

## RIETVELD QUANTITATIVE ANALYSIS OF SUPER DUPLEX STAINLESS STEEL

Jorge L. Garin and Rodolfo L. Mannheim  
Department of Metallurgical Engineering, Universidad  
de Santiago de Chile, Casilla 10233, Santiago, Chile

### ABSTRACT

In order to interpret highly superimposed diffraction patterns, the Rietveld method together with conventional X-ray powder diffraction techniques were carried out on a series of heat-treated weldments of cast super duplex stainless steel. The thermal processing of the samples proceeded at temperatures in the range from 1073 K to 1223 K for periods of time from 1 to 96 h. This procedure permitted an accurate quantification of the microstructural components such as austenite, ferrite and sigma-phase in all studied samples. The contents of sigma-phase in the heat-affected zones of all weldments reached asymptotical values of 30 to 38 wt. % after 96 h of heat treatment.

### INTRODUCTION

A number of high-alloy stainless steels usually known as *duplex stainless steels (DSS)*, are an important class of engineering materials currently being considered for a variety of heavy-service requirements, among many industrial applications (Davis, 1994; Gun, 1997). In fact, the widespread application of duplex steels is based upon their remarkable mechanical and chemical properties such as strength (Liou *et al.*, 2001), chloride stress-corrosion cracking-resistance (Yang and Castle, 2002) and pitting corrosion-resistance (Cvijovic and Radenkovic, 2006). DSS are two-phase alloys based on the Fe-Cr-Ni system. They have approximately equal proportions of the body-centred cubic ferrite and face-centred cubic austenite phases in their microstructure. These materials are further characterized by their very low carbon content (less than 0.03 %) and additions of molybdenum, nitrogen, tungsten and copper. The usual contents of chromium and nickel are in the range from 20 to 30 % for Cr and from 5 to 10 % for Ni. To determine the extent of pitting corrosion resistance offered by the material, the *pitting resistance equivalent (PRE)* is commonly used (Herbsleb, 1982). A minimum PRE value of 40 is often used to define the *super grades*. Among the many manufacturing processes involving wrought and cast DSS, welding metallurgy plays a key role (Badji *et al.*, 2008). However, the performance of DSS can be significantly affected by the welding process (El Koussy *et al.*, 2004). Hence, the high alloy content and the presence of a ferritic matrix renders DSS susceptible to embrittlement, loss of mechanical properties and corrosion resistance when the material is subjected to relatively high temperatures, e.g. 813 K to 1173 K. (Pohl *et al.*, 2007). This is caused by the transformation of the ferritic component into the so-called *sigma-phase* ( $\sigma$ ) (Pohl and Stortz, 2004). This phase is a complex intermetallic compound of Fe, Cr and, to a lesser extent, Mo (Sopousek and Kruml, 1996). The structure type of the compound is based on an ideal stoichiometric composition  $AX_2$ , Pearson symbol tP30 and space group  $P4_2/mnm$  (Sihna, 1972). Since the chemical composition of the compound in the Fe-Cr system is approximately  $Cr_6Fe_7$ , the Cr and Fe atoms are disordered with fractional site occupation among the suitable equivalent positions in the space group,

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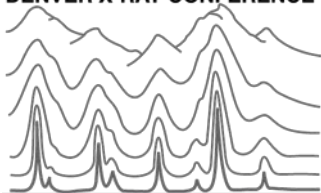
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disclosing a polyhedral array of the Frank-Kasper type (Pearson, 1972). Sigma preferably nucleates along grain boundaries of  $\delta$ -ferrite - austenite,  $\alpha$ -ferrite - austenite or  $\delta$ -ferrite- $\delta$ -ferrite. Compounds with nearly equi-atomic composition in Fe and Cr are formed by an order-disorder transformation of the ferrite phase, while those with a smaller content of Cr precipitate through a eutectoid transformation of the kind  $\alpha = \gamma + \sigma$ , with  $\gamma$  being called *secondary austenite* (Tseng *et al.*, 1994).

