Chromium nitrides effects on low temperature impact toughness and durability of duplex stainless steels forgings

a cura di: **G. Camicia, M. Longin, P. Ferro, F. Bonollo**

The chromium nitrides effects on duplex stainless steels low temperature impact toughness and durability were investigated. A duplex rolled ring was cut as different blocks, and different Cr_2N amounts were obtained by trial heat treatments, with the solution annealing furnace temperature set at low and high levels, 1040 and 1140 °C respectively, and the transfer time ranging between 5 and 120 s in order to prevent the σ phase formation. Micrographic examinations, low temperature Charpy impact tests and durability assessments were carried out on specimens sampled from the blocks cores. The material strength was evaluated by hardness tests. The results showed how an increase in transfer time allows the N diffusion in the austenite phase, reducing the nitrides quantity in the ferrite phase. A synergistic effect between the transfer time and the solution annealing temperature on the amount of intermetallic particles was observed. Clear effects of the Cr_2N presence on both material low temperature impact toughness and pitting corrosion resistance were found.

KEYWORDS: DUPLEX STAINLESS STEELS - FORGING - SOLUTION ANNEALING - CHROMIUM NITRIDES - CHARPY IMPACT TEST - ASTM G48

INTRODUCTION

The production of duplex stainless steels emerged only in the second half of the eighties [1]. The dual phase microstructure gives the optimum compromise between mechanical strength, toughness and durability thus they represents a good answer for the Oil and Gas industry needs. Compared to austenitic and ferritic stainless steels, duplex excels for their resistance to stress corrosion cracking in chloride solutions [2-4], so these grades are nowadays widely used for offshore applications [5; 6]. Low temperature impact toughness and resistance to pitting in corrosive environment are typical requirements, on the other hand these can be detrimentally affected by the formation of secondary phases. Byrne et al. [7] investigated several commercial heats of SDSS UNS S32760 which had a range of nitride contents from none to a large quantity. The impact toughness was significantly reduced when the nitride content was high. They also showed that nitrides reduced the critical pitting temperature in the ASTM G48-C [8] test from 70-75 °C down to 45 °C at the highest nitride content. The studies about the manufacturing process effect on chromium nitrides precipitation and material durability are limited. In this work, the solution annealing temperature and quenching transfer time effects on chromium nitrides precipitation, low temperature impact toughness and resistance to pitting corrosion of duplex stainless steels forgings have been investi-

Giordano Camicia, Matteo Longin
Siderforgerossi Group Spa QA R&D, Arsiero (Italy)

Paolo Ferro, Franco Bonollo
University of Padova DTG, Vicenza (Italy)

gated. A sacrificial duplex rolled ring has been cut in several blocks and these were heat treated according an experimental 2x3 design. Microstructural characterization, mechanical and corrosion tests were carried out on samples machined from these trial blocks. The results highlights a clear link between the tested heat treatment parameters and the material properties and could be applied as reliable guidelines for the correct design and heat treatment of actual duplex forged components.

EXPERIMENTAL PROCEDURE

Rolled ring manufacturing

The starting raw material was a DSS grade UNS S31803 supplied as a Ø 680 mm raw round ingot. The steel melting was by the electric arc furnace, followed by the argon oxygen discharge refining. The table 1 resumes the cast ladle analysis provided by the steel maker.

C	Mn	P	S	Si	Ni	Cr	Mo	N
0,017	1,35	0,027	0,001	0,49	5,54	22,1	3,13	0,17

Tab. 1 - Chemical compositions (wt. %) of the duplex stainless steel used

A ring 1038x528x255 mm sized was manufactured by Siderforgerossi Group Spa by this production route: upsetting, drawing, punching, piercing, ring rolling and water cooling. The average hot forming reduction ratio, calculated according the standard API 20B [9] was 4:1. The hot working temperature ranged from 1250 to 1000 °C. After the ring manufacturing, a solution annealing heat treatment at 1050 °C followed by water quenching according the ASTM standard A182 [10] was carried out.

Trial heat treatments

From a rolled ring slice, six 70x50x40 mm blocks were machined. These have been heat treated at University of Padova - DTG laboratory in an electric resistance furnace according this route:

1. heating rate: about 100 °C/h;
2. holding time at solution annealing temperature: 2 hours;
3. water quenching;

The solution annealing temperatures and quenching transfer times were set according the experimental design stated in table 2.

