MICROHARDNESS OF UNS S31803 (SAF 2205) DUPLEX STAINLESS STEEL AFTER ISOTHERMAL AGING BETWEEN 700°C AND 900°C.

Rodrigo Magnabosco
Professor at Mechanical Engineering Department of "Centro Universitário da FEI" – Av. Humberto A. C. Branco, 3972 – São Bernardo do Campo – SP – BRASIL – 09850-901 – tel# 55-11-43532900 ext. 2173 – rodrmagn@fei.edu.br

Luciane Emi Oiye
Undergraduated student at Mechanical Engineering Department of "Centro Universitário da FEI" – Av. Humberto A. C. Branco, 3972 – São Bernardo do Campo – SP – BRASIL – 09850-901 – tel# 55-11-43532900 ext. 2173 – luciane_oiye@hotmail.com

Clemente Kuntz Sutto
Undergraduated student at Mechanical Engineering Department of "Centro Universitário da FEI" – Av. Humberto A. C. Branco, 3972 – São Bernardo do Campo – SP – BRASIL – 09850-901 – tel# 55-11-43532900 ext. 2173 – clementesutto@hotmail.com

Abstract. This work determines the microhardness after isothermal aging between 700°C and 900°C of UNS S31803 (SAF 2205) duplex stainless steel, and its relation to sigma phase volumetric fraction. The microhardness measurements were conducted in a Shimadzu HMV-2 equipment using 0.5 kg load; 40 measurements were conducted in each specimen. Sigma phase measurement was conducted after electrolytic etching using 10% KOH aqueous solution, 2 Vdc in 1 minute, in a Leica DMLM optical microscope, together with Q500/W image analysis software. It was observed that during aging of SAF 2205 sigma phase was formed in periods up to 10 minutes by precipitation from ferrite, resulting in massive sigma phase; 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 sigma content of all specimens increased with aging, as well as the microhardness of the specimens, changing from 266 HV0.5 for the solution treated specimen (which contains 40.9% ferrite and 59.1% austenite, in volumetric fraction) to up to 490 HV0.5 in long-term aged specimens.

***Keywords**. Duplex stainless steel, phase transformations, sigma phase, microhardness.*

1. Introduction

Duplex stainless steels (DSS) were created to combine the corrosion resistance of ferritic stainless steels (particularly stress corrosion cracking resistance) to the excellent toughness and pitting corrosion resistance of austenitic stainless steels (Argawal, 1988; Sedriks, 1996). They could be produced by hot deformation and solution treatment of Fe-Cr-Ni-Mo-N alloys in temperatures up to 1200°C, followed by rapid quenching (Nilsson, 1992), with a resulting microstruture of approximately 40 to 45% volume fraction of ferrite, rich in chromium and molybdenum, and 55 to 60% volume fraction of austenite, with high fractions of chromium – up to 20% – as a consequence of the high nitrogen content found in those alloys, frequently 0,2% (Solomon and Devine, 1982).

Wrought 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 commom 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.

Considering those facts, this work determines the microhardness evolution of UNS S31803 (SAF 2205) DSS after isothermal aging between 700°C and 900°C, and its relation to sigma phase volumetric fraction.

2. Experimental procedure

The studied material has the chemical composition gave 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 isothermically 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% N_2 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 grounding 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 metabissulphide; 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 using the Q500/W image analysis system, attached to a *Leica* DMLM optical microscope, showed in Fig. (1.b). Vickers microhardness of the specimens were measured in a *Shimadzu HMV-2* micro-durometer, showed in Fig. (1.c), using 0.5 kg load; 40 measurements were conducted in each specimen.

