

CHANGES IN VOLUMETRIC FRACTION OF FERRITE AND SIGMA PHASES AFTER ISOTHERMAL AGING BETWEEN 700°C AND 900°C OF UNS S31803 (SAF 2205) DUPLEX STAINLESS STEEL.

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Abstract. This work determines the changes in volumetric fraction of ferrite and sigma phases after isothermal aging between 700°C and 900°C of UNS S31803 (SAF 2205) duplex stainless steel, using optical microscopy for phase determination, quantitative metallography techniques for sigma phase volumetric fraction determination and magnetic measurements to determine ferrite content. The metallographic preparation were conducted with semi-automatic polishing machine Struers Abramin, and metallographic reveal was possible through modified Behara etching and electrolytic etching using 10% KOH aqueous solution, 2 Vdc in 1 minute. Sigma phase measurement was conducted in a Leica DMLM optical microscope, together with Q500/W image analysis software. Ferrite content was measured using a Fischer MP-30 ferritscope. It was observed that during aging of SAF 2205 sigma phase was formed in periods up to 10 minutes by precipitation from ferrite and austenite, resulting in massive sigma phase and secondary ferrite, an impoverished phase in chromium and molybdenum; other important reaction of sigma phase formation is the ferrite eutectoid decomposition, resulting in sigma (lamellar and massive forms) and secondary austenite, also impoverished in chromium and molybdenum; besides these two major mechanisms of formation, sigma phase growth can occur simultaneously from austenite or ferrite. The ferrite content of all specimens decreased with aging, showing that formation of sigma phase depends mostly on ferrite consumption; however, after total ferrite consumption, sigma phase was formed from austenite.

Keywords. Duplex stainless steel, phase transformations, sigma phase, quantitative metallography.

1. Introduction

Wrought duplex stainless steels (DSS) presents, in the solution treated condition, alternate ferrite and austenite bands of reduced thickness (less than 10 µm), and this microstructure, associated to the higher chromium and molybdenum content of ferrite, and higher chromium, nickel and nitrogen content of austenite, give to DSS high mechanical strength associated to high toughness (Solomon and Devine, 1982; Potgieter, and Cortie, 1991, Leffler, 1990). One of the most common DSS is the UNS S31803 (SAF 2205), which has nominal chemical composition 22% Cr - 5% Ni - 3% Mo - 0,15% N - 0,02% C, and presents tensile strength of 770 MPa, yield strength of 515 MPa (twice the typical value found in austenitic stainless steels UNS S30400 and UNS 31600) and total elongation in 50 mm up to 32% (Eckenrod and Pinnow, 1984; Argawal, 1988; Erbing and Groth, 1993). Regarding this excellent mechanical behavior, UNS S31803 presents higher corrosion resistance than low carbon austenitic steels (Eckenrod and Pinnow, 1984; Nordström and Rung, 1995).

However, undesired phases could form during isothermal aging or welding procedures, resulting in reduction of toughness, ductility and corrosion resistance. Particularly in aging between 700°C and 900°C sigma phase, a hard and brittle intermetallic phase rich in chromium and molybdenum, is present (Nilsson, 1992), formed by eutectoid decomposition of ferrite or by nucleation and growth from ferrite and austenite (Ahn and Kang, 2000).

Magnabosco *et alli* (2002) showed that during aging of UNS S31803 DSS at 850°C in periods up to 10 minutes sigma phase forms by precipitation from ferrite, resulting in massive sigma phase. In aging treatments between 10 minutes and five hours, sigma phase was formed by eutectoid decomposition of ferrite in lamellar and massive sigma phase and secondary austenite. It was found in the same work (Magnabosco *et alli*, 2002) that sigma phase growth can occur simultaneously between 10 minutes and five hours of aging from austenite or ferrite, and after five aging hours, besides the described mechanisms, sigma phase nucleation and growth can occur from austenite.

An accurate description of microstructural changes in aged UNS S31803 DSS by optical microscopy is shown in the work of Magnabosco (2001). The present phases (ferrite, austenite and sigma) were characterized using modified Behara etching, which darkens ferrite phase and turns austenite phase gray, while sigma phase remains without etching. The same work (Magnabosco, 2001) showed that sigma phase selective etching could be achieved by electrolytic etching in 10% KOH aqueous solution, using 2 Vdc during 1 minute; this procedure allowed quantitative metallography of sigma phase.

