INFLUENCE OF HEAT TREATMENTS ON CORROSION

BEHAVIOUR OF ALLOY 625 FORGED ROD

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ABSTRACT

The influence of heat treatments between 500 and 1125°C on corrosion resistance of forged alloy 625 has been studied.
An electrochemical potentiokinetic reactivation method has been perfected and compared to the ASTM G28 test results. Large intergranular corrosion occurs on samples heat treated between 700 and 950°C, due to the intergranular precipitation of Cr- and Mo-rich carbides.
Two of the samples which had the most different behaviour, solution-treated and solution-treated + 8h at 750°C, were then studied in 4M HCl. Dissolution is a little stronger in the passive range for the material treated at 750°C.

Introduction

Nickel alloy 625, typically containing 22 wt.% Cr, 9 wt.% Mo, 3,7 wt.% Nb and < 5 wt.% Fe , combines good mechanical properties, weldability and corrosion resistance (1). It has numerous applications in chemistry, pulp and paper (2), offshore and marine industries (3), and in geothermal power systems (4).

Alloy 625 is an interesting alloy for our line of production because it can be used to :

– weld metals as different as low alloy steels and High Strength Low Alloy steels with alloy 625,
– repair these steels by welding (5–7),
– clad them in order to protect them from corrosion (8–10).

In such cases, post–welding heat treatments may be necessary to keep good properties in the heat affected zone of the ferritic steels. But there are few results (11–13) on the influence of heat treatments on the structure and properties of alloy 625.

The purpose of the work reported in this paper was to determine the relationship between heat treatments at between 500 and 1125°C, structure, and corrosion resistance of forged alloy 625.

Material

Reference condition

A 150 mm x 20 mm forged rod was purchased. The alloy was vacuum remelted. Table I shows the chemical composition of the rod.

Table I Chemical composition of the alloy – Weight %

C	S	P	Si	Mn	Al	Cr	Mo	Co	Ti	Nb	Fe	Ni
0,019	0,001	0,008	0,15	0,07	0,2	21,4	8,7	0,102	0,26	3,4	3,7	61,8

Table II shows the mechanical properties of the as–received material and after 1 h at 1125°C followed by a water–quench. This high temperature solution treatment was chosen for comparison to welded alloy 625 but with a chemical composition as homogeneous as possible to avoid artifacts due to segregation. This is the reference condition for our study.

Table II Mechanical properties at room temperature

	Yield strength (0,2% Offset) MPa	Ultimate tensile strength MPa	Elongation %	Reduction of area %
as received	600 ± 10	1012 ±2	37 ± 7	58 ±,1
1 h at 1125°C	334 ± 2	768 ± 1	61 ± 2	70,8 ± 0,2

Heat treatments

160 mm long pieces of rod were heat treated 8 h at temperature intervals of 50°C between 500 and 1050°C, and also at 1125°C, with a heating rate of 50°C/h and air cooling.

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Previous results

The relationship between heat treatments and microstructure has already been studied, using scanning transmission electron microscopy and X-EDS microanalysis (14).

Results obtained are schematized in figure 1 and can be summarized as follows :

- Up to 650°C, no structural difference exists between the reference condition and heat treated samples,
- before and during gamma double-prime Ni_3Nb precipitation, slip bands appear at 650°C and disappear at 800°C at the same time as Ni_3Nb,
- between 700°C and 950°C, chromium rich $M_{23}C_6$ carbides precipitate in grain boundaries,
- between 800°C and 1050°C, molybdenum rich M_6C carbides also appear in grains boundaries,
- at higher temperature, only niobium- and titanium- rich MC carbides are present in grain boundaries.
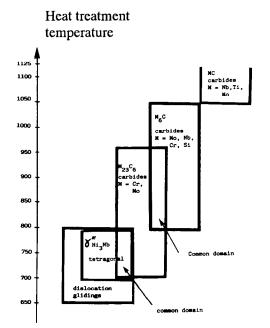
Heat treatment
temperature

Figure 1 – Influence of heat treatment
on microstructure

Tests

ASTM G 28 intergranular corrosion test

The ASTM G 28 test is the normalized intergranular corrosion test for alloy 625 products. It consists of immersion of the sample in a boiling solution containing 25 g of $Fe_2(SO_4)_3$, 236 ml of H_2SO_4 and 400 ml of distilled water during 120 h. The weight loss of each sample is converted into corrosion rate, that must be below 3 mm per year to be acceptable.