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

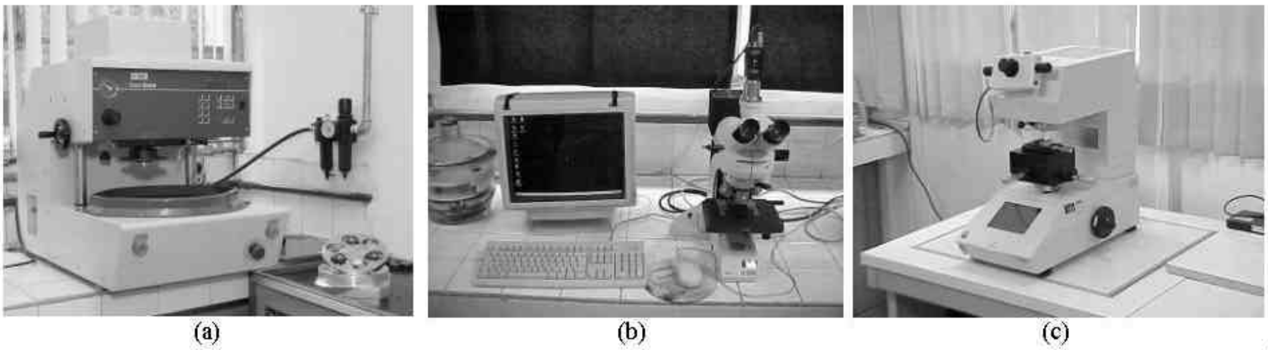

Figure 1. LabMat-FEI equipments used in this study. (a) Semi-automatic polishing machine *Struers Abramin*. (b) *Leica* DMLM optical microscope and Q500/W image analysis system. (c) *Shimadzu HMV-2* micro-durometer.

3. Results and discussion

Figure 2 shows typical micrographs of the DSS studied in eight different heat treatment conditions, after modified *Behara* etching, which darkens ferrite phase and turns austenite phase gray, while sigma phase remains without etching. It could be seen that the solution treated specimen (Fig. (1.a)) presents only austenite (gray) and ferrite (darker) phases, and that isothermal aging at all temperatures studied leads to sigma phase formation. Figure (2.b) represents the microstructure of the specimen aged 1 hour at 900°C, showing sigma phase formation strongly associated to ferrite phase instead of austenite; this happened because of higher chromium and molybdenum contents of ferrite phase, and the higher diffusion coefficients of those elements in ferrite, if compared with those facts in austenite, as stated in literature (Magnabosco, 2002). After 768 hours at 900°C (Fig. (2.c)), the specimen contain only austenite and sigma phases, and the austenite grains are bigger than those found in the solution treated and short-term aged specimens shown respectively in Fig. (2.a) and (2.b).

Similar behavior was found at the other aging temperatures: Fig. (2.d) shows typical microstruture of specimen aged 48 hours at 800°C, and Fig. (2.e) characterizes specimens aged 768 hours at 800°C; both have only sigma and austenite phases; however, austenite grain growth was not observed, and the same happens in the other long-term aging treatments, excepted for the 900°C temperature described before. In some cases, after total ferrite consumption sigma phase formed inside the austenite phase, indicating nucleation and growth of sigma phase from austenite.

Figure (2.f) represents typical microstruture of short-term aged specimens, represented there by specimen aged 40 minutes at 750°C: sigma phase form in small size at the ferrite / ferrite boundaries or ferrite / austenite boundaries. Increasing aging time at 700°C leads to eutectoid decomposition of ferrite, resulting in sigma and austenite phases in lamellar morphology, as could be seen in Fig (2.g), which represents the microstruture after 12 hours aging treatment at

700°C. Once again, in long-term aging treatments as 1032 hours at 700°C, sigma phase formed inside the austenite phase, indicating nucleation and growth of sigma phase from austenite in the absence of ferrite phase.

