Effect of Kolsterising treatment on surface properties of a duplex stainless steel

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In recent years, attempts of engineering the surface of duplex stainless steels were made in order to enhance their hardness and tribological properties, without affecting their corrosion resistance. A possibility of improving these properties is provided by a family of processes developed by Prof. B.H. Kolster in the Netherlands in the late 1980's. These processes (usually referred to as Kolsterising® treatments) consist in a low temperature surface carburizing, which involves the diffusion of large quantities of carbon atoms (up to 6-7 wt.%) into the steel at a diffusion temperature below 450 °C. In the present paper a characterization of the surface layer of Kolsterised duplex SAF 2205 stainless steel was carried out to study the effects of this treatment on surface properties. The characterization includes optical metallographic examination, microhardness tests and SEM-EDS investigation on the Kolsterised steel in the as treated condition and after annealing treatments at 200, 250, 300, 350 and 400°C for 10 hours, to evaluate the stability of Kolsterised layer's properties with a moderate increase in temperature. Moreover, complying with ASTM G48-03 Method E Standard, in order to evaluate the effect of the Kolsterising® treatment on steel pitting resistance, the critical pitting temperature was obtained for Kolsterised duplex SAF 2205 stainless steel compared with the base metal.

Keywords:
Stainless steels, Materials Characterization, Metallography,
Scanning Electron Microscopy, Mechanical tests

INTRODUCTION

The microstructure of duplex stainless steels, with balanced amounts of ferrite and austenite, and a chemistry that is relatively high in chromium and molybdenum, entails good corrosion resistance in pitting, crevice, sulphide and chloride stress corrosion environments, at strength levels about double that of annealed austenitic stainless steels [1].

In many engineering applications a lot of components made of a duplex stainless steel may take advantage of a hardened surface, to improve the wear resistance and reduce the chance of surface initiated cracking, without affecting the corrosion resistance.

Interstitial solid solution hardening, using carbon, is one of the most effective hardening mechanisms for duplex stainless steels, however it is conditioned by the solubility limit of this element in the ferrite part of the metal matrix.

Other hardening mechanisms, such as quenching and tempering, precipitation hardening, or high temperature carburizing, are not possible with duplex stainless steels, due to either the stability of the austenite and ferrite phases or the easy precipitation of chromium carbides at intermediate temperatures.

A possibility of exploiting the interstitial solid solution hardening is provided by a family of processes developed by Prof. B.H. Kolster in the Netherlands in the late 1980's.

The Kolsterising® treatments consist of a low temperature carburizing, which involves the surface diffusion up to 6-7 wt.% of carbon into the steel at a temperature below 450 °C. Due to the low treatment temperature, these processes require long diffusion times (35 to 100 h) to achieve a carburized layer of few tens of μm [2 – 5].

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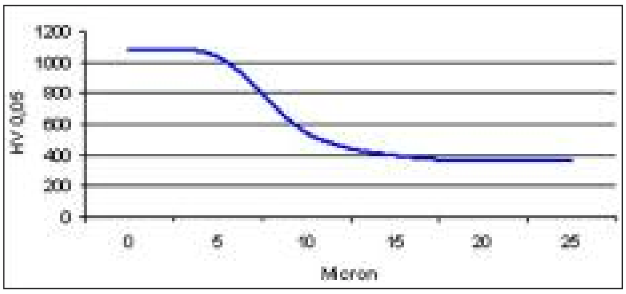


FIG. 1 ***Typical microhardness profile for a Kolsterised SAF2205 steel [6].***

Tipico profilo di microdurezza di un acciaio SAF2205 Kolsterizzato [6].

The maximum value of the achievable microhardness is quite high compared with values obtained by other treatments and it is as high as 1050 $HV_{0,05}$. The typical microhardness profile which is generated by the Kolstering® process onto a SAF2205 steel is hereby reported (Fig. 1) [6].

The Kolsterising® technique was originally developed for austenitic stainless steels: in fact carbon diffuses properly and easily into austenite due to its large solubility in the f.c.c. lattice.

Such a carbon diffusion into an austenitic-ferritic structure is expected to yield a non-homogeneous carbon enriched layer; austenite regions would be easily enriched in carbon, while ferrite regions would be not, because of the c.c.c. lattice where carbon is hardly hosted. In this case, by means of a special surface preparation, a thin fully-austenitic layer is formed making it possible for carbon to diffuse properly and uniformly [6].

