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Sensitization Resistance of Alloy UNS N08825 after different mill-annealing temperatures and times

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ABSTRACT

Designed for applications in the chemical process industry and later also used in the Oil & Gas industry, Alloy UNS(1) N08825 is a fully austenitic nickel-iron-chromium alloy, stabilized by titanium and with additions of copper and molybdenum. It is well known that the susceptibility of the material to intergranular corrosion in the “as delivered” (mill-annealed) condition, so as after the exposure of the material to intermediate temperatures, is strongly dependent on the chemical composition and additionally on the thermal history.

This work consists on the variation of the nickel content within the UNS chemical composition of Alloy N08825 and the variation of the annealing temperatures and times in order to better understand the influence of these variables on the intergranular corrosion resistance of material from large-scale production. Samples were tested according to ASTM(2) G28 method A in the “as delivered” condition and after sensitization heat treatment to verify its intergranular corrosion resistance.

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(1) Unified Numbering System for Metals and Alloys (UNS), SAE International, Warrendale, PA
(2) Americal Sosciety for Testing and Materials (ASTM), West Conshohocken, Pennsylvania

Key words: UNS N08825, Alloy 825, Intergranular corrosion resistance, heat treatment, annealing temperature, ASTM G28 A, sensitization behavior

INTRODUCTION

Designed even before the 1960s for applications in the chemical process industry and later also used in the oil & gas industry, Alloy UNS N08825 is a fully austenitic solid solution nickel-iron-chromium alloy, stabilized by titanium and with additions of copper and molybdenum. Due to its excellent corrosion resistance, especially against stress corrosion cracking in aqueous CO_2 and/or H_2S, it is widely used for cladded tubes and separator vessels in oil and gas production equipment.[1]

With nickel contents that can vary from 38 to 46 % according to the ASTM B424,[2] the susceptibility of the material to intergranular corrosion, in the “as delivered” condition, so as after the exposure of the material to intermediate temperatures, is dependent on the chemical composition and additionally on the thermal history.[3] Such exposures to intermediate temperatures usually happen when the material is cladded to steel, which after the cladding process demands a tempering treatment for the elimination of residual stresses that lead to hardness values that can exceed the specified limits. This tempering heat treatment is usually carried out at temperatures between 600 °C (1112 °F) and 850 °C (1562 °F), depending upon the cladding type,[4] when Alloy UNS N08825 may undergo microstructural changes and become sensitized.

According to W. Z. Friend,[3] when Alloy UNS N08825 in the solution-annealed condition – annealed between 1105 °C (2100 °F) to 1204 °C (2200 °F) – is subjected to a sensitizing heat treatment at intermediate temperatures, chromium-rich carbides $M_{23}C_6$ precipitate at the grain boundaries and the alloy becomes susceptible to intergranular attack. However, the author suggests that if a stabilizing heat treatment is carried out prior to sensitizing heat treatment, at temperatures where diffusion of chromium is sufficiently rapid to prevent significant chromium depletion in the alloy matrix, the material should be resistant to intergranular attack.

In the literature, hot forming temperatures have also been correlated to the susceptibility of Alloy UNS N08825 to intergranular corrosion.[3-6]

According to Raymond,[6] there are some ways to control the sensitization behavior of Alloy UNS N08825. To precipitate the chromium carbides at a temperature where the diffusion of chromium is rapid enough to eliminate chromium depletion, to reduce the carbon content to a value below the solubility limits and to add other carbide formers like titanium or niobium, which are more energetically favorable to form carbides rather than chromium (and thus lower the carbon atoms available in solution) are some of the suggestions given by the author.

This work consists on the variation of the nickel content within the UNS chemical composition of Alloy N08825 and the variation of the annealing temperatures and times in order to better understand the influence of these both variables on the intergranular corrosion resistance of material from large-scale production.

ASTM G-28 method A[7] was used as testing method. According to M. H. Brown,[5] it is one of the principally used test methods for detection of susceptibility to intergranular corrosion, being able to detect the sensitization effects due to the precipitation of $M_{23}C_6$ type carbides.[5]

EXPERIMENTAL PROCEDURE

To carry out the investigation program, hot rolled sheet material from standard production was used. The main chemical composition of the tested materials is shown in Table 1. All tested sheets were (mill)-annealed in an atmospheric, continuous production furnace at different combinations of annealing temperatures and times as summarized on Table 2.

Table 1

Main chemical composition of tested material in weight %

Heat	Cr	Ni	Fe (bal.)	Cu	Mo	Ti	N	C
A	22.67	38.50	31.41	1.86	3.25	0.73	0.010	0.010
B	22.72	39.27	30.71	1.90	3.08	0.76	0.017	0.012
C	22.60	42.29	27.14	2.30	3.21	0.82	0.013	0.008
UNS N08825	19.5-23.5	38.0-46.0	22.0 min	1.5-3.0	2.5-3.5	0.6-1.2	-	0.05

Table 2

Heat treatment parameters used to anneal alloy UNS N08825 for the time vs temperature investigations

Heat treatment condition	Temperature	Holding time	Cooling Media
	[°C]	[min]	
1	980	24	Air
2	980	36	
3	980	48	
4	1010	12	
5	1010	24	
6	1010	36	
7	1010	48	
8	1040	24	
9	1040	36	
10	1040	48	

Post welding heat treatment (PWHT) is a typical treatment carried out on the material after cladding or welding, which can lead to sensitization mostly due to the precipitation of $M_{23}C_6$ type carbides in the grain boundaries. To study the response of the different (mill)-annealing conditions numbered from 1 to 10 to the post welding heat treatments, corrosion samples were heat-treated in an atmospheric laboratory furnace according to Table 3.