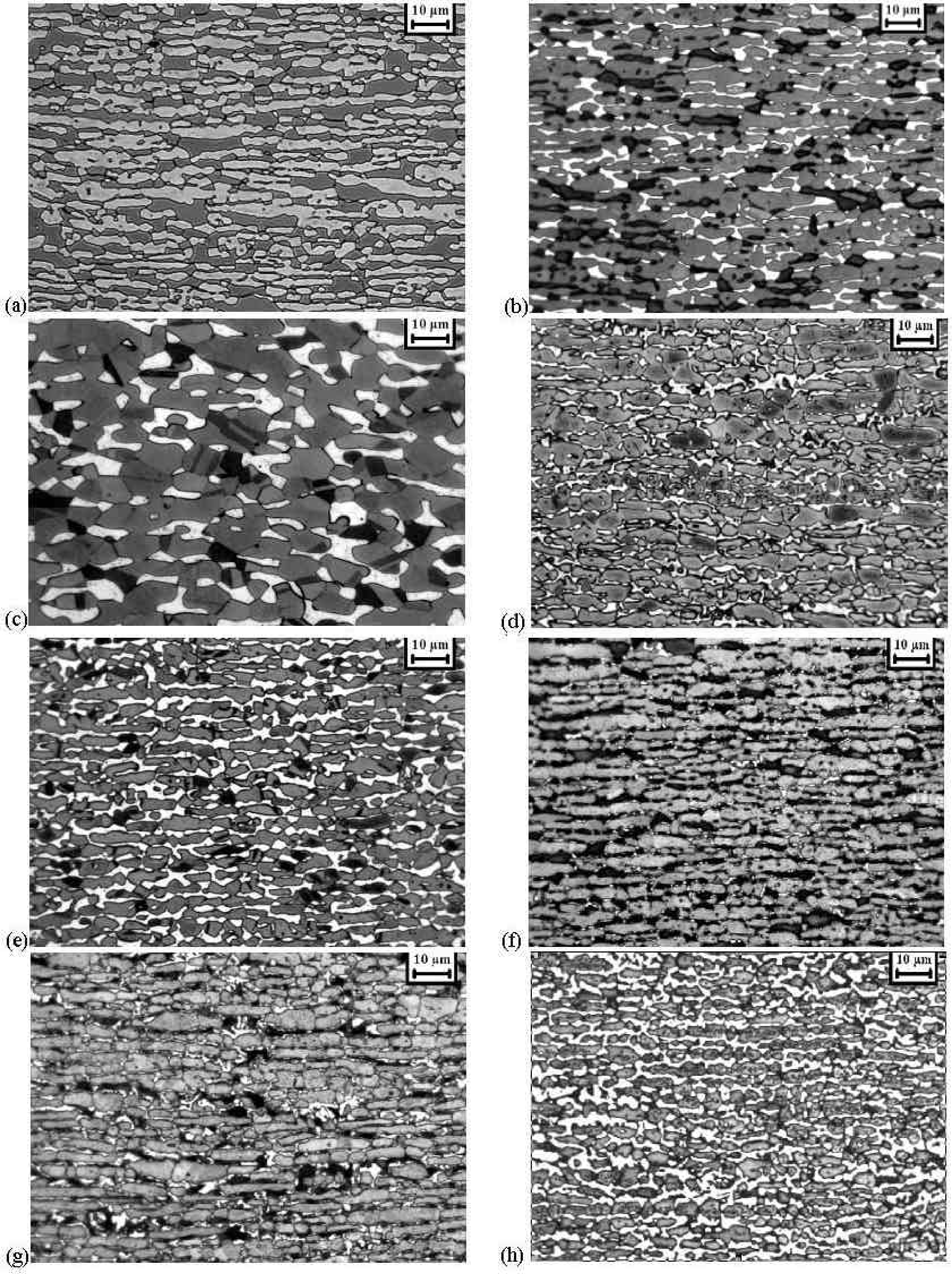

Figure 2. Optical micrographs of UNS S31803 DSS studied: (a) solution treated; (b) aged 1 hour at 900°C; (c) aged 768 hours at 900°C; (d) aged 48 hours at 800°C; (e) aged 768 hours at 800°C; (f) aged 40 minutes at 750°C; (g) aged 12 hours at 700°C; (h) aged 1032 hours at 700°C. All samples etched with modified *Behara* reagent.

The difference between modified *Behara* etching and electrolytic etching in KOH could be seen in Fig. (3), 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. It could be seen in Fig (3.a) eutectoid decomposition of ferrite, resulting in sigma and austenite phases in lamellar morphology.

