Pitting corrosion of sheets of a nickel-base superalloy

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Cold rolled sheets of a nickel-base superalloy are used in building gas turbine engines. After rolling to the final gauge, the sheets were annealed at 1180 °C. Pickling of the sheets was carried out to remove the scale and the oxidized layer. It was observed that there was heavy incidence of pitting with perforations at several locations due to pits penetrating through the thickness. The sheets got rejected, resulting in heavy loss. The superalloy contains 25 wt% chromium, 15 wt% tungsten. Tungsten provides high resistance to pitting corrosion. With such a high level of W, the grade has a high Pitting Resistance Equivalent. Further it is a single-phase material. Pitting attack is thus totally unexpected. The failure was analyzed. Pickling process for this material normally involves the usage of salt bath, sulfuric acid, nitric acid, and/or hydrofluoric-nitric acid baths. In the case under study, satisfactory pickling was not achieved this way; discoloration and deposits were persistently present on the sheet surface. In order to improve the surface quality, the sheets were dipped in hydrochloric acid bath for a long time. Hydrochloric acid bath was in aged condition; by that point of time, the bath went through extensive usage for pickling of different grades of steels. Consequently there was significant accumulation of iron salts in the bath. It is known that ferric and chloride ions cause significant acceleration in pitting. The bath was stagnant and the time of immersion of the sheets in the bath was long. The material failed under the combination of these adverse conditions. The paper brings out the details of the failure analysis carried out.

1 Introduction

AE868 is a Russian grade superalloy produced in the form of bars and sheets for application in building gas turbine engines. The sheets are required in different cold rolled gauges, depending on the component being made.

Pickling is an integral part of the manufacturing process of the superalloy sheets to remove the oxidized layer arising out of the hot working and heat treatment operations. While pickling process had been routinely carried out at both intermediate and finish product stages with no problems, severe quality problems were encountered during pickling of one batch at the finish cold rolled stage. Severe pitting of the sheets was observed at the end of pickling; the sheets got perforated at several places and became unserviceable, leading to large-scale losses.

The material, by virtue of its chemical composition and microstructure in the solution annealed condition in which it is used, is expected to show excellent resistance to pitting corrosion. As such it was totally unexpected that material gets rejected due to severe pitting attack during pickling.

Analysis of the failure was taken up; details of the study carried out and the findings made are reported in the following. Some aspects of the study were earlier presented in CORCON 2005 [1].

2 Description of the material, process, and failure encountered

The material in question is a nickel-base superalloy corresponding to the Russian grade AE868 (henceforth designated as NiCrW superalloy) in the form of cold rolled and annealed sheets. Detailed chemical composition is given in Table 1.

The material was produced through ingot metallurgy route – primary melting, secondary melting, hot forging, hot rolling, and finally cold rolling. Details are given in Fig. 1.

At the end of hot rolling, the sheets were 4.5 mm thick and ~1050 mm wide. The sheets were to be produced to a thin gauge of 0.8 mm for supplying them to the customer enabling him to use them in building gas turbines. As the cold rollability of the material is limited, intermediate annealing is necessary at different stages during cold rolling. Details are given in Fig. 2. After each stage of intermediate annealing as well as after final annealing of the finished rolled sheets, pickling operation was carried out to remove the oxidized layer and get a bright finish.

Figure 3 gives the steps involved in the standard pickling practice to remove the oxidized layer on the NiCrW superalloy sheets. Preheating in fused salt bath is a strongly recommended practice to facilitate pickling of oxidized or scaled surfaces of nickel alloys [2]. In case satisfactory pickling was not achieved by using the standard practice, additional pickling was carried out in a hydrochloric acid bath using the following conditions: concentration of hydrochloric acid bath, 15–20%; temperature of bath, room temperature; time of dip, 2–4 h.

