Paper No.
9459

The Sensitisation Behaviour of Alloy UNS N08825 After Heat Treatment as Used in Clad Materials

Helena Alves, Julia Rosenberg and Peter Maas
VDM Metals International GmbH
Plettenberger Str. 2
58791 Werdohl, Germany

ABSTRACT

Alloy UNS N08825 is widely used in sour service environments of the oil and gas industry. In case of large vessels alloy UNS N08825 is often explosion clad to carbon steel and needs to undergo the same heat treatment requirements as the substrate material. Where post weld heat treatment (PWHT) procedures are required by the Code the behaviour of the clad material has to be considered and standard corrosion tests are frequently used to monitor it.

Most common PWHT procedures require intermediate temperatures in the range of 600-650 °C (1112 - 1202 F). It is well known that depending on the time of heat treatment at these temperatures nickel alloys may undergo microstructural changes that influence the result of the standard corrosion tests.

The aim of this paper is to present recent standard test corrosion data obtained in laboratory for alloy UNS N08825 after PWHT in comparison with as delivered (soft annealed) material.

Keywords: alloy UNS N08825, explosion cladding, PWHT, sensitisation, standard corrosion tests, corrosion rate

INTRODUCTION

Alloy UNS N08825 is a nickel alloy with about 30 wt.% iron, 23 wt.% chromium, 3 wt. % molybdenum, 2 wt.% copper and 0.8 wt.% titanium. Some carbon may be present in addition. The American standard specification [1] is indicating for a corresponding alloy 825 grade a carbon content of max. 0.05 wt.%, an European standard [2] is specifying a carbon content of max. 0.025 wt.%.

The alloy UNS N08825 had been developed before the 1960s [3] and is in well-proven use since then in many applications. It shows a useful performance in a broad range of process media as sufficiently low concentrated phosphoric acid solutions, nitric acid and sodium hydroxide, and has established itself as a standard material for moderately aggressive sulphuric acid applications. It possesses exceptionally high resistance to chloride-induced stress corrosion cracking initiated by pitting in aggressive sour gas environments. It is widely used for clad tubes and separator vessels in oil and gas production equipment due to its excellent resistance to CO_2 and H_2S corrosion and stress corrosion cracking [4].

In case of large vessels alloy UNS N08825 is often explosion clad to a heavy wall carbon steel substrate. Within the explosion clad compound the carbon steel substrate is to carry the mechanical load whereas the nickel alloy cladding has to provide the corrosion resistance. Where welding has to be done on the clad structure and a post weld heat treatment is required for the carbon steel substrate the nickel alloy cladding has to undergo the post weld heat treatment as well without any intolerable loss of its corrosion resistance. Therefore, the corrosion behaviour of the cladding material has to be tested after heat treatments which simulate the conditions of the final post weld heat treatment of the clad structure.

The reason why the corrosion resistance in as-delivered condition and after PWHT may be different is the fact that when nickel alloys are exposed to intermediate temperatures, like in the case of the PWHT mentioned above, they may undergo microstructural changes leading to sensitisation and higher corrosion rates. This is a metallurgical process observed in nickel alloys and can occur regardless of the origin of the material.

It is reported [5,6] that when a corresponding alloy 825 in the solution annealed condition, quenched from a solution annealing temperature of 1150 to 1204 °C (2100 to 2200 F), is subject to a sensitizing heat treatment of 1 hr at 760 °C (1400 F), chromium-rich carbide $M_{23}C_6$ precipitates at grain boundaries, and the alloy is subject to intergranular attack in a nitric acid test [7]. However, if the alloy is given a stabilizing anneal at 940 °C (1725 F) for 1 hr prior to the sensitizing heat treatment, $M_{23}C_6$ precipitates at this temperature where diffusion of chromium is sufficiently rapid to prevent significant chromium depletion in the alloy matrix, and the alloy usually is resistant to intergranular attack. While the titanium content of the alloy is sufficient to stabilize the alloy against intergranular attack in many applications, maximum stabilization requires the application of a 940 °C (1725 F) soft or stabilizing anneal. The alloy normally is supplied by the producer in such a soft annealed or stabilized condition. The VdTÜV material data sheet 432/1 indicates for soft annealing of corresponding alloy 825 materials a temperature range of 920 - 980 °C (1688 - 1796 F).