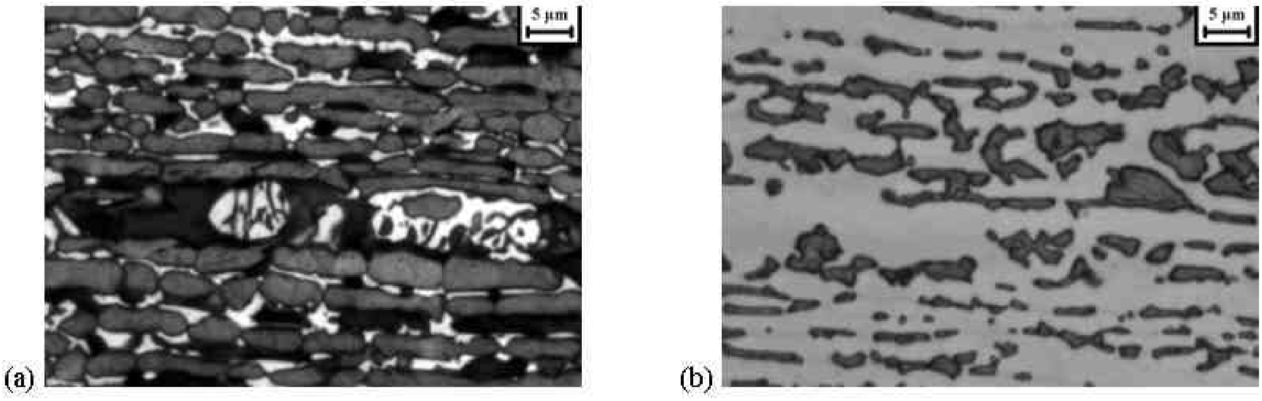

Figure 3. Optical micrographs of UNS S31803 DSS aged 30 minutes at 850°C, showing the difference between (a) modified *Behara* etching (austenite is gray, ferrite is the darker phase and sigma remains unetched) and (b) electrolytic etching in KOH (only sigma is etched).

The result of quantitative metallography of sigma phase and Vickers microhardness of the specimens aged at 850°C is shown in Fig. (4). Those results show that the rate of hardness growing is closely related to the rate of sigma phase formation, confirming the hardness evolution as a consequence of microstructural changes involving sigma phase formation during aging at 850°C.