Temperature (°C)	Transfer time (s)		
1040	< 5	60	120
1140	< 5	60	120

Tab. 2 - heat treatments parameters

In order to record the actual thermal history from the starting heating till the complete cooling, a thermocouple was inserted into an hole drilled from the surface to the block core. The data was collected using a high-speed data acquisition system with a sampling rate of 0,02 Hz, analog-to-digital converter accuracy of 0,1 °C and linked to a personal computer.

Microstructural and mechanical characterizations

The blocks used for trial heat treatments were sectioned for microstructural and mechanical characterizations. For the microstructure investigations, a sample just below the block surface and another one at the block core were machined out. Both were prepared to a 3 μm finish with diamond paste, polished with a commercial 0,4 μm silica slurry for metallographic investigations and finally etched with a ASTM E407 type 219 electrolytic etchant applying 1,0-2,0 V for 10-120 s in a 60% HNO_3 water solution [11]. Microstructural analysis were carried first out using an optical microscope and then the detrimental phases characterization was carried out by a further SEM EDS investigation. and studied by a Quanta FEG-ESEM 250®. The material toughness was checked by Charpy impact tests, performed at - 46 °C (i.e. -50 °F) on V-Notched specimens according ASTM A370 standard [12]. The samples main axis direction were oriented tangentially of the former rolled ring circumference according the reference ASTM standard for the selected grade [10]. The ferrite rate has been calculated by Leica QWin® software analysis according the standard ASTM E1245 [13]. For this purposes the specimens were etched according ASTM E407 type 220 electrolytic etchant applying 1,5-3,0 V for 5-10 s in a 20% NaOH water solution [11]. The material durability was assessed by corrosion tests carried our according ASTM G48 [8]. A standard by ferric chloride solution. The nominal specimens sizes were 50x25x10 mm, polished by a 120 grit paper and cleaned for 5 min in an ultrasonic acetone bath.

RESULTS AND DISCUSSION

Trial heat treatments charts

In the following figures, the quenching charts of the contact embedded thermocouples are shown.

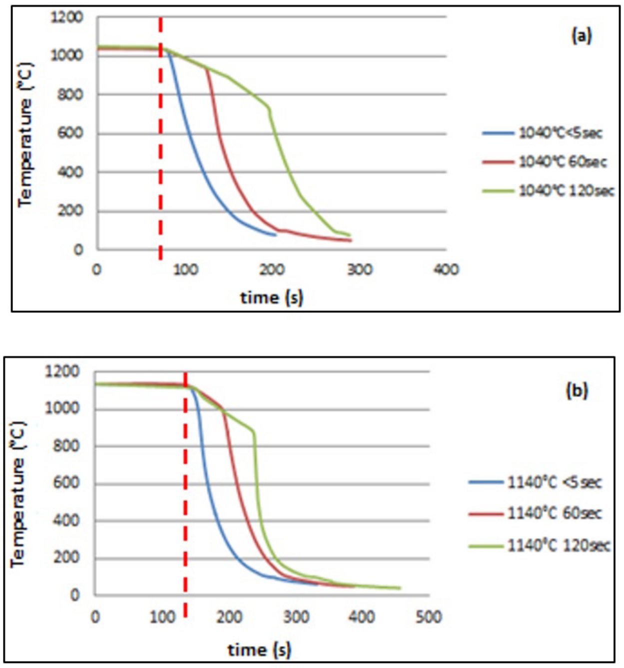
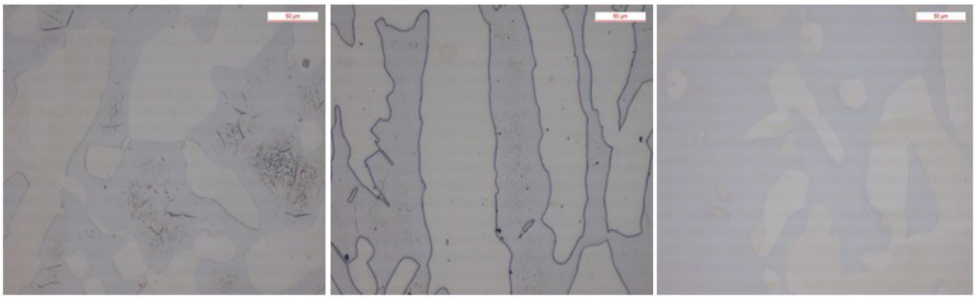


