Hydrogen embrittlement in Nickel-base superalloys Nickel-based superalloys in the petrochemical industry

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Abstract. Due to the excellent properties of nickel-based superalloys, it is often widely used in aircraft engines, petroleum, chemical and nuclear energy. However, the use of nickel-based superalloys in petrochemical industry is usually accompanied by hydrogen embrittlement, which will lead to a decrease in its mechanical properties. Through research, it is found that reducing the generation of σ phase in nickel-based superalloys will reduce the occurrence of hydrogen embrittlement, thereby solving this problem.

Keywords: nickel-based superalloys, petroleum, hydrogen embrittlement.

1. Background

Ni-based superalloys are widely used in aircraft engines, petroleum, chemical and nuclear power because of their excellent high temperature resistance, wear resistance, corrosion resistance and oxidation degradation resistance (Mannan, 2012). When the Ni-based superalloy material is exposed to the electrolyte for a long time, the Ni-based superalloy undergoes an electrochemical reaction. The hydrogen produced by the electrochemical reaction will be adsorbed on the grain boundary of the Ni-based superalloy crystal, which will cause the lattice structure of the alloy to expand and distort. The distorted lattice structure can seriously affect the mechanical properties of the Ni-based superalloy, thereby shortening the service life of the alloy. Hydrogen embrittlement of Ni-based superalloys usually occurs in the petroleum and chemical industry. The purpose of this paper is to select the Ni-based superalloy materials used in the petroleum and chemical industry and how to prevent hydrogen embrittlement from affecting the properties of Ni-base superalloys (Seita et al 2015).

2. Performance requirements in the petroleum and chemical industry

In the petroleum and chemical industry, Ni-based superalloys usually work in the environment of high temperature, strong acid and strong alkali electrolytes, which requires the selected alloys to have high temperature resistance, corrosion resistance and thermal creep resistance. The density of the selected Ni-based superalloy is usually 7.7-9.0g/cm3, and the phase transition temperature(Tm) is 1320℃-1450℃. The elastic modulus of the alloy at room temperature was 210 GPa, the modulus of elasticity of 800 ℃ was 160 GPa. Finally, the alloy needs to work at a minimum of 1000h at 1100 ℃ and a stress of 137 MPa (σ=137MPa) (Pollock and Tin, 2006).

3. Ni-based superalloy system in the petroleum and chemical industry

A series of Ni-based superalloy systems have been developed in order to meet the requirements of the petroleum and chemical industry in different environments.

Ni-based superalloy C276: This alloy is a Ni-Cr-Mo alloy and has good corrosion resistance in both oxidizing and reducing environments. Since the alloy reduces the content of C and Si, the temperature of the heat receiving portion is controlled to suppress precipitation of carbides in the heat-affected zone, and corrosion resistance is improved. This material is especially suitable for use in harsh environments such as high temperature, mixed with mineral acids and organic acids (formic acid and acetic acid) (Zhang et al, 2016).

Ni-based superalloy 718: This alloy is a Ni-Cr-Fe alloy with high tensile strength, fatigue strength, creep strength and flexural strength at 700℃. Corrosion resistance in high and low temperature environments, suitable for various acidic and low temperature environments (Hicks and Altstetter, 1990).

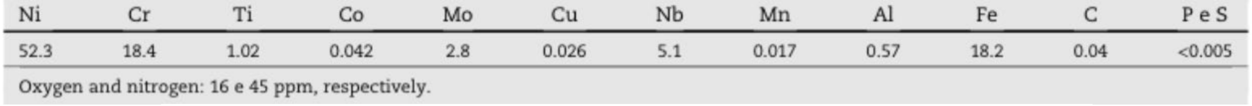
Ni-based superalloy 400: This alloy is a Ni-Cu alloy and has excellent corrosion resistance in fluorine gas, hydrochloric acid, sulfuric acid, hydrofluoric acid and their derivatives.

Ni-based superalloy 725: This alloy is a Ni-Cr-Mo alloy with hydrogen embrittlement resistance and stress corrosion cracking. This alloy is used to make oil hanging tubes for use in an acidic atmosphere.

