Effect of isothermal heat treatments on Duplex Stainless Steels impact toughness

I. Calliari, M. Breda, E. Ramous, M. Magrini
Department of Industrial Engineering, University of Padova, Padova (Italy)
irene.calliari@unipd.it, marco.breda@studenti.unipd.it, emilio.ramous@unipd.it, maurizio.magrini@unipd.it

G. Straffelini
Department of Materials Engineering and Industrial Technologies, University of Trento, Trento (Italy)
giovanni.straffelini@ing.unitn.it

ABSTRACT. Duplex Stainless Steels (DSS) are austenitic-ferritic stainless steels which combine good mechanical and corrosion-resistance properties and, for this reason, are suitable for structural applications in very aggressive environments. However, their aging at 600÷1000°C induces the formation of dangerous intermetallic phases, resulting in serious detrimental effects on both impact toughness and corrosion resistance. Therefore, many standards related to the manufacturing of DSS, require "no intermetallic phases" in the microstructure.
In the present work, the impact toughness behaviour of two DSSs (SAF 2205 and Zeron®100) has been investigated after isothermal heat treatments at different time-temperature combinations, in order to study the influence of different amount of secondary phases on the toughness response.

SOMMARIO. Gli acciai inossidabili Duplex (DSS) sono acciai inossidabili austeno-ferritici che combinano buone proprietà meccaniche e di resistenza alla corrosione e, per questo motivo, si rendono adatti per applicazioni strutturali in ambienti molto aggressivi. Tuttavia, un invecchiamento a 600÷1000°C induce in questi acciai la formazione di pericolose fasi intermetalliche che causano gravi effetti di deterioramento nei confronti sia della resilienza che della resistenza alla corrosione. Pertanto, molti standard relativi alla fabbricazione dei Duplex richiedono "assenza di fasi intermetalliche nella microstruttura".
Nel presente lavoro si è studiata la tenacità ad impatto di due acciai Duplex (SAF 2205 e Zeron ® 100) a seguito di trattamenti isotermici all'interno dell'intervallo critico di temperatura e per diverse combinazioni di tempo-temperatura, al fine di studiare l'influenza di diversi quantitativi di fasi secondarie sul comportamento a resilienza.

KEYWORDS. Duplex stainless steel; Impact toughness; Isothermal heat treatment; Sigma phase.

INTRODUCTION

Duplex Stainless Steels (DSS) have a ferritic-austenitic microstructure which allows the combination of high mechanical and corrosion-resistance properties. The best values of these properties are obtained when the austenite-to-ferrite phase ratio is about one and are increased by the addition of the characterizing alloying elements (Cr, Ni, Mo, N). That implies a very careful balance of the composition in order to get the phase stability at room temperature.

Generally these steels have considerably higher yield strength than the austenitic grades and their enhanced resistance to pitting corrosion makes them suitable for structural applications in very aggressive environments. In DSS, the mechanical properties are modulated by the biphasic microstructure, allowing the achievement of the best features deriving by the peculiar properties of the different lattice structures of the present phases. The tensile properties are essentially governed by the ferritic matrix, while the good toughness is ascribed to the austenitic phase, which retards the cleavage fracture of ferrite [1]. However, the use of DSS is limited, owing to their susceptibility to the formation of dangerous intermetallic phases, such as σ- and χ-phase, which form after ageing the material in a temperature range over 600°C [1, 2]. The critical temperature ranges vary with the steel's grade (i.e. with composition) and at certain temperatures the precipitation can be very fast, occurring only after 3-5 minutes of ageing treatment [3].

The genesis of the precipitates can be attributed to the large amount of alloying element and is promoted by the instability of the ferritic matrix at the high temperatures. Morphology and localization of the secondary phases are well known and already described [1, 2], they precipitate both at triple points and grain boundaries and their growth occurs toward the unstable ferrite, also due the diffusion behaviour of the involved elements (which are mainly Mo and Cr). As already reported, the first precipitating phase is the χ and, by increasing the ageing time, the σ-phase starts to appear in the form of coarser particles [4].

The secondary phases are enriched in chromium and molybdenum and give rise to serious detrimental effect on the DSS properties. The corrosion properties are reduced, especially in correspondence of the interfaces, because the intermetallics cause a depletion of those elements responsible to promote the corrosion resistance. Moreover, the precipitates are structural discontinuities which worsen the mechanical properties by causing stress intensification in correspondence of them and thus becoming the preferential cracks initiation sites. For this reason, after the production cycle, DSS are submitted to a solution annealing treatment followed by water quenching, in order to re-dissolve the secondary phases formed during the previous processes and to obtain an almost equal volume fraction of ferrite and austenite, corresponding to the best mechanical and corrosion properties.

Due to these worsening in properties, many standards related to manufacturing of DSS require "no intermetallic phases" in the microstructure [5]. This restriction implies a careful control of the whole manufacturing process, since a reliable and relatively cheap metallographic procedure is not simple to achieve, especially for the quantitative determination of very small (1-2%) dangerous phase contents.