Fig. 1 - quenching time-temperature charts of the trial blocks starting from a) 1040 °C and b) 1140 °C solution annealing temperatures. The data were collected by a contact thermocouple embedded in the block core. The red dashed lines highlights the instant of the removal from the furnace

The cooling kinetics of the material volume near the thermocouple tip, thus the block core, are reported. In case of a transfer time < 5 s, a substantial direct water quenching from the solution annealing temperature was performed. On the other hand, in case of transfer times 60 and 120 s, the first part of the cooling is in air. In the experimental scenario, the air and water cooling trends seems to be linear and exponential respectively, with a cooling drasticity substantially higher in water as well. Considering the charts for the detrimental phases precipitation available in literature [14-16], the cooling rate around 800 °C is fast enough to prevent the well-known risk of σ phase formation for all the studied conditions [17-20]. On the other hand, different cooling rates were observed around 900 °C, thus the amount of nitrides shall be properly investigated via metallographical and mechanical characterization. The Oil and Gas market forging specifications use to ask for a transfer time less than 60 s. Compared to the typical forging sizes for offshore application, the trial blocks are substantially small, thus the 60 and 120 s tests should be representative of actual small and medium sized forging behavior respectively. The 5 s tests have an industrial significance only for operation with a very high cooling rate within 1200-800 °C, such as the welding processes [21-23].

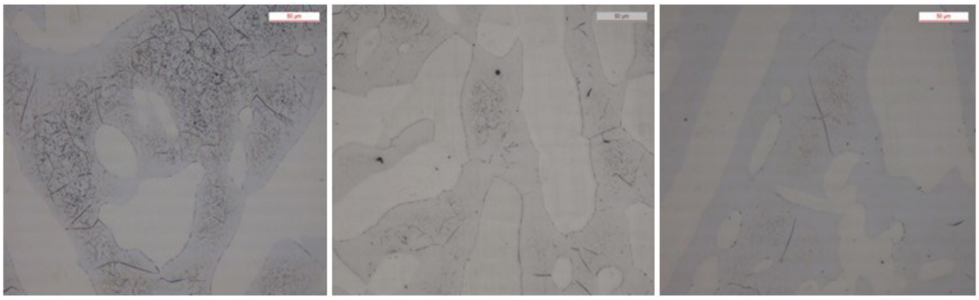
Detrimental phases investigations

As discussed in the previous §, according the precipitation charts in [14-16], σ phase free microstructures are expected due to the thermal history during the trial heat treatments. In the following figures, the optical micrographs are reported.



(a) (b) (c)

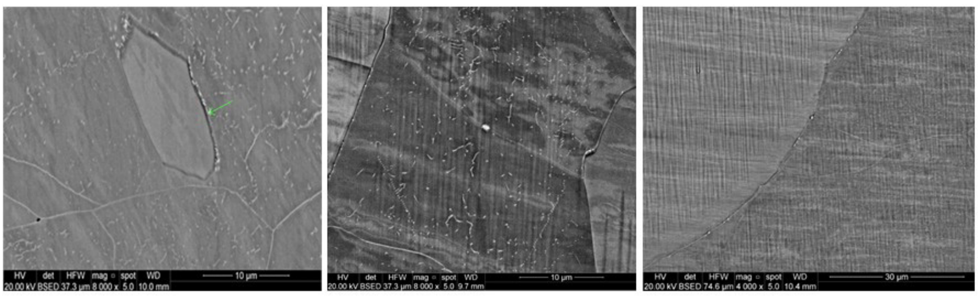
Fig. 2 - optical micrographs of the blocks solution annealed at 1040 °C and quenched with a transfer time (a) < 5 s, (b) 60 s and (c) 120 s. The reference bar in the left bottom corner is for 50 μm. Ferrite is the dark grey phase.