C	Si	Mn	P	S	Cr	Mo	Ni	Al	B	Cu	N
0.024	0.42	1.72	0.020	0.0003	21.96	3.43	5.32	0.028	0.0040	0.167	0.168

TAB. 1 ***Chemical composition in weight percent of the base metal (SAF 2205).***
Composizione chimica, espressa come percentuale in peso, del metallo base (SAF 2205).

The Kolsterising® process is applied to duplex stainless steels by diffusing atoms of carbon at the interstitial level, without the formation of undesired chromium carbides and the consequent degradation of the corrosion resistance.

Accommodation of the carbon within the austenitic layer is claimed to cause expansion of the austenite crystal lattice that is contrasted by the unexpanded, and unhardened, substrate. This creates compressive stresses in the surface layer. These stresses, combined with the changes in chemical composition, significantly harden the material.

Few attempts are reported in the existing literature to characterize the effect of Kolsterising® treatment on surface properties of duplex stainless steels.

In the present study, a characterization of the surface layer of Kolsterised duplex SAF 2205 stainless steel was carried out to study the effects of this treatment on surface properties.

EXPERIMENTAL METHOD

The duplex stainless steel (base metal) investigated in the present paper is characterised by the chemical composition shown in Table 1.

The SAF 2205 steel is a second generation duplex stainless steel, with a medium nitrogen content (≈ 0.15%).

The samples were machined from a 340 mm diameter forged round block. The bar was previously subjected to a solution treatment at 1050 °C, followed by a quenching in stirred water, which resulted in a 50/50 ferrite/austenite ratio microstructure. Afterwards the specimens were Kolsterised by Bodycote S3P Group, Italy.

The characterization of the samples includes optical metallographic examination, SEM-EDS investigation and microhardness tests on the Kolsterised steel in the as treated condition and after annealing treatments at 200, 250, 300, 350 and 400°C for 10 hours, to evaluate the stability of Kolsterised layer's properties with a moderate increase in temperature.

Duplex stainless steels, in fact, because of their high Cr concentration, are prone to the so called 475°C embrittlement, so their application is frequently confined to temperatures below about 300-350°C. Up to these temperatures whichever surface hardening treatment must therefore be unaffected by any thermal treatment.

Light microscopy and SEM investigations were carried out on a cross-section piece cut normal to the surface of the Kolsterised specimens. The samples were mechanical polished and etched with Beraha reagent to reveal the austenitic-ferritic microstructure and the austenitic Kolsterised layer.

At the beginning, the samples were examined using a Reichert-Jung MeF3 optical microscope, equipped with QWin image analyser. Afterwards, SEM observations and semi-quantitative chemical analyses, using a LEO EVO-40XVP scanning electron microscope with a Link Analytical eXL microprobe, were carried out to evaluate any change in the chemical composition of the austenitic Kolsterised layer after annealing treatment.

The microhardness of the austenitic Kolsterised layer was measured in two ways: one directly on the surface and the other on a cross-section piece cut normal to the surface.

As reported in [7], indentations made at normal HV microhardness loads around 500 gr would penetrate through the thin Kolsterised layer in the on-face tests, giving a falsely low measure of the microhardness, because both the Kolsterised layer and the unhardened substrate would be sampled. On the other hand, very light loads mostly investigate the hardened layer but the size of the indentation is small and is possibly affected by both greater influence of the elastic recovery during unloading and appreciably larger errors of measurement.

To optimize the surface microhardness value a load of 30 g was used. Three tests were made and the average of the measured values was calculated.

The microhardness tests on the cross-section of the samples were made after mechanical polishing and etching with Beraha reagent to reveal the austenitic Kolsterised layer and the base metal microstructure. As only a thin surface layer is hardened, the size of the indentation has to be small to avoid the risk of a falsely low measure of the Kolsterised layer microhardness, therefore a load of 30 g was used again. Three tests were made and the average of the measured values was calculated.

Further microhardness tests were made on the cross-section of the samples under the austenitic Kolsterised layer in the as treated condition, at a distance of 30 μm from the surface, both in the ferritic islands and in the austenitic ones. A load of 200 g was used. The obtained values also in this case are the average of three measurements. They were compared with the base metal ones.