EXPERIMENTAL

Materials investigated

Within the scope of this investigation three heats of alloy UNS N08825 have been tested. The principal alloying constituents of these heats are shown in Table 1. The carbon content ranged between 0.008 and 0.012 wt.-% which is far below the above mentioned maximum carbon values.

Heats A and B were submitted to final soft annealing in the regular production. Heat C has been diverted from production before the final soft annealing step and submitted to laboratory annealing at different temperatures ranging from 940 to 1120°C in order to investigate the effect of the heat treat history.

Table 1
Main chemical alloying elements of the investigated alloy UNS N08825 heats, wt.-%

Heat	Ni	Fe	Cr	Mo	Cu	Ti
A	39.38	30.27	22.80	3.28	1.98	0.81
B	39.26	30.64	22.75	3.19	1.94	0.69
C	39.20	30.66	22.73	3.12	1.94	0.69

Selected heat treatment conditions

Material samples have been tested both in the as delivered condition (1) and in different selected laboratory heat treatments intended to simulate the post weld heat treatments of the explosion clad structures (2-7).

1) as delivered: soft annealed after hot rolling

2) as delivered + post weld heat treatment at 600 °C (1112 F) for 4 hrs, 8 hrs and 16 hrs

3) as delivered + post weld heat treatment at 650 °C (1202 F) for 4 hrs, 8 hrs and 16 hrs

4) as delivered + post weld heat treatment at 700 °C (1292 F) for 4 hrs, 8 hrs and 16 hrs

5) as delivered + post weld heat treatment at 630 °C (1166 F) for 18 hrs, 24 hrs and 36 hrs

6) as delivered + post weld heat treatment PWHT 1 = 350°C/30°C/h (662 F/86 F/h) -> 620°C/5h/30°C/h (1148 F/5h/86 F/h -> 350 °C (662 F)/air

7) as delivered + post weld heat treatment PWHT 2 = 350°C/30°C/h (662 F/86 F/h) -> 620°C/15h/30°C/h (1148 F/5h/86 F/h -> 350 °C (662 F)/air

Methods of corrosion testing

In practice testing on intercrystalline corrosion of the cladding is recommended to see if a post weld heat treatment of an explosion clad structure may impair the corrosion behaviour of the cladding material. Current methods of testing are those according to ASTM A262 Practice C - Nitric Acid Test for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels [7] and ASTM G28 Method A - Ferric Sulfate - Sulfuric Acid Test [8]. While the Ferric Sulfate - Sulfuric Acid Test does detect susceptibility to intergranular corrosion in Alloy UNS N08825 [8], the boiling 65 % nitric acid test ASTM A 262, Practice C, for detecting susceptibility to intergranular corrosion in stainless steels should be used if the intended service is nitric acid [7]. However, handling of boiling 65 % nitric acid over five boiling periods of 48 hrs each as the recommended time of testing according to ASTM A 262 [7] is more difficult and takes more time than testing over a time between 24 - 120 hrs in the boiling ferric sulfate-sulfuric acid test solution according to ASTM G 28 Method A [8], where it is emphasized in the standard [8] that the test does detect susceptibility to intergranular corrosion in alloy UNS N08825.

RESULTS AND DISCUSSION

Fig. 1 shows the corrosion rate obtained on heat A of alloy UNS N08825 in the test according to ASTM A 262 Practice C (nitric acid test) after post weld heat treatments of 16 hrs at 600, 650 and 700 °C. In this test the alloy is exposed in 5 consecutive cycles to boiling azeotropic nitric acid over 48 hrs. The standard ASTM A 262 Practice C [7] states in section 15 the following: "The presence or absence of intergranular attack in this test is not necessarily a measure of the performance of the material in other corrosive environments; in particular, it does not provide a basis for predicting resistance to forms of corrosion other than intergranular such as general corrosion, pitting, or stress-corrosion cracking."

In Fig. 1 the corrosion rate after the post weld heat treatment of 16 hrs at 600°C is more or less the same as in the soft annealed delivery condition, whereas the corrosion rates obtained for the post weld heat treatments of 16 hrs at 650 °C and at 700°C are increased due to these sensitisation treatments. This becomes more obvious when the corrosion rates per test cycle are considered as shown in **Fig. 2**. This increase of the apparent corrosion rate with increasing number of test cycles is due to an increase of the true surface caused by the intercrystalline corrosive action of the foregoing cycles, not by a decrease of the material's corrosion resistance. The apparent increase of the corrosion rate after the first test cycles indicates simply that an intercrystalline corrosion had taken place during the foregoing test cycles.