ASTM G 28 tests were performed on samples of 70 mm x 10 mm x 3 mm after each heat treatment.
One of the sides with the 10 mm width was mechanically polished with 6 μm diamond, to make possible microscopical investigations after the corrosion test. The other sides were polished under water with P120 abrasive paper.
In all cases, the ASTM G 28 intergranular corrosion test was strictly applied on three samples, with a normal exposure time of 120 h.
For the most sensitive conditions, the same test was shortened to 6 or 70 h. This avoided a depletion of Fe^{3+} ions in the solution and allowed examination of the beginning of attack.
All the samples were examined in a Scanning Electron Microscope SEM JEOL 840 equipped with an inclined Energy-Dispersive X-ray Spectrometer (X-EDS) EDAX ECON 9100.

Electrochemical Potentiokinetic Reactivation (EPR) test

EPR technique is a quantitative, non-destructive, rapid method for detecting sensitization of stainless alloys to intergranular corrosion. It has been mainly developed by CIHAL et al. (15, 16), NOVAK and coworkers (17) and has been widely applied to quantify the degree of sensitization (DOS) of austenitic stainless steels (18, 19), nickel-base alloys such as Inconel 600 (20) and Alloy 800 (21).

Two versions of the EPR method are available: single-loop and double-loop reactivation tests. In the single loop method, the sample is polarized in the passive range and the potential is scanned toward electronegative potentials. The charge corresponding to the anodic reactivation current is a measure of the DOS. In the double loop method, this reactivation scan

is preceded by a scan from the corrosion potential to the passive range, which enables measurement of the charge corresponding to activation. DOS is quantified by C_a/C_p, where C_a and C_p are respectively the activation and reactivation charges. Both methods were employed in our work, and their results compared with those of the ASTM G 28 test.

The samples are cylinders of material in each heat treatment condition, with the axis perpendicular to the original bar length, i.e. the surface to be studied is the same as for the ASTM G28 test. The thickness of the cylinders is 4 mm and the diameter 11,27 mm (surface area: S=1 cm²). The specimens were polished with a 4 μm diamond, rinsed in ethanol and distilled water, air dried and mounted on a rotating disc electrode. The rotation speed was 2000 r.p.m.. The electrochemical set-up consisted of a 100 ml five-necked flask with a thermostat, a platinum grid counter electrode and a saturated sulfate reference electrode.

Preliminary tests were performed to define the electrolyte giving the best results: it consists of a solution containing 236 ml H_2SO_4 (density: d=1.83), 400 ml H_2O and 58 mg NaCl, deaerated by bubbling purified nitrogen and controlled at 303 K.

The reactivation polarization curves were obtained using a Princeton Applied Research model 273 potentiostat. The electrochemical parameters are given in table 3.
Samples were observed after the test, in the same way as previously.

Table III Electrochemical parameters for EPR test

Single–loop method	Double–loop method
– corrosion potential during 120 s; – passivation at + 200 mV/ESS during 240 s; – potential scan down to corrosion potential at a rate of 2 mV.s^{-1}.	– corrosion potential during 120 s; – potential scan up to + 200 mV/ESS at a rate of 2 mV.s^{-1}; – passivation at + 200 mV/ESS during 240 s; – potential scan down to corrosion potential at a rate of 2 mV.s^{-1}.

Electrochemical characterization in 4M HCl by i–E curves and impedance spectroscopy

To determine if there could be a relationship between intergranular corrosion of alloy 625 and its behaviour in a highly corrosive environment, hydrochloric acid was chosen.
Electrochemical behaviour was described by plotting current–potential curves.
Electrochemical Impedance Spectroscopy (EIS) diagrams were plotted in the anodic regions of curves, to determine corrosion mechanisms.

