Inconel 625 (UNS N06625) is a nickel-chromium-molybdenum alloy with an excellent corrosion resistance in a wide range of corrosive media. Up to now this material has been applied in oil and gas field in annealed condition, with the aim to have the best corrosion resistance properties. However, the chemical composition of this alloy is compatible with the application of a precipitation hardening (PH) heat treatment, which should increase its mechanical properties. Unfortunately there are no information in literature about the effect that this heat treatment can have on the corrosion resistance, especially in terms of sulfide stress cracking, stress corrosion cracking, galvanically induced hydrogen stress cracking and intergranular corrosion, which are the typical tests applied to NACE Oil & Gas materials.

Forged round bars with different diameters (6 [152mm], 8 [203mm] and 10 [254mm] inches) and a defined chemical composition have been precipitation-hardened and tested to measure their corrosion resistance (accordingly to NACE requirements) and their mechanical properties in PH state.

JMat PRO simulation and DSC analysis were performed to define the optimal ranges of times and temperatures for the PH heat treatment.

Optical microscope analysis and SEM/TEM investigations have been carried out to correlate the microstructure and the distribution, types and size of precipitates to the final corrosion and mechanical properties.

Oil and gas companies are very interested in increasing the mechanical resistance of used materials in form of forged bars produced starting from ingots; basically with 517MPa $Rp_{0.2}$ with the corrosion resistance comparable to that is required for solution annealed UNS N06625. Unfortunately up to now no literature or research are available to confirm the possibility to use UNS N06625 in PH condition in Oil & Gas project.

Develop a standard UNS N06625 in PH condition with the cooperation of Italfond S.p.A. and CSM – Centro Sviluppo Materiali and produce a complete characterization starting from real forged material in terms of mechanical and corrosion resistance properties is so the aim of the study. A deep metallurgical analysis of the material will allow to understand the precipitation effect on the material in terms both of mechanical properties and corrosion behavior.

Nickel can be alloyed with most metals. It shows wide ranges of solubility respect to iron, chromium and niobium and the face-centered cubic structure of the nickel matrix (γ) can be strengthened by solid-solution hardening, carbide precipitation, or precipitation hardening. [1]

Depending on the heat treatment and production process many different phases and microstructural constituents can be found in a nickel base alloy, some of them are useful for the material mechanical and anti-corrosion properties and some others are deleterious.

UNS N06625 is a nickel base superalloy with the following chemical composition.

Ni	Cr	Mo	Nb + Ta	Fe	Ti	C	Mn	Si	S	P	Al	Co
58.0 min	20 - 23	8 -10	3.15 - 4.15	5.0 max	0.40 max	0.10 max	0.50 max	0.50 max	0.15 max	0.15 max	0.40 max	1.0 max

Tab.1 Chemical composition for UNS N06625 [2]

The most important hardening phase for UNS N06625 is gamma double prime (γ’’), coherent disk-shaped particles that form on the {100} planes (average diameter approximately 60 nm, thickness approximately 5-9 nm). It is a metastable phase with the chemical composition Ni_3Nb. It was observed that the nucleation of γ'' particles starts at 10 hours in the range of 923-973K (650-700°C). The first stages of γ'' precipitation are almost exclusively intragranular and resulted in an increase of the Vickers microhardness. The nucleation time of the γ'' phase from 923K to 1023K (650°C to 750°C) and its consequences on the microhardness had been studied by Cortial et al. [3]

At the beginning, γ'' particles are almost spherical while a progressive morphological change appears increasing the aging duration at both temperatures. The first stages of γ’’ precipitation are heterogeneous, γ’’ particles nucleate along straight lines that are likely to be sub-grain boundaries, dislocation segments, or twin boundaries. The evolution of the γ’’ in terms of size as a function of temperature and aging time, results from a diffusion-controlled process according to the LSW theory [8]. By increasing the aging time or temperature, it was observed that the metastable γ'' particles progressively transform into the stable Ni_3Nb (δ) phase, by a coalescence process, with a detrimental effect on the alloy mechanical and corrosion properties.