Table 3

Heat treatment parameters used to sensitize the corrosion samples of alloy UNS N08825

Start Temperature	Heating Rate	Holding Temperature	Holding Time	Cooling Rate	End Temperature
[°C]	[°C / h]	[°C]	h	[°C / h]	[°C]
350	30	620	15	30	350

The chosen (simulated)-PWHT consists of a process of inserting the material in the furnace at a temperature of 350 °C (662 °F) and heating the material until it reaches the temperature of 620 °C (1148 °F). The material is then held at this temperature for 15 hours and cooled down to 350 °C (662 °C), when it is taken out of the furnace and air cooled to room temperature. The described heat treatment was chosen since it is known that Alloy UNS N08825 sensitizes after exposure to these temperatures for the described times and therefore the comparison between the heat treatment conditions is possible. The described (simulated)-PWHT is also used by several users as requirement for material qualification.

In order to well understand the microstructural changes that happen in the material as a result of the annealing and (simulated)-PWHT, a thermodynamical analysis of the precipitated phases was made by the use of phase diagrams, which were calculated using the software JMatPro(3).

The susceptibility to intergranular attack on alloy UNS N08825 was then determined by the application of ASTM G28 Method A, a ferric sulfate – sulfuric acid test. At least two samples were tested per heat treatment condition with and without sensitization heat treatment.

After the corrosion tests, the corrosion rate was reported and the depth of intergranular corrosion on each sample was measured by means of optical microscopy and images were taken for exemplification.

RESULTS

With the use of the before mentioned numerical simulation software, phase diagrams were calculated for low- and high-Nickel chemical compositions of Alloy UNS N08825 and the zoomed area of interest is

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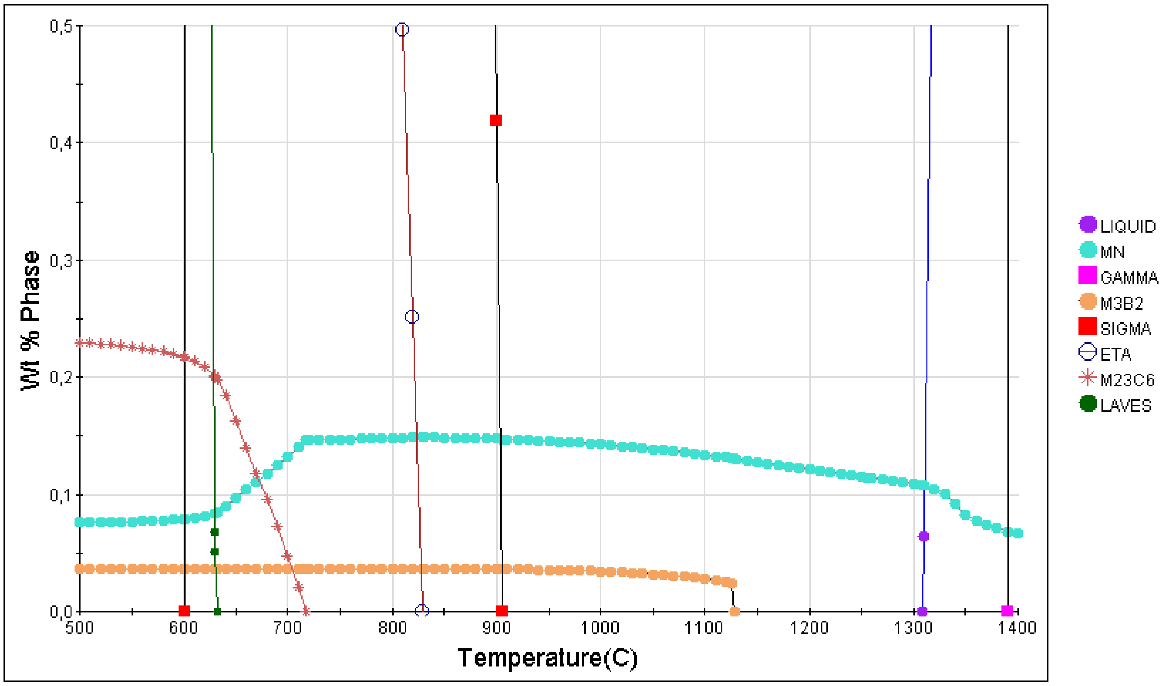
(3) Trade name. Java-based Materials Properties.

shown in Figure 1. The complete diagram will not be shown in this paper. According to the calculations, Alloy UNS N08825 should precipitate $M_{23}C_6$ type of carbides at temperatures below approximately 730 °C (1346 °F) and the temperature of 620 °C (1148 °F) – chosen for the sensitization heat treatment – should correspond (or be close) to the maximum precipitation.