The present work is aimed to study the impact toughness of two different DSS grades after a set of isothermal heat treatments in order to relate the impact behaviour to the quantity of the secondary phases, with particular emphasis on the early stages of precipitation. The investigated steels were a "standard" Duplex UNS S31803 (SAF 2205 DSS) and a "super" Duplex UNS S32760 (Zeron®100 SDSS). The impact toughness was investigated by means of instrumented impact testing, by using Charpy V-notched specimens at room temperature. Different contents of intermetallic phases have been produced by isothermally treating the steels within their critical temperature range, which is known to be at 800-950°C [3, 6]. Both σ- and χ-phases negatively affect the impact toughness behaviour, even if, when both are present, their effects are not distinguishable.

EXPERIMENTAL

The investigated materials were a wrought UNS 31803 (SAF 2205) DSS in form of rod (30 mm) and an UNS S32760 (Zeron®100) Super DSS plate (14.5x1350 mm), whose chemical compositions are reported in Tab. 1. The steels were solution-annealed at the proper solubilisation temperature and subsequently water quenched.

Grade	Chemical composition [wt.%]										
	C	Cr	Ni	Mo	Cu	W	Mn	P	S	Si	N
2205	0.030	22.75	5.04	3.19	-	-	1.46	0.025	0.002	0.56	0.16
Zeron®100	0.014	25.23	6.89	3.67	0.72	0.62	0.88	0.023	0.001	0.25	0.28

Table 1: Nominal chemical composition of the investigated steels.

The isothermal aging treatments were designed to obtain the precipitation of various amounts of secondary phases and the time-temperature combinations, which are listed in Tab. 2, were chosen on the basis of previous results [3, 6].

Grade	Ageing temperature [°C]	Ageing time [min]	Absorbed energy [J]	Secondary phases [%]
2205	780	20	242.5	not present
		25	231.5	not present
		30	173	< 0.1
		40	141	< 0.1
	850	10	229	not present
		15	219	not present
		20	125	<0.1
		25	87.5	<0.1
		30	83.5	0.5
		40	28.5	2.5
	900	10	222	< 0.1
		15	181	< 0.1
		20	97	0.6
		25	37.5	1.9
		30	15.5	5.7
		40	14	9.2
Zeron®100	850	5	~300	not detected
		8	281	<0.1
		10	138	0.5
		15	26.5	6.2
		25	4.2	15.3
	900	3	>300	not present
		5	>300	not present
		8	55	2.3
		10	50	2.5
		15	11.2	9.5
	950	3	~300	not detected
		5	237	<0.1
		8	105	1
		15	10.2	11.9
		25	4.2	15.4

Table 2: Nominal chemical composition of the investigated steels.

The microstructural observations were carried out by a Leica Cambridge Stereoscan 440 scanning electron microscope (SEM) equipped with a Philips EDAX PV9800 energy dispersive X-ray spectroscope (EDS) in backscattered-electron mode (BSE at 29 kV), without etching the specimens. The different average atomic number of the phases (Z-contrast) allows for their identification: ferrite appears darker than austenite (depending on the considered grade), while the secondary phases appear lighter, with χ brighter than σ, owing to its higher molybdenum content. The amount of secondary phases was estimated using of an image-analysis software on the SEM-BSE micrographies (5 fields at 2000x).

The impact toughness of both steels was investigated by means of an instrumented impact testing machine on Charpy V-notched specimens at room temperature (RT), using an available energy of 300 J. The load-deflection curves were partially smoothed using the moving average method [7] with a cut-off frequency of 50 Hz. For the fracture behaviour investigation, the fracture surfaces were also observed by means of SEM in secondary-electron mode (SE at 15 kV), in order to obtain information on crack nucleation and fracture propagation.

RESULTS AND DISCUSSION

Microstructure

The as-received materials were composed by a ferritic matrix in which were dispersed the austenitic grains, oriented toward the previous hot rolling direction. The phases were present in almost equal volume fraction but, as previously explained, the isothermal heat treatments gradually lowered the ferrite content. As a matter of fact, not all the considered aging times were sufficient to obtain the precipitation of significant amounts of intermetallic phases (see Tab. 2): this implies different impact toughness responses, depending on their effect on the microstructure.
As confirmed by other studies [3, 6], in both the steels, the precipitation sequences were the same, but with different kinetics and phases amounts. The χ-phase was the first precipitating ones, in correspondence of triple points and grain boundaries, and, by increasing the treatment time, its formation was followed by the rise of the σ-phase, which grown toward ferrite (see Fig. 1). The σ particles were coarser than the χ ones and also grown faster, progressively embedding the χ precipitates. As can be seen from Fig. 1, the precipitation kinetics was faster in the Zeron®100 DSS owing to its higher alloying element content.

