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Short Communication

Spinodal decomposition mechanism study on the duplex stainless steel UNS S31803 using ultrasonic speed measurements

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ABSTRACT

This work, focuses on the spinodal decomposition mechanism study on the duplex stainless steel duplex UNS S31803, composed by austenite (γ) and ferrite (α) phases, at 425 °C and 475 °C temperatures by ultrasonic speed measurements. This temperature range is responsible for the transformation mechanism of $\alpha_{initial}$ phase to α phases (poor in chromium) and α′ (rich in chromium) by spinodal decomposition. The techniques to accomplish this analysis are based mainly on X-ray diffraction measures and ultrasonic speed. The obtained results show that it is possible to conclude that the use of ultrasonic speed measurements indicates a promising technique for following-up the phase transformation and spinodal decomposition on the steel studied.

1. Introduction

Duplex stainless steel (DSS) comprises a two-phase microstructure with quantities practically similar represented by austenite (γ) and ferrite (α) [1]. They present special mechanical properties, such as high mechanical resistance and to corrosion cracking due to their composition based essentially on high concentrations of chromium (Cr) and molybdenum (Mo) elements, and therefore, may be used in aggressive environments [2]. Hence, DSS becomes competitive when in comparison to other types of stainless steel. Due to those properties, DSS is highly used by chemical, nuclear, petrochemical, pulp and marine industries, among others [3–5].

DSS suffers phase transformation by spinodal decomposition for temperatures below 525 °C having higher kinetics for temperatures around 475 °C. This mechanism is responsible for the transformation of $\alpha_{initial}$ phase into α phases (poor in chromium) and α′ (rich in chromium) [6,7].

In this context, the main objective of this work was to study phase transformation for spinodal decomposition by sonic speed measurements. Therefore, it is possible to develop a non-destructive approach to anticipate the best moment for change or maintenance of DSS under spinodal decomposition when in service.

This paper is organized as follows: next section describes the material and method considered, as well as material and techniques used for preparation of this work. In Section 3, it is presented a thorough analysis and discussion of results and, finally, in Section 4, is done an analysis of the main advantages of this work pursuant to employment of the proposed approach.

2. Materials and methods

In this work was used a stainless steel duplex UNS S31803 to evaluate the phase transformation at temperature of 425 °C and 475 °C. In Table 1, it is presented the duplex stainless steel chemical composition as-received in weight percent (wt.%).

Samples used for this work were aged inside an electric resistance oven at temperatures of 425 °C and 475 °C. Aging periods of 12 h (hours), 24 h, 50 h, 100 h and 200 h were used for each sample, as well as sample receiving status (0 h).

For the study of α′ formation phase, it was carried out X-ray diffraction (XRD) test around a peak (200), scanning angle (2θ) from 63° to 65.5° for different types of treatment. An X-ray diffraction

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Table 1
Duplex stainless steel UNS-S31803 chemical composition as-received in weight percent (wt.%). (C – carbon, Mn – manganese, P – phosphorus, S – sulfur, Si – silicon, Cr – chromium, Ni – nickel, Co – cobalt, Cu – copper , Mo – molybdenum , N – nitrogen, Nb – niobium , Al – aluminum, Sn – tin, Ce – cerium, Fe – iron).

C	Mn	P	S	Si	Cr	Ni	Co
0.018	1.480	0.019	0.001	0.450	22.220	5.590	0.130
Cu	Mo	N	Nb	Al	Sn	Ce	Fe
0.280	3.080	0.180	0.021	0.003	0.012	0.020	66.496

meter was used, XRD-6000 vertical type and copper potassium alpha (Cu Kα) radiation.

Ultrasonic testing was carried out in a Krautkramer USD 15, by a pulse echo technique using a V112-RM normal contact transducer 5 MHz longitudinal wave, manufactured by OLYMPUS. Dimension of samples tested were $55 \times 25 \times 10\ mm^3$.

Sonic speed was determined by as:

$$v = \frac{d}{t}, \tag{1}$$

where d is the sample thickness and t is the time that the ultrasonic signal takes to scan sample thickness and to return to the transducer. Time is determined by overlapping two consecutive peaks of tension diagram versus time.

To obtain the modulus of elasticity (E), the density and longitudinal and transversal velocities associated with the sample were determined. Hence, modulus of elasticity was measured based on standard practice for measuring ultrasonic velocity in materials:

$$E = \frac{\rho Vt(3Vl^2 - 4Vt^2)}{Vl^2 - Vt^2}, \tag{2}$$

where ρ is density and Vt and Vl are longitudinal and transversal velocities, respectively.

