SAF 2205 DUPLEX STAINLESS STEEL HAZ MICROSTRUCTURAL CHANGES DURING LONG TERM AGEING AT 380 °C

MAURIZIO FERRANTE, MARCELO DE MELLO, ANDREJ LEŠKO

Microstructural observation plus chemical and structural analysis of the real heat-affected zone (HAZ) of a TIG weld performed on a 2205 Duplex stainless steel were carried out, both in the as-welded state and after long ageing periods of time at 380 °C. The weld thermal cycle re-transforms the 50/50 austenite/ferrite duplex original microstructure into large ferritic grains and a combination of grain boundary Widmanstätten plates and small intragranular islands of austenite. Intensive precipitation of 0.5–1.0 μm long platelets identified as Fe-Cr-Mo carbonitrides was observed in the ferritic grains. These features were homogeneously dispersed in the central part of the ferritic grains and heterogeneously arranged along curved lines, the latter being possibly associated with previous ferritic or austenite/ferrite grain boundaries. Close to the fusion line the weld thermal cycle caused the onset of spinodal decomposition in the HAZ ferritic grains, characterized by a typical "mottling" contrast detected by transmission electron microscopy. After 5000 h at 380 °C the spinodal decomposition became more intense and gave rise to the homogeneous precipitation of particles identified as the G-phase.

MIKROŠTRUKTÚRNE ZMENY V TEPELNE OVPLYVNENEJ ZÓNE DUPLEXNEJ OCELE SAF 2205 POČAS DLHODOBÉHO STARNUTIA PRI 380 °C

Tepelne ovplyvnenú zónu (TOZ) TIG zvaru duplexnej ocele SAF 2205 sme podrobili mikroštruktúrnemu štúdiu, chemickým a štruktúrnym analýzam v stave po zváraní a počas dlhodobého starnutia pri 380 °C. Zvárací tepelný cyklus pretransformoval pôvodnú 50/50 austeniticko-feritickú duplexnú štruktúru na veľké feritické zrná a austenit vo forme Widmanstättenových latiek po hraniciach feritu a malé ostrovčeky vo vnútri feritických zŕn. Vo ferite sme pozorovali výraznú precipitáciu doštičkovitých častíc s dĺžkou 0,5–1 μm, ktoré sme identifikovali ako karbonitridy Fe-Cr-Mo. Tieto častice boli homogénne rozložené v strede feritických zŕn alebo usporiadané do zahnutých línií, ktoré pripomínali

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Prof. Dr. M. Ferrante, M. de Mello, MSc., Federal University of Sao Carlos, Department of Materials Sciences, Via Washington Luis, km 235, CEP 13.565-905 Sao Carlos – SP Brazil.

Dr. Andrej Leško, visiting researcher, on leave from the Institute of Materials Research of the Slovak Academy of Sciences, Watsonova 47, 043 53 Košice, Slovak Republic.

pôvodné hranice zŕn. V TOZ v blízkosti zvarového kovu zvárací tepelný cyklus vyvolal istý stupeň spinodálneho rozpadu, ktorý sa prejavuje ako „mottling“ kontrast v transmisnom elektrónovom mikroskope. Po 5000 h pri 380 °C spinodálny rozpad dosiahol takú intenzitu, že vyvolal homogénnu precipitáciu častíc, identifikovaných ako G-fáza.

Key words: Duplex stainless steel, heat affected zone, spinodal decomposition, G-phase precipitation

