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The Effect of σ-Phase Formation on Long-Term Durability of Welding Joints in SUPER 304H Steels

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Article presents results on the analysis of secondary phases formed in the medium-term static isothermal ageing welding joints of a SUPER 304H (675 °C/2 × 10^4 h). The investigations of the precipitates were focused on the occurrence of σ-phase because its formation leads to significant deterioration of mechanical properties. The microstructure was investigated on microscopic level by scanning/transmission electron microscopy. The distribution and quantification of brittle σ-phase were studied on macroscopic level by color etching method using light optical microscopy. The effect of microstructural changes (σ-phase formation) on the impact strength of an aged base material was investigated. For comparison impact tests on received state material were also performed. The results showed that long-term ageing led to the significant reduction of impact strength as a result of the formation of the σ-phase. It was found that the σ-phase distribution is influenced by welding process. The influence of brittle σ-phase on long-term durability of the degraded steel regarding its insufficient impact strength has been discussed.

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1. Introduction

There is a worldwide tendency to improve efficiency of coal fired power-units. The economic analysis is reported in [1]. Difference in efficiency between subcritical and supercritical power-units should be up to 12%. In numbers it means for 700 MW power unit reducing of the cost of coal by 16.4 M$/year. One of the most thermal exposed components is the superheater. In literature the new steel type SUPER 304H is recommended for the superheaters [1, 2]. It is generally accepted that long-term service of stainless steels leads to the degradation of microstructure thus to the change of mechanical properties. Main reason of microstructure degradation in stainless steels after long-term service is formation of the σ-phase. It was found that σ-phase precipitates inhomogeneously at temperatures between 600 and 1000 °C [3, 4]. The studies of precipitation behavior found that σ-phase precipitates in particular at triple points between δ-ferrite, incoherent twin boundaries and inclusions [5] or δ-ferrite/austenite interphase boundaries [6]. Nevertheless after long ageing time at high temperature σ-phase can precipitate on coherent twins and intragranular inclusions or in austenite [7, 8]. Long term performance can be predicted by acquiring new knowledge. Therefore, the aim of the present work is to investigate the effect of long-term ageing on microstructure which could significantly influence ductility of both base material and heat affected zone.

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2. Experimental material and procedures

Experimental material SUPER 304H is a fully austenitic, creep-resistant, alloyed steel. The ratio of base alloying elements Cr/Ni is 18/9. In addition, the steel contains 0.4% Nb, 1% N and 3.0% Cu. The SUPER 304H tubes were welded by automated orbital welding technology by multilayer weld with three layers denoted as a root, central and crown layer. In present study Thermanit 304HCu was used as welding material. Thermanit 304HCu has a similar chemical composition as welded steel. The chemical composition can be listed in [9].

The welded tubes were annealed at 675 °C for 2×10^4 h in order to obtain degraded experimental material. Microstructure was investigated in the base material and in the heat affected zone (HAZ) in selected layers (root, central, and crown) by light microscopy and also by scanning electron microscope (SEM) using a JEOL JSM 7600F equipped by EDX. The amount of σ-phase was quantified by image analysis of microstructure using color etching Beraha II etchant. For quantification of objects and determination area fraction Nis Elements software was used. Transmission electron microscope (TEM) foils were prepared by focused ion beam (FIB) technique using SEM Tescan Lyra 3 and observed by TEM microscope JEOL 2100F. Impact strength of as-received and aged base material was tested at room temperature.

3. Experimental results and discussion

Figure 1a shows microstructure of initial state in the crown layer of HAZ. Analysis of microstructure of unaged crown layer showed that the mean grain size area in the crown layer in HAZ was about 193 μm^2 and the σ-phase was not detected for initial state. Long-term isothermal ageing caused no significant coarsening of austenitic grains (Table I), however led to the formation of brittle σ-phase (Fig. 1(right)). A detailed investigation of the microstructure showed that σ-phase was predominantly situated at triple points and also along boundaries of austenitic grains. In the structure of aged based material approximately 2.3% of σ-phase was present. Slightly higher values of the σ-phase concentration and mean grain size were derived in HAZ of crown layer (Table I). In this area σ-phase was also predominantly formed at triple points and grain boundaries (Fig. 2(left)). The largest changes in microstructure were observed in central and root layers of HAZ (Fig. 2(right)). Results demonstrate that these areas contain significantly larger grains and reduced portion of σ-phase in comparison with based material and crown layer after long-term isothermal ageing (Table I).

TABLE I

Microstructure characteristics in base material and welding joints zones.

	Zone	Objects	Portion of area [%]	Grain size [G]	Grain size [µm^2]
	as-received state	0	0	9	267
aged	base material	54	2.265	9	234
	crown layer	67	2.734	9.5	118
	middle layer	25	1.002	6.5	1830
	root layer	13	0.489	5	3924

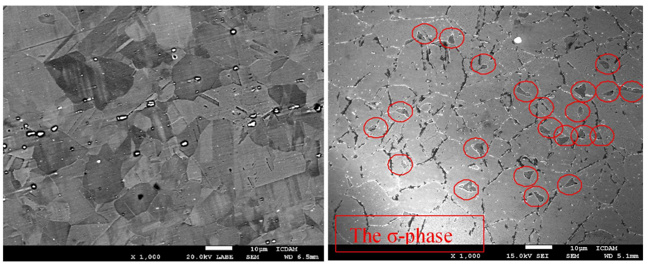

Fig. 1. Microstructure of as-received state in crown layer (left) and (right) formation of σ phase after ageing 2×10^4 h.