Considering those facts, this work determines the changes in volumetric fraction of ferrite and sigma phases after isothermal aging between 700°C and 900°C of UNS S31803 (SAF 2205) duplex stainless steel, using optical

microscopy for phase determination, quantitative metallography techniques for sigma phase volumetric fraction determination and magnetic measurements to determine ferrite content.

2. Experimental procedure

The studied material has the chemical composition presented in Tab. (1), and was received as a 3 mm thickness sheet, solution treated at 1120°C and water quenched. Specimens of 20 mm length and 15 mm wide were obtained, and the length described was maintained parallel to the rolling direction. All specimens were isothermally aged at 700°C, 750°C, 800°C, 850°C and 900°C between 10 minutes and 1032 hours, in a tubular electric furnace with solid-state controller, which maintained aging temperature 1°C around the chosen temperature. All heat treatments were conducted under a 99,9% N₂ atmosphere, in order to suppress oxidation of the specimens' surfaces and prevent nitrogen loss from the DSS; water quenching interrupted the aging treatments.

After the heat treatments the specimens were metallographic polished in a semi-automatic grinding and polishing machine *Struers Abramin*, showed in Fig. (1.a); final polishing were provided by 1 μm diamond abrasive. After metallographic polishing samples were etched with modified *Behara* reagent, which composition is 20 mL chloridric acid, 80 mL distilled water and 1 g potassium metabisulfide; to this stock solution, 2 g of ammonium bifluoride were added just before the etching, conducted in two minutes. This etching procedure allowed the distinction between ferrite, austenite and sigma phases.

To obtain selective etching of sigma phase, electrolytic etching were performed in 10% KOH aqueous solution, using 2 Vdc during 1 minute; this procedure allowed quantitative metallography of sigma phase, measuring its volumetric fraction, using the Q500/W image analysis system, attached to a *Leica DMLM* optical microscope, showed in Fig. (1.b). Magnetic measurements in a *Fischer ferritoscope*, showed in Fig (1.c), were performed to determine ferrite content.

Table 1. Chemical composition of UNS S31803 (SAF 2205) DSS studied.

Element	Cr	Ni	Mo	Mn	Si	V	N	C	S
weight %	22.2	5.7	2.98	1.60	0.44	0.07	0.161	0.016	0.001

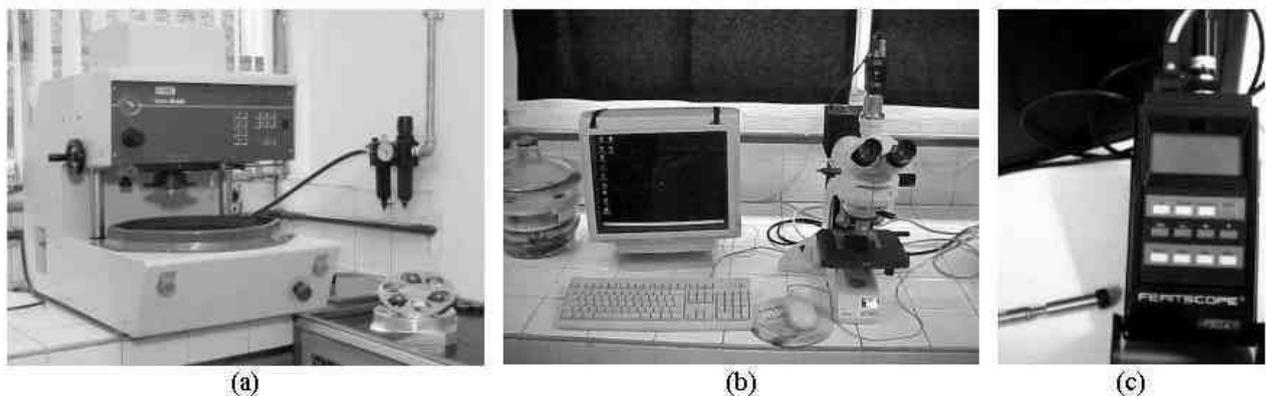


Figure 1. LabMat-FEI equipments used in this study. (a) Semi-automatic polishing machine *Abramin*. (b) *Leica DMLM* optical microscope and Q500/W image analysis system. (c) *Fischer ferritoscope*.