4. Processing and microstructure of nickel-based superalloys

Take the processing of nickel-base superalloy 718 as an example(the nominal composition is shown in Table 1).Since the composition of the Ni-based superalloy 718 has Al and Ti is easily oxidized, the smelting of the nickel raw material is usually performed under vacuum. Vacuum induction melting (VIM), electro slag remelting (ESR) and vacuum consumable arc melting (VAR) are commonly used to smelt nickel raw materials (Pollock and Tin, 2006). At the same time, these technologies can effectively remove contaminants and oxygen from nickel raw materials. The smelted nickel raw material is cast to obtain a homogeneous alloy ingot, the microstructure of the alloy ingot is very rough (particle size larger than 10 mm) and has a residual coarse columnar grain structure (Pollock and Tin, 2006). By observing the microstructure, the grains of the ingot crystal are homogeneous γ phase grains. Ni-based superalloy ingots need to be forged to reduce grain size. Uniform equiaxed grains having a diameter of about 5-50μm are required during the forging process (Fig 1). Dynamic and metadynamic recrystallization of grains of the original microstructure during hot working by controlling process variables such as strain, strain rate, and workpiece temperature.

Table.1 chemical composition of Ni-based superalloy 718 (wt.%) (Rezende et al, 2015).



Ni	Cr	Ti	Co	Mo	Cu	Nb	Mn	Al	Fe	C	P e S
52.3	18.4	1.02	0.042	2.8	0.026	5.1	0.017	0.57	18.2	0.04	<0.005

Oxygen and nitrogen: 16 e 45 ppm, respectively.

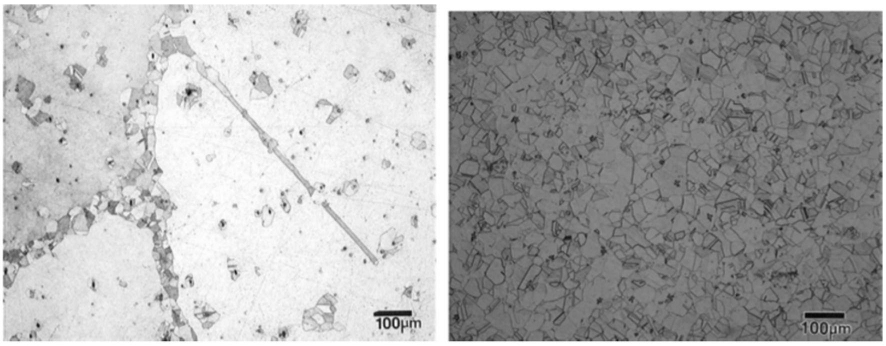


Fig.1 recrystallization of Ni-based superalloy(Pollock and Tin, 2006)

The forged Ni-based superalloy 718 requires heat treatment and effective hardening treatment to obtain alloy strength. The Ni-based superalloy 718 is hardened by precipitation of the second phase ($\gamma' phase\ and\ \gamma'' phase$) in the metal strip. The precipitation of Ni-Al and Ni-Ti phases in the alloy is usually formed by heat treatment between 1100K and 1500K. If the alloy is precipitated in other phases or combined into other forms, the alloy cannot achieve the corresponding mechanical strength. Therefore, it is necessary to dissolve the aging elements such as Al and Ti before the alloy hardens. The specific steps are: (1) The alloy is rapidly cooled in water after solution heat treatment at 1900K-1950K. (2)The cooled alloy was precipitation hardened at 1400 K for 10 hours. (3) Cool to 1200K in air and keep until the total aging time is 20 hours. (4) cooling to room temperature in air. The purpose of aging is to ensure uniform precipitation of the $\gamma' phase\ and\ \gamma''\ phase$, so that the strength of the Ni-based superalloy 718 is obtained. The microstructure of the Ni-based superalloy 718 is shown in Figure 2 (Furrer and Fecht,1999. Zhang et al, 2019).

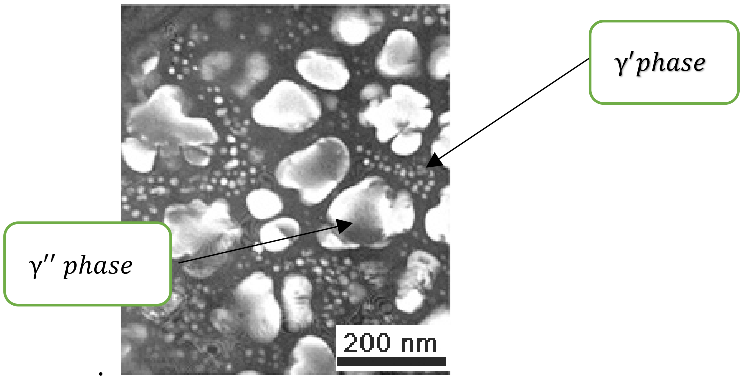


Fig.2 Microstructure of the Ni-based superalloy 718

5. Performance test of Ni-based superalloy

The production of nickel-based superalloys requires a series of performance tests to verify compliance. The main mechanical properties include high temperature tensile testing, creep testing, hydrogen analysis and Corrosion test

Any of these four properties can affect the life of the alloy.