Owing to the highly detrimental effects of sigma-phase precipitation on the mechanical and chemical properties of the DSS alloys, the determination of relative amounts in the microstructure by means of quantitative X-ray diffraction demands a rather precise processing of the experimental data. Taking into account the usually complex powder diffraction patterns of these alloys, which disclose many overlapping reflections, and the strong preferred orientations of the matrix components caused by solidification dendrites formed in castings as well as in welded joints, the present article describes the application of the Rietveld method to resolve the referred difficulties in weldments of a super duplex stainless steels subjected to annealing at various temperatures and processing times.

## EXPERIMENTAL

The raw alloy utilized in the present study was supplied on demand by a commercial steel producer. All casts were poured in the classical Y-shape moulds, according to ASTM A395 standard, to deliver samples of 50 mm thickness. The average chemical composition of the resulting Y-shaped ingots, determined by means of emission spectroscopy, is detailed in Table 1. The contents of the main elements are within the composition ranges defined by ASTM A 890/A 890 M standard (UNS J93404).

Table 1. Chemical composition of the cast alloy (mass %)

Element	Sample	Standard
C	0.026	0.03 max
Si	0.56	1.00 max
Mn	0.90	1.50 max
P	0.01	0.04 max
S	0.001	0.04 max
Cr	24.77	24.0-26.0
Ni	6.41	6.0-8.0
Mo	3.94	4.0-5.0
N	0.25	0.10-0.30

Specimens suitable for heat treatment, light microscopy and X-ray powder diffraction experiments, of dimensions 45x25x5 mm<sup>3</sup> were machined from the test section of the Y-blocks. Observation surfaces were prepared by usual metallographic techniques, up to a final step of wet polishing with alumina of 0.05  $\mu$ m particle size. The manufacturing of the weldments (butt joints with "X" bevels) was carried out by means of the usual manual arc welding technology (SMAW) with INOX 2509MoB electrode. The heat treatment process included 1 h homogenization annealing at 1323 K followed by heating for sigma-phase induction at 1073 K, 1133 K, 1173 K,

and 1223 K, for various periods of time over the range from 1 to 96 h. The X-ray powder diffraction data were collected on a SIEMENS D5000 diffractometer (40 kV, 30 mA) equipped with a diffracted beam graphite monochromator, Cu K $\alpha$  radiation ( $\lambda_{K\alpha1}=0.15406$  nm,  $\lambda_{K\alpha2}=0.154439$  nm,  $I_{K\alpha1}/I_{K\alpha2}=0.5$ ), Bragg-Brentano geometry,  $\theta$ - $\theta$  scan, sample spinning, divergence slit of 1 mm, antiscatter slit of 1 mm and receiving slit of 0.1 mm. The X-ray diffraction measurements were carried out within the scan range of 30° to 85° (2 $\theta$ ) with step size of 0.02° (2 $\theta$ ) and step counting time of 15 s.

## RESULTS AND DISCUSSION

Due to the extensive number of processed samples, the experimental results of this study are now described in terms of representative samples of the raw alloy and weldments annealed at selected temperatures for 3, 6, 12, 24, 48, 72 and 96 h. The light-microscopy metallography shows the morphology and particle size distribution of the diffracting surfaces of the specimens. Hence Fig. 1 reveals the microstructure of the as-cast material, where a distribution of irregular-shape

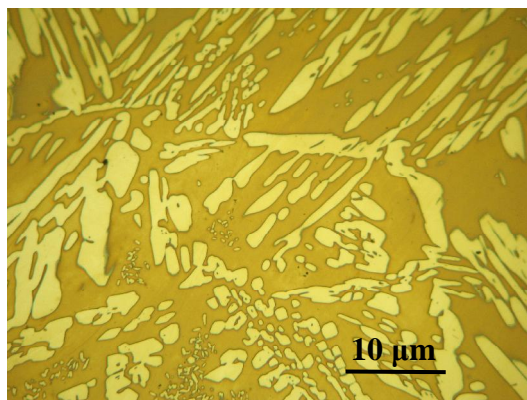


Fig. 1. Microstructure of the as-cast alloy. (500 X)