1. Introduction

The use of Duplex stainless steels has been growing very fast since modern control of their production technology guaranteed the optimisation of chemical composition, microstructure, and final properties. Once the basic metallurgy was sufficiently understood, attention began to be given to the determination of the residual service life of products and components already in use and to life prediction of new components. Residual and expectancy life are controlled by relatively very slow microstructural changes taking place at service temperatures up to 350 °C in the ferrite only, since austenite is considered virtually stable. These changes reduce both toughness and corrosion resistance, and a number of recent studies have been carried out aiming at their description. Most investigations observed spinodal decomposition followed by the precipitation of several types of complex intermetallic phases, as well as carbides, nitrides, and carbonitrides [1–5]. The precipitation preferred sites appear to depend on the thermal cycle characteristics and vary from grain boundary, dislocations and the interior of the ferritic grains. Both spinodal decomposition and the above mentioned precipitation are harmful to the corrosion resistance, the former through Cr and Fe redistribution and the latter by removing important alloy elements from the matrix. Finally, by increasing the proportion of ferrite and promoting further transformation and precipitation, the long term anneal decreases the HAZ toughness. It has been shown that the most critical part of a Duplex steel weld joint is the HAZ, where the original rolled sheet 50/50 austenite/ferrite elongated microstructure is completely modified by the weld thermal cycle [6, 7]. For low energy weld processes the HAZ typical width is $\sim$ 0.1 mm. During the heating cycle the ferritic grains grow at the expense of the austenite, meaning that at peak temperatures the whole HAZ is composed only by large ferritic grains. During the cooling cycle however, partial re-formation of austenite takes place and proceeds up to volume fractions in the range 0.35–0.40. The austenite nucleates preferentially at the ferrite boundaries and grows as Widmanstätten needles into the grains, where some austenite islands nucleate and grow as well, albeit to a lesser extent. As a consequence of this phase volume changes a redistribution of alloy elements takes place; nickel partitions to the austenite while the chromium partitions to the ferrite [8], and the intergranular secondary austenite in all weld metals was found to be depleted in chromium and nitrogen relative to primary austenite [9].

In conclusion, the microstructural and compositional changes caused by the weld thermal cycle have profound effect on the toughness and corrosion resistance behaviour at service temperature. The present work is a study of such changes after a long exposure at 380 °C of an actual HAZ produced by TIG welds on a SAF 2205 rolled plate, and their correlation with microhardness evolution.

2. Experimental techniques

Two SAF 2205 steel plates were TIG welded normal to the rolling direction. Plate thickness and nominal composition were 3.0 mm and 22Cr-5.5Ni-3.2Mo, respectively, and the weld heat input was close to 0.5 J mm^{-1} giving a cooling rate of about 25 °C s^{-1}. Sections of the weld were placed in a tube furnace at 380 °C and the scheduled removal time was 500, 750, 1000, 1500, 2000, 3000, 5000, and 7500 h. Samples were observed by optical, scanning (SEM), and transmission electron microscopy (TEM). Precipitate identification was carried out by EDS microanalysis and electron diffraction on carbon-plastic extraction replicas and on thin foils. In order to precisely locate the HAZ, weld transverse sections were cut as ~ 5 mm deep bars, etched on both sides, and the region of interest was extracted using a small hand saw. Finally, Vickers microhardness transverse measurements (the microhardness indenter was loaded with 50 g and 100 g for the base plate/weld

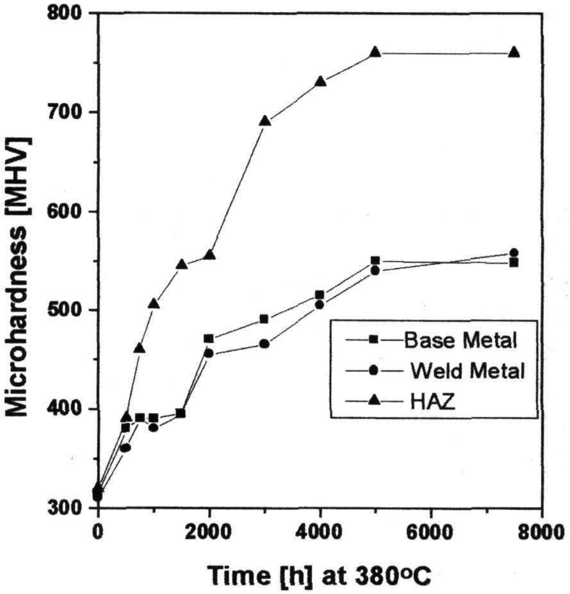

Fig. 1. Base metal, weld metal, and heat affected zone microhardness evolution with time.

metal, respectively) were performed along the joint; each value is the average of 20 measurements.

3. Results and discussion

Fig. 1 shows the hardness evolution of the weld joint, with time at 380 ℃. Measurements were performed only on the ferritic grains and it can be seen that the HAZ was the most affected region since its hardness almost doubled after 3000 h. This is an indication that this region was significantly affected by the already mentioned ferritic grain growth and alloy elements/phases redistribution. Fig. 1 also shows that with further anneal the hardness increase of the HAZ continues to be much faster than in the other two regions, showing a different response to the 380 ℃ anneal. Thus, at 5000 h the hardness reached 760 HV then levels off, showing that either the phenomenon causing the hardening ceased or that other mechanisms took place in the opposite direction.