3. Results and discussion

Figure 2 shows typical microstructures found in DSS studied. Figure (2.a) shows the material in the solution treated condition, showing ferrite (darker phase) and austenite (gray). Magnetic measurements showed a ferrite volumetric fraction of 40.9%, resulting in 59.1% of austenite. Aging treatments were conducted over this microstructure, resulting in sigma phase formation in all temperatures studied.

Sigma phase assumed massive morphology in specimens which aging time is greater than 1 hour, as could be seen in Fig. (2.b), where the darker phase is ferrite, the gray regions are austenite and sigma remains unetched. In all specimens containing ferrite, sigma phase formed at ferrite / ferrite or ferrite / austenite boundaries, consuming preferably the ferrite.

Long-term aging, however, leads to total consumption of ferrite phase, as could be noticed in Fig. (2.c) and (2.d), where only sigma and austenite phases were present (the darker regions in those micrographs are related to annealing twins in austenite). Only at 900°C long-term aging austenite grain growth was observed, as could be seen in Fig. (2.d).

Figure (2.e) is an example of short-term aged specimens. In this case, it could be noticed the same small grain size found in the solution treated material, resulting in massive formation of sigma phase, but in small size precipitates, preferably associated to the original ferrite phase. Figure (2.f) shows the difference between modified *Behara* etching and electrolytic etching in KOH, where the selective etching of sigma phase in the procedure using KOH is clearly

noted. All specimens were electrolytic etched with KOH to allow sigma phase volumetric fraction measurements by quantitative metallography.