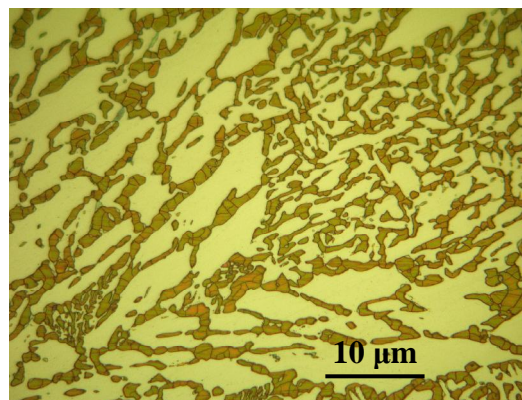


Fig. 2. Microstructure of the weldment (HAZ) at 1173 K, 72 h. (1000 X)

austenite grains (light particles) is superimposed on a matrix of ferrite (dark background). On the other side Fig. 2 illustrates the precipitation of sigma-phase in the heat-affected zone (HAZ) of the weldment annealed at 1173 K during 72 h. As depicted in the micrograph sigma particles were brought in dark brown tones after etching with the proper reagent. Here a massive distribution of small sigma particles is encountered along the austenite-austenite grain boundaries, where nucleation preferably takes place. The formation of sigma-phase with longer treatment times shows much thicker particles, distributed along ferrite-ferrite boundaries. This clearly indicates that particles which originally nucleated along grain boundaries grew towards the ferritic phase, increasing their relative presence in the alloy, while the content of ferrite was conversely diminished. Next, a qualitative identification by X-ray powder diffraction was performed on all studies samples. Hence, ternary ferrite (Fe-Cr-Ni) and ternary austenite (Fe-Cr-Ni) were found in the parent alloy, in close agreement with the pattern shown in Fig. 3. According to this diffraction pattern, formation of sigma-phase does not occur in this kind of specimens. Furthermore, the pattern evidences strong preferred orientations effects of the {200} lattice planes in the ferrite solid solution phase. Fig. 4 - 10 show the XRD patterns of samples corresponding to the annealed weldments at 1133 K for 3, 6, 12, 24, 48, 72 and 96 h respectively.

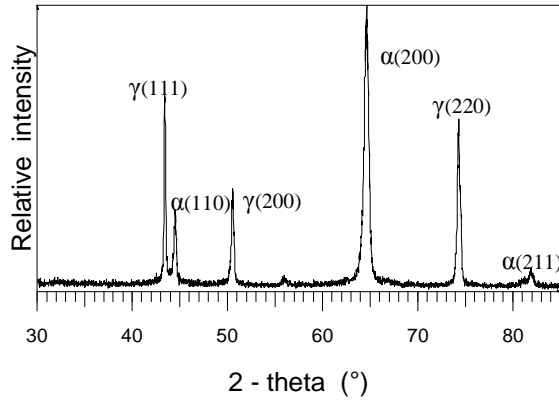


Fig. 3. XRD pattern of parent alloy ( $\gamma$ : austenite,  $\alpha$ : ferrite)

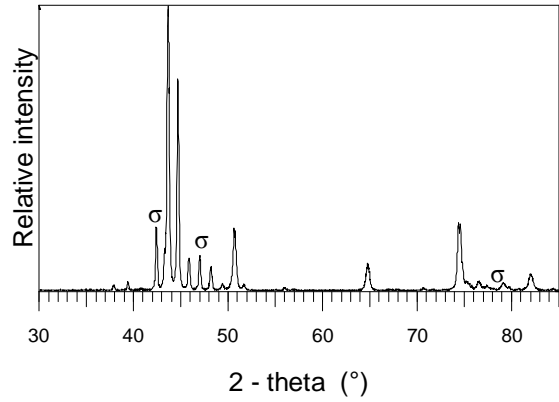


Fig. 4. XRD pattern of weldment (HAZ) annealed at 1133 K, 3 h. ( $\sigma$ : sigma-phase)