The tests were performed on two heat treatment conditions only: reference conditions and after 8 h at 750°C, which is one of the most sensitized condition for intergranular corrosion as will be shown in the results.
The samples were cylinders 8 mm in diameter and 12 mm thick. Preparation and electrochemical set-up were the same as for the EPR tests, except for the reference electrode which is a saturated calomel electrode. The electrolyte was a 4M HCl solution controlled at 298 K and deaerated by bubbling purified nitrogen.
Potentiostatic i–E curves were plotted for each sample using a PAR model 273 potentiostat. A PAR model 5208 two phase lock–in analyser was added to obtain EIS diagrams. They were plotted using a potential sinusoidal perturbation of 5 mV amplitude, in the frequency range 100 kHz–10 mHz.
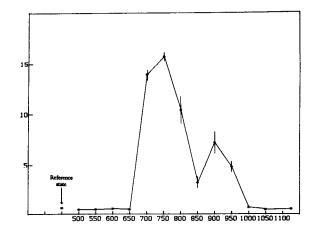
ASTM G 28

ASTM G 28 corrosion rates for samples heat treated 1 h at 1125°C and 1 h at 1125°C + 8 h at 500 to 1125°C are shown in figure 2. Vertical lines represent the spread in results at each temperature.

Two maxima appear on the curve, one between 700 and 750°C and the second at 900°C. Between 700 and 950°C, the spread in measured values is important, because grain fall-off occurred during subsequent handling.

Examination of samples after corrosion testing leads to the following observations:
Corrosion rate is low on samples heat-treated 1 h at 1125°C and 1 h at 1125°C + 8h at 500, 550, 600 and 650°C. Figure 3a shows that the attack areas are the grain boundaries and the segregation bands which contain Al- and Mg-, Si- and Al- or Ca- rich inclusions (14).
Grain boundaries of samples treated 1 h at 1125°C + 8 h at 700 and 750°C

Corrosion rate
(mm/year)

Heat treatment temperature (°C)

Figure 2 – Effect of heat treatment on
ASTM G 28 results

are severely corroded (fig.3b). Inside the grains, the attack follows crystallographic planes as shown by twins, steps and facets.
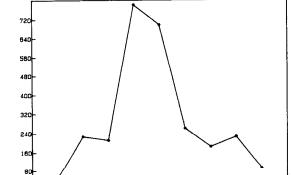Intergranular corrosion is still very important for samples treated 1 h at 1125°C + 8 h at 800°C (fig.3c). Corrosion of grains is different from previously: there are no more faceted grains, corrosion gives a sponge aspect to the surface.
For treatments at higher temperatures, samples are corroded along grain and twin boundaries and segregation band inclusions. In grain and twin boundaries, corrosion is reduced as the temperature grows: it is continuous up to 950°C (fig.3d), it becomes discontinuous at 1000 and 1050°C (fig.3e), and it almost disappears at 1125°C (fig.3f). For this temperature, the morphology is the same as for the samples treated at 500-650°C.

EPR tests results

Figure 4 shows the reactivation charges obtained for the different samples during single loop tests. The maximum of corrosion appears for 800-850°C. The examination of samples treated at 750°C shows that the reactivation charge measured is not only due to intergranular sensitization, but also to transgranular attack.

Ca (mC/cm²)

Figure 4 – Effect of heat treatment
temperature on reactivation charges
obtained with single-loop method

Heat treatment temperature (°C)

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a – 650°C

b – 700°C

c – 800°C
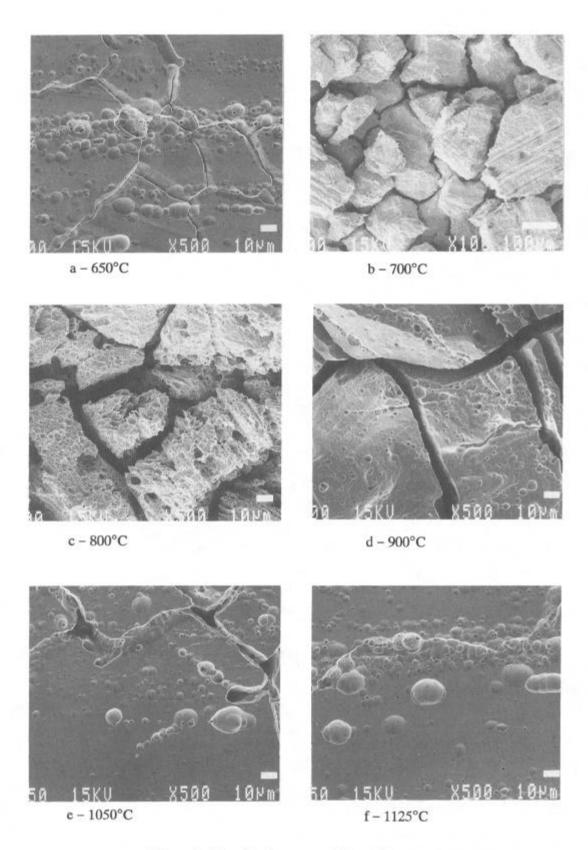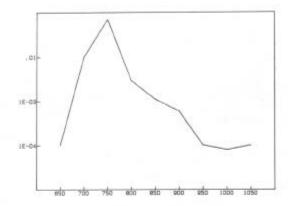
d – 900°C

