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TU Graz

F. R. PUCCI[1], T. A. LOPES[1], J. W. CALDERON-HERNANDEZ[2], R. MAGNABOSCO[1]

APPLICATIONS OF X-RAY DIFFRACTOMETRY ON PHASE QUANTIFICATION IN STAINLESS STEELS

Abstract

Performance of stainless steels (SS) is a direct function of the microstructure, and phase quantification is an important experimental procedure for microstructural characterization. X-ray diffratometry (XRD) is widely used in phase identification of SS, and analysis of the diffracted intensity peaks of the phases allows the determination of their volume fractions. X-ray diffraction patterns using copper or chromium X-ray sources were obtained for two different SS. The first group of samples are composed of a duplex stainless steel (DSS) solution-treated at three different temperatures, in order to obtain different ferrite-to-austenite volume fraction ratios. The other group was composed by quenched and tempered samples of a supermartensitic stainless steel (SMSS) with different amounts of retained and/or reversed austenite. It was found that XRD results using copper targets as source of X-rays lead to better quantification of phases for both SS studied. However, the technique was influenced by crystallographic texture in DSS phases quantification; in the absence of marked texture, XRD results in quantification similar to other techniques. Only SMSS samples with higher amounts of coarse reversed austenite (as in samples tempered for 2 h at 625 or 650 °C) could have austenite partially quantified, being magnetic measurements a better indirect technique for quantification of phases in SMSS.

Keywords

X-ray diffratometry. Duplex stainless steel. Supermartensitic stainless steel.

1. Introduction

Duplex Stainless Steels (DSS) are applied in situations where mechanical resistance, toughness and high corrosion resistance are needed. Their typical microstructure approximately equal amounts of ferrite and austenite, which can be obtained after solution heat treatment between 1000 and 1200 °C followed by fast cooling, usually in water. This processing route maintain DSS in a metastable equilibrium, and for this reason subsequente heating cycles could lead to the formation of undesirable phases, like sigma, chi or chromium nitrides [1,2].

Supermartensitic Stainless Steels (SMSS) belongs to another important class of materials, and were developed to provide the high mechanical resistance associated to martensitic structures, together to the ability of receiving welding procedures without a loss in corrosion resistance. The low content of carbon in SMSS allows the martensitic phase to have a body centered cubic (BCC) crystal structure, the same found in the ferrite phase. Martensite, in SMSS, is crystallographic equivalent to the ferrite phase, differing from this phase in the phase transformations that lead to its formation. Ni content of SMSS can lead to expressive amounts of retained austenite after quenching, and/or reversed austenite during tempering heat treatment. [3].

[1] FEI University, [2] USP

Considering that desired properties of DSS and SMSS are close related to the amounts of ferrite and austenite (for DSS), or the amount of retained/reversed austenite in SMSS, this work will analyse the possibility of X-ray diffraction (XRD) as a technique for phases characterisation and quantification, comparing the quantification results by XRD to the quantification of ferrite and martensite performed by magnetic measurements using a ferritscope. A UNS S31803 DSS and an experimental SMSS alloy were used, both in different heat treatment conditions.

2. Experimental Procedures

Samples of UNS S31803 DSS were obtained from a 3 mm thickness sheet, and were solution-treated for 30 min at 1070, 1130 or 1180 °C and water quenched. Samples of an experimental SMSS were austenitized at ,050 °C, oil quenched and then tempered for 2 hours at 550, 575, 600, 625, 650 or 700 °C. Chemical compositions of both alloys are presented in Table 1.

Table 1 – Chemical compositions (wt%) of the DSS and SMSS studied.

	Cr	Ni	Mo	N	C	Mn	Si	Nb	Ti	Cu	Fe
DSS	22.48	5.74	3.20	0.162	0.018	1.42	0.35	-	-	0.15	bal.
SMSS	13.35	5.10	1.08	0.17	0.008	0.63	0.39	0.11	0.008	-	

Specimens are metallographic polished before X-ray diffraction analysis, which were performed in a Shimadzy XRD-7000 diffractometer. Copper target X-ray source generated Cu Kα1 X-ray (λ = 0.15406 nm, using a monochromator crystal just before the X-ray detector) were used for XRD analysis, with scanning angle in the range of $40° < 2\theta < 100°$ for the DSS and $40° < 2\theta < 85°$ for the SMSS. Chromium target X-ray source generated Cr Kα1 X-ray (λ = 0.22897 nm, using a vanadium filter in the X-ray source) were also used in XRD analysis, with scanning angle in the range of $60° < 2\theta < 160°$ for both steels. Independent of the X-ary source, a step of 0.02° and a scanning rate of 0.5 °/min were employed; acceleration voltage in source was 30 kV, and filament current was 30 mA, generating a 0.9 kW power X-ray beam. For each sample, ten XRD patterns were obtained.