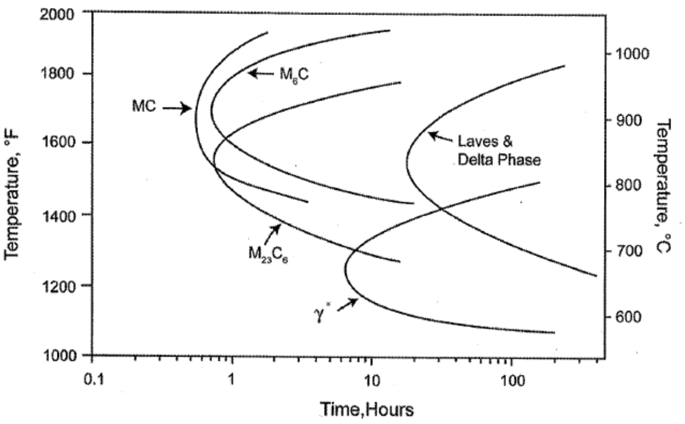

Fig.1 TTT Diagram – Alloy 625 [4]

Figure 1 shows the TTT diagram for a generic UNS N06625 with the nominal analysis. Temperature around 670°C should be chosen to obtain a hardened material with aging time compatible to an industrial process, time of treatment should be calibrated to reach the hardening effect and to avoid the coalescence of Ni_3Nb precipitates.

The corrosion testing to be performed on heat treated material are those prescribed by the NACE specifications and market requirements:

NACE TM 0177 Method A - Dead weight - constant load:

- Stress corrosion cracking (SCC).
- Galvanic hydrogen stress cracking (GHSC).

NACE TM 0177 Method C – C Ring – with the Level VII environment

ASTM G28-A – Susceptibility to intergranular corrosion

NACE tests are performed to demonstrate the material resistance to cracking failure under the combined action of tensile stress and corrosion in aqueous environments containing hydrogen sulfide (H_2S). This phenomenon is generally termed sulfide stress cracking (SSC) when operating at room temperature and stress corrosion cracking (SCC) when operating at higher temperatures. In recognition of the variation with temperature and with different materials this phenomenon is herein called environmental cracking (EC).

SSC of metals exposed to oilfield environments containing H_2S was recognized as a materials failure problem by 1952. Laboratory data and field experience have demonstrated that even extremely low concentrations of H_2S may be sufficient to lead to SSC failure of susceptible materials. In some cases, H_2S can act synergistically with chlorides to produce corrosion and cracking (SSC and other mode) failures. However, laboratory and operating experiences have also indicated to materials engineers the optimum selection and specification of materials having minimum susceptibility to SSC. NACE TM0177 covers test methods for SSC (at room temperature) and SCC (at elevated temperature).

The need for better understanding of the variables involved in EC of metals in oilfield environments and better correlation of data has become apparent for several reasons. New design requirements by the oil and gas production industries call for higher-strength materials that, in general, are more susceptible to EC than lower-strength alloys. These design requirements have resulted in extensive development programs to obtain more resistant alloys and/or better heat treatments. At the same time, users in the petroleum refining and synthetic fuels industries are pushing present materials much closer to their mechanical limits.

Room-temperature (SSC) failures in some alloys generally are believed to result from hydrogen embrittlement (HE). When hydrogen is cathodically evolved on the surface of a metal (as by corrosion or cathodic charging), the presence of H2S (and other compounds, such as those containing cyanides and arsenic) tends to cause hydrogen atoms to enter the metal rather than to form hydrogen molecules (see Fig.2) that cannot enter the metal. In the metal, hydrogen atoms diffuse to regions of high triaxial tensile stress or to some microstructural configurations where they become trapped and decrease the ductility of the metal. Although there are several kinds of cracking damage that can occur in metals, delayed brittle fracture of metals resulting from the combined action of corrosion in an aqueous sulfide environment and tensile stresses (failure may occur at stresses far below the yield stress) is the phenomenon known as SSC. [5]