(a) (b) (c)

Fig. 3 - optical micrographs of the blocks solution annealed at 1140 °C and quenched with a transfer time (a) < 5 s, (b) 60 s and (c) 120 s. The reference bar in the left top corner is for 50 μm. Ferrite is the dark grey phase.

A substantial reduction of detrimental intermetallic phases in the ferrite phase is noted increasing the transfer time, in particular moving from < 5 s to 60 s. The samples solution annealed at 1140 °C seems to be more prone to the secondary phases precipitation. The electronic microscope analysis enhanced the intermetallic phases morphology, as shown in fig. 4.



(a) (b) (c)

Fig. 4 - electronic micrographs of the blocks solution annealed at 1140 °C and quenched with a transfer time (a) < 5 s, (b) 60 s and (c) 120 s. The reference bars are for (a)-(b) 10 μm and (c) 30 μm. Ferrite is the dark grey phase

Again, the intermetallic phases were found mainly within the ferrite phase and their content falls with increasing the quenching transfer time up to 120 s. In the fig. 4.c is shown how the grain boundaries are free from σ phase particles also for the 120 s quenching, as supposed in the previous §. A chemical investigation of several precipitates by X-EDS has been performed, in the following figure one example is reported.

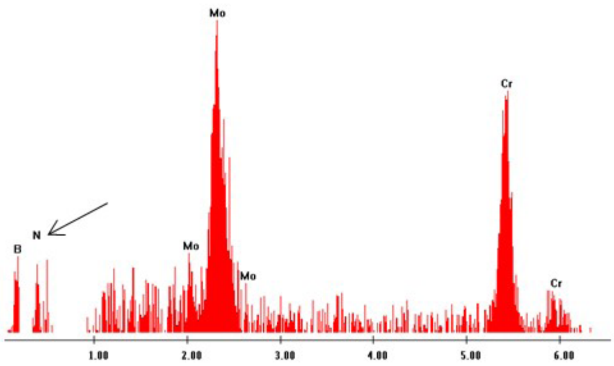


Fig. 5 - X-EDS analysis of the precipitate highlighted by the green arrow tip in fig. 4.a

The N peak in fig. 5 let classify the intermetallic particle as a nitride. Several authors reported the Cr_2N precipitation, mainly within the ferrite phase, for rapid cooling from a solution annealing temperature between 1000-1300 °C [24]. At this range, the N solubility in the ferrite phase arises up to the austenite phase value. In case of too fast cooling the N diffusion to the austenite phase is hindered, thus the ferrite phase becomes oversaturated in N and this precipitates as fibrous chromium nitrides [25].

Charpy impact tests

The duplex stainless steels are widely used in the Oil and Gas industry for their excellent low temperature impact properties, a ductile behavior is generally required down to -46 °C [26]. In the following figure, the Charpy impact tests results for the 2x3 tested heat treatment conditions are reported.

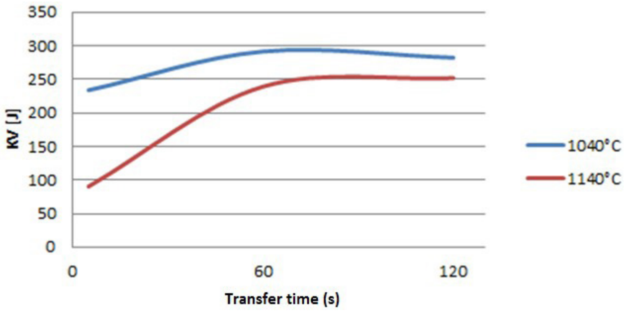


Fig. 6 - Effect of the solution annealing temperature and quenching transfer time on the -46 °C Charpy impact test fracture energy trend (average of 3 values).

The material fracture can be considered as ductile for all 60 s and 120 s quenching tests, thanks to the resilience values above 250 J. A substantial resilience drop is noted for the 1140 °C solution annealed specimens quenched within 5 s, on the other hand for the one solution annealed at 1040 °C and quenched within 5 s the resilience reduction is less marked. In all the tested conditions, the lower solution annealing temperature seems to increase the material impact resilience. The effect of the austenite spacing on CVN -46 °C results has been reported in [27] as negligible.