The cross-section of σ-phase obtained by FIB technique used for TEM-foils preparation enabled more detailed investigation of σ-phase situated at boundaries. Figure 3(left) shows the distribution of Cr (green color), Nb (dark blue) and Cu (magenta) around grain boundaries. It can be seen that colonies of relatively fine σ-phases (mean size ≈300 nm) were formed along grain boundaries which is covered by large Cr and Nb carbides. It was also observed that Cu particles (denoted B) are located very often at interphase boundaries between σ-phase and matrix (Fig. 3(right)). In the σ-phase interior (denoted A) there were observed Nb carbides (denoted C), Cu particles (donated B) sitting on the σ-phase edges (Fig. 3).

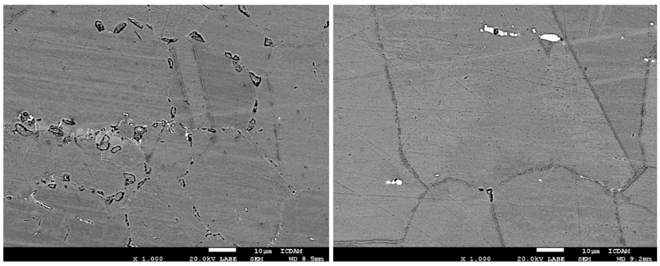

Fig. 2. Distribution of σ-phase in the crown layer a and in the root layer (right).

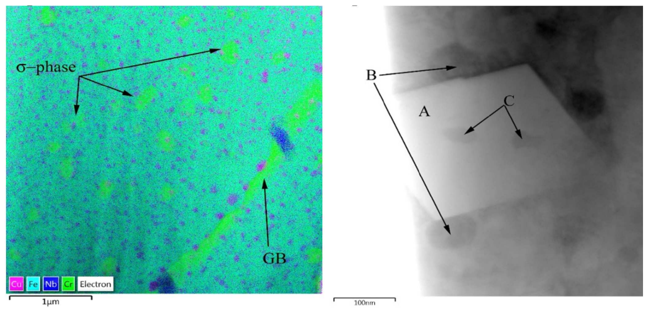

Fig. 3. a Distribution of elements around austenitic grain boundary (left) and TEM image of σ-phase cross-section (right).

Difference in grain size across welding joint layers is caused by absorbed heat energy during welding process. It means that the root layer was exposed longer to higher temperatures than the last crown layer because it was repetitively heated by additional welding passes. Coarsening of grains in root layer led to the significant reduction of σ-phase formation. This result indicates that σ-phase is predominantly formed at triple points and grain boundaries due to higher Cr content and defect concentration [7, 8]. It was proposed that σ-phase is formed from $M_{23}C_6$ by carbon elimination. It was also observed that σ-phase formation occurred independently of $M_{23}C_6$ [8]. In alloys without $M_{23}C_6$ carbides there will be slow precipitation.

Steel SUPER 304H is alloyed with ≈3% Cu. Addition of copper may lead to increase of mechanical properties of steel [10, 11]. Recently it was suggested that Cu particles cannot only increase mechanical properties but may also pin the motion of σ-phase/austenite interfaces.

The impact strength decreases from 109.4 ± 0.4 J/cm^2 measured in as-received base material to value about 28.2 ± 0.6 J/cm^2 determined in aged state. It can be suggested that higher contents of σ-phase in the crown layer and significantly larger grain size in root and central layers probably cause further reduction of impact strength. Recently, it was reported that significant decrease in impact energy may be expected already after short-time annealing (for about 10^3 h) at 650 and 700 °C [12, 13].

On the basis of microstructure results it can be suggested that a drop of impact strength after long-term

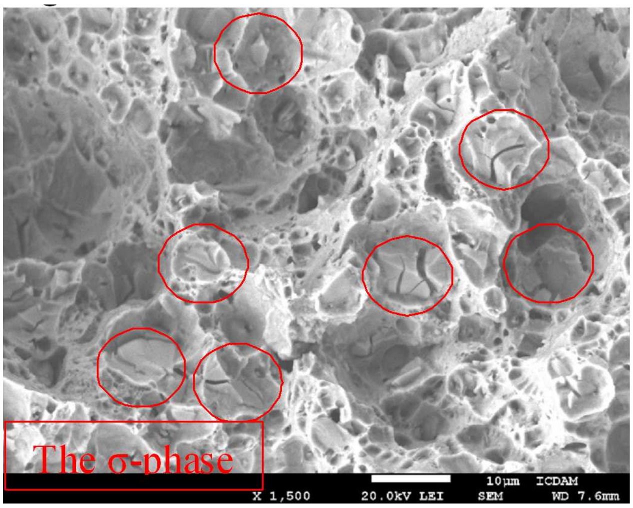

Fig. 4. Fracture surface of as-received state after long-term ageing.

ageing is significantly influenced by σ-phase formation. This suggestion could be supported by analysis of fracture surfaces obtained from impact strength tests. The aged state exhibited the mixture of transgranular ductile fracture of matrix and intragranular fracture along σ-phase (Fig. 4).

4. Conclusion

Long-term ageing of SUPER 304H tube led to σ-phase formation which was predominantly situated at triple points and austenitic grain boundaries. The coarsening of austenitic grain in HAZ of root layer considerably reduced the content of σ-phase. The reduction of impact strength in degraded state at room temperature can be explained by σ-phase formation.

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