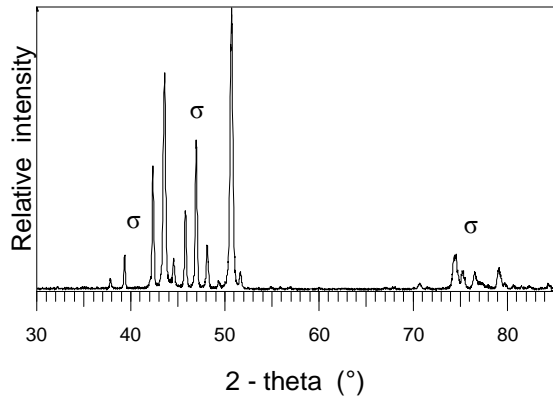


Fig. 5. XRD pattern of weldment (HAZ) annealed at 1133 K, 6 h.

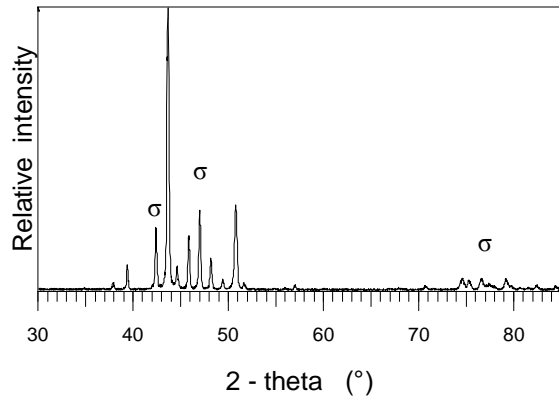


Fig. 6. XRD pattern of weldment (HAZ) annealed at 1133 K, 12 h.

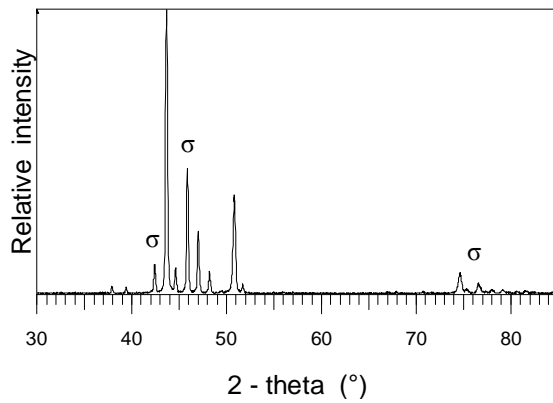


Fig. 7. XRD pattern of weldment (HAZ) annealed at 1133 K, 24 h.

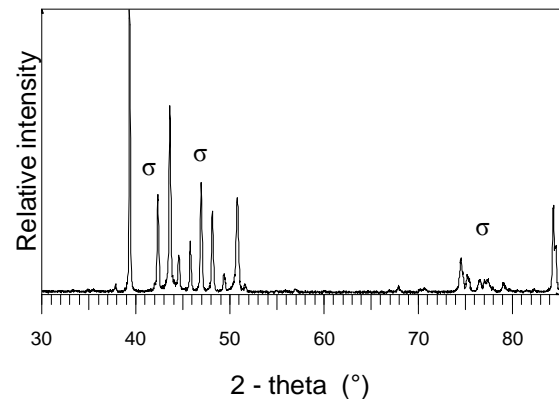


Fig. 8. XRD pattern of weldment (HAZ) annealed at 1133 K, 48 h.