e – 1050°C

f – 1125°C

Figure 3 – Samples heat treated 8 h at indicated temperatures.
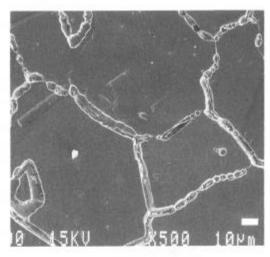Micrographs after ASTM G28 test

C_a/C_p values obtained by double-loop test for all the samples are plotted on figure 5. Maximum corrosion appears at 700–750°C. Micrographs of samples after testing show that corrosion is mostly along grain and twin boundaries (fig.6).
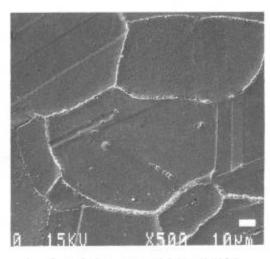
Ca/Cp

Heat treatment temperature (°C)

Figure 5 – Influence of heat treatment on Ca/Cp values determined with double-loop method

a – Sample heat-treated 8 h at 750°C

b – Sample heat treated 8 h at 950°C

Figure 6 – Micrographs after double-loop reactivation test

Electrochemical characterization of the alloy behaviour in 4M HCl

Electrochemical behaviour of the alloy in 4M HCl has been characterized for two samples: material treated 1 h at 1125°C (reference condition) and material treated 1 h at 1125°C + 8 h at 750°C (most sensitive condition of intergranular corrosion).
Two potentiostatic i–E curves have been plotted for each sample, with good repeatability. Figure 7 shows the potentiostatic anodic i–E curves obtained on the two samples. The activation peak is the same for both heat treatments, the difference is in the passive range: current density is higher for the material treated at 750°C.
Examples of impedance NYQUIST diagrams obtained on the samples for anodic overpotentials are shown on figure 8. Diagrams plotted in the active dissolution range show a capacitive arc associated with double-layer capacitance and charge transfer resistance, and an inductive loop which probably corresponds to an adsorption phenomenon.
As passivation occurs, a second capacitive arc appears, associated with a positive polarization resistance (R_p) before the critical passivation potential and a negative R_p after it.
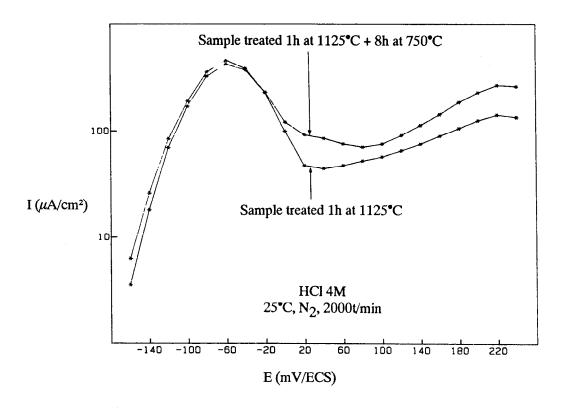
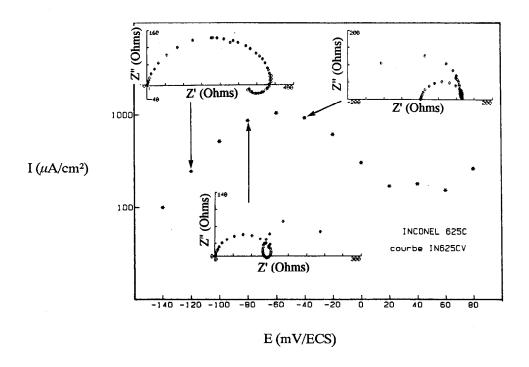Figure 7 – Potentiostatic I – E curves in 4M HCl

Figure 8 – Electrochemical impedance diagrams obtained
on sample heat treated 1 h at 1125°C

The diagrams obtained are the same for both samples. Only the charge transfer resistance values (R_t) are different above -20 mV/ECS (fig.9): R_t values are smaller for sample heat treated at 750°C, which is in agreement with the observation that the current density is greater for this state in the same range, as shown on figure 7.