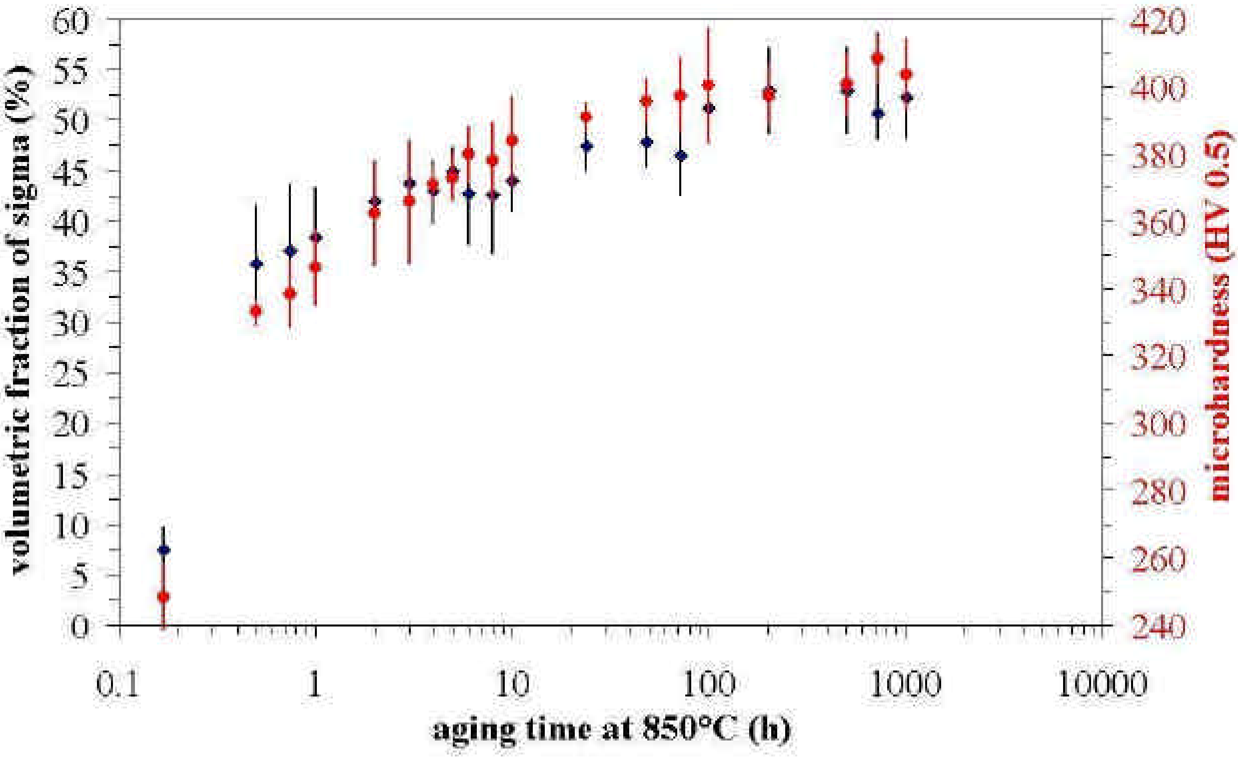

Figure 4. Microhardness and volumetric fraction of sigma phase (determined by quantitative metallography) evolution as a function of aging time at 850°C UNS S31803 (SAF 2205) DSS studied.

Figure (5) presents microhardness evolution as a function of aging time and temperature for UNS S31803 (SAF 2205) DSS studied. It was found that for short-term aging at 700°C a light reduction in hardness occurs, compared to the hardness of the solution treated material (266±8 HV0.5), probably associated to reduction in solute contain of ferrite to nucleate sigma phase, particularly reduction in chromium and molybdenum content. The same behavior is observed in specimens aged at 750°C; however, the hardness of those aged specimens reaches the solution treated hardness in a short period of time (approximately 40 minutes), if compare to the time at 700°C needed to achieve 266 HV0.5 (up to 4 hours).

Considering the hardness behavior discussed before, and the results of sigma phase formation and hardness of specimens aged at 850°C showed in Fig. (4), it could be concluded that sigma phase formation is the reason for the hardness growing described in Fig. (5), and it also shows that the rate of hardness growing is higher at 800°C, and is very similar to the one found at 850°C aging temperature. The maximum hardness, 490±18 HV0.5, could be found at 1032 hours of aging at 800°C.

