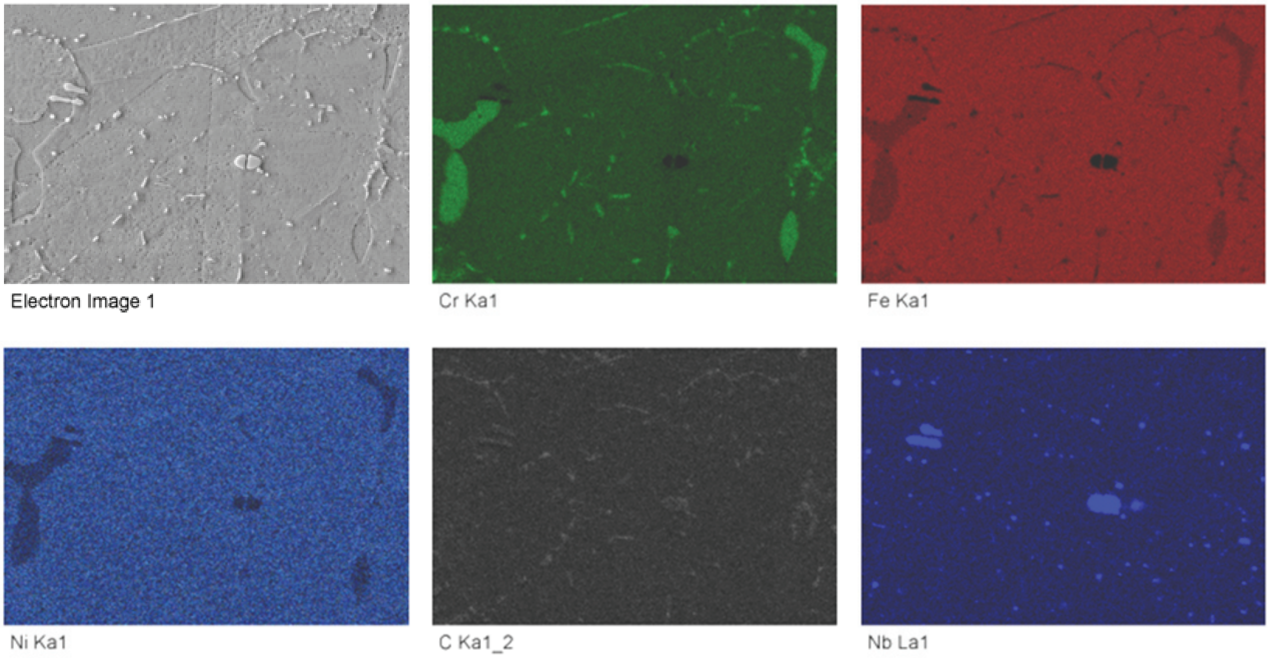

Fig. 7 Maps of chemical composition SEM/EDS - state after 20 000 h of ageing

2.4. Possible approach to quantification amount of sigma-phase in microstructure

It is possible to say that amount of Sigma-phase in microstructure lead to decreasing of the impact strength. Possible approach for quantification of sigma-phase in quite lower magnification would be using of light-microscopy/color etching (LM). Comparison of the microstructure from LM and the microstructure from SEM is shown in **Fig. 8** and **Fig. 9**. White particles in **Fig. 8** are sigma-phases. These white particles have sufficient contrast in comparison with matrix. Thus, image analysis for quantification of amount of sigma-phase will be possible to use.

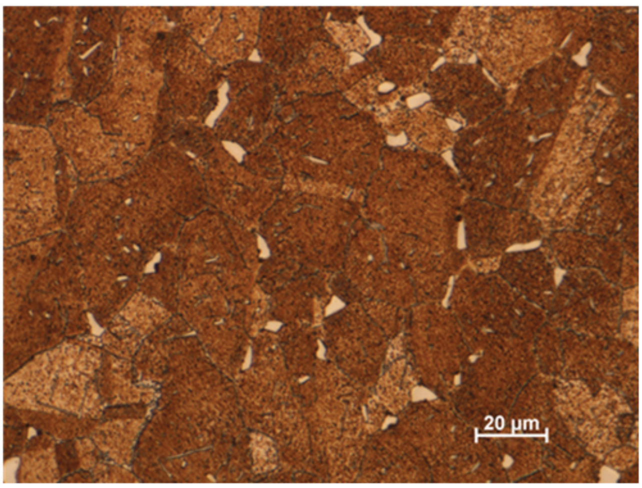

Fig. 8 Microstructure after color etching (sigma-phase is white) [4]

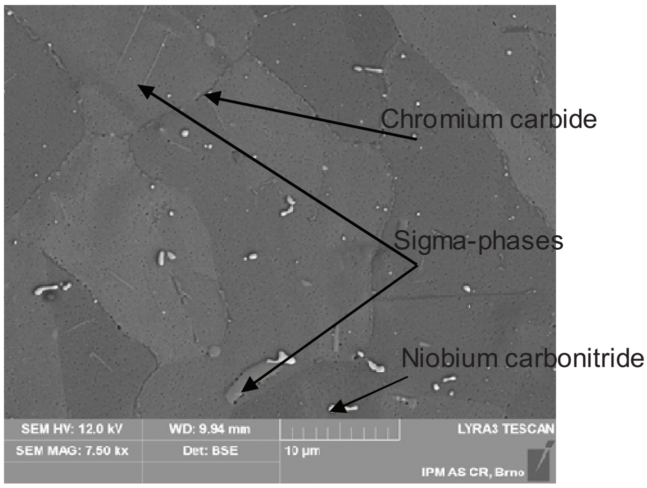

Fig. 9 Microstructure with marked phases for comparison with **Fig. 8** [4]

3. CONCLUSIONS

Initial state

The particles observed in the microstructure of initial state were niobium carbonitride and in the less amount chromium carbide. Two different shapes of niobium particles were observed:

- Separated niobium particles with the size up to 20 µm (**Fig. 1**)
- Niobium particles with linear orientation and the size up to 5 µm (**Fig. 1**)

Chromium carbides were precipitated at intersection of grain boundaries.

No sigma-phase was observed.

The impact strength of initial state was 109.4 ±4.4 J/cm^2 (average value from 6 measurement)

State after 15 000 hours of ageing

Particles observed after 15 000 of ageing were niobium carbonitride, chromium carbide and sigma-phase. Niobium particles were observed inside grain and had dimension up to 3 µm (**Fig. 2**). Chromium carbides were located at grain boundaries with dimension of about 0.4 µm. sigma-phase precipitated in two different shapes (**Fig. 2**):

- Round shape with dimension about 3 µm (max. up to 6.5 µm)
- Lamellar with thickness about 1 µm, length up to 5 µm

State after 20 000 hours of ageing

Particles observed after 20 000 hours of ageing were niobium carbonitride, chromium carbide and sigma-phase. No changes for niobium particles and chromium carbides were observed. Dimension of sigma-phase precipitated at intersection of grain boundaries increased to max. dimension 10 µm.

The impact strength of state after 20 000 hours of ageing was 28.2 ± 0.6 J/cm^2 (average value from 3 measurement)

It is possible to say that the sigma-phase in the microstructure precipitate and grows during ageing. It lead to an embrittlement of SUPER 304H steel. Precipitation of sigma-phase at intersection of grain boundaries and a decrease in the impact strength of steel SUPER 304H can lead to serious problems during lifetime of super heaters.

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