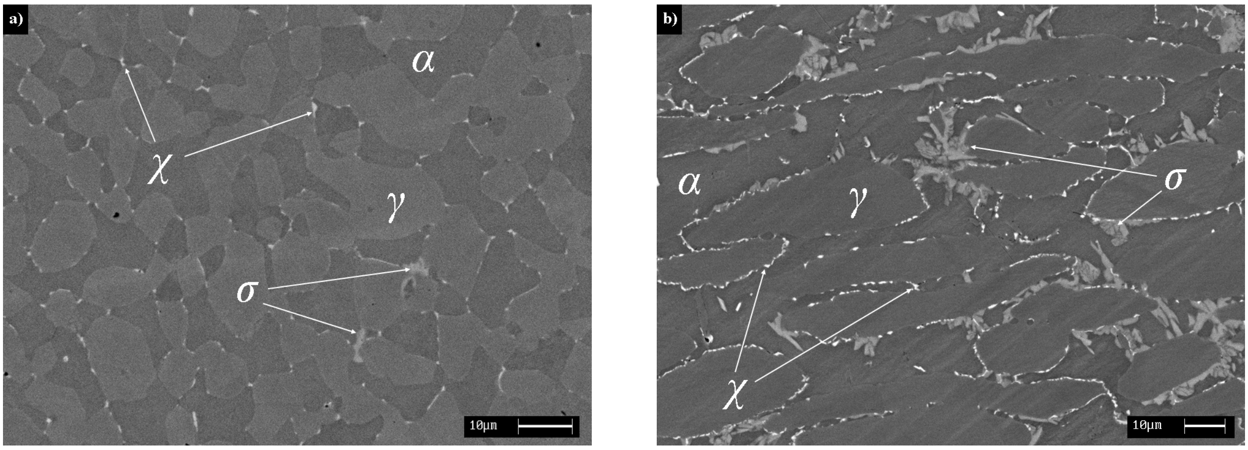

Figure 1: Microstructure of the aged samples at 900°C: a) 2205 after 25 min and b) Zeron®100 after 15 min.

The microstructural damage depends not only on the ageing time, but is also related to the local microstructural conditions. Composition differences at a local level may lead to unevenly distributions of the new generated phases and also to slight different chemical composition of such particles. In agreement with the precipitation kinetics [3, 6], which are strictly related to the steel's grade, the treatment times influence the intermetallic content and also the size of the precipitating particles. Therefore, the observed impact toughness must be related to the phase's volume fraction and also to the particle's dimensions and their distribution inside the ferritic matrix. Furthermore, the mechanical properties of such phases can be affected by the composition of the parent phase, resulting, for instance, in a greatest hardening of the particles in the Zeron®100 DSS due to the presence of W, which can promote their rupture.
The average amounts of secondary phases detected are reported in Tab. 2, but their dimensions and distribution inside the microstructure were anything but homogeneous. This was evident in those specimens which were treated at the same time-temperature conditions and which were failed at different impact energy values. Besides the distribution of such phases, by increasing the aging time the particles dimensions also increased, promoting the embrittling effect.

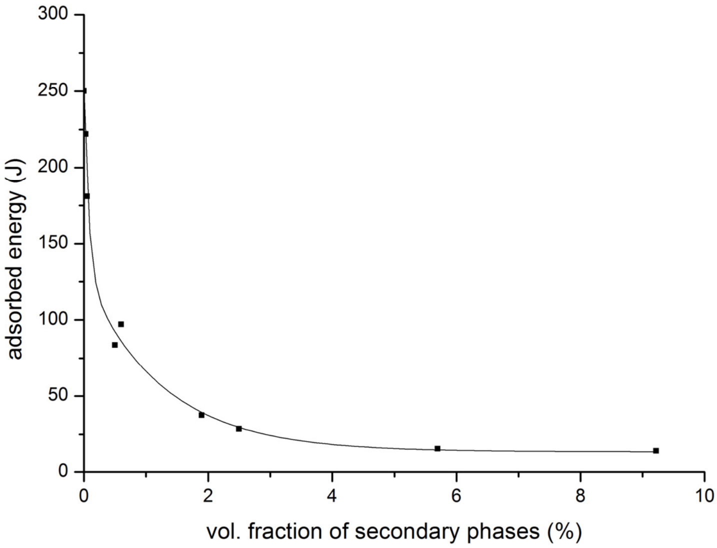

Figure 2: Impact energy reduction in 2205 DSS.

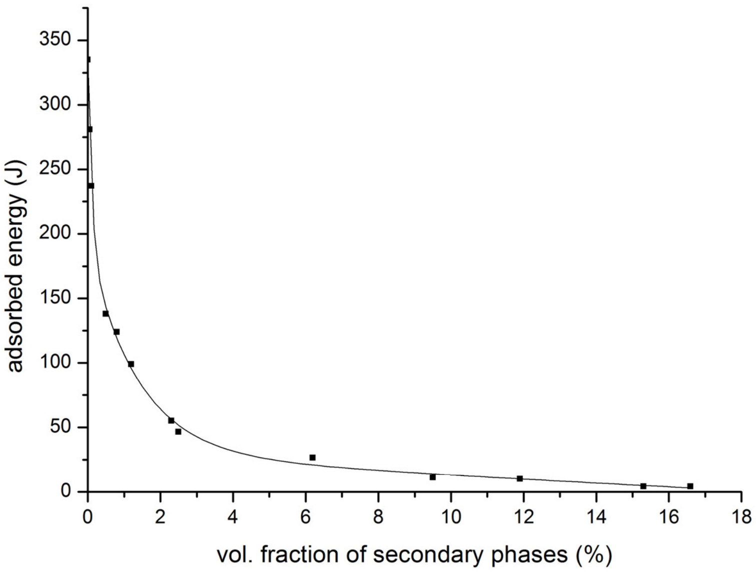

Figure 3: Impact energy reduction in Zeron®100 DSS.