According to the calculations, Sigma, Eta and Laves phase are stable at temperatures lower than 900 °C (1652 °F), but the formation of these phases are avoided by the application of correct heat treatment temperatures, times and cooling rates, therefore the precipitation of these phases are not considered here.

As shown on Figure 1, at the annealing temperatures used for this study, 980 °C (1796 °F), 1010 °C (1850 °F) and 1040°C (1904 °F), MN types of precipitates are supposed to be present in the Gamma-matrix (and are expected to remain in the matrix after cooling). This type of precipitate represents the titanium nitrides, which are mainly formed by titanium and nitrogen. The MN precipitate type does not contain chromium in its composition, although carbon may be present at temperatures higher than that of $Cr_{23}C_6$ precipitation. M_3B_2 borides are also stable at annealing temperatures, but may not play an important role on the sensitization resistance of the material, because, although having some chromium in its chemical composition, this phase is expected to precipitate in very low volumes according to the thermodynamic calculations. The wt.% of carbon distributed on both carbon-containing phases MN and $M_{23}C_6$ depending on the temperature are shown on Figure 2.

(A)



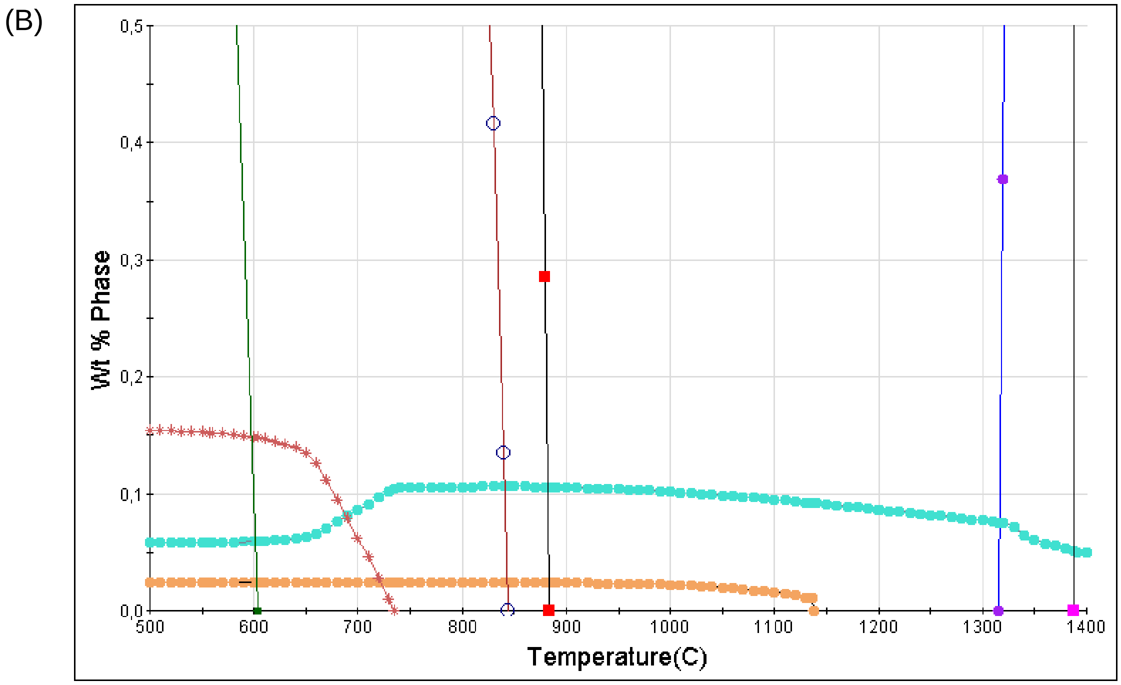


Figure 1: Zoom of calculated phase diagram of alloy UNS N08825 with (A) 39.27 % Ni and (B) 42.29 % Ni