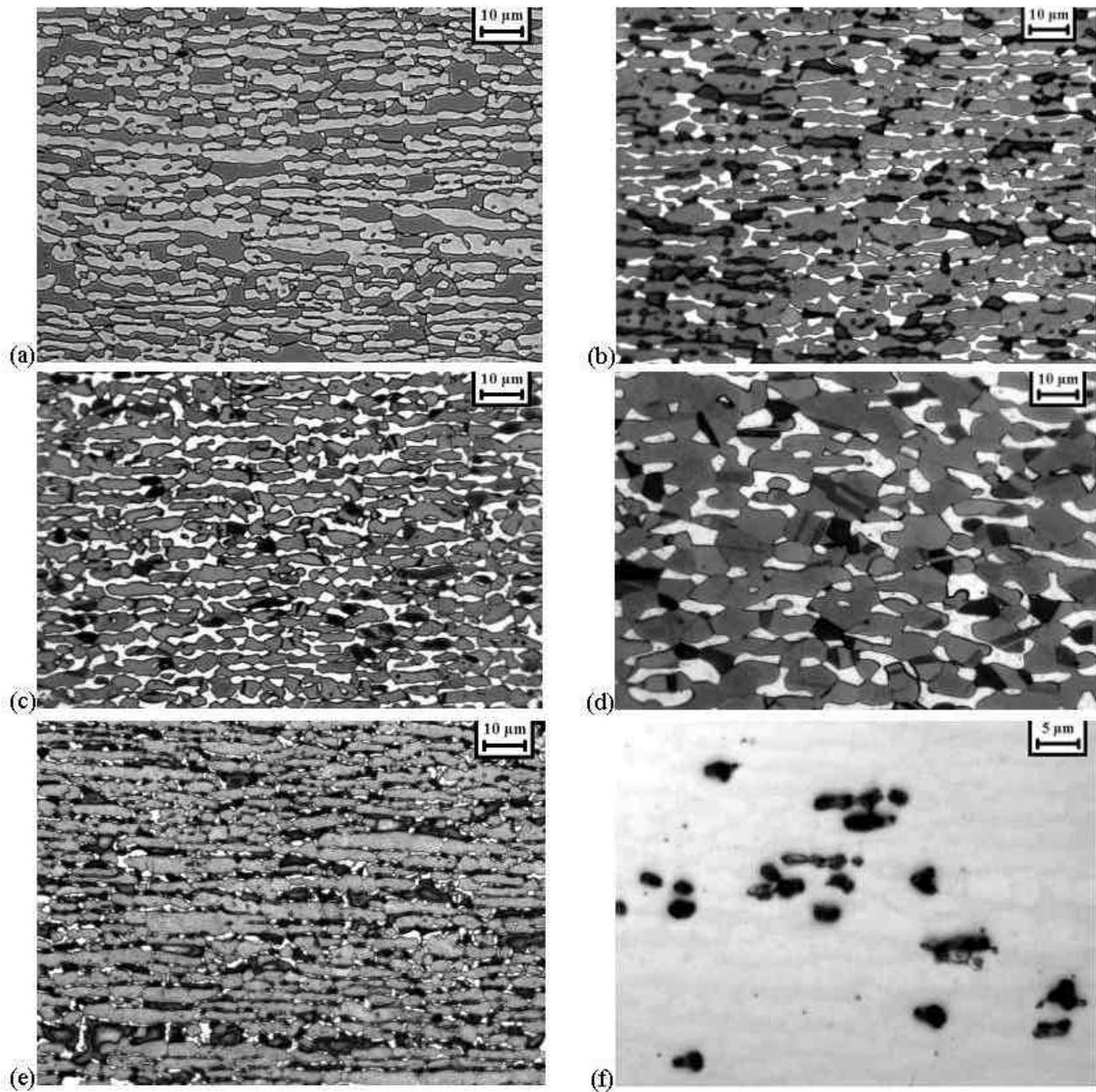


Figure 2. Optical micrographs of UNS S31803 (SAF 2205) DSS studied: (a) solution treated; (b) aged 1 hour at 900°C; (c) aged 768 hours at 800°C; (d) aged 768 hours at 900°C; (e) aged 1 hour at 750°C; (f) aged 20 minutes at 900°C. Etching for (a) to (e): modified *Behara* reagent; for (f): electrolytic etching in KOH solution.

It could be seen in Fig (3.a) eutectoid decomposition of ferrite, resulting in sigma and austenite phases in lamellar morphology; in some short-term aging, this formation mechanism could be found, especially where larger lamellae of ferrite phase could be found. In long-term aging between 700°C and 850°C sigma phase was nucleated and growth inside the austenite lamellae, as could be noticed in Fig (3.b); in those treatments, however, there is stable lamellae and grain sizes, contrasting with huge austenite grain size found in long-term aging at 900°C, discussed before and showed in Fig. (2.d). The only phases found after long-term aging are sigma and austenite, but after 1008 hours aging at 850°C Cr₂N type chromium nitride could be found after scanning electron microscopy examination using backscattered electrons, in small volumetric fraction (less than 0.8%), as could be seen in Fig. (4).