Fig. 3 and **Fig. 4** show the effect of the holding time during a post weld heat treatment at 630 °C on the corrosion rate of two different heats A and B of alloy UNS N08825 in the test according to ASTM A 262 Practice C (nitric acid test) and in the test according to ASTM G28 Method A (ferric sulfate sulfuric acid test). In both cases, there is a tendency to an increase of the corrosion rate with increasing holding time, and the corrosion rate of Heat A is somewhat higher than the corrosion rate of Heat B.

Fig. 5 shows the corrosion rate of alloy UNS N08825, Heat A in the test according to ASTM G 28 Method A (ferric sulfate - sulfuric acid test) after a sensitizing post weld heat treatment of increasing duration at different temperatures of 600, 650 and 700 °C. After a sensitizing post weld heat treatment at 600 °C no influence on the corrosion rate in the following ASTM G 28 Method A tests is to be seen, independently of the duration of the sensitizing heat treatment. However, if the sensitizing anneal is done at 650 or still more at 700 °C the corrosion rate is somewhat increased after 8 hrs sensitizing anneal or considerably increased after 16 hrs sensitizing anneal. In case the test according to ASTM A 262 Practice C is applied similar behaviour can be observed.

Fig. 6 demonstrates the influence of the temperature of soft annealing which had been done before delivery of the material. Such effect of heat treat history was investigated on the third heat (Heat C) which has been diverted from production before the final soft annealing step and submitted to laboratory annealing at different temperatures ranging from 940 to 1120°C. The material was tested in such "as delivered" condition and also after performing the subsequent simulating heat treatments 6) and 7) as described in the chapter EXPERIMENTAL. No influence of the temperature of soft annealing between 940 °C and 1120 °C on the corrosion rate in the ASTM G 28 Method A test solution is discernible if only the "as delivered" condition is considered. However, if post weld heat treatments are applied the corrosion rate in the ASTM G 28 Method A test solution is increased for the lower soft annealing temperatures of 940 and 980 °C. This behavior was confirmed by the results obtained with the nitric acid test ASTM A 262 Practice C Test, see **Fig. 7**.

It should be kept in mind that quality approval corrosion tests like ASTM G-28 Method A and ASTM A-262 Practice C do not give any information on the corrosion behavior on site under real service conditions. These tests are solely intended to show that materials are fabricated according to the corresponding production specifications and that important production steps are properly done.

The overall corrosion rate in ASTM G-28 Method A test is dependent on the ratio of Cr/(Mo+W) elements [3]. If this ratio is sufficiently high the corrosion behavior is stable and the obtained corrosion rates are well reproducible. This is the case for alloy UNS N08825. This means that corrosion criteria can more easily be defined and compared. The test conditions are such that material is tested in its passive state, which is in most cases the way nickel alloys containing chromium and molybdenum are used in industrial services.

On the other hand, testing conditions according to ASTM A 262 Practice C imply testing under very strong oxidizing conditions, which may result in a very strong scatter of the test results, which need to be evaluated statistically. Therefore, the test needs to be repeated several times (5 cycles at 48h with evaluation after each cycle) resulting in very long total testing time. In addition, each sample must be tested individually. The test requires nitric acid of special quality and extreme care in handling and special safety requirements. For all these reasons, ASTM A 262 Practice C is a very long, laborious, cumbersome and environmental unfriendly test.

In contrast, ASTM G-28 Method A is to be conducted more easily and faster and is, therefore, a more adequate test for detecting intergranular susceptibility of Alloy UNS N08825 in the quality approval process also after post weld heat treatment (PWHT).

CONCLUSIONS

1) A sensitisation treatment of alloy UNS N08825 of 16 hrs at 650 and at 700°C is effective in increasing the corrosion rates in a subsequent nitric acid test, whereas a post weld heat treatment of 16 hrs at 600°C is less problematic. In view of the cladding material alloy UNS N08825 post weld heat treatments at those higher intermediate temperatures should be avoided.

2) In case of the nitric acid test an observed increase of the corrosion rate with increasing number of test cycles indicates an intercrystalline corrosion which had taken place during the foregoing test cycles resulting in an increased true sample surface.