Finally microhardness tests were made on the cross-section of the samples under the austenitic Kolsterised layer in the as treated condition, at a distance of 30 μm, 60 μm and 90 μm from the surface, both in the ferrite islands and in the austenite ones to evaluate carbon diffusion depth.

Moreover, complying with the ASTM G48-03 Method E Standard, in order to evaluate the effect of the treatment on steel pitting resistance, the critical pitting temperature was measured for Kolsterised steel and compared with the base metal.

RESULTS AND DISCUSSION

Metallographic Examination

The austenitic-ferritic microstructure and the austenitic Kolsterised layer, which is less etched than the underlying steel, are shown in Fig. 2. An austenitic Kolsterised layer with a thickness of 12 – 13 μm was measured on all specimens.

Similar metallographic examination was carried out on the samples after annealing treatments at 200, 250, 300, 350 and 400°C for 10 hours: as foreseeable, no visible alteration of either the austenitic Kolsterised layer was observed.

SEM investigation and microhardness tests were necessary to evaluate the stability of the austenitic Kolsterised layer properties with increasing temperature.

Carbon content obtained by EDS analyses, being carbon a light element, must be regarded only on a qualitative basis; nevertheless, differences in carbon content from point to point can be considered as representative, independently of the absolute value.

Carbon concentration in the austenitic Kolsterised layer progressively decreases at increasing annealing temperature. The most significant decrease is however observed at the highest temperatures, i.e. 350°C and 400°C, as shown in Fig. 3 - spectra 1; a carbon diffusion towards deepest layers, favoured by car-

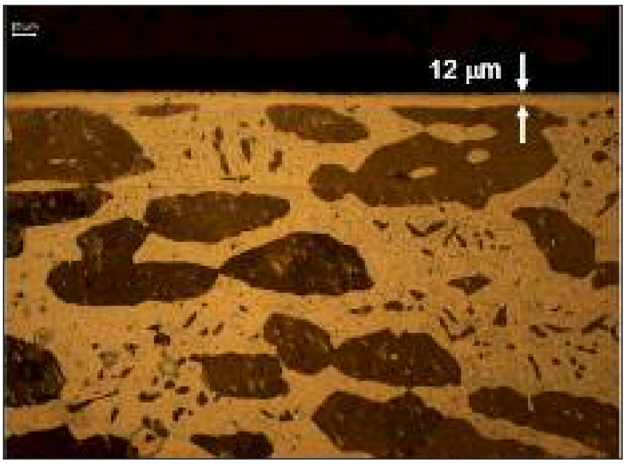
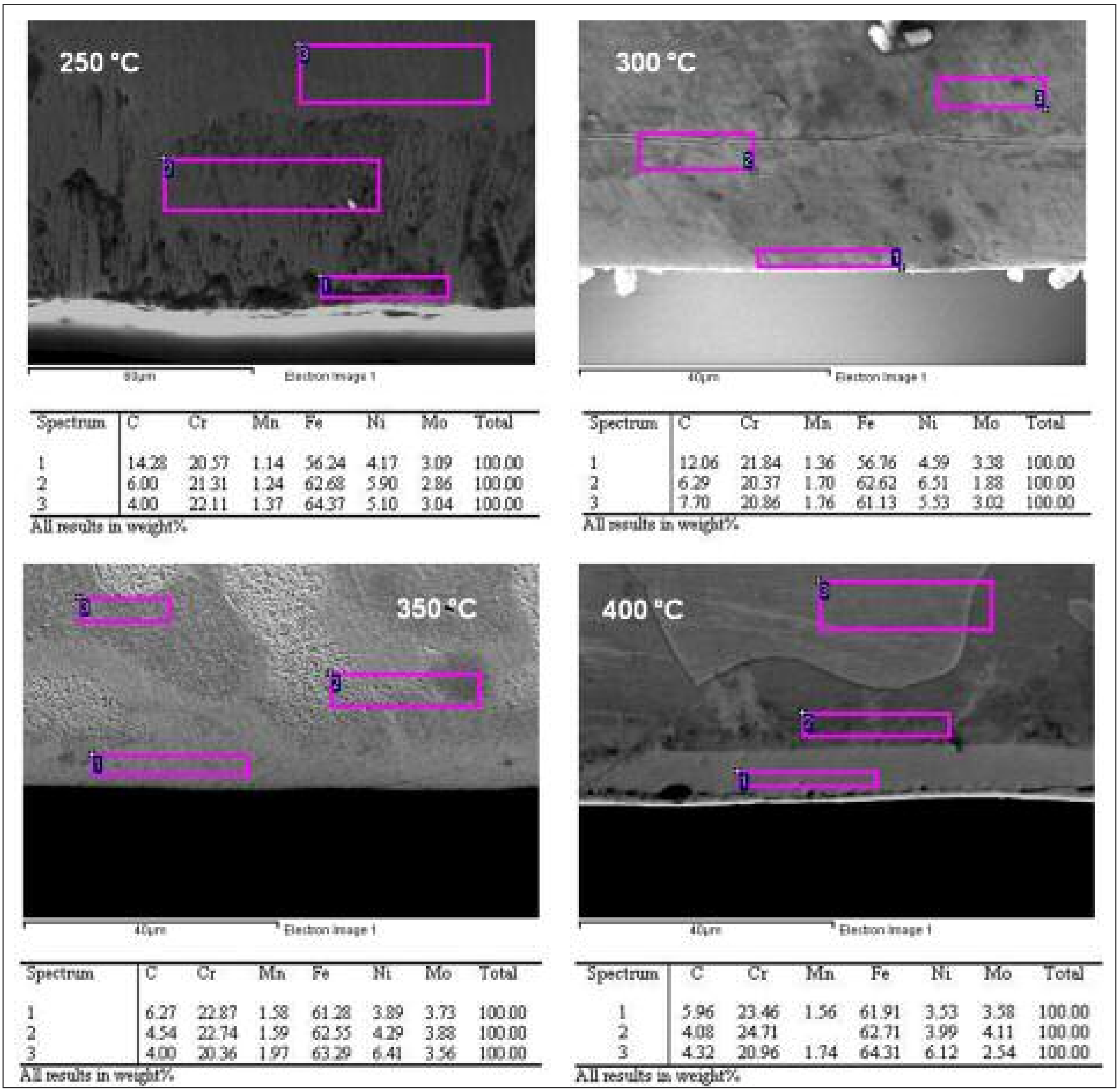