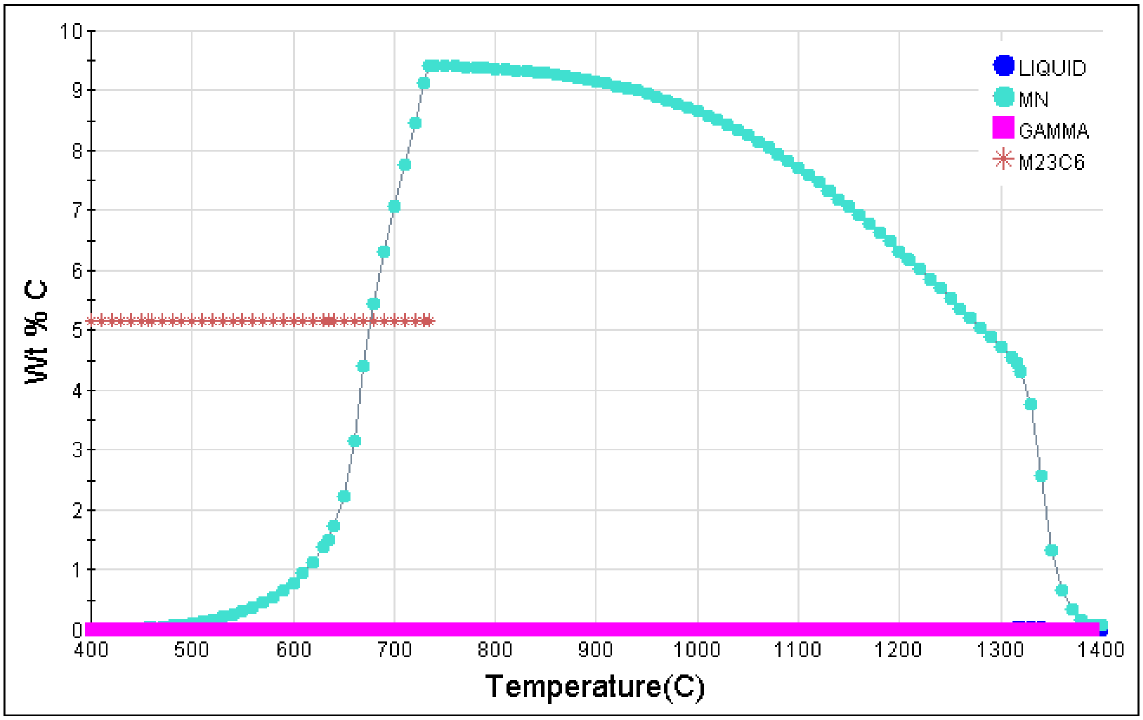


Figure 2: Calculated weight percent of carbon present in both carbon-containing phases MN and $M_{23}C_6$

At the corresponding simulated-PWHT temperature, as it can be seen on the diagrams (considering the long heat treatment duration, kinetic limitations will not be addressed), $M_{23}C_6$ carbides and MN precipitates are stable. At this temperature, MN is mainly formed by titanium and nitrogen. The expected composition of the $M_{23}C_6$ phase should be mainly chromium and molybdenum, combined with carbon.

All other phases present on the material, according to the numerical calculations, do not play a direct role on the sensitization behavior of alloy UNS N08825, since none of them contains a relevant amount of carbon, chromium, titanium or nitrogen, which may play a role on the carbides precipitation and therefore will not be described in details here, and/or, due to kinetics, are not precipitated.

The calculated amount in wt.% of each element present in $M_{23}C_6$ is shown on the diagram of Figure 3 and should be similar for all tested heats. Due to the high chromium content consumed by the $M_{23}C_6$ precipitate to form, the area that surrounds this phase is expected to be depleted of Cr and therefore more susceptible to corrosion attack. As $M_{23}C_6$ carbides mainly precipitate on the grain boundaries, these regions are known to be more susceptible to corrosion.

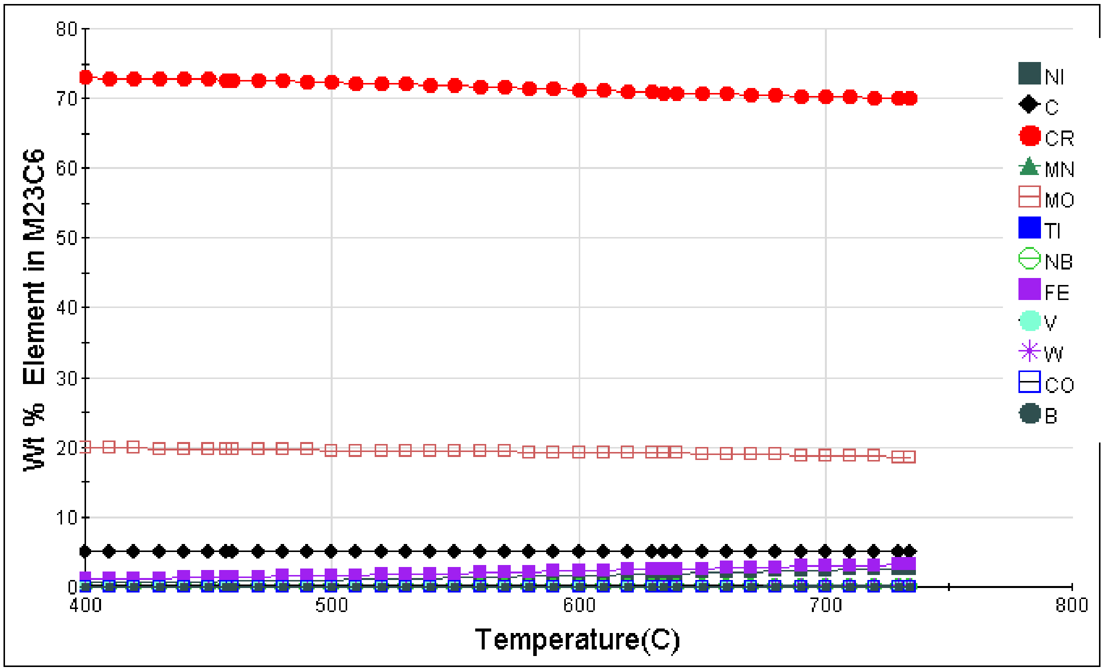


Figure 3: Calculated composition of $M_{23}C_6$ carbides on alloy UNS N08825

Time vs Temperature investigations

In order to comprehend the mill annealing time and temperature influence on the sensitization behavior of Alloy UNS N08825, heat A was annealed in an atmospheric production furnace at different combinations of holding times and temperatures. Some of the corrosion samples were given a (simulated)-PWHT. Samples with and without (simulated)-PWHT were tested according to ASTM G28 Method A and the corrosion rates and Intergranular corrosion (IGC) depth are presented in the diagrams of Figure 4.