Figs. 2 and 3 are micrographs of the welded joint in the as-welded condition of the HAZ and the detail, respectively. It can be seen that the region of interest is approximately 100 mm wide and consists of large ferritic grains and grain boundary austenite, besides Widmanstätten plates and rather small intragranular islands of that phase. The proportion of austenite was estimated by point counting as

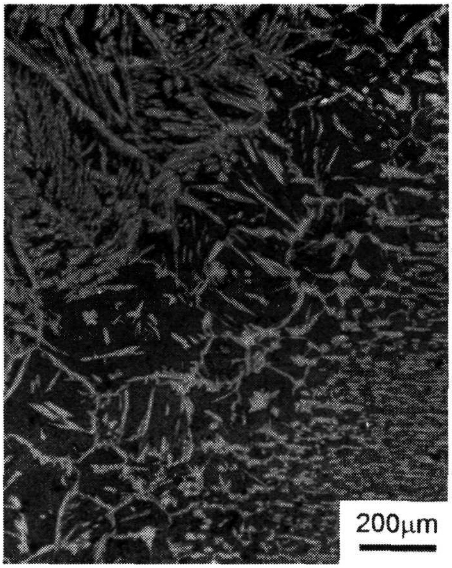

Fig. 2. Optical micrograph of the heat affected zone, base metal, and weld metal.

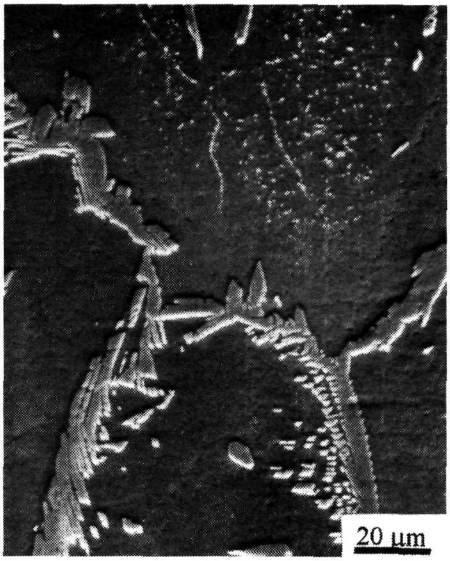

Fig. 3. SEM micrograph of the heat affected zone ferrite with precipitation along curved lines.

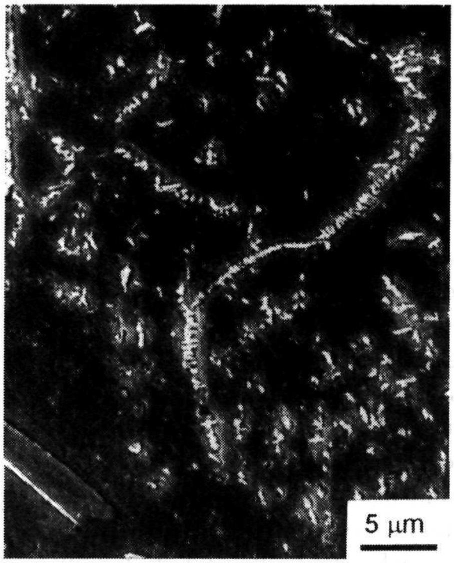

Fig. 4. SEM micrograph of the heat affected zone: ferritic grain and precipitates.

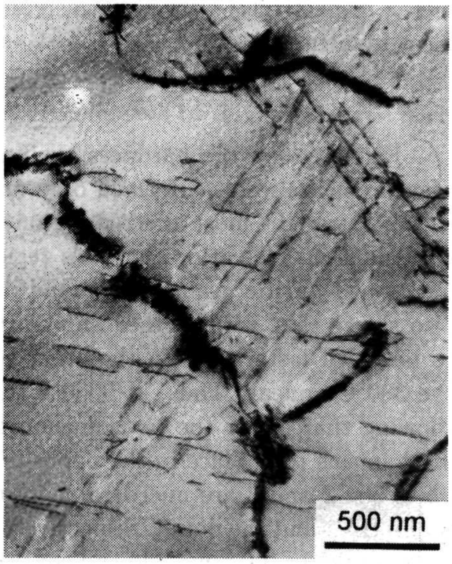

Fig. 5. TEM micrograph of the heat affected zone: ferritic grain and precipitates.