As described elsewhere [4, 5, 6], when only two phases are identified in XRD, the quantification of phases corresponding to the peaks found was possible through the use of Eq. (1), which relates the volumetric fraction (X), the integrated intensity (I) of the diffraction peak and the scattering factor (R) of the (n) peaks related to α' phase and (m) peaks related to γ phase.

$$X_{\alpha'} = \frac{\frac{1}{n}\sum_1^n \frac{I_{\alpha'}}{R_{\alpha'}}}{\frac{1}{n}\sum_1^n \frac{I_{\alpha'}}{R_{\alpha'}} + \frac{1}{m}\sum_1^m \frac{I_\gamma}{R_\gamma}} \tag{1}$$

Scattering fator (R) was calculated from Eq. (2) for each crystallographic (hkl) Miller index plane, knowing: i) structure factor (F), ii) the multiplicity factor (p) associated with the plane (hkl), iii) diffraction angle θ of the Bragg Law (Eq. 3), iv) Debye- Waller (DWF) temperature factor, and v) the volume of unit cell (V) of the phase. V was calculated using the

unit cell parameter (a) obtained for all (hkl) plane spacing (d) using Eq. 4, since both phases are cubic crystal structures [4,5]. All d values obtained were used for the Nelson-Riley adjustment (eq. 5) [7], obtaining a in each XRD for both phases.

$$R_{hkl} = \left(\frac{1}{V^2}\right)[F^2 p(\frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta})]DWF \tag{2}$$

$$n\lambda = 2d_{(hkl)}\sin\theta \tag{3}$$

$$a = d_{(hkl)}\sqrt{h^2 + k^2 + l^2} \tag{4}$$

$$CP_{N-R} = \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) \tag{5}$$

The DWF factor is a function of the diffraction angle 0 and the wavelength of the X-ray source (λ), and according to ASTM E 975- 13 [8], DWF can be estimated by Eq. (6).

$$DWF_{(hkl)} = e^{-0,71.\left(\frac{\sin\theta}{\lambda}\right)^2} \tag{6}$$

The structure factor F(hkl) is dependent on the atomic scattering factor (f), determined by the mean influence of atomic species in a phase. With the weighted (f), the value of structure F(hkl) is calculated using simplifications according to the type of structure, BCC or FCC in the case of this work [4, 5, 6].

After XRD analysis, the volume fraction of magnetic phase (ferrite in DSS and martensite in SMSS) were obtained with the aid of a ferritscope MP30 FISCHER, which was calibrated using standard samples containing 14.4 %, 30.7 %, 86.2 % or 100% of magnetic phase. In each sample, 10 to 30 measurements were taken, determining mean values and standard deviation.