FIG. 2
Microstructure and austenitic Kolsterised layer of a sample etched with Beraha reagent.

Microstruttura e strato austenitico Kolsterizzato ottenuti mediante attacco chimico Beraha.

bon gradient and increasingly effective annealing temperature is responsible for these variations.

The analyses in Fig. 3, indicated as spectra 2 and 3, refer to zones below the austenitic Kolsterised layer, at increasing distance from the surface. From these analyses it can be observed that carbon diffusion during the Kolsterising treatment is not limited to the outer austenitic layer, but extends to deeper layers. From EDS analysis it emerges that carbon content starts to be constant nearly at 0.1 – 0.12 mm from the surface. As it could be foreseen, carbon enrichment in the duplex matrix below the au-



Spectrum	C	Cr	Mn	Fe	Ni	Mo	Total
1	14.28	20.57	1.14	56.24	4.17	3.09	100.00
2	6.00	21.31	1.24	62.68	5.90	2.86	100.00
3	4.00	22.11	1.37	64.37	5.10	3.04	100.00

All results in weight%

Spectrum	C	Cr	Mn	Fe	Ni	Mo	Total
1	12.06	21.84	1.36	56.76	4.59	3.38	100.00
2	6.29	20.37	1.70	62.62	6.51	1.88	100.00
3	7.70	20.86	1.76	61.13	5.53	3.02	100.00

All results in weight%

Spectrum	C	Cr	Mn	Fe	Ni	Mo	Total
1	6.27	22.87	1.58	61.28	3.89	3.73	100.00
2	4.54	22.74	1.59	62.55	4.29	3.88	100.00
3	4.00	20.36	1.97	63.29	6.41	3.56	100.00

All results in weight%

Spectrum	C	Cr	Mn	Fe	Ni	Mo	Total
1	5.96	23.46	1.56	61.91	3.53	3.58	100.00
2	4.08	24.71		62.71	3.99	4.11	100.00
3	4.32	20.96	1.74	64.31	6.12	2.54	100.00

All results in weight%

Fig. 3 ***SEM micrographs and EDS analyses of the samples after annealing treatment at 250, 300, 350 and 400°C for 10 hours.***

Micrografie SEM e analisi EDS dei campioni dopo trattamento termico di ricottura a 250, 300, 350 e 400°C per 10 ore.

stenitic Kolsterised layer progressively decreases at increasing distance from the surface.