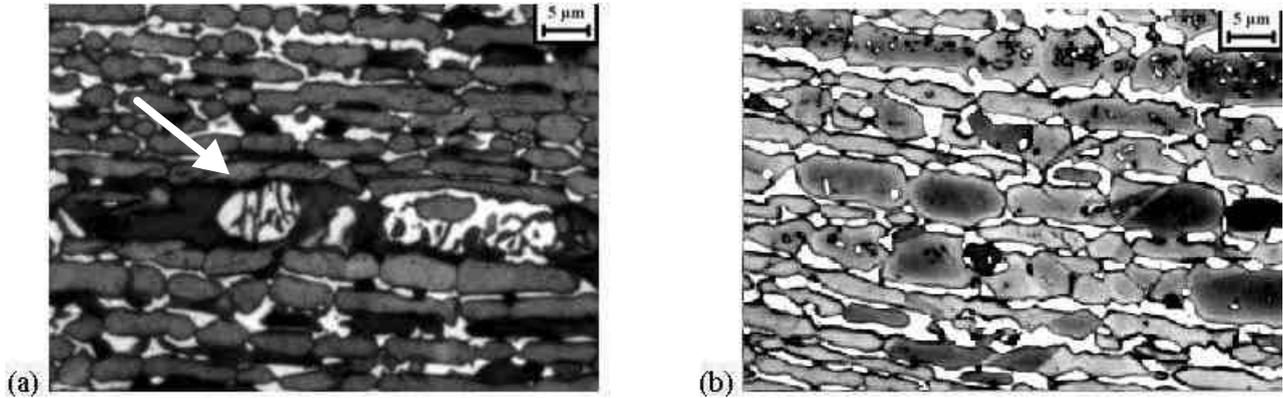


Figure 3. Optical micrographs of UNS S31803 (SAF 2205) DSS studied. (a) Aged 30 minutes at 850°C, showing austenite and sigma phases as lamellar products of eutectoid decomposition of ferrite, indicated by an arrow. (b) Aged 100 hours at 850°C, showing nucleation of sigma phase inside austenite. Etched with *Behara*.

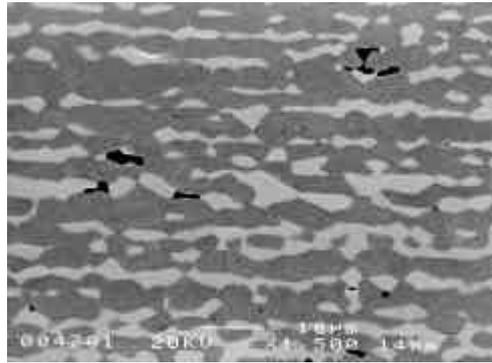


Figure 4. Scanning electron microscopy examination using backscattered electrons of UNS S31803 (SAF 2205) DSS studied, aged 1008 hours at 850°C, showing sigma phase (white), austenite (gray) and Cr₂N type chromium nitride (black).

Figure (5) shows the results of sigma phase quantitative metallography, confirming that aging between 700°C and 900°C leads sigma phase volumetric fraction grow with evolution of aging time. It could be noticed an stabilization of sigma phase volumetric fraction (approximately 41%) for specimens aged between 12 and 384 hours at 900°C, followed by reduction to a value near 36% after 768 hours. This fact could be associated to the austenite grain growth occurred in long-term aging treatments at 900°C, as shown in Fig (2.d). The reduction in volumetric fraction of sigma phase and the associated austenite grain size growth are strong indications of differences in sigma phase composition during its formation at 900°C.

The maximum volumetric fraction of sigma phase could be found after long-term aging in 700°C (near 57%), and the maximum rate of sigma phase formation is found between 800°C and 850°C. Considering the differences between sigma phase volumetric fractions and rate of formation found in different aging temperatures showed in Fig. (5), and the change in austenite grain size and reduction in sigma phase fraction at 900°C mentioned before, it could be concluded that sigma phase composition is a function of aging time and temperature.

Magnetic measurements in a *Fischer* ferritscope, performed to determine ferrite content, give the results showed in Fig. (6), showing the higher rates of ferrite consumption in the same temperatures of the higher rates of sigma phase formation (800°C and 850°C), confirming that sigma phase is formed preferably from ferrite when this phase is present. Figure (6) also shows that total consumption of ferrite could be found after 192 hours of aging at 700°C and 900°C, respectively the lowest and highest aging temperatures studied. At 750°C, however, the rate of ferrite phase consumption is larger, and ferrite could not be found after 24 hours of aging treatment, and the highest rates of ferrite phase consumption are found in 800°C and 850°C, where ferrite could not be found after 12 hours of aging treatment. This fact, associated to the maximum rate of sigma phase formation is found between 800°C and 850°C, confirms that sigma phase formation occurs preferably from ferrite when this phase is present.

Neglecting the small chromium nitride formation after long-term aging at 850°C, it could be considered that only ferrite, austenite and sigma phases exist in the microstructure, and the austenite volumetric fraction could be calculated using Eq. (1):

$$\%g = 100 - \%a - \%s \quad (1)$$

where %g is the calculated austenite volumetric fraction and %s and %a are respectively the volumetric fractions of sigma and ferrite phases extracted from Fig. (5) and (6).