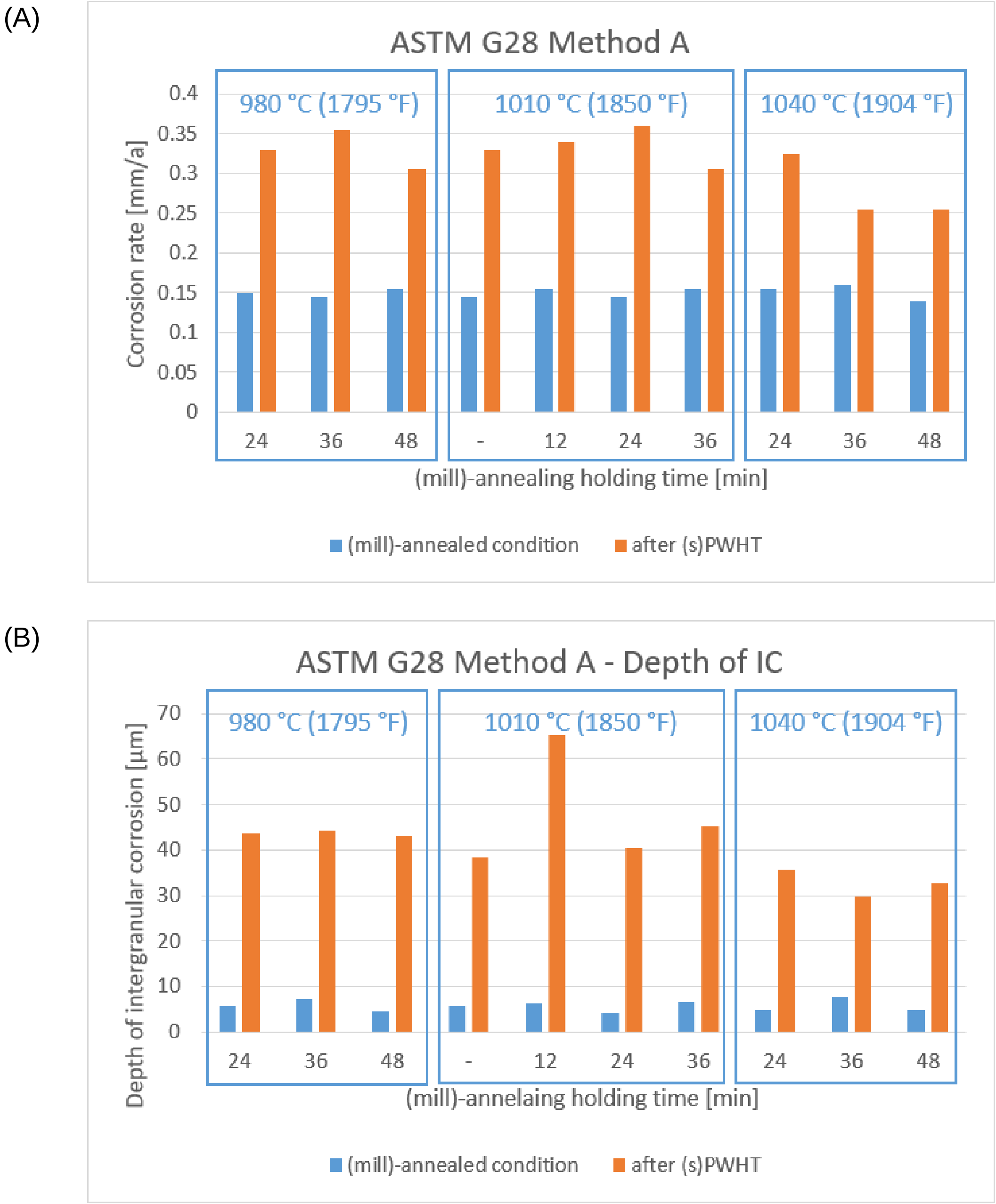


Figure 4: (A) Corrosion rates and (B) depth of intergranular corrosion of heat A after tests according to ASTM G28 Method A on as-delivered and sensitized conditions of material mill-annealed at different combinations of holding times and temperatures

Although there is a slight tendency of less susceptibility to intergranular corrosion after (mill)-annealing at higher temperatures (1040 °C, 1904 °F), the standard Alloy UNS N08825 is susceptible to sensitization after (simulated)-PWHT and presents corrosion rates that can vary from 0.25 to 0.36 mm/a after being submitted to the intermediate temperature of 620 °C.