Microhardness tests

The surface microhardness of the Kolsterised steel in the as treated condition is shown in Fig. 4, compared with the base metal. It is important to note that a 975 HV microhardness was measured for the Kolsterised layer represents a noticeable hardening compared with the 357 HV for the base metal.

The surface microhardness of the Kolsterised steel after the annealing treatments at different temperatures for 10 hours is shown in Fig. 5.

The results show that the surface microhardness (above 950 HV) is weakly affected by annealing temperatures up to 300°C.

A considerable decrease of the surface microhardness is evident after the annealing treatment at 400°C, most probably to be related to the more favoured diffusion of carbon at further distances from the original Kolsterised surface layer.

The results of the microhardness tests on the cross-section of the samples after the annealing treatments are shown in Fig. 6. On the transverse section microhardness is somewhat lower than that measured on the surface (Fig. 5) because of the microhardness gradient within the Kolsterised layer and represents a rough average value throughout the layer itself.

Microhardness keeps above 700 HV for annealing treatments up to 350°C, while a considerable decrease is observed at 400°C, due to the favoured carbon diffusion out of the surface layer.

The results of microhardness tests made on the cross-section of the samples under the austenitic Kolsterised layer in the as surface-treated condition, at a distance of 30 μm from the surface, both in the ferrite islands and in the austenite ones, are shown in Fig. 7, along with their comparison with the base metal.

The increase in microhardness in both phases of the Kolsteri-

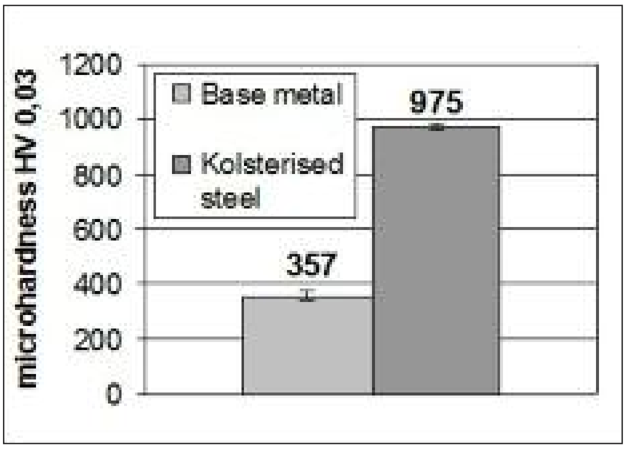


FIG. 4 ***Surface microhardness of the Kolsterised steel in the as treated condition compared with the base metal.***

Microdurezza superficiale dell'acciaio Kolsterizzato a confronto con il metallo base.

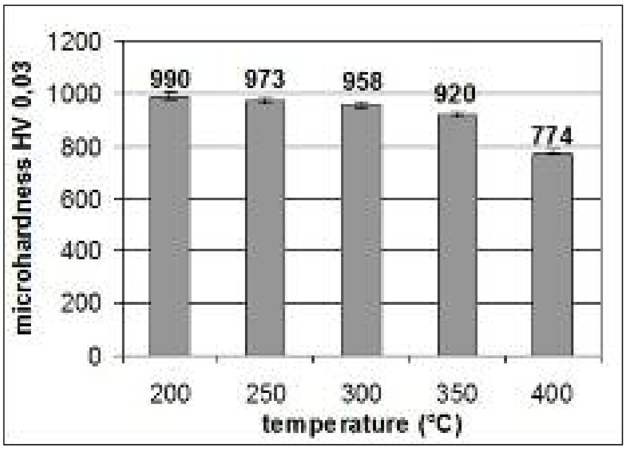


FIG. 5 ***Surface microhardness of the Kolsterised steel after annealing treatment at 200, 250, 300, 350 and 400°C for 10 hours.***

Microdurezza superficiale dell'acciaio Kolsterizzato sottoposto a ricottura a 200, 250, 300, 350 e 400°C per 10 ore.