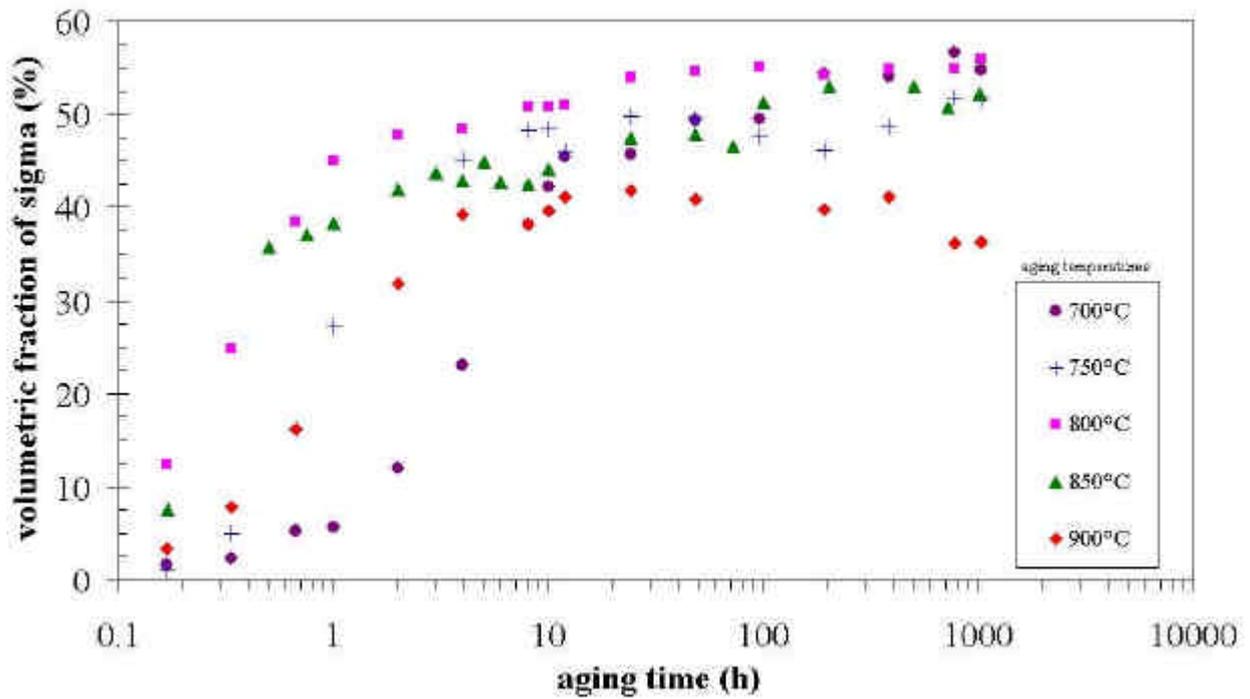


Figure 5. Volumetric fraction of sigma phase (determined by quantitative metallography) as a function of aging time and temperature for UNS S31803 (SAF 2205) DSS studied.