3) An increase of corrosion rate with increasing holding time on the temperature of sensitisation may be interpreted as a result of a sensitisation being still in progress.

4) An increasing duration of a sensitising post weld heat treatment between 600 and 700 °C is the more effective the higher the temperature.

5) The heat treat history of the material may influence the resistance to intergranular corrosion. Whereas in the "as delivered" condition such influence may not become visible, differences may evolve when post weld heat treatments, e.g. at 620 °C, are applied.

6) The results obtained in this investigation are laboratory results and have to be further verified in normal production.

7) Both corrosion tests, ASTM G 28 Method A and ASTM A 262 Practice C can be used to study the material's susceptibility to intergranular corrosion. The testing according to ASTM G 28 Method A is easier and less cumbersome to perform and leads to results which, in general, show less scatter. Therefore, this test should be preferred unless the intended service is nitric acid.

REFERENCES

[1] Standard Specification for Ni-Fe-Cr-Mo-Cu Alloy (UNS N08825 and UNS N08221) Plate, Sheet and Strip, Designation B 424 - 98a, ASTM International, West Conshohocken, PA

[2] DIN 17744: 2002-09: Nickel-Knetlegierungen mit Molybdän und Chrom - Zusammensetzung - Wrought nickel alloys with molybdenum and chromium - Chemical composition

[3] U. Heubner: Corrosion resistance of nickel alloys and high-alloy special stainless steels, in U. Heubner, J. Klöwer: Nickel alloys and high-alloyed special stainless steels, 4th completely revised ed., expert verlag, 2012, pp. 40-75

[4] R. Behrens: Nickel alloys and high-alloy special stainless steels for the oil and gas industry, in U. Heubner, J. Klöwer: Nickel alloys and high-alloyed special stainless steels, 4th completely revised ed., expert verlag, 2012, pp. 238-254

[5] E. L. Raymond, Corrosion, 24, 180 (1968), referred to in [6]

[6] Wayne Z. Friend: Corrosion of nickel and nickel-base alloys, John Wiley & Sons, New York - Chichester - Brisbane - Toronto, 1980

[7] Standard Practices for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels, Designation: A262 - 13, ASTM International, West Conshohocken, PA

[8] Standard Test Methods for Detecting Susceptibility to Intergranular Corrosion in Wrought, Nickel-Rich, Chromium-Bearing Alloys, Designation: G28 - 02 (Reapproved 2008), ASTM International, West Conshohocken, PA