Corrosion tests

The durability against ASTM G48-A solution [8] was investigated on specimens from the material treated by the six trial solutions annealing. The material was firstly assessed after 24 h / 25 °C as commonly required by Oil & Gas specifications for forgings [26]. No weight loss and visible pitting at 20x was found in all the tested conditions. In the following figure are shown the results at higher (i.e. 40 °C) testing temperature.

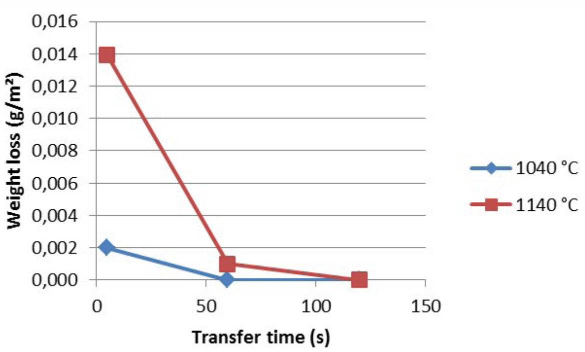


Fig. 7 - Effect of the solution annealing temperature and quenching transfer time on the ASTM G48-A 24h / 40 °C pitting corrosion weight loss. The specimens with a weight loss were affected by pits visible at 20x magnification.

In this case a clear pitting corrosion at 20x was found in the hottest solution annealed and fastest quenched sample, with an actual weight loss of 0,014 g/m². Increasing the transfer time and decreasing the solution annealing temperature, the trend is substantially equal and opposite of the low temperature impact toughness, with a negligible pitting corrosion in case of 120 s quenching. The resistance to the pitting corrosion can be estimated from chemical composition according the well-known formula, PREN= wt.% Cr + 3,3 wt.% Mo + 16 wt.% N and by the critical pitting temperature CPT. A CPT over 40 °C is generally found [28], in [29] a decrease of the CPT by the increase of the solution annealing temperature was obtained in a superduplex stainless steel as related to the unfavorable unbalanced high α and low γ microstructure produced. In the following table the amount of the average ferrite rate in the analyzed samples are reported.

Sol. annealing T (°C)	Transfer time (s)	Average ferrite rate	St. dev.
1040	< 5	52%	2%
	60	50%	1%
	120	52%	2%
1140	< 5	59%	3%
	60	60%	2%
	120	58%	1%

Tab. 3 - Effect of the solution annealing temperature and quenching transfer time on the average ferrite rate values

The amount of the ferrite phase increases by the solution annealing [30-32], but no significant effect were found ranging the transfer time between < 5 up to 120 s. The presence of pitting corrosion for the fastest quenched samples, in particular for the one treated at 1140 °C, can be considered as Cr_2N related, thus due to the local drop of the PREN due to the Cr and N depletion in the α phase. Yang et al. [33] studied the pitting corrosion resistance of laser welded duplex, the CPT in the base material is 56 °C, on the other hand it drops down to 42 °C in the fusion zone due to the unbalanced ferrite rich microstructure (92 vol.%) and precipitation of Cr_2N in the α phase. A 40 °C CPT is kept in the studied stainless steel only for after a proper thermal history. In [34], the CPT is estimated by a statistical regression analysis on alloying elements, considered as independent variables, thus it does not address the process effect.

CONCLUSIONS

In this paper, the chromium nitrides effects on low temperature impact toughness and durability of duplex stainless steels forgings was discussed. Several nitrides amounts were obtained by a 2x3 design with different combinations of solution annealing temperature and quenching transfer time.

The following conclusions can be drawn from this work.

a) Both solution annealing temperature and quenching transfer time regulate the actual Cr_2N amount in the ferrite phase.

b) The Cr_2N presence plays a main role for the low temperature impact resilience determination, a drop was noted for the samples quenched within 5 s, in particular for the specimens solution annealed at the highest temperature.

c) The nitrides amount increases by the solution annealing temperature thanks to the higher N solubility in the α phase at the higher temperature, on the other hand a rapid quenching (i.e. low transfer time) creates an α phase N supersaturated enabling the Cr_2N precipitation.

d) The pitting corrosion resistance is also affected by the Cr_2N presence. Whilst the durability against the ASTM G48-A 24 h / 25 °C is preserved, on the other hand a CPT over 40 °C cannot be ensured with high nitrides contents due to an unfavorable manufacturing process.

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