5.1 High temperature tensile test

The Ni-based superalloys with a diameter of 5 mm were measured at four high temperature values of 500℃, 550℃, 575℃, 600℃, 650℃ for tensile strength, yield strength, elongation at break and reduction in area. The alloy to be tested was incubated for 1 h before the test. The control strain was 0.04%/s in the test (Nazmy et al, 2003). Compare the experimental values with the standard parameters of the alloy to determine compliance.

5.2 Creep test

Since superalloys undergo long-term strain under high temperature stress, they are highly resistant to time-dependent creep deformation, which is important for Ni-based superalloys in the petrochemical and chemical industries. The creep test measures the deformation of the alloy by subjecting the alloy material to be tested to constant temperature and constant stress for a long time. The higher the temperature or the greater the stress, the more pronounced the creep. In order to meet the mechanical properties of alloys in complex environments, high-temperature creep tests and low-temperature creep tests are required for Ni-based superalloys. Calculating the creep strength of the material (Diologent et al, 2003).

5.3 Hydrogen analysis

Superalloy samples require hydrogen analysis to determine whether they have hydrogen embrittlement resistance. In the petrochemical industry, Ni-based superalloys often work under harsh environmental conditions, so there is a strict requirement for hydrogen content in the sample. Quantitative hydrogen depth analysis of Ni-based superalloys can be performed using secondary ion mass spectrometry (SIMS) (Eicke and Bilger, 1991). The method is characterized by high detection sensitivity and depth resolution of a few nanometers (Louthan et al, 1972). The hydrogen content of the NI-based superalloy samples was measured using a SIMS instrument (shown in Fig.3) and compared to standard values.

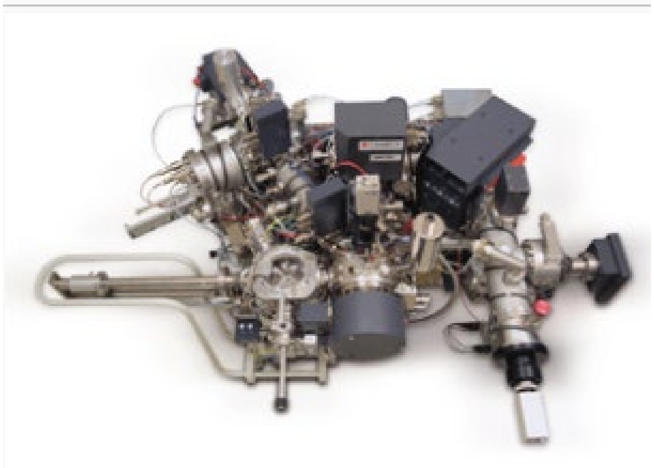


Fig.3 SIMS instrument

5.4 Corrosion test

In the petrochemical industry, Ni-based superalloys often work in an electrolyte environment such as strong acid, strong alkali or seawater, and the alloy must have strong corrosion resistance. Using the sample intergranular corrosion test method, the sample was placed in a boiling 23% sulfuric acid + 1.2% hydrochloric acid + 1% ferric chloride + 1% copper chloride solution to measure the intergranular corrosion sensitivity of the sample.

6. Degradation problems in Ni-based superalloy systems

In the petrochemical industry, Ni-based superalloy systems usually operate under hydrogenation media such as acid-base, seawater, and sulfide gas (H2S) (Mannan, 2012). The alloy absorbs hydrogen due to corrosion and causes hydrogen embrittlement. When the material is in a catholically protected state, an electrochemical reaction occurs. Hydrogen is generated on the surface of the alloy, resulting in hydrogen embrittlement. From a microscopic point of view, the phase σ in the Ni-based superalloy is directly related to the hydrogen embrittlement sensitivity. Due to incorrect solution or heat treatment, the Ni-based superalloy may be present in the σ-rich phase. The σ phase of the grain boundary covering the hydrogen promotes the interfacial bonding between the σ phase and the matrix (Tarzimoghadam et al, 2017). The needle-like phase σ provides a linear crack path, which internal hydrogen and hydrogen produced by electrochemical reaction are more likely to propagate along the crack. This will result in a decrease in ductility of the Ni-based superalloy, a decrease in tensile strength, and failure of aging of the alloy. Therefore, the production of σ phase should be reduced during the production process, thereby reducing hydrogen embrittlement. In addition, Nickel-based superalloys may generate residual stress during the welding process, and the formation of hydrogen at the cathode reaction generates stress. These stresses will eventually lead to stress corrosion cracking of the Ni-based superalloy, causing brittle fracture of the alloy and permanent failure (Brass & Chene 1998).