FIGURES

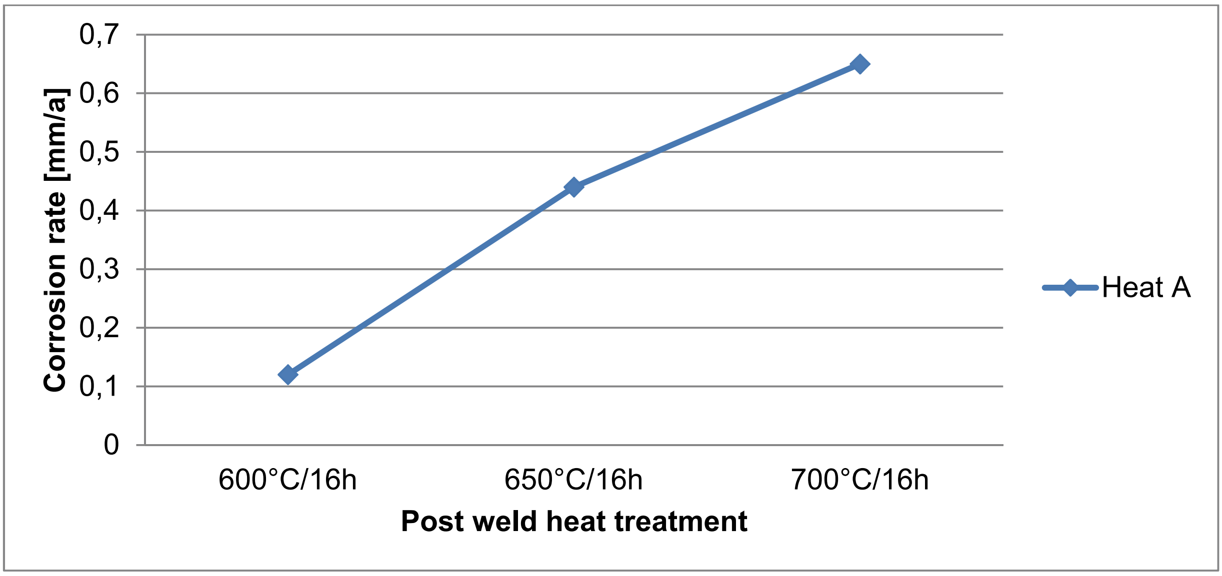

Fig. 1: Corrosion rate of alloy UNS N08825 - Heat A in the test according to ASTM A 262 Practice C (nitric acid test) after post weld heat treatments of 16 hrs at 600, 650 and 700 °C. The indicated corrosion rates are an average of 5 consecutive cycles.

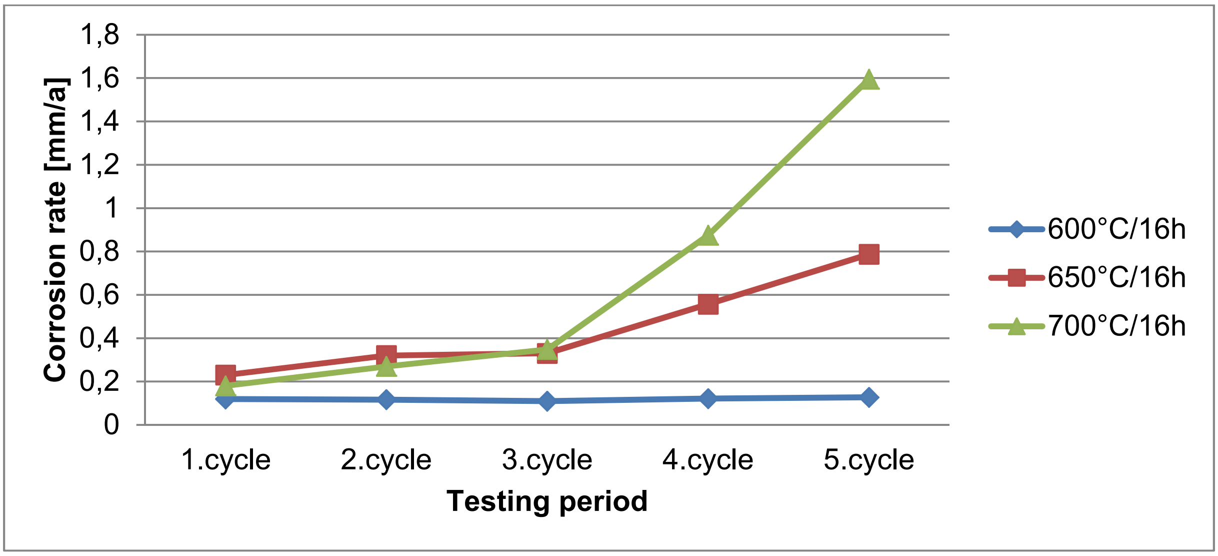

Fig. 2: Corrosion rate of alloy UNS N08825 - Heat A in the test according to ASTM A 262 Practice C (nitric acid test) after sensitisation post weld heat treatments of 16 hrs at 600, 650 and 700 °C. For the corrosion rate the results of each test cycle of 48 hrs are indicated.