Investigations on the nickel content variation

Table 4 shows the corrosion rates and IGC depth after corrosion testing according to ASTM G28 Method A for the heats B (39.27 % Ni) and C (42.29 % Ni) annealed at 1010 °C (1850 °F) and 1040 °C (1904 °F) in (mill)-annealed condition and after sensitization heat treatment. The corrosion rates are also summarized in Figure 5. Both heats show sensitization after exposure to the intermediate temperatures as described above, since the corrosion rates, as well as the depth of intergranular corrosion, are significantly higher in the samples exposed to the (simulated)-PWHT, with one exception, which is heat C annealed at 1010 °C (1850 °F).

Table 4

Corrosion rates and depth of intergranular corrosion after tests according to ASTM G28 Method A on as-delivered and sensitized conditions

Heat	Annealing Temperature	PWHT	Average Corrosion Rate	Average IGC depth
	[°C]	[yes / no]	[mm/a]	[µm]
B (39.27 % Ni)	1010	no	0.15	5
		yes	0.47	64
	1040	no	0.15	5
		yes	0.39	61
C (42.29 % Ni)	1010	no	0.09	3
		yes	0.09	0
	1040	no	0.14	4
		yes	0.86	101

On Figures 6 to 9, exemplification micrographs of intergranular corrosion of the tested samples can be found.

The results show that the heat containing higher amount of nickel (heat C) does not sensitize after exposure to intermediate temperatures after being (mill)-annealed at 1010 °C (1850 °F). If annealed at a higher temperature of 1040 °C (1904 °F), this heat shows to be susceptible to intergranular corrosion after being submitted to the (simulated)-PWHT and the corrosion rates reach values close to the 0.9 mm/a, which is usually set by end users as a threshold for material qualification. A deeper investigation here is required. Heat C has around 3 % higher nickel content and this tendency of increased corrosion rates after mill annealing at 1040 °C has been observed systematically. So far this observation could not be verified by thermodynamic calculations.

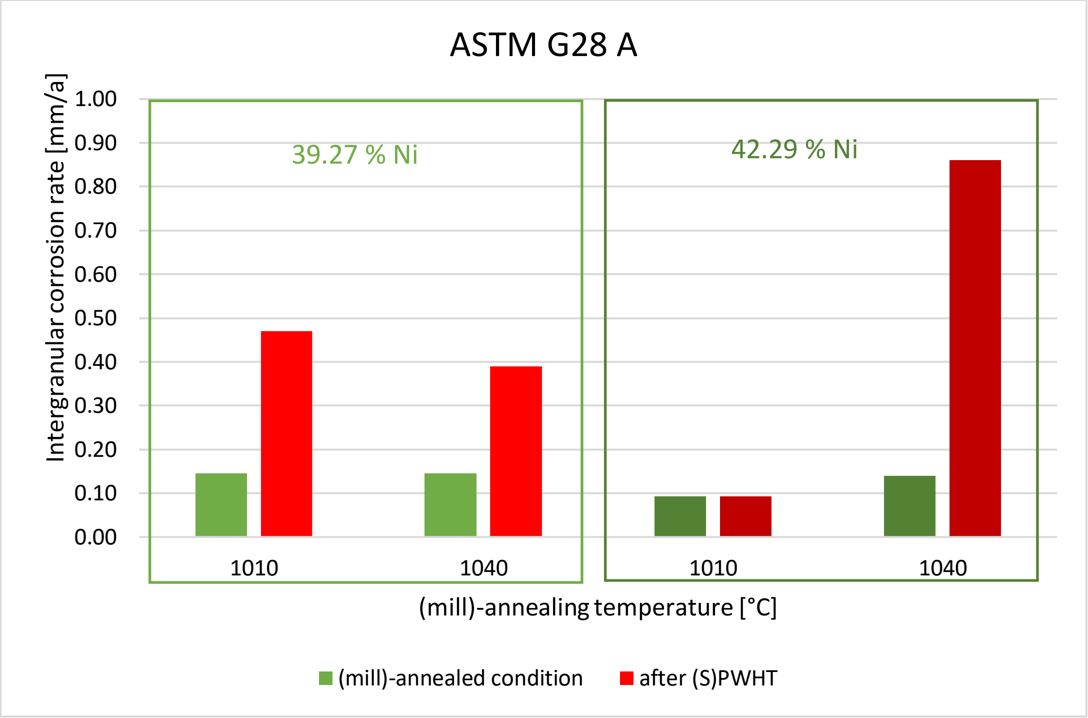


Figure 5: Corrosion rates after tests of according to ASTM G28A on as-delivered and sensitized conditions of material with lower (heat B) and higher nickel contents (heat C).