In the present case, the sheets were cold rolled to the final dimension (0.8 mm thickness). Final annealing was carried out at 1180 °C using the roller hearth furnace. The time of dwell of the sheets at 1180 °C was of the order of 6 min. The sheets were forced air cooled to room temperature. Pickling was carried out as per the standard practice. However, satisfactory pickling could not be achieved. The sheets did not have a clean surface. Discoloration of the surface was observed, possibly due to reminiscence of oxides which were strongly adherent and did not get removed by the pickling process used. Repickling was done using hydrochloric acid bath with 15–20% concentration and operating at room

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Table 1. Chemical composition of the NiCrW superalloy

Element	Wt%
Carbon	0.064
Sulfur	0.0012
Phosphorous	0.007
Chromium	24.95
Titanium	0.49
Aluminum	0.25
Tungsten	14.85

Raw material preparation
↓
Vacuum induction melting
↓
Cast into 350 mm Φ electrodes, ~2.5 MT in weight
↓
Vacuum arc remelting to realize 400 mm Φ remelt ingots
↓
Forging to 50 mm x 250 mm cross section, using a 1500 MT capacity forge press
↓
Hot sheet rolling to 4.5 mm thick x ~1050 mm wide sheets
↓
Cold rolling to 0.8 mm thick x ~1050 mm wide sheets

Fig. 1. Manufacturing process steps in the production of cold rolled sheets of the NiCrW superalloy

As hot rolled sheets 4.5 mm thick x ~1050 mm wide
↓
First intermediate anneal in Roller Hearth Furnace (RHF) at 1160 °C
↓
Pickling to remove surface oxide
↓
Cold roll to 2.5 mm thick x ~1050 mm wide sheets
↓
Second intermediate anneal in RHF at 1160 °C
↓
Pickling to remove surface oxide
↓
Cold roll to1.6 mm thick x ~1050 mm wide sheets
↓
Third intermediate anneal in RHF at 1160 °C
↓
Pickling to remove surface oxide
↓
Cold roll to 0.8 mm thick x ~1050 mm wide sheets
↓
Final annealing in RHF at 1180 °C
↓
Pickling of finish rolled product

Fig. 2. Steps involved in cold rolling of the NiCrW superalloy sheets

Dip the annealed sheets in salt bath furnace at 480 °C and hold for 30 min.
↓
Quench the sheets into water
↓
Dip the sheets into ~20% sulfuric acid for 1-2 hours
Bath temperature ~80 °C
↓
Rinse the sheets in water
↓
Dip the sheets for 3-5 minutes in HF (3-4%) – HNO_3 (15-20%) bath at 30-40 °C
↓
Rinse the sheets in water

Fig. 3. Standard practice for pickling of the NiCrW superalloy sheets to remove the oxidized layer

temperature. In the process, the sheets got severely pitted and a number of small pinholes (penetrating through the thickness) distributed nonuniformly over the sheet surface were seen.

Material of this grade was being regularly pickled in the pickling shop and this type of problem was never encountered in the past. In fact, the sheets of the batch under discussion were pickled after every stage of intermediate annealing in the roller hearth furnace. As shown in Fig. 2 intermediate annealing was carried out three times during the process of bringing down the thickness by cold rolling of the hot rolled sheets. Problem of pitting and perforations occurring was not encountered during these intermediate pickling stages.

Since the damage was severe and irreparable, the sheets had to be rejected and scraped, resulting in a heavy financial loss. As it was necessary to prevent recurrence of such costly rejections, an investigation was carried out to understand the reasons for the heavy pitting observed.

The investigation was first focused on identifying process deviations if any made during pickling. It was noticed that there was an important deviation with respect to dipping time in hydrochloric acid bath. Whereas the normal of dipping time was 2–4 h, the sheets in the present case were dipped for more than 24 h continuously at a stretch. In view of the difficulties encountered in getting a clean surface, the operator hoped to get the desired result by extending the soaking time; in the process he allowed a much longer dwell time in the hydrochloric acid bath than what normally the case was. The bath condition during this long period of dipping was still/static.