3. Results and discussion

Typical XRD patterns for studied DSS and SMSS can be observed in Fig. 1. Quantification of the ferromagnetic martensite volume fraction (obtained in ferritscope measurements) compared to the martensite volume fraction (obtained by XRD analysis) are presented in Fig. 2. In a similar way, in Fig. 3 the ferromagnetic ferrite volume fraction is compared to ferrite volume fraction of the DSS samples.
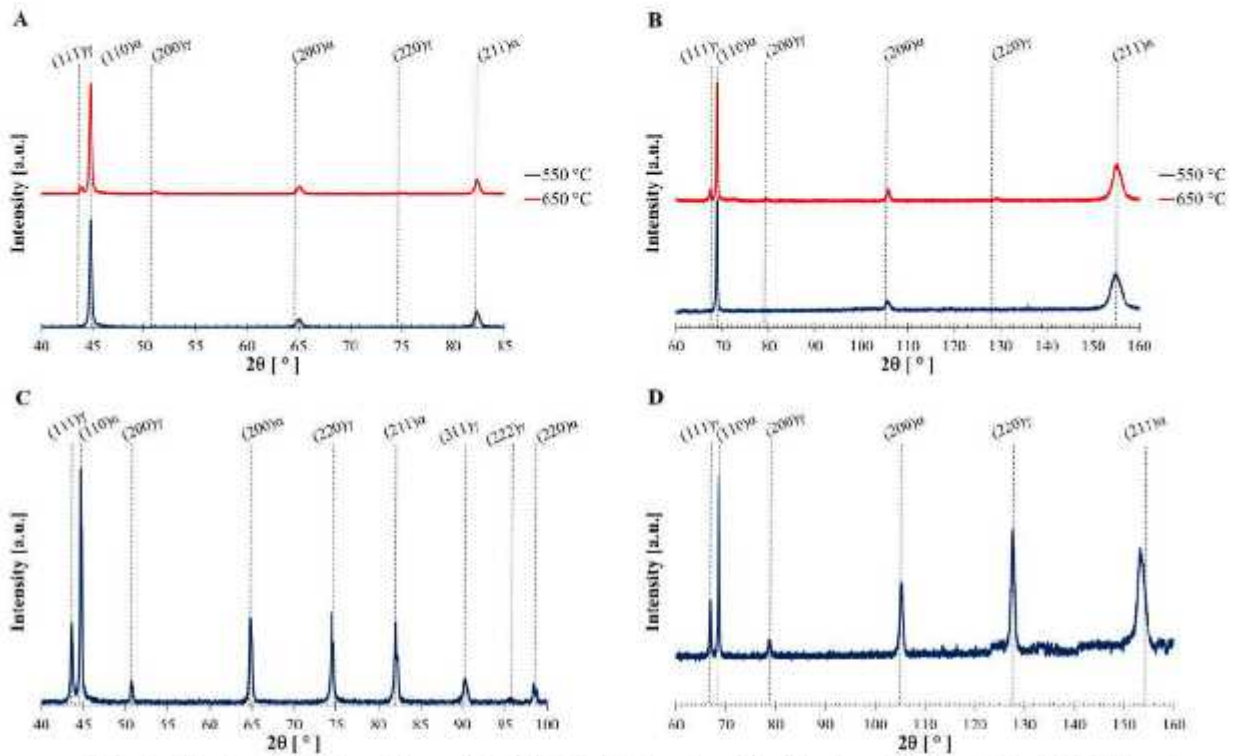
Fig 1. Typical XRD patterns for (A) SMSS using Cu Kα1 radiation, (B) SMSS using Cr Kα1 radiation, (C) DSS using Cu Kα1 radiation, and (D) DSS using Cr Kα1 radiation. Crystallographic planes of the phases are identified in each XRD pattern.
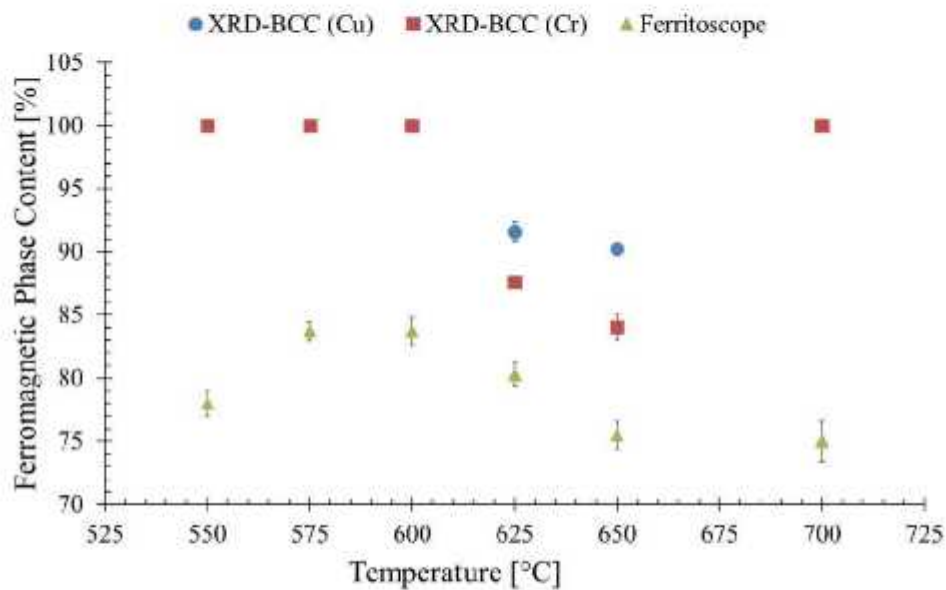