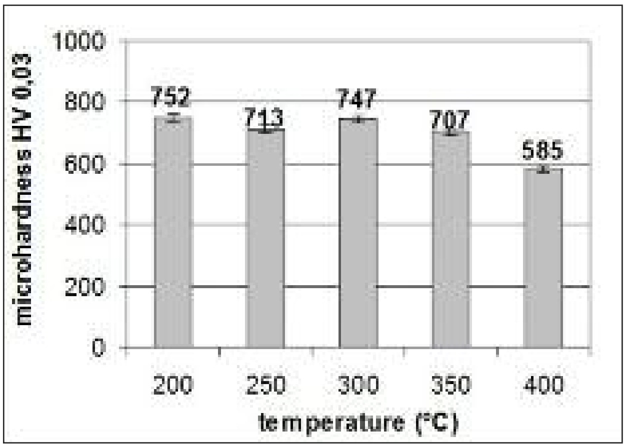


FIG. 6 ***Microhardness of the austenitic Kolsterised layer after annealing treatment at 200, 250, 300, 350 and 400°C for 10 hours.***

Microdurezza dello strato austenitico Kolsterizzato sottoposto a ricottura a 200, 250, 300, 350 e 400°C per 10 ore.

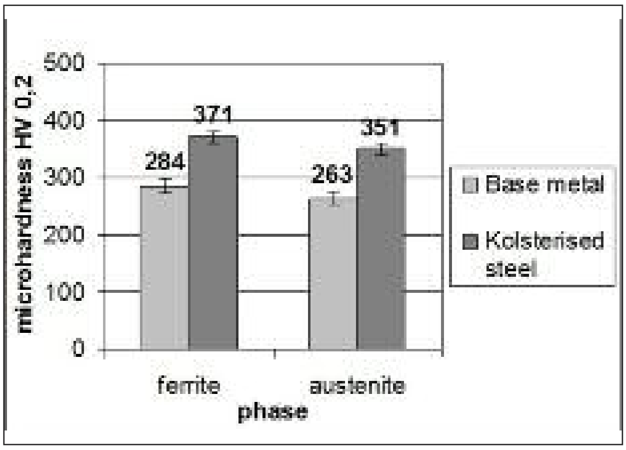


FIG. 7 ***Microhardness of the ferritic phase and the austenitic one at a distance of 30 μm from the surface of the Kolsterised steel in the as treated condition.***

Microdurezza della fase ferritica e di quella austenitica ad una distanza di 30 μm dalla superficie dell'acciaio Kolsterizzato.

sed steel in the as treated condition shows that carbon diffusion below the austenitic surface layer during the Kolsterising® treatment is not limited to austenite, but contributes also to the increase of the ferrite phase hardness.

Finally, the results of microhardness measurements on the cross-section in the ferrite and austenite islands under the austenitic Kolsterised layer in the as treated condition, at a distance of 30 µm, 60 µm, and 90 µm from the surface, are shown in Fig. 8. These values are compared with the base metal ones.

Microhardness variation at increasing distance from surface is consistent with the observed carbon diffusion below the austenitic surface layer during the Kolsterising treatment up to 0.1 – 0.12 mm from the surface, where carbon content starts to be unaffected by the treatment.

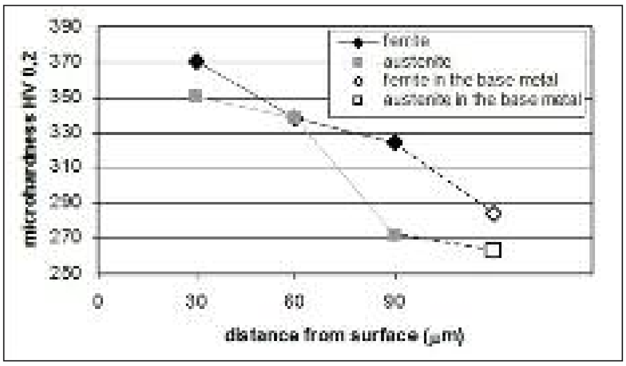


FIG. 8 ***Microhardness of ferrite and austenite as a function of the distance from surface on Kolsterised steel in the as treated condition compared with the base metal.***

Microdurezza della ferrite e dell'austenite in funzione della distanza dalla superficie Kolsterizzata a confronto con il metallo base.

Critical Pitting Temperature (CPT) test

The standard ASTM G48 solution was used for the corrosion tests, with 6% $FeCl_3$ by mass and 1% HCl, to evaluate the effect of the Kolsterising® treatment on steel pitting resistance.