Impact toughness

In the as-received conditions, the RT impact toughness was very high in both the steels and, as expected, was greater for Zeron®100 (about 330 J) than for SAF 2205 (about 240 J). The enhanced mechanical properties of the Zeron®100 SDSS can be attributed to the higher alloying element content which promotes the mechanical strengthening of the phases.

The ageing treatments caused the secondary phases precipitations, leading to a worsening of the impact toughness responses. For each time-temperature condition, the average toughness values are reported in Tab. 2, while the impact energy values (as a function of the content in intermetallic phases) are plotted in Figs. 2 and 3. The effect of the secondary phases is evident starting from 0.5% volume fraction, value at which the most drastic reductions of impact toughness were observed. The absorbed energy was reduced by more than 50% in both cases, underlining the severe detrimental effect of these phases. A further reduction was registered at 1÷1.5% of secondary phases and over the 2% volume fraction a great deterioration in toughness was again observed. In this latter case, small entities of plastic deformations are enough to cause a prevailing brittle fracture mechanism. The relation between the impact energy and the volume fraction of secondary phases is clearly evident (Figs. 2 and 3): a very low content was enough to produce very dangerous effects and, by increasing the precipitates amounts, the fracture mechanism showed an ever more prominent brittle behaviour until, for 6÷8% volume fraction (depending on the considered grade), the ductile component was totally absent.

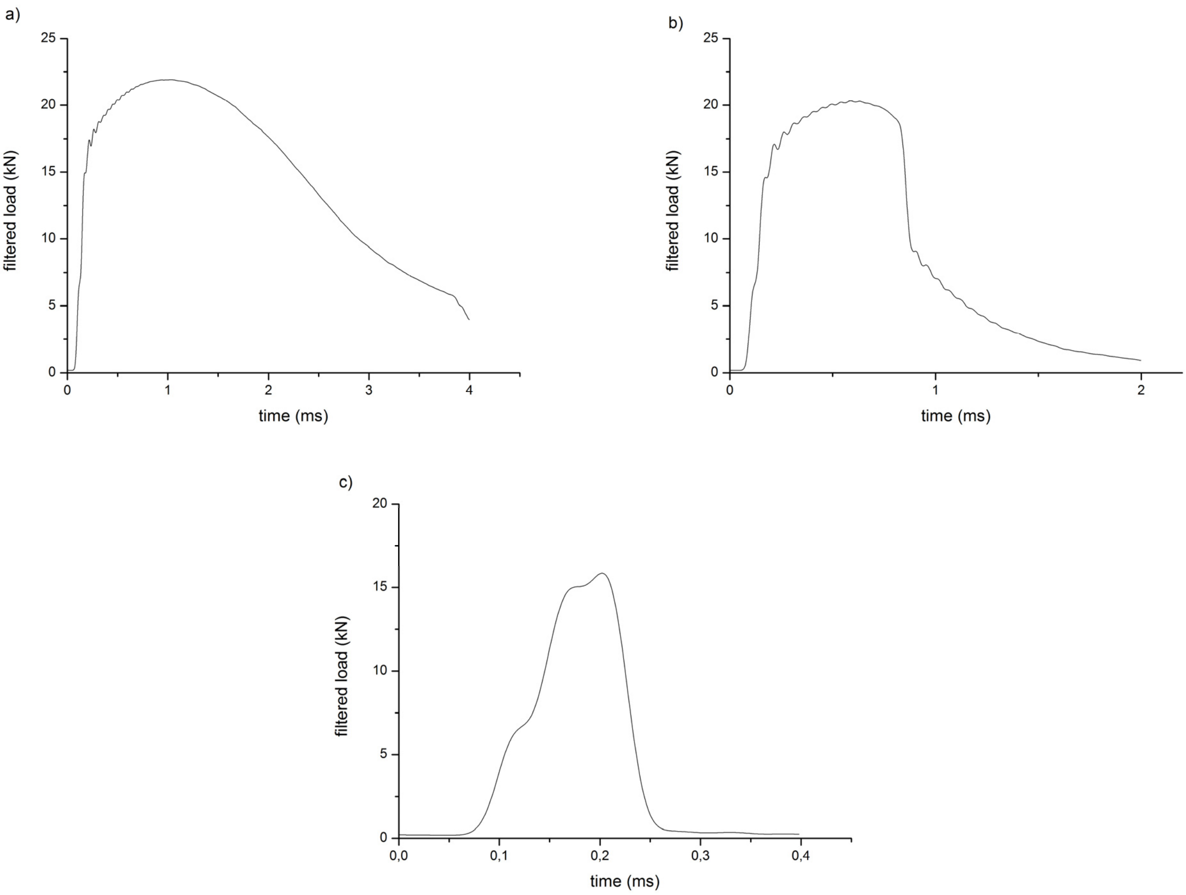

Figure 4: Load curves of 2205 DSS specimens: a) with impact energy >150 J (780°C for 20 min), b) with impact energy 50-150 J (900°C for 20 min) and c) with impact energy <50 J (900°C for 40 min).