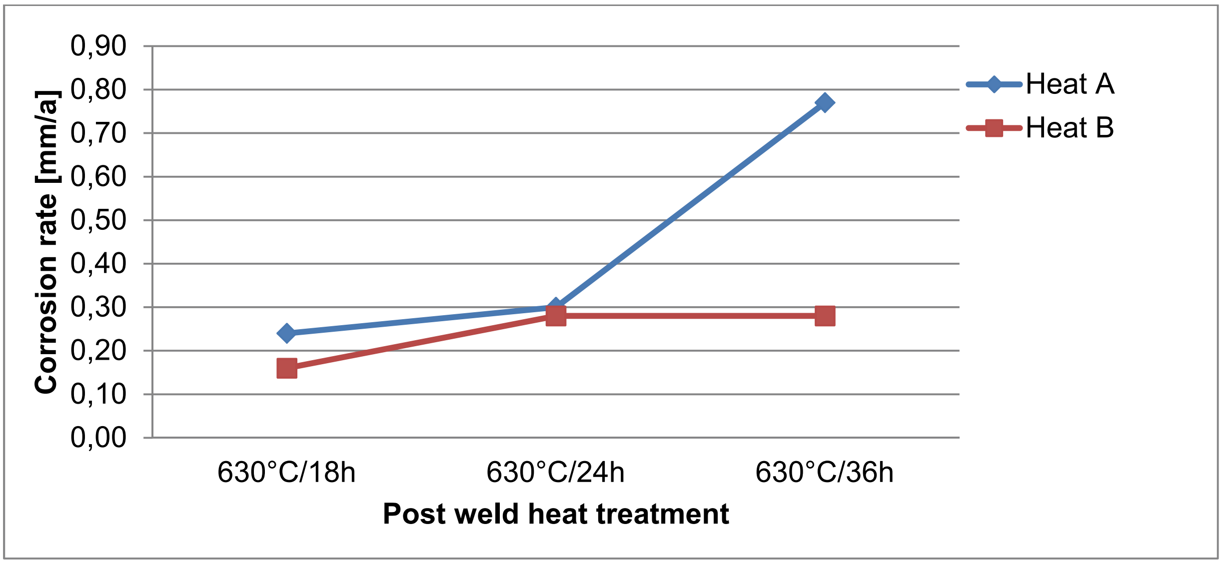

Fig. 3: Corrosion rates of alloy UNS N08825, Heats A and B in the test according to ASTM A262 Practice C (nitric acid test) for post weld heat treatments at 630 °C with increased holding times. The indicated corrosion rates are an average of 5 consecutive cycles.

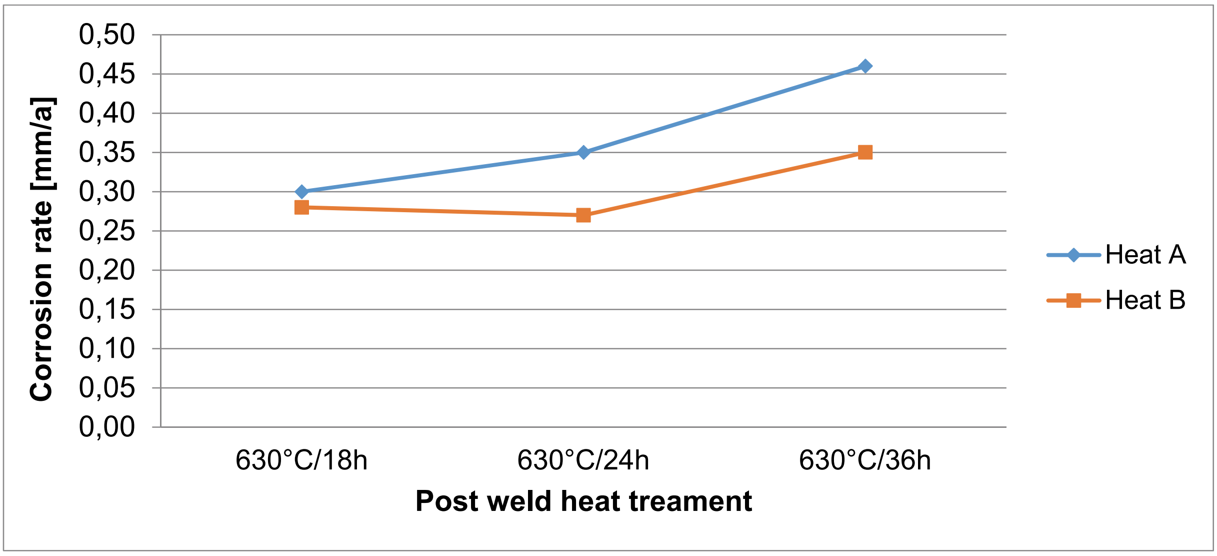

Fig.4: Corrosion rates of alloy UNS N08825, Heats A and B in the test according to ASTM G28 A (ferric sulfate - sulfuric acid test) for post weld heat treatments at 630 °C with increased holding times.