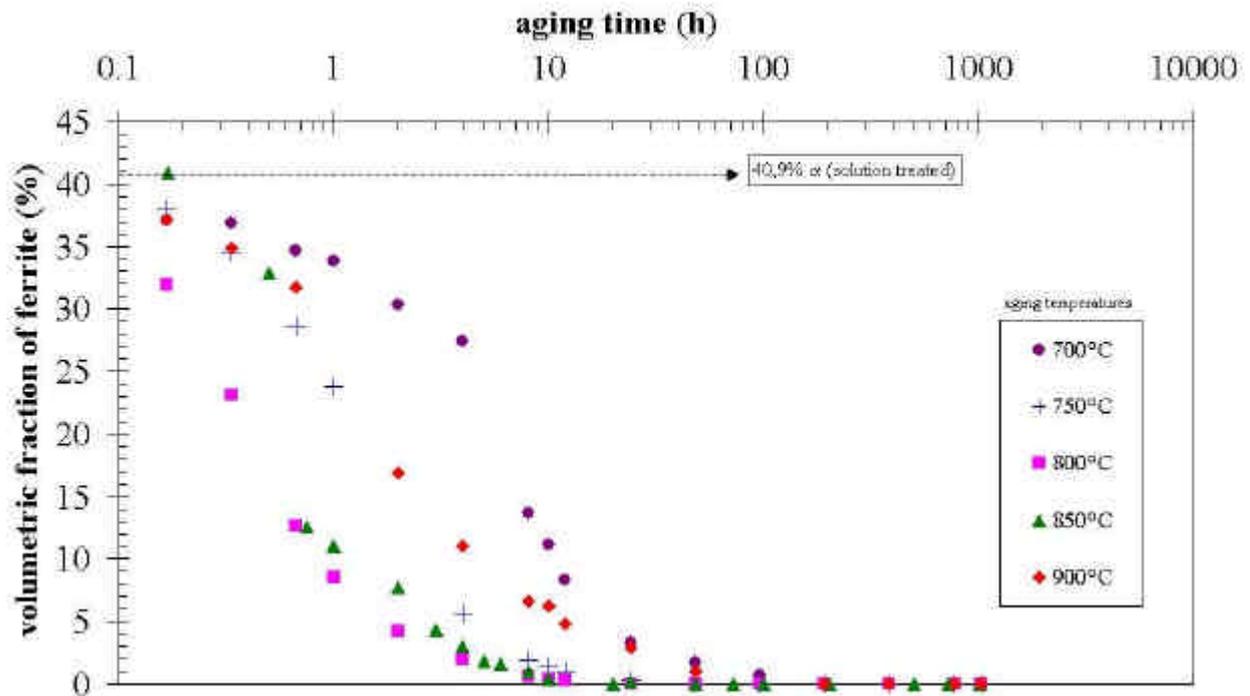


Figure 6. Volumetric fraction of ferrite phase (determined by magnetic measurement with *Fischer* ferritscope) as a function of aging time and temperature for UNS S31803 (SAF 2205) DSS studied.

The evolution of austenite volumetric fractions shows that austenite is formed in two different aging periods. At 700°C, austenite volumetric fraction grows between 2 and 96 hours of aging, reaching 50%, followed by a reduction to 43% at 768 hours and new growing after this aging time. The same behavior could be found at 850°C (austenite volumetric fraction grows between 30 minutes and 8 hours until 57% of austenite; this is followed by reduction and a new growing after 203 hours of aging).

Comparison of Fig. (6) and (7) shows that the first periods of austenite volumetric fraction grow are always associated to the presence of ferrite for all temperatures; on the other hand, the second periods of austenite volumetric fraction grow occurs in the absence of ferrite. From those facts, it is possible to state that the major sigma phase formation mechanism in short-term aging cannot be eutectoid decomposition of ferrite (which forms sigma and austenite), and the most probably mechanisms are nucleation in ferrite / ferrite or ferrite / austenite boundaries and preferably growth from ferrite, since the rate of ferrite consumption are higher than austenite one in short-term aging. After this period, the major sigma phase formation is eutectoid decomposition of ferrite, which allows the austenite volumetric fraction growth. After total ferrite consumption sigma phase growth occurs from austenite, leading to the second austenite volumetric fraction reduction. However, the clearly second growth of austenite volumetric fraction occurred in long-term aging at 900°C, and its presence in the other studied aging temperatures as stated in Fig. (7), shows that sigma and austenite phases formed in the long-term aging treatments are not in equilibrium, which was reached only after 768 hours at 900°C, when volumetric fractions of sigma and austenite remained constant (36% and 64% respectively).