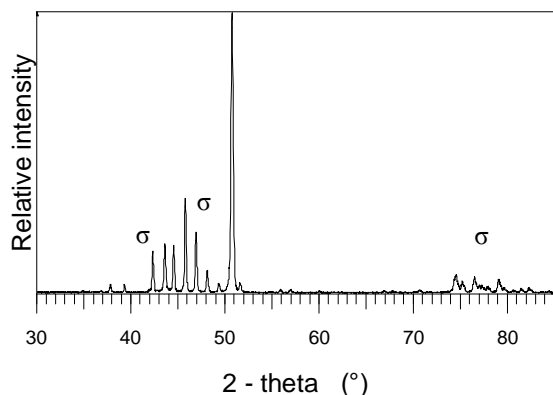


Fig. 9. XRD pattern of weldment (HAZ) annealed at 1133 K, 72 h.

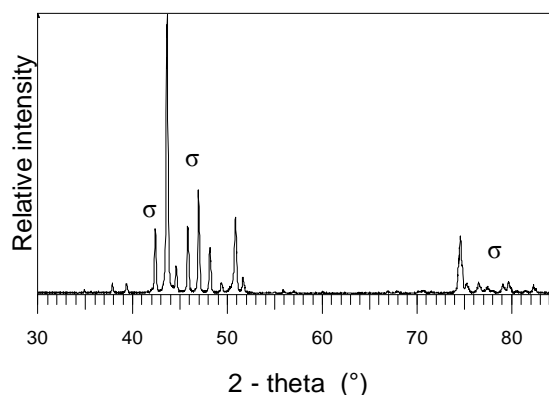


Fig. 10. XRD pattern of weldment (HAZ) annealed at 1133 K, 96 h.

Formation of sigma as well as significant preferred orientations of the component phases can be corroborated in all heat-treated samples. In order to determine the relative amount of phases in the heat-treated alloys, particularly sigma-phase, quantitative X-ray powder diffraction based on the Rietveld processing of the data (McCusker *et al.*, 1999), was performed on all samples. The refinements were carried out assuming the split Pearson VII function for the simulation of the peaks shape, while the background was modelled by a 4rd order Chebychev polynomial; the refinement cycles were based upon the variation of structural and instrumental parameters. The correction term for the presence of textures utilized the March-Dollase function (Dollase, 1986), represented by:

$$P_K = (G_1^2 \cos^2 \alpha + (1/G_1) \sin^2 \alpha)^{-3/2} \quad (1)$$

where  $\alpha$  is the angle between the normal to the diffracting plane and the presumed cylindrical-symmetry axis of the texture and  $G_1$  is a numerical refinable parameter. Due to the somewhat simple formation of dendrites in the weldments, the uniaxial March-dollase model is applicable to welded specimens of duplex stainless steels. The crystal data utilized in the calculation of the structure factors were those reported from single-crystal analysis of sigma-phase (Yaquel, 1983a, 1983b), detailed in Table 2. The relative amount of phases was calculated by means of the equation (Hill, 1991):

$$W_p = \frac{S_p (ZMV)_p}{\sum_{i=1}^N S_i (ZMV)_i} \quad (2)$$

where  $W_p$  is the mass concentration of phase p,  $S_p$  is the scale factor of phase p, ZM is the molecular weight of the unit cell, V is the volume of the unit cell and N is the number of crystalline phases in the specimen. The Rietveld code used was the DBWS-9807a system of programs (Young *et al.*, 1999). The numerical results obtained by application of the described procedure to a metallurgical problem, are graphically represented in Fig. 11 and Fig. 12. It can be observed that the fraction of precipitated particles of sigma increases with heating time at a given temperature, resembling the well-known mechanism of Johnson-Mehl-Avrami (Cahn and Haasen, 1996), based on the nucleation and growth phenomenon in metals and alloys, as described by the equation (3):

$$X_{\sigma} = a[1 - \exp(-kt^n)] \quad (3)$$

where  $X_{\sigma}$  is the fraction of precipitated sigma-phase, which nucleates and grows from ferrite particles,  $t$  is the transformation time and  $a$ ,  $k$  and  $n$  are transformation parameters.