$R_t i$ values (fig.10) are the same for both samples, which means that the corrosion mechanism is the same. Only the magnitude of dissolution in the passive range is greater for the sample heat-treated at 750°C.
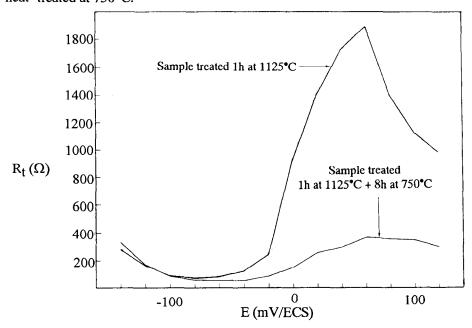

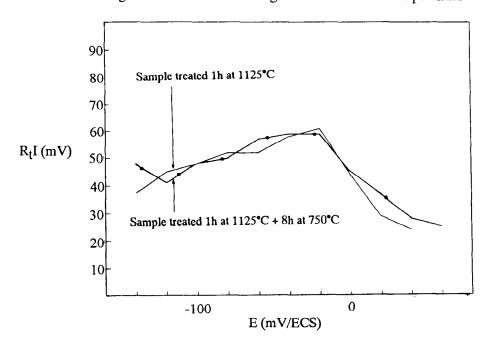Figure 9 – Evolution of charge transfer resistance Vs potential

Figure 10 – Evolution of RtI products Vs potential

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Discussion

Comparison between the different corrosion tests

The influence of heat treatments is more pronounced in intergranular corrosion tests, EPR in sulfuric acid and ASTM G 28 tests, than on electrochemical tests in hydrochloric acid. For both sorts of tests, results vary in the same way.

EPR double loop test is more representative of intergranular corrosion, and is more consistent with ASTM G 28 test than single loop test. During the single loop test, severe transgranular corrosion takes place, and the maximum of corrosion is shifted towards higher temperatures.

The EPR double loop test is more sensitive than the ASTM G28 test at the beginning of intergranular corrosion.

Influence of structure on corrosion resistance of IN 625

Intergranular corrosion takes place after heat treatments between 700 and 950°C, at the same time as precipitation of chromium– and molybdenum–rich $M_{23}C_6$ and M_6C carbides in grain and twin boundaries. Intergranular corrosion is due to chromium and probably also molybdenum depleted zones along grain and twin boundaries, as shown in (14) and (22). The two maxima observed at 700–750 and 950°C for the ASTM G28 results correspond to the depletion due respectively to $M_{23}C_6$ and M_6C precipitation. The range of sensitization is the same as that found by other authors, with the ASTM G28 test (1) or with the nitric acid HUEY test (23).

Corrosion inside the grain takes place between 700 and 800°C, at the same time as dislocation glides and gamma double–prime Ni_3Nb precipitation. This precipitation is responsible for the grain attack.

Electrochemical behaviour in HCl has shown that the corrosion mechanism is the same for all heat treatments. The magnitude is greater for the sample heat treated at 750°C. The explanation must be the same as for intergranular corrosion tests: corrosion occurs on the areas where the passive layer is weaker.

Conclusion

The influence of heat treatments between 500 and 1125°C on the corrosion resistance of forged alloy 625 has been studied.

An electrochemical potentiokinetic reactivation method has been perfected and compared to the ASTM G28 test results. Large intergranular corrosion occurs on samples heat treated between 700 and 950°C, due to the intergranular precipitation of chromium–rich $M_{23}C_6$ and molybdenum–rich M_6C carbides. At the same time, between 700 and 800°C, transgranular corrosion occurs by Ni_3Nb attack. The EPR double loop test is more sensitive than the ASTM G 28 test.

Two of the samples which had the most different behaviour, solution–treated and solution–treated + 8h at 750°C, were then studied in 4M HCl. No difference appears in the active range of potentiostatic voltammograms and electrochemical impedance diagrams. Dissolution is a little stronger in the passive range for the material treated at 750°C. This result is in agreement with intergranular corrosion results.

Heat treatments of INCONEL 625 between 700 and 950°C must be avoided to prevent attack in very corrosive environments.

ACKNOWLEDGEMENTS

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