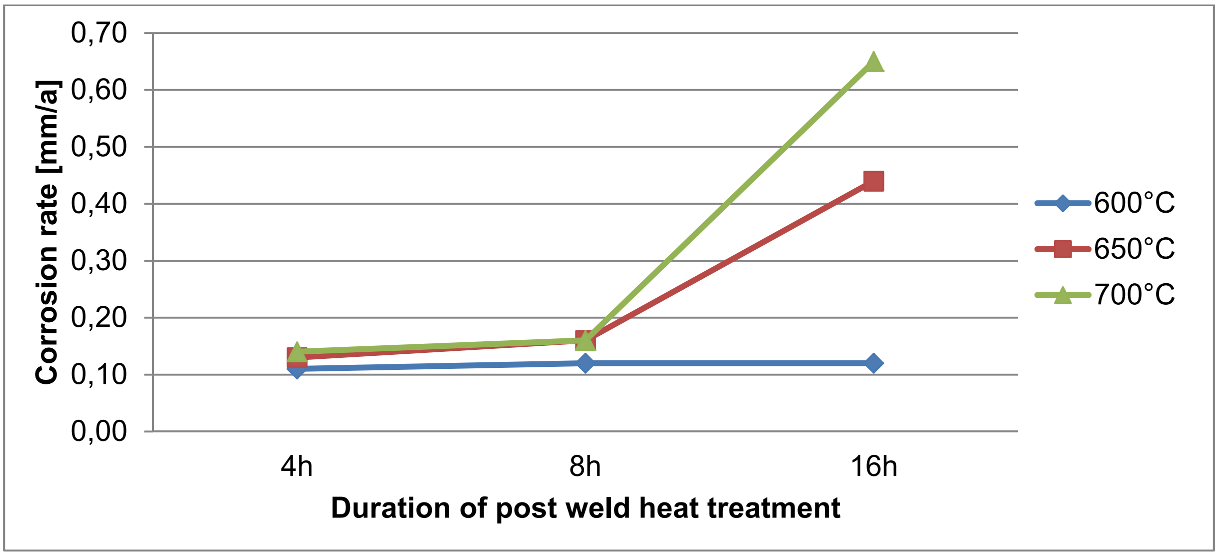

Fig. 5: Corrosion rate of alloy UNS N08825, Heat A in the test according to ASTM G 28 Method A (ferric sulfate - sulfuric acid test) after post weld heat treatments of increasing duration at 600, 650 and 700 °C.