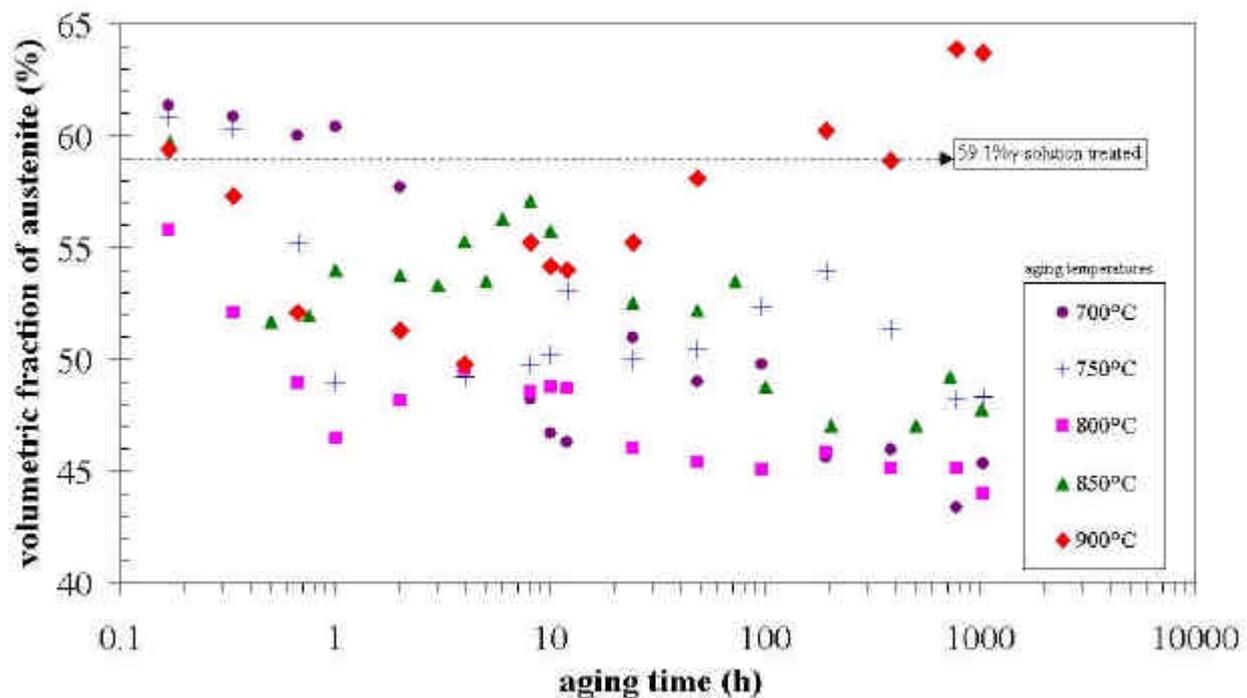


Figure 7. Volumetric fraction of austenite phase as a function of aging time and temperature for UNS S31803 (SAF 2205) DSS studied, calculated using Eq. (1) and considering that only ferrite, sigma and austenite could be present.

4. Conclusions

It could be concluded from this work that:

- After short-term aging of UNS S31803 (SAF 2205) DSS between 700°C and 900°C sigma phase is found as small size precipitates, preferably associated to the original ferrite phase.
- In UNS S31803 (SAF 2205) DSS aged between 700°C and 900°C, sigma phase was formed at ferrite / ferrite or ferrite / austenite boundaries, consuming preferably the ferrite.
- Long-term aging of UNS S31803 (SAF 2205) DSS between 700°C and 900°C leads to total consumption of ferrite phase.
- Only at 900°C long-term aging of UNS S31803 (SAF 2205) DSS austenite grain growth was observed, and Cr₂N chromium nitride was observed, in small volumetric fraction, only after 1008 hours aging at 850°C.
- The reduction in volumetric fraction of sigma phase and the austenite grain size growth during aging at 900°C of UNS S31803 (SAF 2205) DSS, associated to the differences between sigma phase volumetric fractions and rate of formation found in different aging temperatures, are strong indications of differences in sigma phase composition during its formation, showing that sigma and austenite phases formed in the long-term aging treatments are not in equilibrium, which was reached only after 768 hours at 900°C.
- The major sigma phase formation mechanisms in short-term aging of UNS S31803 (SAF 2205) DSS between 700°C and 900°C are nucleation in ferrite / ferrite or ferrite / austenite boundaries and preferably growth from ferrite, since the rate of ferrite consumption are higher than austenite one in short-term aging.

- After the initial period of sigma formation in UNS S31803 (SAF 2205) DSS between 700°C and 900°C by nucleation in boundaries and preferably growth from ferrite, the major sigma phase formation is eutectoid decomposition of ferrite.
- After total ferrite consumption, sigma phase growth in UNS S31803 (SAF 2205) DSS between 700°C and 900°C could occur from austenite.

5. References

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