As can be seen from Tab. 2, some Zeron®100 SDSS specimens were not completely broken and the registered absorbed impact energies were >300 J (i.e. the available energy in the impact was totally absorbed by the samples without causing the complete rupture). In these samples no secondary phases were detected and for them the fracture was completely ductile. A completely ductile behaviour was also observed in some 2205 DSS specimens aged for the shorter times. In both cases the heat treatments were not sufficient to allow for the precipitation of the secondary phases.
The obtained results are suitable to define a subdivision of the energy plots reported in Figs. 2 and 3 on the basis of the content in intermetallic phases. Each region is characterized by the similarity of the load curves obtained in the impact test, while different shapes of the curves correspond to different fracture behaviours (see Figs. 4 and 5). It is important to note that the boundaries between the three regions are not well defined and the materials exhibited a gradual transition from the completely ductile to completely brittle fracture mechanism.
In the materials pertaining to the first region and in which the intermetallics content were <0.5% (absorbed energy >150 J), the dynamic yielding were about 15 kN for the 2205 DSS and 20 kN for Zeron®100 SDSS (Figs. 4a and 5a). After the yielding, the applied loads increased, owing to the strain hardening, the fractures nucleated in relation to the maximum loads and the following decreasing was associated to stable crack propagation, due to the ductile mechanism. The microstructural analysis revealed small amounts of secondary phases, identified as mainly χ particles. In this region, an increasing of the intermetallics content caused a progressively change in the curve slope after the maximum load and a reduction of the fracture propagation time.

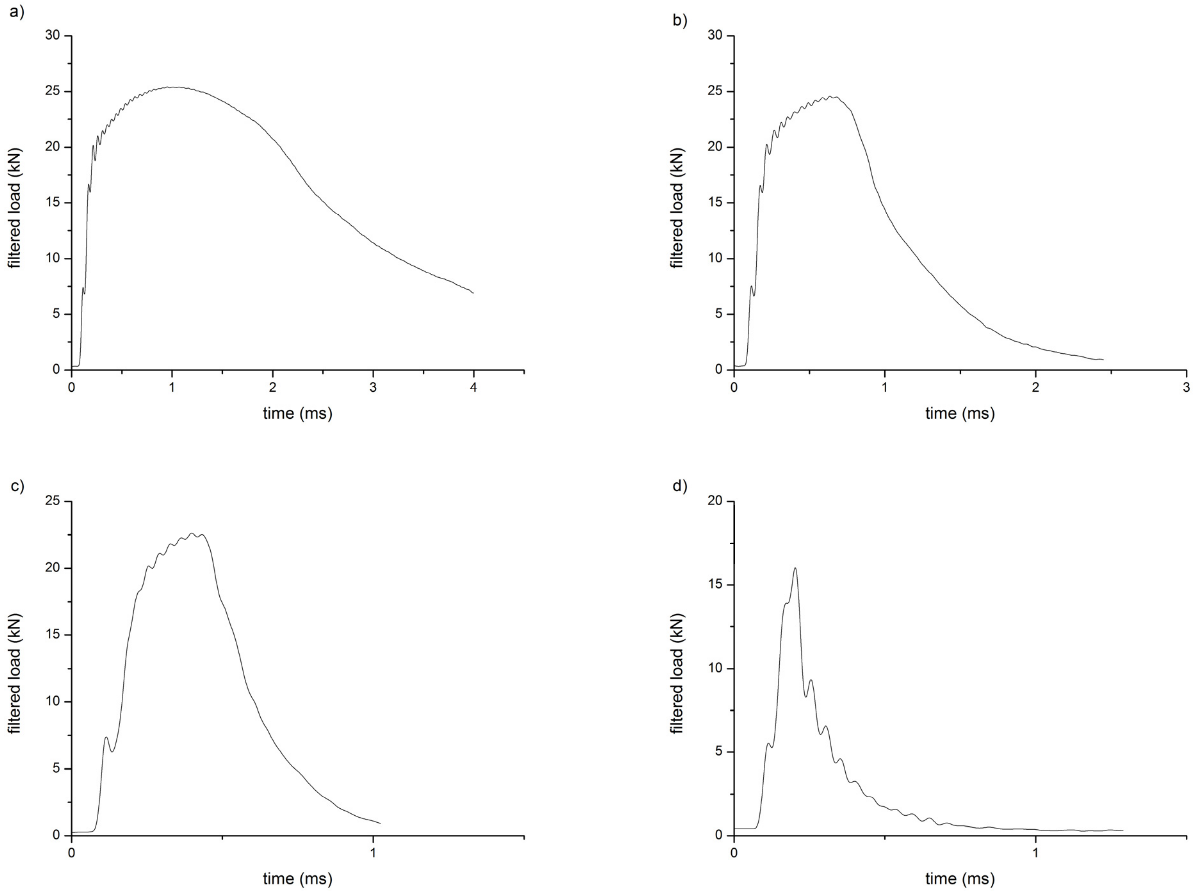

Figure 4: Load curves of Zeron®100 SDSS specimens: a) with impact energy >150 J (850°C for 8 min), b) with impact energy 50-150 J (950°C for 8 min), c) with impact energy <50 J (900°C for 8 min) and d) with impact energy <50 J (900°C for 15 min).