Table II. Crystal data for sigma-phase

Unit formula	$\text{Cr}_6\text{Fe}_7$
Pearson symbol	tP30
Structure type	$\text{D8}_b(\text{Cr}_6\text{Fe}_7)$
Space group	$\text{P4}_2/\text{mmn}$
Unit cell parameters ( $\text{\AA}$ )	$a = 8.785$ $c = 4.579$
Volume ( $\text{\AA}^3$ )	353.39
Z	10
M ( $\text{g mol}^{-1}$ )	702,95
Density ( $\text{g cm}^{-3}$ )	7,63
Atom positions in space group	0,75Cr+0,25Fe in 4 (g); 0,66Cr+0,34Fe in 8 (j); 0,62Cr+0,34Fe in 8 (i); 0,16Cr+0,84Fe in 8 (i); 0,12Cr+0,88Fe in 2 (a);

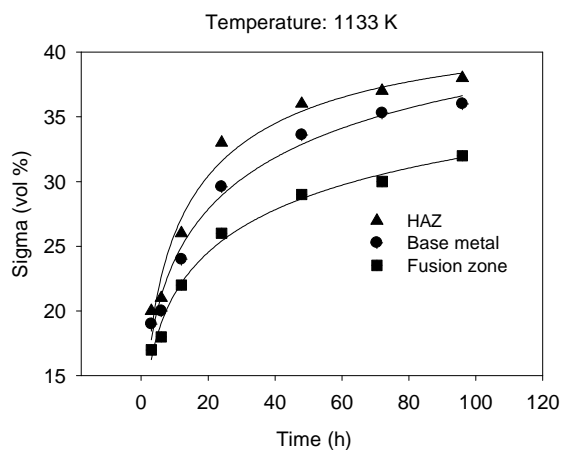


Fig. 11. Relative amount of sigma-phase versus annealing time of the weldment.

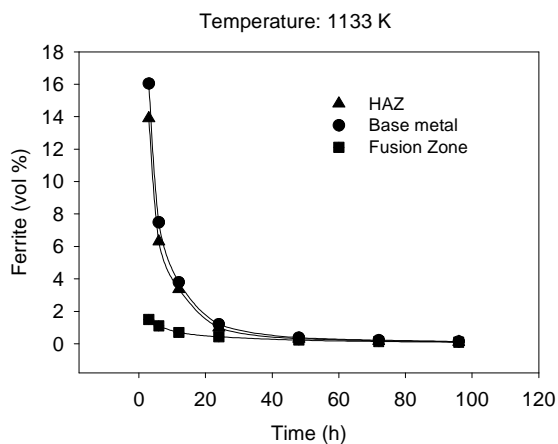


Fig. 12. Relative amount of ferrite versus annealing time of the weldment.

## CONCLUSIONS

In summary, the results of the present study have assessed the application of the Rietveld method to quantify the formation of sigma-phase in weldments of duplex stainless steels subjected to annealing at relatively high temperatures. The main advantage of this methodology was the use of the March-Dollase model for correction of the strong texture effects on the diffraction pattern, which yielded the lower R-values and much better represented the relative amounts of phases in the samples. In fact, the alternative

technique of computer-aided microscopy, where image analysis depends greatly upon the ability of the optical system to resolve the subject, generally yields poor-quality data when more than two phases are involved. From the metallurgical point of view, the results of XRD followed by Rietveld analysis indicated that the larger the annealing time of the welded parts, the larger will be the volume fraction of the precipitated particles of the intermediate phase, in good agreement with the Johnson-Mehl-Avrami relationship. Furthermore, sigma particles nucleate and grow reaching saturation levels depending on the specific type of the alloy.

## ACKNOWLEDGEMENTS

Support for this work was provided by Universidad de Santiago de Chile (USACH) and the Chilean Research Funding Agency (FONDECYT Project No 1085053). The authors greatly appreciate this assistance, as well as experimental assistance given by Mrs. Alicia Duran, Ms. Gladys Olivares and Mr. Felipe Gutiérrez.

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