equal to 32%. The variation of both phase balance and morphology is certainly responsible for significant changes of mechanical properties, toughness reduction in particular [10]. Additionally, in some grains, see Fig. 3, numerous small particles either homogeneously dispersed or arranged as "strings" are visible. This particular feature is more clearly shown in the detailed SEM image, see Fig. 4, where it appears as thin platelets with the largest dimension in the range of 0.5–1.0 μm and with the two different spacial arrangements mentioned above. When random, the particles are mostly located in the central part of the ferritic grains; however, when arranged along curved lines they suggest heterogeneous nucleation on grain boundaries or on dislocation lines. The latter possibility can be discarded, because the continuity of those lines indicate that they are in fact surfaces intersecting the plane of observation, hence grain boundaries. Therefore, it can be suggested that precipitation took place on previous δ/δ or δ/γ boundaries which were moving under the effect of the weld heat cycle during heating, in other words, when the duplex microstructure was transforming into ferrite. This reformed delta ferrite begins to grow at 1250 °C, approximately, and as a consequence of the sudden decrease of solubility, a number of alloy element precipitate, both homogeneously within the ferritic grains or heterogeneously along their boundaries. The partial $\delta \rightarrow \gamma$ re-transformation during cooling does not change the pattern of second phase

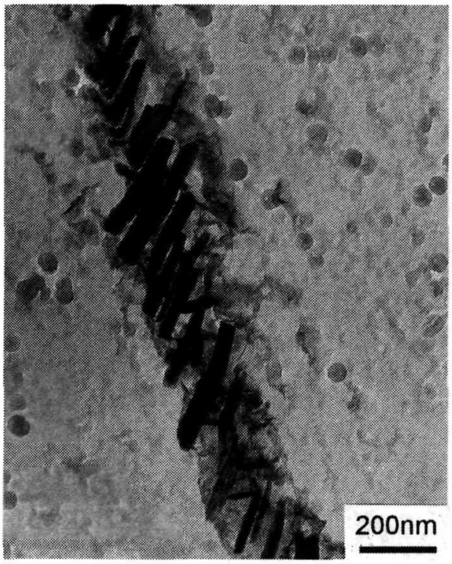

Fig. 6. TEM micrographs of extracted precipitates. Carbon replica.

Fig. 7. TEM micrograph showing mottling contrast indicating the onset of spinodal decomposition in the ferrite.

precipitation, except by possible solutionizing of the above-described precipitates.

TEM observation and EDS chemical analysis of the precipitates were performed on thin foils and on extraction replicas, see Figs. 5 and 6. Microanalysis measurements combined with electron diffraction patterns interpretation show that the precipitates are complex Fe, Cr, and Mo carbonitrides, with different solubilities for these elements. It can be mentioned that in high nitrogen Superduplex stainless steels similar particles were identified as CrN or CrN_2 [5, 11]. Additionally, the present TEM work revealed the presence of a mottled contrast, which is a typical feature of spinodal decomposition. This phenomenon was observed in the as-welded HAZ samples but confined to some grains only and it can be suggested that these were closer to the fusion line than the ones in which no decomposition was observed.

Observation of samples annealed at 380 °C showed that the spinodal decomposition spreads out to an increasingly larger number of grains. As for its intensity, different grains have different contrast, depending on their distance from the fusion line; however, after 1000 h the contrast became sharper with time, see Fig. 7, and takes up the entire HAZ. Finally, after 5000 h at 380 °C a new microstructural feature was observed, beginning in regions where the spinodal decomposition appears

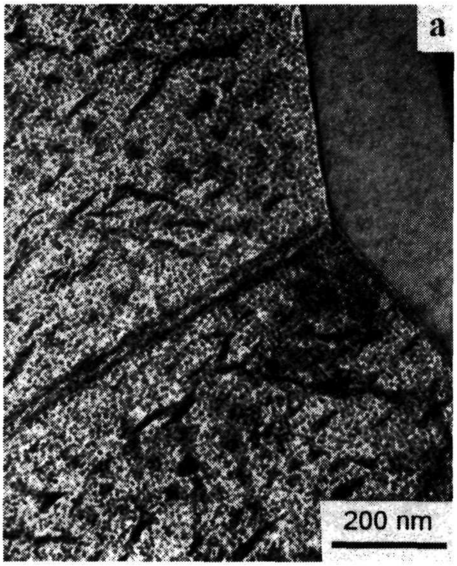

Fig. 8a. TEM micrograph showing G-phase precipitation in the heat affected zone after 7500 h at 380 °C.