The second region includes the samples with an intermetallics amount from 0.5 to 1% for 2205 DSS and between 0.5 and 1.5% for Zeron®100 SDSS (absorbed energy about 50÷150 J). In these specimens the fractures were not completely ductile and the brittle component started to manifest itself. The dynamic yielding remained almost unchanged for both the examined steels (see Figs. 4b and 5b) but, after an initial stable crack propagation, the brittle mechanism takes place causing a changing in the impact curves slope and reducing the absorbed energy. However, depending on the considered grade, the fracture behaviours were different. The observed reduction in impact toughness, from the completely ductile mechanism to the prevailing brittle behaviour, was more marked in the 2205 grade (Fig. 4b), while in the Zeron®100 the transition was more gradual (Fig. 5b). Nevertheless, in both cases the greater content in secondary phases strictly affected the fracture behaviour and the brittle mechanism was promoted when the phase's amount increased. The hard intermetallics, which were identified as both σ- and χ-phases, preferentially broke and caused a reduction of the average crack-free-paths, facilitating the crack propagation into the adjacent ferritic phase.

In the third region, the materials were characterized by a secondary phases content which overcomes the 1÷1.5% (absorbed energy <50 J) and the situation was again different depending on the considered grade. After the dynamic yielding, which still occurred at 15 kN (Fig 4c), the 2205 DSS exhibited an abrupt drop in the absorbed energy and the fracture propagation was completely brittle. On the contrary, the Zeron®100 SDSS showed a progressive changing in fracture behaviour. In this latter steel, even if the fracture was prevailingly brittle, the ductile behaviour was initially not negligible (Fig 5c) and, by increasing the intermetallic content, the brittle component was even more pronounced. For Zeron®100 SDSS, the fracture was initially mixed and the rupture only occurred for shorter times with a general yielding still at 20 kN. Greater intermetallics contents reduced the fracture time and the yielding value until the fracture became completely brittle (Fig 5d).

In all the materials pertaining to the third region, a small amount of plastic deformation at the notch root was enough to reach the critical brittle fracture conditions, the fracture propagation was very rapid and the absorbed energies were low. The secondary phases allowed for an easy crack nucleation and contributed to determine an energy-favoured path for the crack propagation. For secondary phases volume fractions greater than 6÷8% the fracture behaviour was completely brittle and no plastic deformations at the notch root were observed in both the steels. The results showed that when the intermetallics amount is maintained below the 2÷3%, the microstructural damage has no influence on the dynamic yielding and on the overall yielding behaviour, even if it occurs for shorter times and the following strain hardening contribution is smaller.

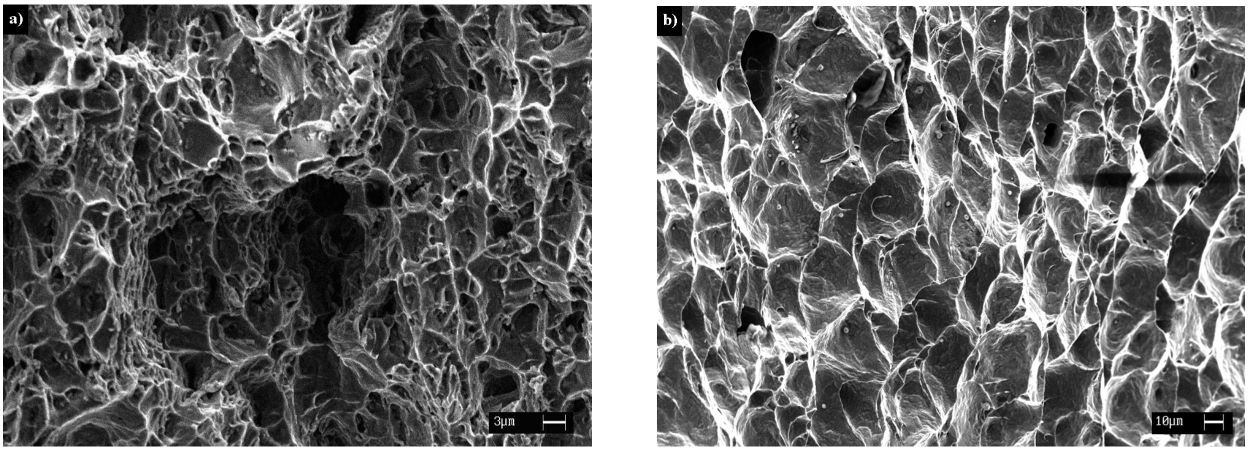

Figure 6: Samples failed in the first (ductile behaviour). Fracture surfaces (SEM-SE): a) 2205 DSS (high magnification) and b) Zeron®100 SDSS (low magnification).