3. Results and discussion

Phase changes were studied at temperature range of 425–475 °C for duplex stainless steel UNS S31803. Diffraction measurement with an X-ray, Fig. 1, which was carried out in samples as received and samples aged at temperature of 525 °C at 50 h only show the presence of γ phase and peaks related to α phase, Fig. 2, falling outside the purpose of this work since the main objective was to evaluate just the effect of α phase. Temperature

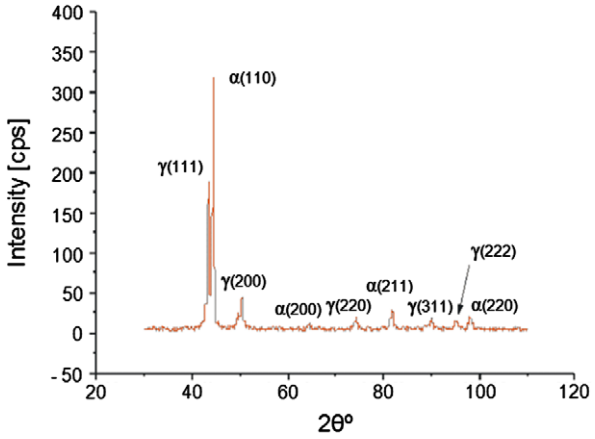

Fig. 1. Diffractiongram of sample received, showing only the presence of α and γ phases (2θ = values of abscissa $\times 10^{-4}$).

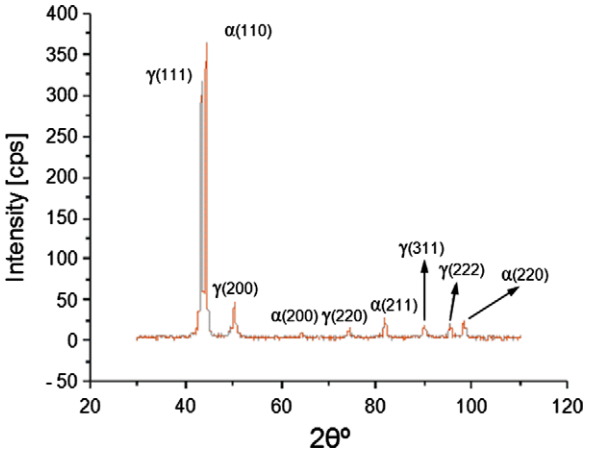

Fig. 2. Diffractongram of sample aged at temperature of 525 °C at 50 h (2θ = values of abscissa $\times 10^{-4}$).

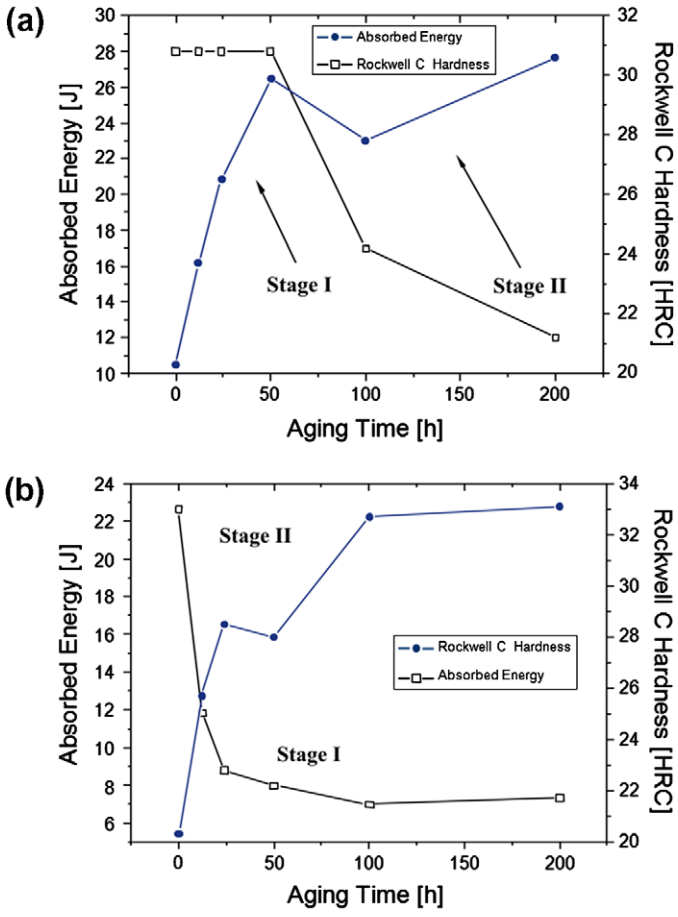

Fig. 3. Presence of two-stage hardening on samples treated at 425 °C and 475 °C. Variation of Rockwell C hardness measures due to aging time at temperature of 425 °C (a) and 475 °C (b).