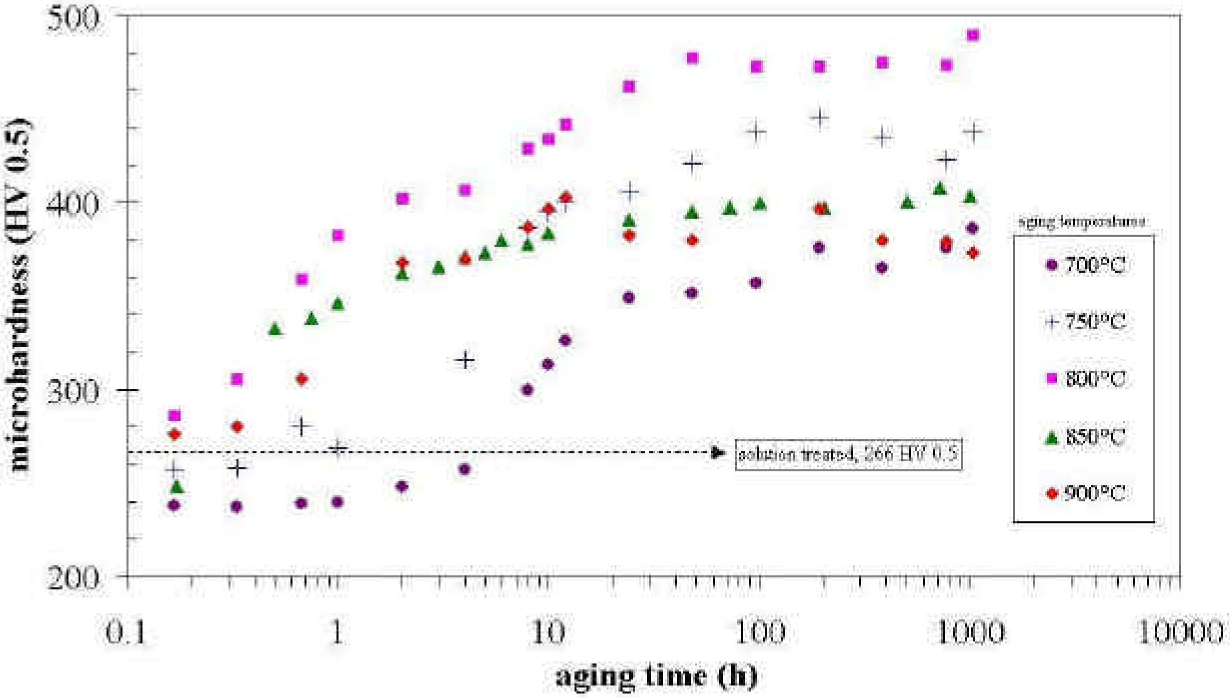

Figure 5. Microhardness evolution as a function of aging time and temperature for UNS S31803 (SAF 2205) DSS studied.

The quantitative metallography of sigma phase resulted in the volumetric fraction of sigma phase data showed in Fig. (6), confirming that aging between 700°C and 900°C leads to sigma phase formation. Comparison of Fig. (5) and Fig. (6) shows again that the rate of hardness growing is closely related to the rate of sigma phase formation, and this comparison is well done in Fig. (7). However, hardness evolution in aged samples is also a consequence of the microstructural changes involving sigma phase formation, as showed in Fig. (7); despite of hardness grow as a function of sigma phase volumetric fraction, there are differences in hardness values for samples that contains similar sigma phase content if they were treated in different temperatures.

It could also be noticed that the light reduction in hardness observed in short-term aging at 700°C showed in Fig. (5), is related to the smallest sigma phase volumetric fraction, reaffirming the relation between reduction in chromium and molybdenum contain of ferrite and the reduction in hardness. Figure (5) also shows stabilization in hardness for specimens aged for more than 12 hours at 900°C, followed by hardness reduction after 100 hours of aging. This fact could be associated to the austenite grain growth occurred in long-term aging treatments at 900°C, as shown in Fig (2.c), and to the reduction in volumetric fraction of sigma phase showed in Fig. (6).

The reduction in volumetric fraction of sigma phase and the associated austenite grain size growth are strong indications of changing in sigma phase composition during aging at 900°C. Considering the differences between hardness evolution and volumetric fraction of sigma phase found in different aging temperatures, it could be concluded that sigma phase composition, and the microstructure formed, are functions of aging temperature.

4. Conclusions

It could be concluded from this work that:

- Short-term aging between 700°C and 900°C of UNS S31803 (SAF2205) DSS leads to sigma phase formation at the ferrite / ferrite boundaries or ferrite / austenite boundaries.
- Increasing aging time at 700°C of UNS S31803 (SAF2205) DSS leads to eutectoid decomposition of ferrite, resulting in sigma and austenite phases in lamellar morphology.
- After long-term aging between 700°C and 900°C, the microstructure of UNS S31803 (SAF2205) DSS is composed only by austenite and sigma phase.

- The reduction in volumetric fraction of sigma phase and the associated austenite grain size growth are strong indications of changing in sigma phase composition during aging at 900°C in UNS S31803 (SAF2205) DSS.
- Sigma phase formation during aging of UNS S31803 (SAF2205) DSS implies in hardness rising, and the maximum hardness (490±18 HV0.5) was found in specimens aged 1032 hours at 800°C.