The specimens had a standard size (12.5x25x50 mm). All surfaces of the base metal specimens were polished to a uniform finish with a 120-grit abrasive paper.

The CPT start temperature was determined in accordance with the formula in the ASTM G48 standard, as detailed below:

$$\text{CPT } (^{\circ}\text{C}) = (2.5 \times \%\text{Cr}) + (7.6 \times \%\text{Mo}) + (31.9 \times \%\text{N}) - 41.0 \qquad (1)$$

Test was first carried out at the nearest increment of 5°C, estimated by the above equation for both the base metal specimens and the Kolsterised ones. A start temperature of 50°C was therefore used, since the calculated CPT was 45°C.

The standard test period is 24 h. Following removal from the test solution the specimens were cleaned in water, flushed with acetone and air dried. The specimens were then optically examined at magnifications up to 200x. The presence of any pitting attack was recorded.

When pitting is present with a depth of 25µm or greater and no pitting attack is present at the 5°C immediately lower temperature, the test temperature is the critical pitting temperature (CPT).

The results of the tests are reported in Table 2.

The start temperature of 50°C proved to be too high for both the base metal and the Kolsterised steel as it promoted pitting attack on the specimens in both the examined conditions.

This start temperature is considered to be too high for duplex SAF 2205 stainless steel also in the literature [8].

For this reason, in accordance with ASTM G48, the test temperature was reduced to 45°C. Also this test temperature promoted pitting attack on the specimens in both treated and untreated conditions.

On the contrary, tests performed at 40°C on the Kolsterised specimens showed variable results, with one specimen being free from pitting attack and one specimen showing localised pitting. The 40°C test temperature promoted pitting attack on both the base metal specimens.

At the next temperature decrement, i.e. at 35°C, no visible pitting was noted on both the Kolsterised specimen and the untreated one. Consequently the CPT for the base metal results 40 °C.

Due to the not certain result obtained on Kolsterised sample in the 40 °C test, the experiment was repeated at a slightly lower temperature (37°C) for a further check on the effect of the Kolsterising® treatment on steel pitting resistance. This test confirmed the 35°C test result, with both treated and untreated specimens being free from pitting attack. It follows that the CPT for the Kolsterised layer is at least 40 °C, with the possibility that it could be between 40 °C and 45 °C.

This result points out that the Kolsterising® treatment of duplex SAF 2205 stainless steel has no detrimental effect on the chloride pitting resistance.

Test temperature [°C]	Treated/Untreated	Pitting evident
35	Kolsterised	No
	base metal	No
37	Kolsterised	No
	base metal	No
40	Kolsterised	No/Yes
	base metal	Yes/Yes
45	Kolsterised	Yes/Yes
	base metal	Yes/Yes
50	Kolsterised	Yes
	base metal	Yes

TAB. 2 ***Results Summary for CPT tests on the base metal specimens and on the Kolsterised ones.***

Risultati dei CPT test sui campioni di metallo base e su quelli Kolsterizzati.

CONCLUSIONS

In the present paper a characterization of the surface layer of Kolsterised duplex stainless steel SAF 2205 was carried out to study the effects of this treatment on surface properties. The results are summarised as follows.

It was shown that the Kolsterising® treatment causes significant enhancement of the surface microhardness of the duplex SAF 2205: 975 HV was measured on the Kolsterised steel, compared with 357 HV for the base metal.

Surface microhardness (above 950 HV) is only weakly affected by subsequent annealing treatment at increasing temperature up to 300°C, while at 400°C a noticeable microhardness decrease was recorded.

Similarly, the through-thickness microhardness of the austenitic Kolsterised layer shows a very small decrease, with values above 700 HV, after annealing up to 350°C, while a considerable decrease is observed after annealing at 400°C, due to the diffusion of the carbon out of the surface layer.

These results agree with SEM investigations and EDS analyses. Microhardness tests made on the cross-sections under the austenitic Kolsterised layer in the as treated condition, both in the ferrite and austenite islands, show a carbon diffusion in both phases below the austenitic surface layer during the Kolsterising® treatment at least up to 90 μm from the surface, with a hardening of the steel also under the austenitic surface layer.