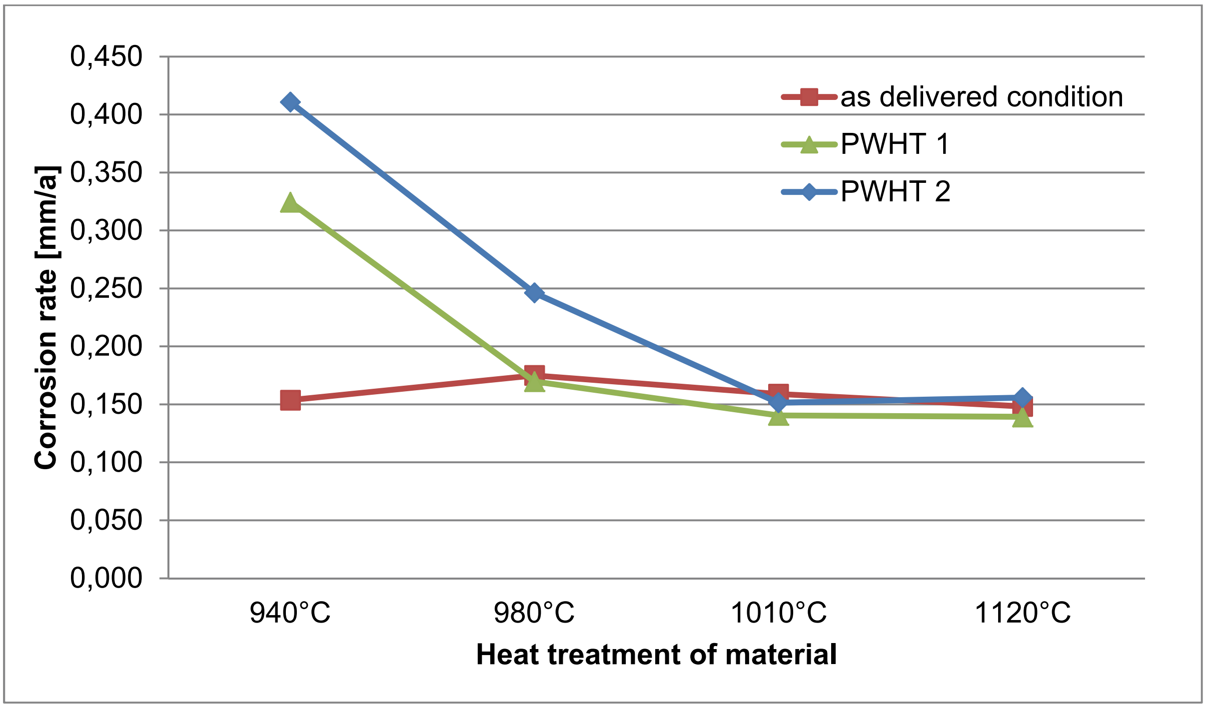

Fig. 6: Corrosion rate of alloy UNS N08825, Heat C in the test according to ASTM G28 Method A (ferric sulfate sulfuric acid test), the alloy having been heat treated at different temperatures and subsequently submitted to different post weld heat treatment conditions: without PWHT (as delivered), with PWHT 1 and PWHT 2.

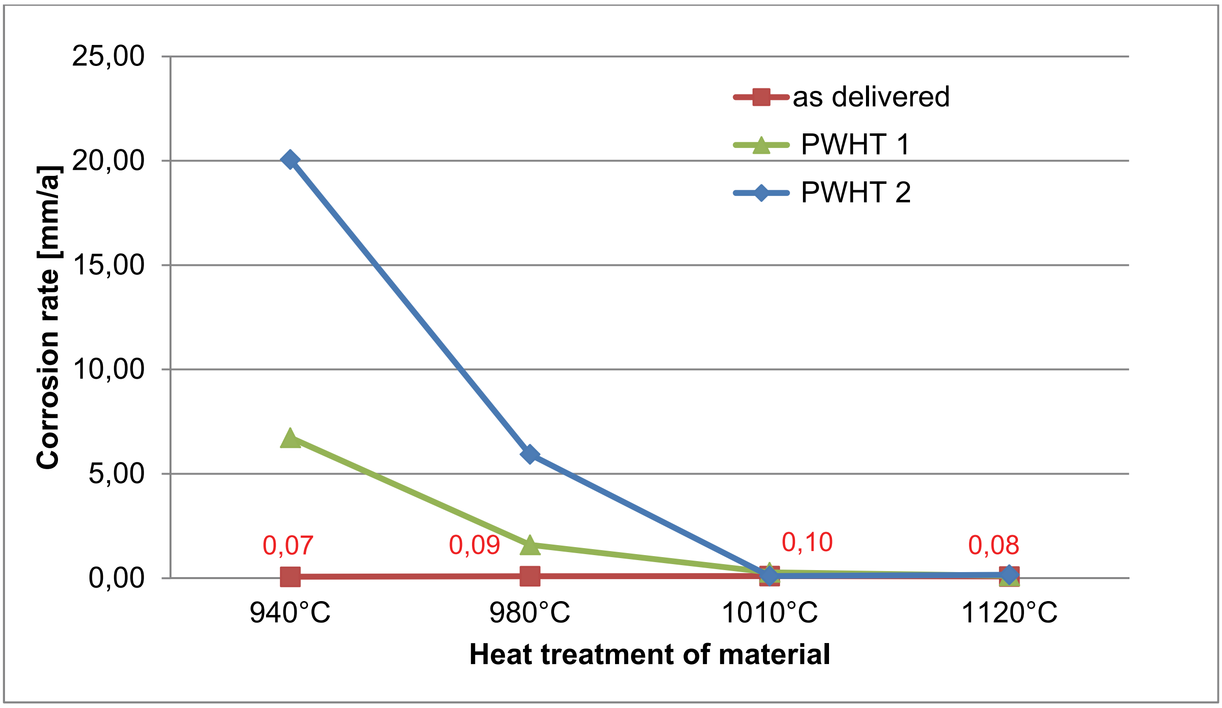

Fig. 7: Corrosion rates of alloy UNS N08825, Heat C in the test according to ASTM A262 Practice C (nitric acid test), the alloy having been heat treated at different temperatures and subsequently submitted to different post weld heat treatment conditions: without PWHT (as delivered), with PWHT 1 and PWHT 2. The indicated corrosion rates are an average of 5 consecutive cycles.