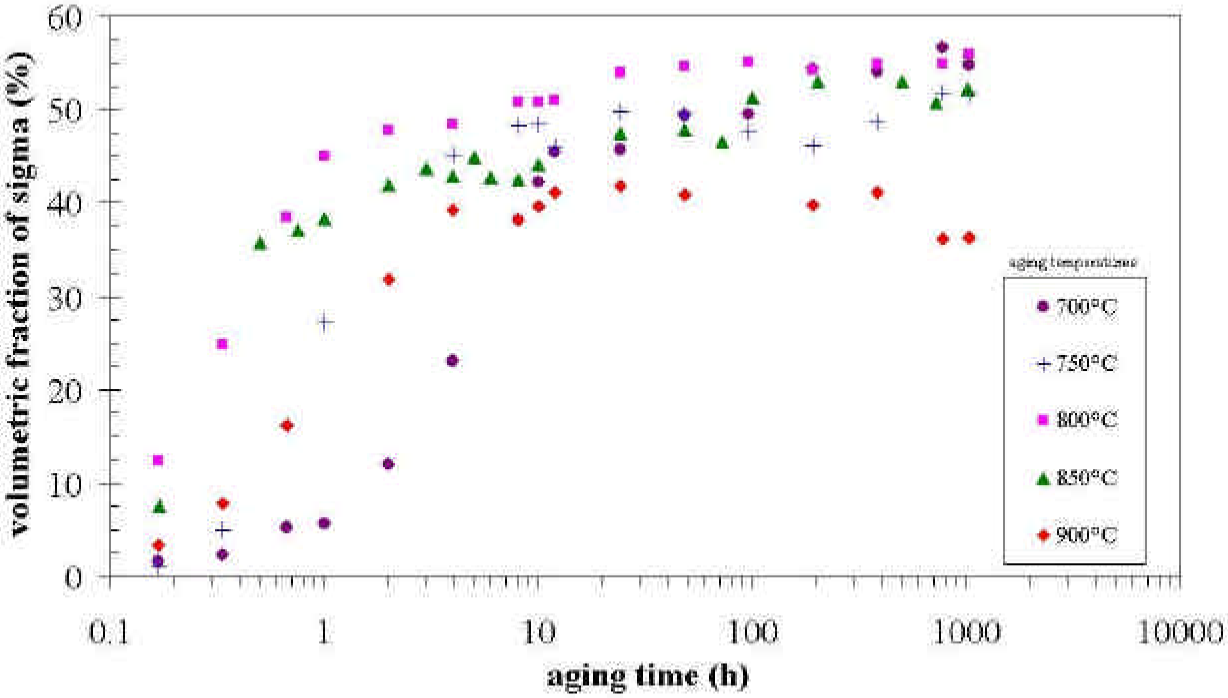

Figure 6. Volumetric fraction of sigma phase (determined by quantitative metallography) as a function of aging time and temperature for UNS S31803 (SAF 2205) DSS studied.