Concentration of hydrochloric acid bath was checked and found to be in the permissible range. It was noticed that many iron-bearing materials were pickled in the hydrochloric acid bath before it was used to pickle the NiCrW superalloy sheets. Contamination from dissolved salts is hence expected to be correspondingly high. In particular since previous usage of the bath involved pickling of iron bearing materials, a significant accumulation of ferric ions in the bath is to be expected. However the iron content in the bath was not checked at the time of investigation.

3 Discussion

Once a pit appears at a point on the sheet, due to the expected preferential attack at that point and the low thickness of the sheets, the pit transforms into a perforation in no time.

The material in question is a nickel-base superalloy containing ~25 wt% chromium, ~15 wt% tungsten as the two major alloying elements (Table 1). Tungsten behaves similar to molybdenum in providing improved resistance to localized corrosion – pitting and crevice corrosion [3,4]. The pitting resistance equivalent number (PREN) can be calculated using the alloy chemical composition to estimate the relative pitting resistance of alloys. For stainless steel PREN is given by [5]

$$\mathrm{PREN} = \%\mathrm{Cr} + 3.3\,(\%\mathrm{Mo}) + 16\,(\%\mathrm{N}) \tag{1}$$

and for stainless steels containing tungsten

$$\mathrm{PREN} = \%\mathrm{Cr} + 3.3\,(\%\mathrm{Mo}) + 1.65\,(\%\mathrm{W}) \tag{2}$$

Table 2. Chemical composition and PREN for several corrosion-resistant Ni-Cr-Mo alloys and the NiCrW superalloy

Alloy	UNS no.	Fe	Ni	Cr	Mo	W or Nb	Cu	PREN
686	N06686	1	58	20.5	16.3	3.9		50.8
C2000	N06200	1	57.4	23	16		1.6	47.0
22	N06022	2.5	59	21.5	13.6	3.1		46.6
C276	N102676	6	57	15.5	16	3.9		45.4
625	N06625	3	62	22	9	3.6		40.8
C4	N06455	2	66	16	16			40.0
AE868			59	24.95		14.85		47.2

The standard PREN equation used for stainless steels cannot be used for the more highly alloyed nickel-base alloys, for which the following equation is used to calculate PREN [6]:

$$\text{PREN} = \%\,\text{Cr} + 1.5\,(\%\,\text{Mo} + \%\,\text{W} + \%\,\text{Nb}) \qquad (3)$$

The percentages are by weight.

With the high level of tungsten present in the alloy (14.85 wt%), in addition to $\sim$25 wt% Cr, the PREN of the NiCrW superalloy is very high. Table 2 compares the PREN for several highly alloyed nickel–chromium–molybdenum alloys known for their high resistance to pitting corrosion [6] with PREN for the AE868. It can be seen that PREN of 868 (47.2) is second only to that of grade AE686 with PREN of 50.8. Accordingly, the NiCrW superalloy is supposed to exhibit an excellent resistance to pitting corrosion.

Second phase if present may in some instances act detrimentally to the pitting resistance of nickel containing alloys. For example, delta ferrite in austenitic stainless steels was found to be detrimental to the pitting resistance when present in small amounts [5]. The NiCrW superalloy is a single phase material and no second phase is there at the solution annealing temperature (1180 °C), nor does any second phase form during the cooling carried out from solution annealing temperature to room temperature. Sigma and chi phases form in certain grades of stainless steels and superalloys; they have the effect of decreasing the pit initiation times and increase the weight loss due to pitting [4]. But in the NiCrW superalloy, formation of such topologically close packed phases has not been reported.

Solution treatments at high temperatures helps in dissolving second phase particles, leading to marked improvement in the pitting resistance [5]. In the present case, the material is solution annealed at a high temperature (1180 °C) and forced air cooled to room temperature, before undertaking pickling. Accordingly, $M_{23}C_6$ and M_6C type carbides are not expected to be present in the microstructure [7].

In view of the foregoing, it is totally unexpected that material suffers damage through pickling attack.