Fractography

Deformation and fracture behaviour of examined materials are strongly influenced by the secondary phases and an examination of both fracture morphology and microstructure close to the notch root can reveal the distinguishing features.
In the first region the materials were failed in a completely ductile manner after a large plastic deformation and the morphology showed the characteristic dimpled surface (Fig. 6). In both the steels the low volume fraction of secondary phases was not enough to promote the brittle fracture and the intermetallics acted as nucleation sites for the ductile fracture. The presence of a large plastic deformation was confirmed by the grain shearing close to the notch root (Fig. 7). Nevertheless, the presence of some micro-voids at the triple points and at the grain boundaries near the fracture surface can be attributed to the original presence of small particles which were broken during the impact.

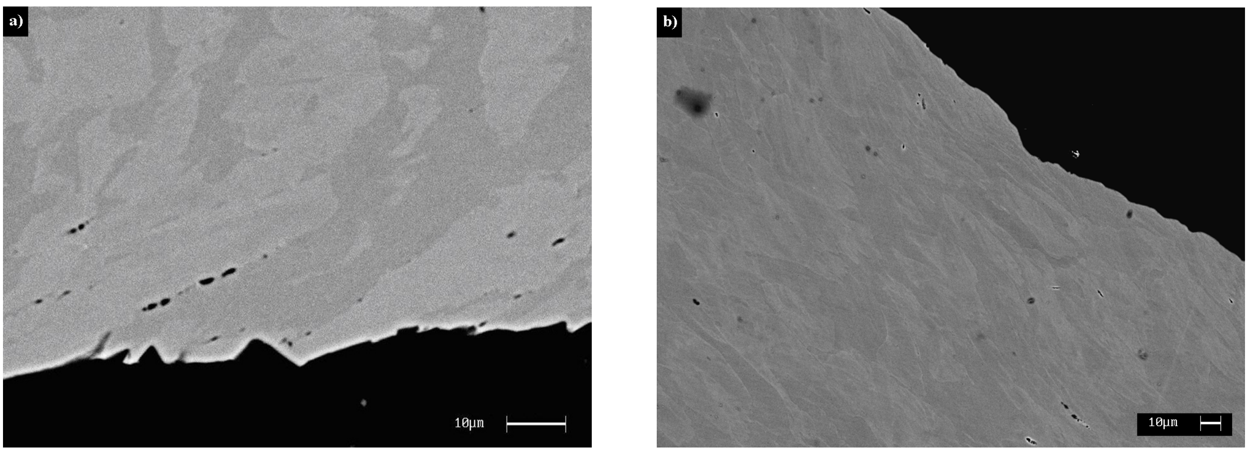

Figure 7: Samples failed in the first region. Grain shearing near the notch root (SEM-BSE): a) 2205 DSS and b) Zeron®100 SDSS.

On the contrary, the materials pertaining to the third region failed in a brittle manner. For both the steels, although the fracture was completely brittle when the secondary phase's amounts reached the 6÷8%, the approaching to the brittle rupture was different. In the 2205 DSS (see Fig. 8), the 2% of volume fraction was enough to cause the brittle failure and the fracture surfaces were characterized by the presence of quasi-cleavage facets. The microstructure at the notch root revealed a high density of micro-cracks which formed before the occurrence of the final fracture. In the Zeron®100 SDSS (see Fig. 9), the same behaviour was observed in those samples with a secondary phases amount >4% and where cleavage and quasi-cleavage facets were detected. On the contrary, in the range 1.5÷4% the fracture of the Zeron®100 was mainly mixed, the dynamic yielding gradually decreased and the ductile component gradually disappeared. In the third region, a small plastic deformation was enough to reach the critical conditions for the brittle fracture. The density of such micro-cracks was large and their size was also big, owing to the large content of the secondary phases due to the higher treatment times. This allowed an easier nucleation of the brittle crack.