7. Summary

This paper mainly introduces the application of Ni-based superalloy system in petrochemical industry. Several super alloy systems for this field are briefly introduced. Taking Ni-based alloy 718 as an example, the synthesis steps and performance detection methods of Ni-based superalloys are introduced in detail. Explain from the microscopic principles of the alloy hydrogen embrittlement, the possible hazards and how to prevent hydrogen embrittlement.

References

[1] Brass, A. M., & Chene, J. (1998). Influence of deformation on the hydrogen behavior in iron and nickel base alloys: a review of experimental data. Materials Science and Engineering: A, 242(1-2), 210-221.

[2] Diologent, F., Caron, P., d'Almeida, T., Jacques, A., & Bastie, P. (2003). The γ/γ′ mismatch in Ni based superalloys: In situ measurements during a creep test. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 200, 346-351.

[3] Eicke, A., & Bilger, G. (1991). SIMS for hydrogen quantification and structural analysis of amorphous silicon germanium compounds. Fresenius' journal of analytical chemistry, 341(3-4), 214-218.

[4] Furrer, D., & Fecht, H. (1999). Ni-based superalloys for turbine discs. Jom, 51(1), 14-17.

[5] Jambor, M., Bokůvka, O., Nový, F., Trško, L., & Belan, J. (2017). Phase transformations in nickel base superalloy Inconel 718 during cyclic loading at high temperature. Production engineering archives, 15(15), 15-18.

[6] Louthan Jr, M. R., Caskey Jr, G. R., Donovan, J. A., & Rawl Jr, D. E. (1972). Hydrogen embrittlement of metals. Materials Science and Engineering, 10, 357-368.

[7] Hicks, P. D., & Altstetter, C. J. (1990). Internal hydrogen effects on tensile properties of iron-and nickel-base superalloys. Metallurgical Transactions A, 21(1), 365-372.

[8] Mannan, S. K. (2012). Alloy 718 for oilfield applications. Jom, 64(2), 265-270.

[9] Nazmy, M., Denk, J., Baumann, R., & Künzler, A. (2003). Environmental effects on tensile and low cycle fatigue behavior of single crystal nickel base superalloys. Scripta Materialia, 48(5), 519-524.

[10] Pollock, T. M., & Tin, S. (2006). Nickel-based superalloys for advanced turbine engines: chemistry, microstructure and properties. Journal of propulsion and power, 22(2), 361-374.

[11] Seita, M., Hanson, J. P., Gradečak, S., & Demkowicz, M. J. (2015). The dual role of coherent twin boundaries in hydrogen embrittlement. Nature communications, 6(1), 1-6.

[12] Tarzimoghadam, Z., Ponge, D., Klöwer, J., & Raabe, D. (2017). Hydrogen-assisted failure in Ni-based superalloy 718 studied under in situ hydrogen charging: the role of localized deformation in crack propagation. Acta Materialia, 128, 365-374.

[13] Rezende, M. C., Araujo, L. S., Gabriel, S. B., Dos Santos, D. S., & De Almeida, L. H. (2015). Hydrogen embrittlement in nickel-based superalloy 718: Relationship between γ′+ γ ″precipitation and the fracture mode. international journal of hydrogen energy, 40(47), 17075-17083.

[14] Zhang, C., Zhang, L., Shen, W., Liu, C., & Xia, Y. (2016). The kinetics of metadynamic recrystallization in a Ni-Cr-Mo-based superalloy Hastelloy C-276. Journal of Materials Engineering and Performance, 25(2), 545-552.

[15] Zhang, Z., Moore, K. L., McMahon, G., Morana, R., & Preuss, M. (2019). On the role of precipitates in hydrogen trapping and hydrogen embrittlement of a nickel-based superalloy. Corrosion Science, 146, 58-69.