The hydrochloric acid bath used for pickling had been under heavy usage and many iron bearing materials were pickled in this bath before pickling of the final-annealed NiCrW superalloy sheets was taken up. Due to aging there was significant accumulation of dissolved salts in the bath. Since iron bearing materials were previously pickled, it is believed that ferric ion concentration had built up to a relatively high level in the bath. The presence of ferric ions has a profound effect on many metals. In particular ferric chlorides are known to attack nickel alloys [8].

The sheets were held in the hydrochloric acid bath for a very long time, more than 24 h; in all earlier instances where pickling of the NiCrW superalloy sheets could be successfully carried out, the dwell times were in the range of 2–4 h. The long duration of exposure to hydrochloric acid bath is hence believed to have contributed importantly to the debacle. It has been reported that pitting can indeed occur during pickling when the material remains in the bath for long times [2].

Pitting of corrosion-resistant alloys can indeed occur if stagnant conditions prevail [5]. In the present case, the sheets were held in the bath for a very long time without any interruption; there was no stirring/agitation of the bath during this time. There were no convection currents either, as the bath was operating at room temperature. This still/stagnant condition of the bath is believed to have contributed importantly to the observed pitting attack.

It is possible that the remnant oxides on the surface of the sheets facilitated the nucleation of the corrosion pits. *Esih* et al. [9] have demonstrated that thermal oxides facilitate the nucleation of corrosion pits on the surface of plates of grade 316L stainless steel in chloride solutions. That remnant oxides/deposits persistently present on the sheet surface played a role in causing pitting can thus not be ruled out.

4 Summary

Cold rolled and annealed sheets of a nickel-base superalloy were taken up for pickling to remove the scale/oxidized layer. The pickling resulted in heavy incidence of pitting of the sheets; perforations were observed at several locations on the sheets, with the pits penetrating through the thickness. The superalloy contains 25 wt% chromium and 15 wt% tungsten and hence is expected to have a high resistance to pitting attack. The damage caused to the sheets was thus surprising. The failure was analyzed. It appears that three factors have contributed to the superalloy sheets getting severely afflicted by pitting corrosion – (i) use of a hydrochloric acid bath heavily contaminated with oxidizing ferric chloride, (ii) excessively long dwell time of the material in the hydrochloric acid bath, and (iii) the still/stagnant condition that prevailed during the hydrochloric acid bath treatment. Remnant oxides/scale adherently present on the surface of the sheets could have facilitated the pitting reaction.

5 References

[1] R. K. Dinnappa, M. Nageswar Rao, presented at *CORCON 2005*, Chennai, India, November 28–November 30, **2005.**

[2] *Metals Handbook, 9th Edn., Vol. 5, Surface Engineering*, ASM International, Metals Park, OH **1994.**

[3] W. Z. Friend, *Corrosion of Nickel and Nickel-Base Alloys*, John Wiley & Sons, New York **1980.**

[4] *Metals Handbook, 9th Edn., Vol. 13, Corrosion*, ASM International, Metals Park, OH **1987.**

[5] A. J. Sedriks, *Corrosion of Stainless Steels*, John Wiley & Sons, New York **1996.**

[6] S. A. McCoy, L. E. Shoemaker, J. R. Crum, *Corrosion Performance and Fabricability of the New Generation of Highly*

Corrosion Resistant Nickel-Chromium-Molybdenum Alloys, a publication of Special Metals Corporation.

[7] M. J. Donachie, S. J. Donachie, *Superalloys A Technical Guide, 2nd Edn.*, ASM International, The Materials Information Society, Metals Park, OH **2002.**

[8] C. M. Schillmoler, *Alloys to resist Chlorine, Hydrogen Chloride and Hydrochloric Acid*, NiDi Technical Series No. 10020, Nickel Development Institute, Toronto **1988.**

[9] I. Esih, V. Alar, I. Juraga, *Corros. Eng. Sci. Technol.* **2005**, *40*, 110.

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