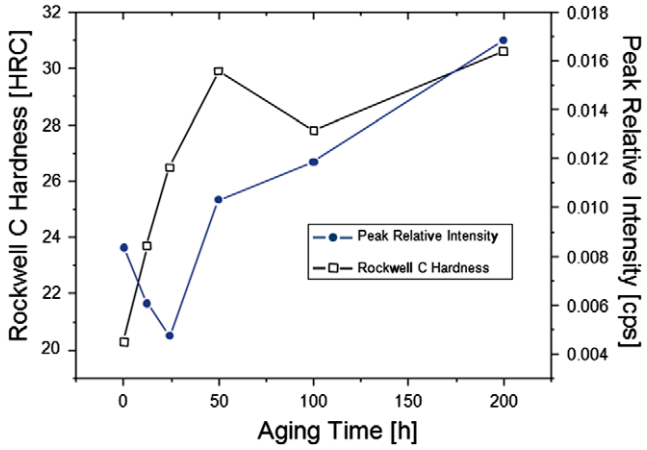

Fig. 4. Relationship between relative intensity of peak 200 Rockwell C hardness for samples aging at a temperature of 425 °C.

range for the study of this work stays below 525 °C, which corresponds to the transformation region of α phase.

Studied temperature range is characterized by the decomposition of the $\alpha_{initial}$ phase into two phases: one poor in chromium and another one rich in chromium. A mechanism responsible of this transformation is known as spinodal decomposition [8], and γ phase does not suffer any transformation within this temperature range [9]. For an easy understanding of the transformations taking place during ageing at the temperature range of 425–475 °C, the hardness was analyzed through energy absorbed and hardness measurements, Fig. 3. This figure shows that hardness curve may be split into two-stage hardness. The presence of two-stage hardness has been noticed in other spinodal decomposition systems [10,11] a fast increase in hardness at I stage is followed by a transition level. Afterwards, a second stage begins at a less hardened rate and with tendency for a hardness level. According to Choo et al. [10], two sources of hardness responsible for stages I and II are spinodal decomposition and the growth of particles of phase organization, respectively.

At the second stage, hardness growth rate is less, especially due to the coalescing of α′ phase particles.

The presence of side bands derived from the phases organization due to the mechanism of spinodal decomposition have been observed by a diffraction of the selected area in scanning electronic microscopy and by X-ray diffraction [12,13].

The organization of α′ phase was analyzed in this work by X-ray diffraction. The study of variation of peak intensity (200) shows that samples aged at temperature of 425 °C, Fig. 4, indicating a drop of peak relative intensity to values within 24 h, as presented in [14]. At this temperature, decomposition kinetic is slower, allowing a better follow-up of spinodal decomposition. Relative intensity reduces due to the spread of peak 200, as far as rich in chromium and poor in chromium regions grow, resulting in side bands which increase the peak and reduce its relative intensity; this same effect was also observed by Miyazaki and Koyama [15].

Phase transformations were followed-up by sonic speed measurements at temperatures 425 °C and 475 °C, Fig. 5, and we observed that sonic speed has a direct relationship with hardness. This indicates that sonic speed can follow up transformations of phases occurred on two stages of hardness successfully.

Matsubara et al. [16,17] conducted studies in samples of duplex stainless steel at temperature of 450 °C and verified that sonic speed measures were promising for the follow-up of aging kinetics at this temperature.

Bouda et al. [18] observed that the variation of microstructure and hardness is correlated to sonic speed and as thinner the steel