Fig 2. Ferromagnetic martensite volume fraction (obtained in ferritscope measurements) compared to the martensite volume fraction (obtained by XRD analysis using Cu Kα1 or Cr Kα1 radiation) for the SMSS.
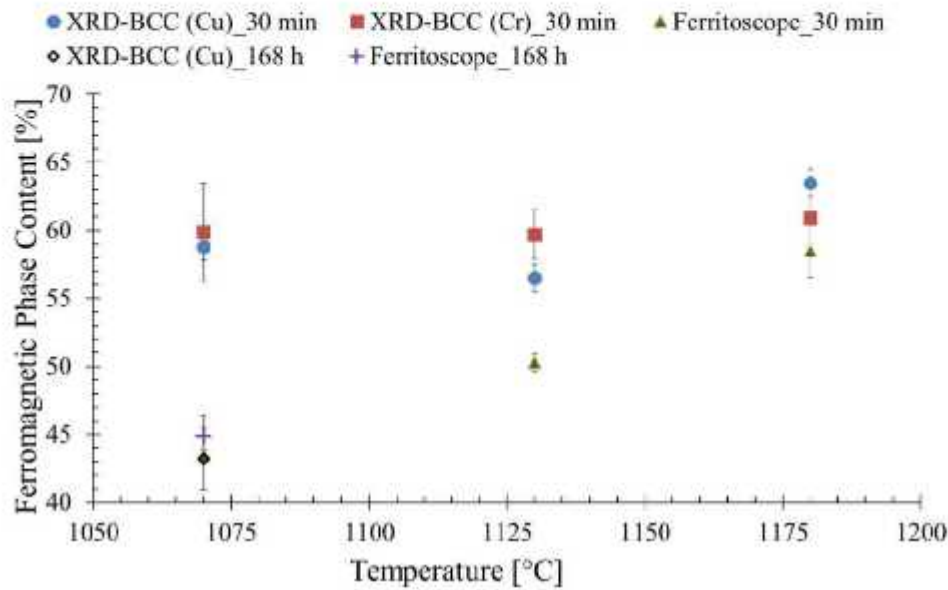
Fig 3. Ferromagnetic ferrite volume fraction (obtained in ferritscope measurements) compared to the ferrite volume fraction (obtained by XRD analysis using Cu Kα1 or Cr Kα1 radiation) for the DSS.

The SMSS only showed γ(200), γ(111) and γ(220) peaks for the samples tempered at 625 or 650°C, in both radiation sources (Fig. 1A and 1B). For this reason, only at those temperatures austenite was quantified through XRD (Fig. 2). For all other temperatures, XRD analysis showed only martensite. Those results are very different from ferritscope measurements, which demonstrates that there are retained and/or reversed austenite in all samples. One explanation for this occurence is the probable morphology of the austenite in those samples.

Retained austenite (more prone to occur at lower tempering temperature) was retained between martensite laths. The small thickness of these interlath austenite did not provide a sufficient volume of FCC crystal to allow X-ray diffraction, and the intensity of the peaks related to FCC will be much smaller than the diffraction peak intensities for martensite.

At 625 or 650 °C tempered samples, as reported elsewhere [3] reverse austenite can be formed during tempering. Retained austenite from quenching, in those samples, act as nucleation sites for reversed austenite formation during tempering, allowing this phase to grow. Larger volume of austenite allow a more intense diffraction of specific austenite planes, allowing its detection and quantification. The volume fraction of austenite measured by XRD, however, are smaller than the volume fraction of austenite measured by ferritscope, indicating that part of the retained austenite remained thinner, or part of the reversed austenite was transformed into martensite during cooling after tempering. This is probably what was happened in the sample tempered at 700 °C: a higher reversed austenite volume fraction lead to higher martensite formed after tempering.

Quantification by XRD of retained/reversed austenite in samples tempered at 625 °C or 650 °C, however, are more closer to ferritscope results if Cr Kα1 radiation is employed. This could be a result of the better separation between γ(111) and α(110) peaks when Cr radiation is used (Fig. 1A and 1B), making the definition of the integrated intensity (I) of the diffraction peaks more precise.