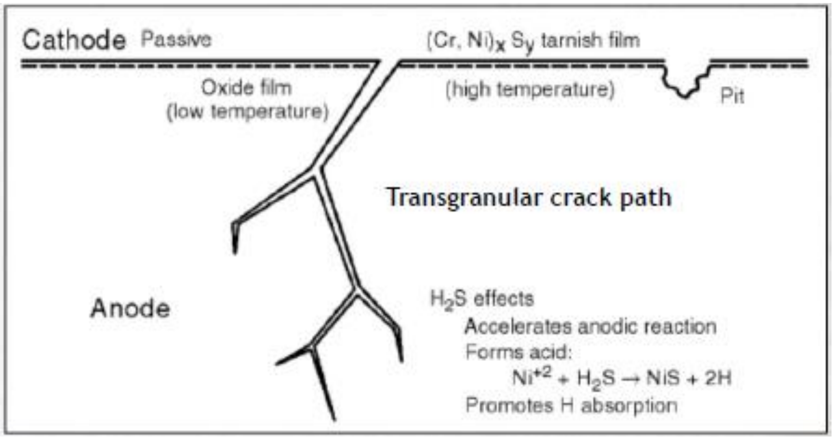

Fig.2 SSC phenomena [6]

ASTM G28 describes the procedure for conducting the boiling ferric sulfate—50 % sulfuric acid test which measures the susceptibility of certain nickel-rich, chromium-bearing alloys to intergranular corrosion which may be encountered in certain service environments. [7]

Starting from the literature analysis, the first step will be to determine the proper heat treatment parameters. DSC testing and simulations using JMat Pro will be done to have a guideline to define times and temperatures. Samples taken from different bars located on top and bottom positions (traceability to the starting ingot will be maintained during the production process) will be heat treated in laboratory furnace. On the same specimens, ASTM G28 test will be performed in order to have a first idea about the corrosion behavior of the heat treated material.

After this preliminary laboratory test, bars will be heat treated with an industrial process and retested with the same procedure used for the laboratory tests to evaluate possible differences related to the different scale.

A metallurgical analysis will be done in every production step to control the microstructure evolution and any other possible issue.

If the material will satisfy the required mechanical properties ($Rp_{0.2}$ higher than 517MPa) the next step will be the execution of the corrosion tests in H_2S environment. Actually, this is the more interesting part of the work, as there is no literature that describes the corrosion behavior of UNS N06625 in PH condition tested in accordance with NACE requirements.

A careful analysis will performed on the corroded samples to determine the effect of precipitates on the corrosion mechanisms and the heat-treated material will be analyzed by SEM and TEM to define the composition and the volume fraction of precipitates.

If the precipitation hardening behavior of UNS N06625 has been deeply studied in the past, the effect of this heat treatment on the corrosion resistance in environments typical to Oil & Gas applications is already to be explored. In the literature, there are not information about the corrosion behavior of precipitation-hardened UNS N06625 in H_2S-bearing environments. A part from the industrial comeback given by the development of a material with increased mechanical properties at almost constant corrosion resistance and price, the scientific return of the research will involve the understanding of corrosion mechanisms of the forged precipitation-hardened UNS N06625 in H2S environments, and their relation with microstructure, composition and volume fraction of precipitates.

[1] ASM Handbook 2 Properties and selection: Nonferrous Alloys and Special-Purpose Materials, ASM International, 1990, p. 1366.

[2] H. L. Eiselstein and D. J. Tillack, “The Invention and Definition of Alloy 625,” in Superalloys, Pittsburgh, 1991.

[3] F. Cortial, J.M. Corrieu, and C. Vernot-Loier: Metall. Mater. Trans. A, 1995, vol. 26A, pp. 1273–86.

[4] L. E. Shoemaker, “Alloys 625 and 725: Trends in properties and applications,” in Superalloys 718, 625, 706 and derivatives, Pittsburgh, 2005.

[5] NACE TM 0177 Standard.

[6] A. Smith, “CSM experience with design and testing of Ni alloys for SCC resistance”, Roma, 2017.

[7] ASTM G28 Standard.

[8] Lorena Mataveli Suave, Jonathan Cormier, Patrick Villechaise, Aure´ Lie Soula, Ze´ Line Hervier, Denis Bertheau and Johanne Laigo, “Microstructural Evolutions During Thermal Aging of

Alloy 625: Impact of Temperature and Forming Process”, METALLURGICAL AND MATERIALS TRANSACTIONS A, VOLUME 45A, June 2014 pp. 2963.