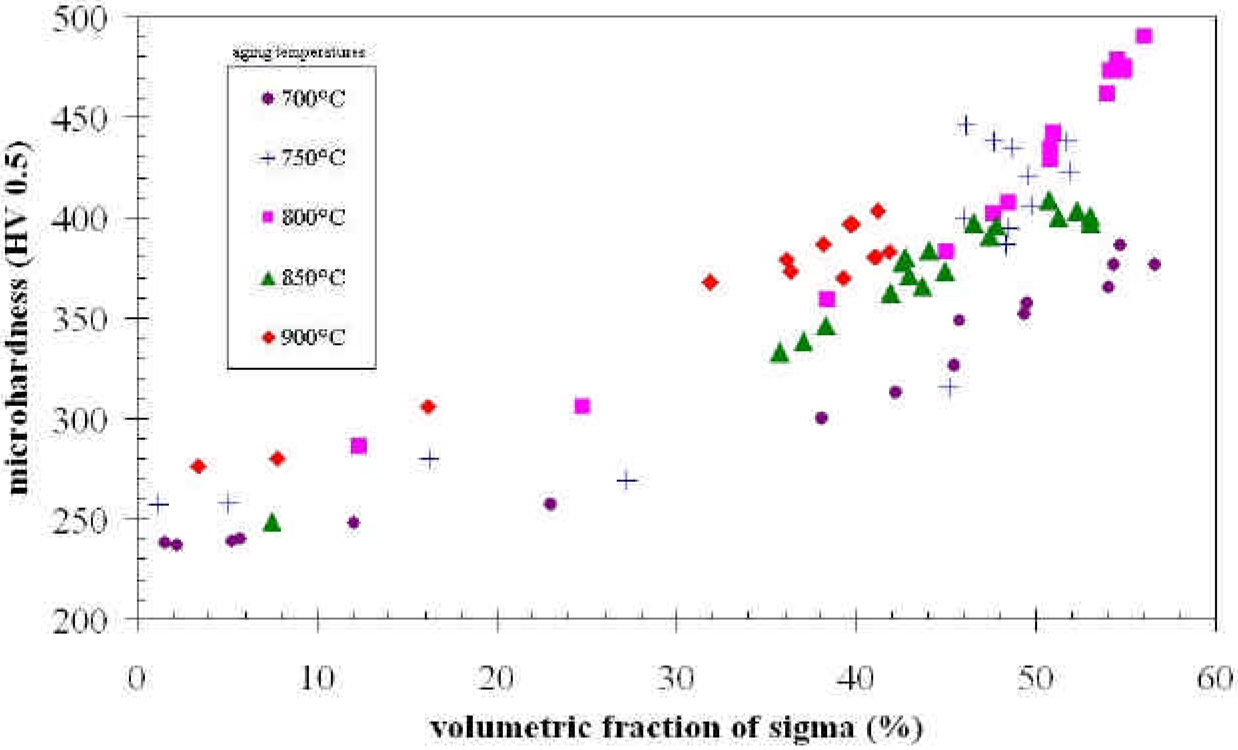

Figure 7. Microhardness evolution as a function of volumetric fraction of sigma phase (determined by quantitative metallography) for various aging temperatures for UNS S31803 (SAF 2205) DSS studied.

5. References

AGARWAL, D. C., 1988, "*Duplex stainless steels – The cost effective answer to corrosion problems of major industries.*", Key Eng. Mater., No. 2, Vol. 20-28, pp. 1677-1692.

AHN, Y. S., KANG, J. P., 2000, "Effect of aging treatments on microstructure and impact properties of tungsten substituted 2205 duplex stainless steel.", Materials science and technology, Vol. 16, pp. 382-8.

ECKENROD, J. J., PINNOW, K. E., 1984, "*Effects of chemical composition and thermal history on the properties of alloy 2205 duplex stainless steel.*", In: New developments in stainless steel technology, Detroit, pp.77-87.

ERBING, M. L., GROTH, H. L., 1993, "*Duplex-un'alternativa all'acciaio inossidabile 316 per il risparmio di peso in applicazioni offshore*", L' acciaio inossidabile, No. 2, pp. 10-13.

LEFFLER, B., 1990, "*Alloy 2205 for marine chemical tankers*", Materials performance, pp. 60-63.

MAGNABOSCO, R. *et alli*, 2002 "*Transformações de fase durante o envelhecimento a 850°C do aço inoxidável UNS S31803*", 57th Annual International Congress of ABM, São Paulo, Brasil (electronic media).

NILSSON, J. O., 1992, "*Super duplex stainless steels.*", Materials science and technology, Vol. 8, pp. 685-700.

NORDSTRÖM, J., RUNG, B, 1995, "*Bollitori e torri di stoccaggio di pasta per carta in acciai inossidabili duplex consentono risparmio di peso e di costi*", L' acciaio inossidabile, Vol. 2, pp. 7-12.

POTGIETER, J. H., CORTIE, M. B, 1991, "*Determination of the microstructure and alloy element distribution in experimental duplex stainless steels.*", Materials characterization, Vol. 26, pp. 155-165.

SEDRIKS, A. J., 1996, "*Corrosion of stainless steels*", John Wiley : NY, 2. ed., pp. 1-4.

SOLOMON, H. D., DEVINE Jr., T. M., 1982, "*Duplex stainless steels – a tale of two phases.*", In: Duplex stainless steels – conference proceedings., ASM, Metals Park : Ohio, pp. 693-756.