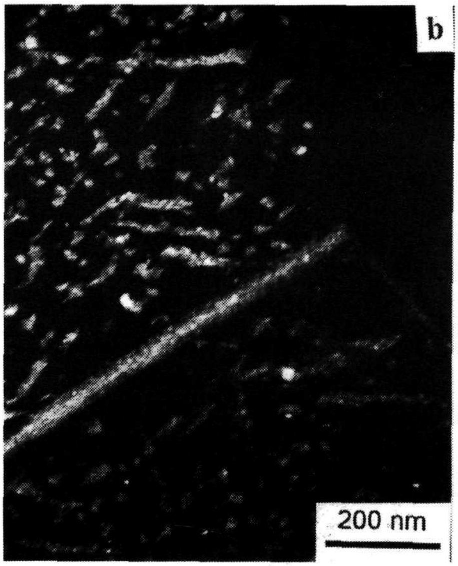

Fig. 8b. G-phase; dark field in 333G reflexion.

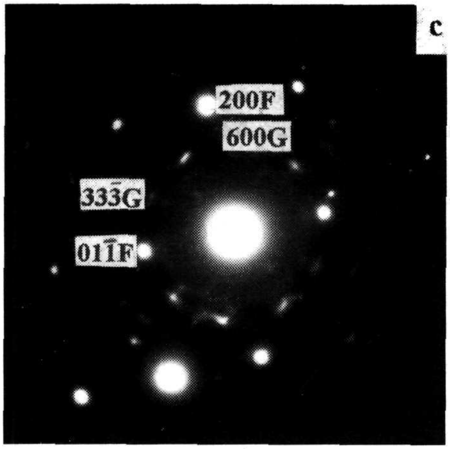

Fig. 8c. Diffractogram of G-phase precipitates. Ferritic zone axis is [011].

to be more intense. This is the precipitation of very small particles as shown in Fig. 8a, 8b, and 8c, bright field, dark field, and diffractogram, respectively. Comparing the diffraction pattern analysis with literature data [2, 4], the particles were identified as G-phase, having a cube on cube orientation relationship with the ferritic matrix. This G-phase is a complex silicide with average size up to 10 nm [2] and chemical formula equal to $Ni_{16}Si_7Ti_6$, in which Ti and Ni can be substituted by Cr, Fe, Mo, and/or Mn [12]. It must be pointed out that in Duplex steels such phase has been observed only after much longer times at service temperature [4] showing that the weld thermal cycle had a profound accelerating effect on the G-phase precipitation. This microstructural description is in very good agreement with the microhardness development, shown in Fig. 1. The hardness increase of the HAZ reflects the extent of the spinodal decomposition since it is known that matrix demixing causes the appearance of stresses which oppose further decomposition. However, after 5000 h the hardness does not change further, suggesting that by introducing a great number of interfaces in the de-mixed ferritic matrix, the G--phase precipitation contributes to the reduction of the above mentioned stresses. This mechanism appears to be valid from the early stages of G-phase precipitation, when stress relief prevails over precipitation hardening.

5. Conclusions

This paper deals with microstructural observations of the real HAZ of a 2205 Duplex stainless steel low energy weld, aged at 380 ℃ for times up to 7500 h. The results lead to the following conclusions:

– The weld thermal cycle modified the original 50/50 austenite/ferrite microstructure, which in the as-welded HAZ consisted of large ferritic grains plus austenite distributed as a network of grain boundary allotriomorph, Widmanstätten plates, and small intragranular islands.

– Intense precipitation of (Cr, Fe, Mo) complex carbonitrides took place within the as-welded ferritic HAZ grains, both homogeneously distributed and along curved lines. The onset of spinodal decomposition within ferritic grains adjacent to the fusion line was also observed after welding.

– The microhardness of the HAZ increased with ageing time at 380 ℃, levelling up only after 5000 h.

– The spinodal decomposition intensified with time at 380 ℃. Matrix demixing corresponding to the formation of Ni, Si, and Ti(Mo)-rich microvolumes culminated after 5000 h at 380 ℃ in the G-phase formation. This event coincided with microhardness stabilization.

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