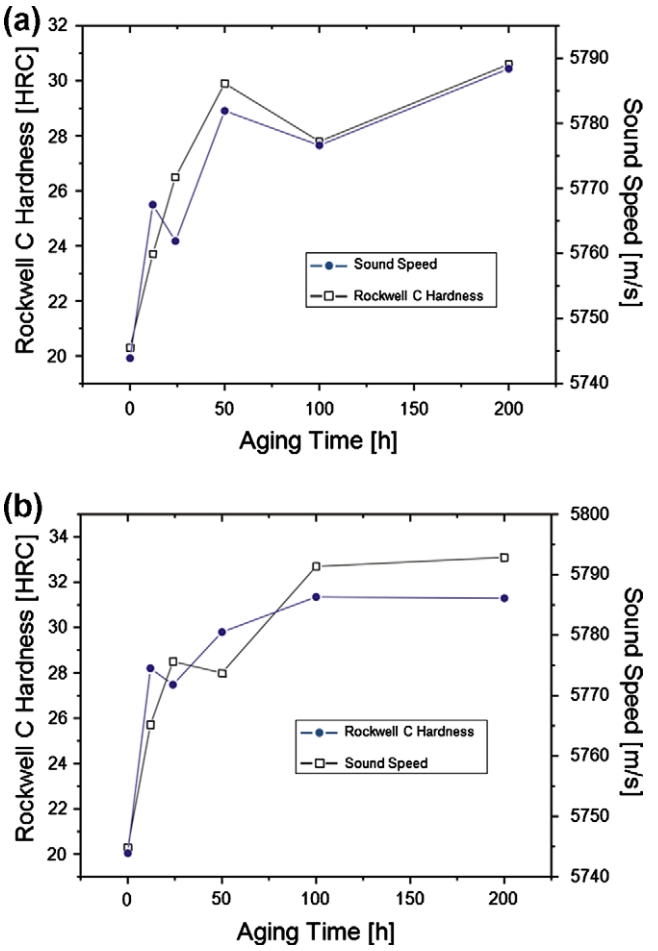

Fig. 5. Variation of sound speed and Rockwell C hardness with aging time for temperatures of 425 °C (a) and 475 °C (b).

Table 2
Modulus of elasticity results from of longitudinal and transversal velocities, and density material.

Thermal conditions		ρ (kg/m^3)	*Vl* (m/s)	*Vt* (m/s)	*E* (GPa)
As-received			5746.72	3310.68	211.54
425 °C	12 h		5765.52	3305.77	211.50
	24 h		5757.42	3308.05	211.53
	50 h		5769.39	3310.54	212.02
	100 h	7709.99	5773.44	3312.52	212.28
	200 h		5786.02	3313.48	212.64
475 °C	12 h		5773.76	3308.35	211.91
	24 h		5774.62	3307.09	211.82
	50 h		5781.38	3311.58	212.37
	100 h		5784.11	3321.74	213.35
	200 h		5797.85	3338.43	215.17

microstructure, the larger the outlining surface, increasing material hardness and as a consequence, raising the sonic speed.

In materials where micro structural transformation is caused by a mechanism of spinodal decomposition during the α′ phase decomposition, alternate rich in chromium and poor in chromium regions are formed. Chromium-rich regions are responsible by changing ferrite matrix rigidity and to cause raising of sonic speed. At first stage, spinodal decomposition of matrix occurs and consequently, formation of α′ phase coherent to the matrix; at the second stage, cohesion with matrix is lost and α′ phase grows. With that, rigidity tends to become constant and a level for sonic speed

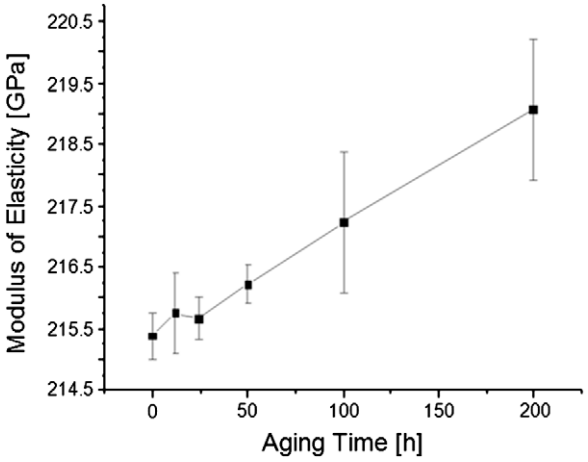

Fig. 6. Modulus of elasticity at temperature of 475 °C.

values is observed. Composition fluctuation generated by α′ phase decomposition changes modulus of elasticity values during phase transformation. Material zones which start becoming solute-rich for further consolidation with formation α′ phase will have their rigidity value changed with aging time.

The modulus of elasticity of those regions will vary with aging time, as shown in Table 2. Those zones formed by spinodal decomposition increase ferrite matrix rigidity and will block plane slide and plastic deformation, thus increasing material hardness, see Fig. 6. This way, sonic speed measures seem promising to follow up small micro structural variations, such as transformation by spinodal decomposition which is not detected by conventional techniques.

4. Conclusions

Spinodal decomposition mechanism study of UNS S31803 duplex stainless steel was carried out at temperatures of 425 °C and 475 °C. Transformations analysis was based on sonic speed, X-ray diffraction and hardness test.

Results obtained by this work allow concluding that:

- Sonic speed measurements could detect phase transformations by spinodal decomposition. Duplex stainless steel studied presented a two-stage hardness verified through sonic speed. The first hardening stage is characterized by a spinodal decomposition mechanism and the second stage by a growth of formed phases.

The variation of modulus of elasticity is related to composition fluctuations due to decomposition mechanism of α phase, thus causing the hardening of ferrite matrix and causing a change in modulus of elasticity. Sonic speed measurements could detect a development of modulus of elasticity successfully.

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