The critical pitting temperature was obtained for Kolsterised steel compared with the base metal, the CPT was measured to be 40 °C for the base metal and it is al least 40 °C (with the possibility that it could be between 40 °C and 45 °C) for the Kolsterised steel. It was then possible to conclude that the Kolsterising® treatment of duplex SAF 2205 stainless steel tested has no detrimental effect on the chloride pitting resistance.

ACKNOWLEDGEMENTS

The authors thank Valentina Ferrari for her collaboration in the corrosion tests.

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Abstract

Effetto del trattamento di Kolsterizzazione sulle proprietà superficiali di un acciaio inossidabile duplex

Parole chiave: acciaio inox, caratterizzazione materiali, metallografia, microscopia elettronica, prove meccaniche

Gli acciai inossidabili duplex sono caratterizzati da un elevato contenuto di cromo che, associato a opportuni tenori di nichel e molibdeno, consente di ottenere una microstruttura bifasica, costituita da austenite e ferrite, spesso in uguali proporzioni.

Il successo di tali acciai, se confrontati con i più tradizionali acciai inossidabili austenitici, è principalmente dovuto alle loro maggiori caratteristiche meccaniche; presentano ad esempio una resistenza allo snervamento circa doppia, da associare ad un migliore comportamento nei confronti della corrosione per pitting e sottotensione [1].

Negli ultimi decenni sono stati condotti molteplici tentativi per migliorare le caratteristiche meccaniche superficiali di questi acciai, in particolare la loro durezza e le loro proprietà tribologiche, senza, però, peggiorarne la resistenza alla corrosione.

Una possibilità per migliorare queste caratteristiche è data dall'impiego di alcuni processi sviluppati dal Prof. B. H. Kolster alla fine degli anni '80.

Tali processi, noti come trattamenti di Kolsterizzazione®, consistono in una cementazione condotta a bassa temperatura, inferiore a 450 °C, che consente la diffusione del carbonio negli strati appena al di sotto della superficie dell'acciaio. A causa della bassa temperatura del trattamento, la Kolsterizzazione® richiede lunghi tempi di diffusione del carbonio, da 35 a 100 ore, per raggiungere spessori dello strato carburato di poche decine di μm.

I valori di microdurezza massimi raggiungibili sono piuttosto alti se confrontati con quelli ottenibili attraverso altri trattamenti e sono attorno a 1050 HV.

Originariamente la Kolsterizzazione® è stata messa a punto su acciai inossidabili austenitici, così da sfruttare la facilità di assorbimento e di diffusione del carbonio all'interno del reticolo c.f.c.

Viceversa, la diffusione del carbonio in una microstruttura austenitico-ferritica porterebbe ad una condizione di disomogeneità di composizione chimica, poiché il carbonio diffonderebbe con più facilità nell'austenite rispetto a quanto accadrebbe nella ferrite.

Per ovviare a questo inconveniente, che si rifletterebbe su una disomogeneità delle proprietà dello strato superficiale kolsterizzato, si opera pretrattando opportunamente la superficie dell'acciaio, così da ottenere un sottile strato omogeneo austenitico. Ottenuto il reticolo cristallino ottimale per accogliere il carbonio, mediante la Kolsterizzazione® il carbonio forma una soluzione solida interstiziale con il ferro, senza dare origine alla formazione di carburi di cromo indesiderati, che potrebbero comportare un peggioramento della resistenza alla corrosione dell'acciaio.

Nel presente lavoro si è condotta una caratterizzazione dello strato superficiale kolsterizzato di un acciaio inossidabile duplex SAF 2205, allo scopo di studiare l'effetto di tale trattamento sulle proprietà superficiali dell'acciaio.

Tale caratterizzazione comprende un'indagine metallografica condotta al microscopio ottico, osservazioni al microscopio elettronico a scansione completate da analisi chimiche semiquantitative e misure di microdurezza dell'acciaio sia allo stato kolsterizzato sia dopo Kolsterizzazione® e trattamenti termici a 200, 250, 300, 350 e 400°C per 10 ore, allo scopo di valutare la stabilità delle proprietà dello strato kolsterizzato al crescere della temperatura in potenziali impieghi al di sopra della temperatura ambiente.

Inoltre, facendo riferimento alla normativa ASTM G48-03, si è ottenuta la temperatura critica di pitting dell'acciaio kolsterizzato e del metallo base per valutare l'effetto del trattamento di Kolsterizzazione® sulla resistenza a pitting dell'acciaio.