Analysis of the XRD patterns for the DSS (Fig. 1C and 1D) clearly shows that all austenite peaks have higher intensities when compared to the austenite peaks observed in the SMSS samples (Fig. 1A and 1B). This corroborates the previous idea: being austenite in DSS

present in higher volume fractions, and in a more block morphology, its detection by XRD are facilitated. This lead to the closer results between XRD quantification using Cu Kα1 radiation and magnetic measurements for the DSS solution-treated at 1130 °C or 1180 °C (Fig. 3). However, results obtained from XRD patterns using Cr Kα1 radiation were almost the same for the three temperatures studied. Nine different diffraction peaks were found using Cu Kα1 radiation, while only six were found during Cr Kα1 radiation XRD. Using Cr source, the number of peaks were smaller, and the definition of area under peaks (or the integrated peak intensity I) is worse. This is probably caused by the use of a V filter instead of a monochromator crystal, which intensify the presence of background and noise in Cr source XRD. The better separation of γ(111) and α(110) peaks, which allowed a better quantification in SMSS, was not an advantage in DSS phase quantification: the lack of more well defined peaks was mandatory in this case.

At the lower solution-treatment temperature of DSS (1070 °C) XRD quantification of phases, even using a copper source, resulted in values different from ferritscope quantification. The microstructure of the sample solution treated for 30 min at 1070 °C (Fig. 4A) showed a heavily banded microstructure, which can be associated to a crystallographic texture of that sample. If this happened, the quantification by XRD (which suppose a non-oriented sample) was compromised.

Evaluation of the possible influence of texture in XRD quantification of phases, using a copper source, was done by treating another sample of DSS for 168 h at 1070 °C. Microstructure of this sample presented larger grain sizes for both phases, and the equiaxial grains were more randomly distributed in the microstructure (Fig. 4B), and this can be an indication of the reduction of the previous texture. Ferritscope analysis of that sample (Fig. 3) showed that this higher solution-treatment time did not altered the volume fraction of phases, confirming that both samples, treated for 30 min or 168 h, reached the equilibrium volume fraction of ferrite and austenite.

XRD quantification of phases in the 168h solution-treated sample showed that values of ferrite and austenite obtained by this method are equivalent to the ferritscope measurements, confirming the influence of microstructure in the XRD technique.
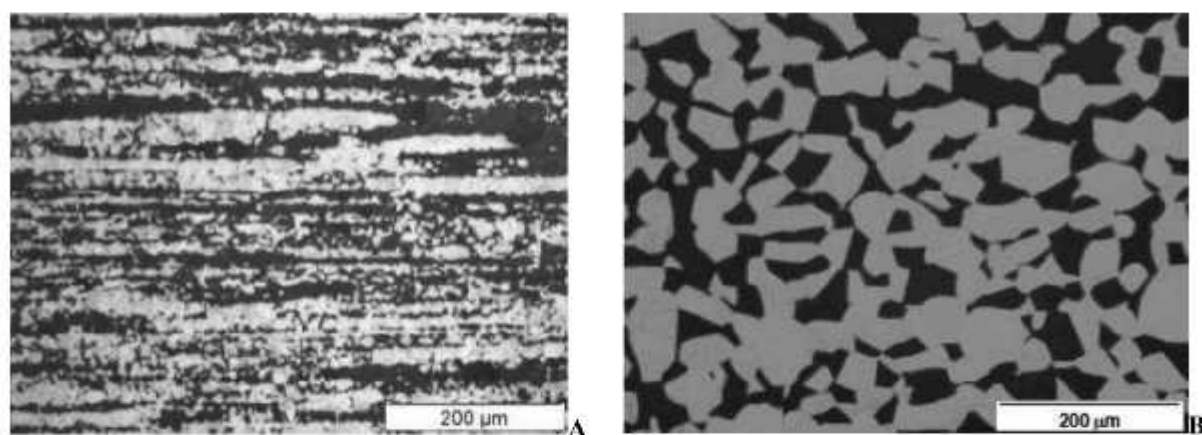

Fig 4. Microstrutures of the DSS solution-treated at 1070 °C for (A) 30 min and (B) 168 h, after modified Beraha etching. Ferrite is the darker phase, austenite is the lighter..

4. Conclusions

➤ Ferritscope analysis of SMSS showed that retained and/or reversed austenite is present in all tempering conditions. However, XRD quantification were only able to detect and

quantify austenite in samples where the morphology of austenite lead to a higher volume, enhancing austenite peaks intensity.

- For the SMSS, the better separation between $\gamma(111)$ and $\alpha(110)$ peaks when Cr Kα1 radiation was used lead to a better quantification of the reversed austenite formed at 625 °C and 650 °C tempered samples. However, detection of thinner laths of retained austenite was not possible even using Cr Kα1 radiation.
- For the DSS, quantification of phases by XRD was only possible using Cu Kα1 radiation, and the samples can not present preferential orientation of phases.

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