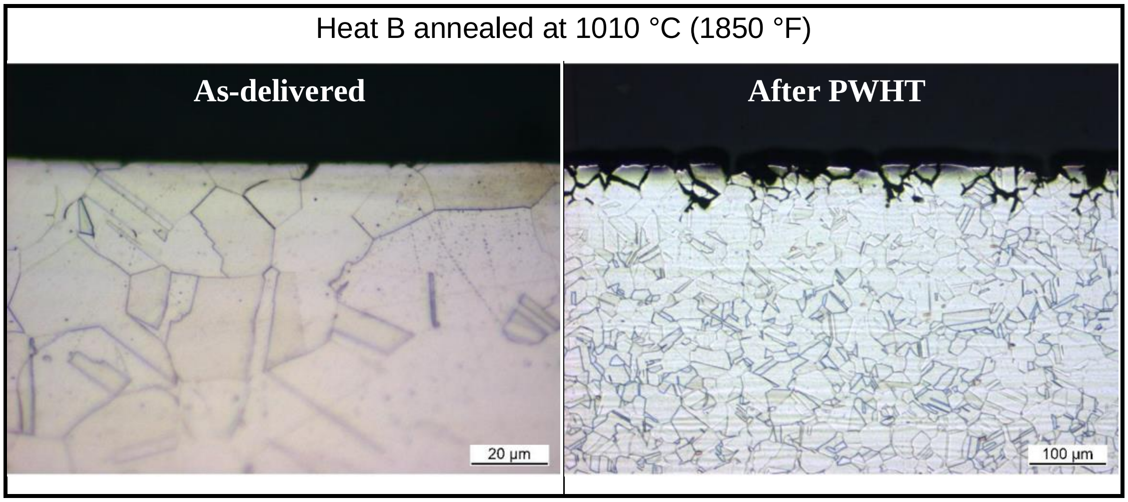


Figure 6: Depth of intergranular corrosion on samples of heat B heat-treated at 1010 °C (1850 °F) after ASTM G28A on as-delivered and sensitized conditions.

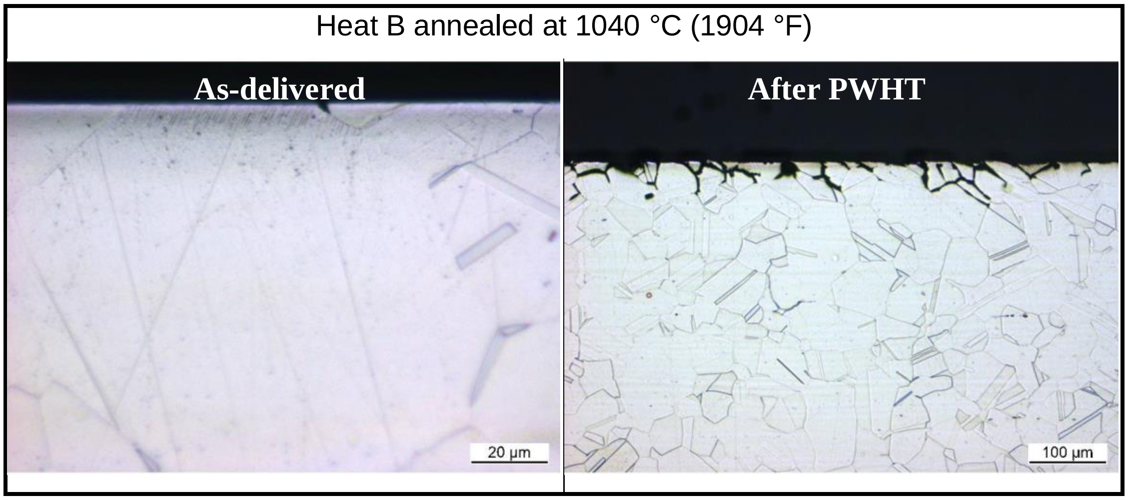


Figure 7: Depth of intergranular corrosion on samples of heat B heat-treated at 1040 °C (1904 °F) after ASTM G28A on as-delivered and sensitized conditions.

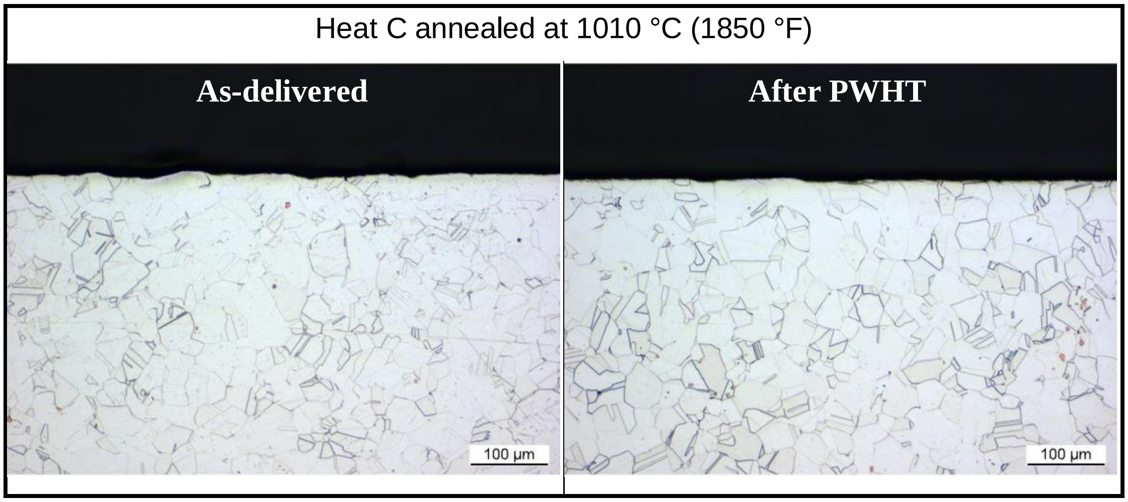


Figure 8: Depth of intergranular corrosion on samples of heat C heat-treated at 1010 °C (1850 °F) after ASTM G28A on as-delivered and sensitized conditions.