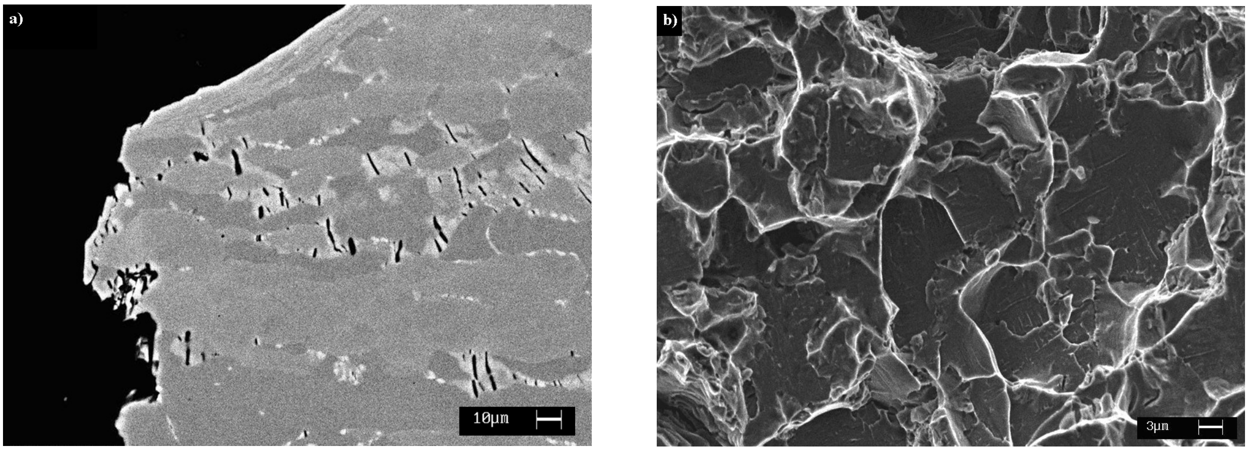

Figure 8: 2205 DSS failed in the third region: a) micro-cracks close to the notch root (SEM-BSE) and b) fracture surface (SEM-SE).

Finally, the second region is characterized by a large plastic deformation before reaching the critical conditions at the notch root, density and size of the micro-cracks are intermediate between the first and the second region and lower amounts of embrittling secondary phases were detected. This is a transient region and the behaviour of the material changed when considering the upper and the lower energy limits showing an ever more brittle fracture mechanism and an ever smaller plastic deformation as the intermetallic amount increases. For both the steels, the fracture was mixed and the morphology exhibits the characteristic features of both brittle and ductile fracture, shifting toward the first or the second depending on the secondary phase's amount.

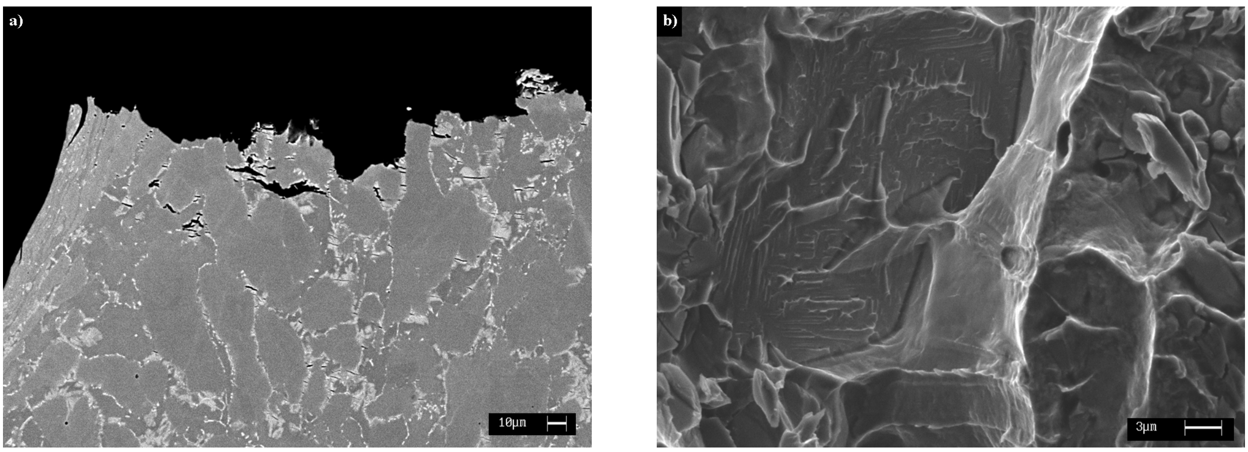

Figure 9: Zeron®100 SDSS failed in the third region (prevailing fragile behaviour): a) micro-cracks close to the notch root (SEM-BSE) and b) fracture surface (SEM-SE).

CONCLUSIONS

In the present work, the effect of the isothermal heat treatments on the impact toughness of two Duplex Stainless Steels (DSS) has been examined. A UNS S31803 (SAF 2205 DSS) and a UNS S32760 (Zeron®100 SDSS), isothermally heat treated at different time-temperature conditions, were investigated. .

For both the steels, the impact testing results showed that for about 0.5% of intermetallic phases the impact toughness was reduced by over 50% and for contents <0.5% the main effect was a reduction of the absorbed energy by facilitating the ductile fracture. Up to 1÷1.5% of volume fraction the fracture was mixed and for greater amounts the fracture was mainly brittle. The results were in agreement with some DSS specifications, which limit the intermetallic phase content at values <1%, in order to assure a minimum impact energy of 40-50 J [5].

Small amounts of secondary phases were enough to severely compromise the toughness of the materials, which instead was very high in the as-received conditions. For greater volume fractions of intermetallics the impact toughness was further reduced, small entities of plastic deformations are enough to cause a prevailing brittle fracture mechanism until, for 6÷8% of volume fraction, the ductile component was totally absent.

The plastic deformation the specimens were subjected to caused the secondary phases breakage with the formation of a high density of micro-cracks, inducing an easy nucleation and propagation of the final fracture crack. Both σ- and χ-phase have been found to be responsible for the embrittling of the steels under study and the observed impact toughness mainly depended on their amount, dimensions and distribution inside the duplex microstructure.

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