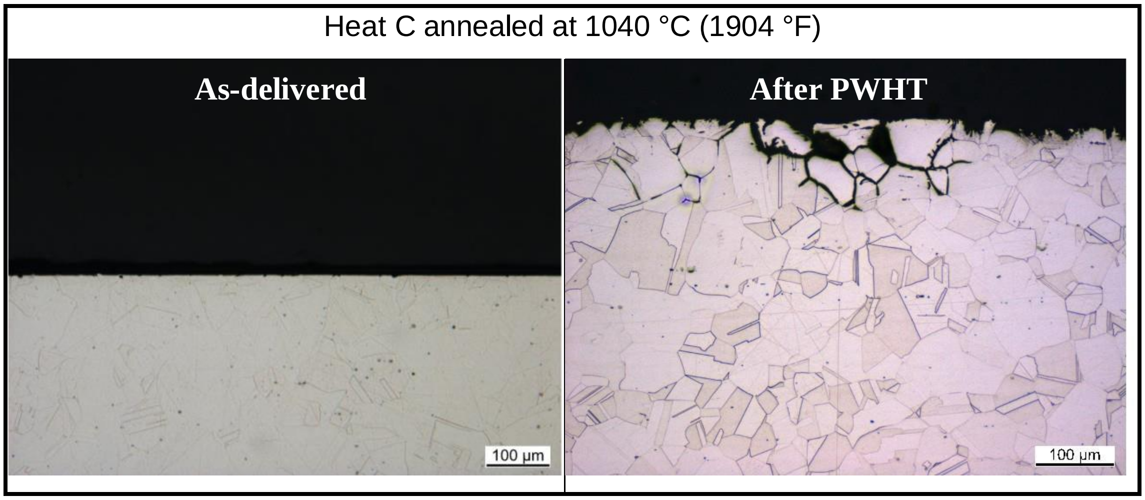


Figure 9: Depth of intergranular corrosion on samples of heat C heat-treated at 1040 °C (1904 °F) after ASTM G28A on as-delivered and sensitized conditions.

When talking about the heat containing a lower amount of nickel (heat B), the situation seems to be different and comparable to the first investigations with heat A, which has a similar chemical composition. This lower amount of nickel leads to sensitization in both annealed conditions since the corrosion rates after exposure to the (simulated)-PWHT are higher in comparison to the corrosion rates on the (mill)-annealed condition. Nevertheless, a difference between the two annealing conditions still can be seen: the samples of material annealed at lower temperature (1010 °C / 1850 °F) show higher corrosion rates after being exposed to the intermediate temperatures when compared to the samples of material annealed at higher temperature (1040 °C / 1904 °F).

The IGC depth tends to be higher as the corrosion rates increase. Although the comparable DICs presented by heat B after (simulated)-PWHT on material annealed at 1010 °C (1850 °F) and 1040 °C (1904 °F) – 64 and 57 µm respectively – it can be visually noted that, by trend, the intergranular corrosion is more intense and homogeneous in the material annealed at 1010 °C (1850 °F), which also presented the slightly higher corrosion rate.

CONCLUSIONS

The results obtained by this investigation program allowed the authors to conclude that applications that do not require post-weld-heat-treatments are safe in terms of sensitization to intergranular corrosion, since (mill)-annealed conditions of Alloy UNS N08825 present very low corrosion rates and very low depth of intergranular corrosion, regardless of having lower or higher nickel contents. The reason for these low corrosion rates is probably due to having most of the chromium in solution, since at the selected (mill)-annealing temperatures, the numerical calculations predict that the chromium-carbides are not precipitated or diffusion takes place and the originally Cr-depleted zone is enriched of chromium again due to kinetics.

The optimal (mill)-annealing temperature to grant better resistance to sensitization after PWHT is dependent on the chemical composition of the alloy and seems to be directly correlated to the content of nickel. Material with higher nickel contents require lower annealing temperatures to minimize the sensitization behavior, while material with lower nickel contents seems to require higher annealing temperatures to minimize the sensitization behavior, although sensitization still takes place.

In general, the higher the nickel content, the higher the resistance to sensitization, when material is properly annealed. Alloy UNS N08825 with nickel contents closer to the upper limits of the material composition range should be favored when material will be submitted to PWHT before the application.

It is known that carbon plays a role on the sensitization behavior of Alloy UNS N08825, but these studies did not allow a deep interpretation of the correlation between carbon content and intergranular corrosion susceptibility. If the carbon is considered, although all heats have a low carbon content, the slightly lower amount of carbon in heat C in comparison to heats A and B seems to strengthen the positive effect of nickel on increasing its general resistance to intergranular corrosion.

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