

High Temperature Corrosion Resistance of Alloy N07740 In Solar and Low Emission Ultra-Supercritical Power Generation

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ABSTRACT

Nickel superalloys are of increasing interest in new and emerging energy production applications for their high temperature mechanical properties, stability, durability and corrosion resistance. The precipitation hardenable Ni-Co-Cr superalloy N07740 has been developed for high pressure – high temperature environments and is an ASME code approved material and originally designed for fossil fuel power generation. New applications for the material include concentrated solar power receiver tubes due to its very high creep and fatigue strength in the temperature range 580 to 825C . The solar receiver tubes contain a heat transfer medium of molten salts used to transfer and store the solar energy. Solar receiver technology is also being combined with new

ultrasupercritical power cycles which have potential advantages of high efficiency and reduced demand for water in desert environments. The paper includes molten salt corrosion testing of alloys N06625, N06230 and N07740 in Nitrate salt at 600C for exposure periods up to 4000 hours. Corrosion weight loss data is presented including optical and SEM surface and analysis of cross sections. The paper also reviews corrosion data in other molten salt media and in the ultrasupercritical carbon dioxide used in high efficiency – low emission power generation systems. The development of lower cost product forms and fabrication techniques for the precipitation hardened superalloy N07740 to enable the salt containing receiver tubes and high pressure-high temperature components are also discussed.

INTRODUCTION

In recent years, solar energy technology has received particular emphasis in the interest of reducing CO₂ emissions. Concentrated solar power (CSP) technology received an initial boost from the installation of nine parabolic trough-based electricity-generating systems totaling 354 megawatts of capacity in the 1980's. Solar One, operational in 1982 and supported by the DOE and an industrial consortium, illustrate utilization of a circulating heat transfer fluid to produce steam to drive a turbine generating electricity. Solar Two in 1996 demonstrated energy storage so that solar power could be generated during the night.¹ In the ensuing decades, additional capacity has increasingly been installed worldwide, comprised primarily of both parabolic trough and central tower CSP technologies. As of 2019, global installed capacity totaled 6.2 GW, with an additional 21 GWh planned of installed thermal energy storage (TES) comprised primarily of molten salts.

Given the significant material challenges inherent to designing such a system, and the added challenge imposed by molten salt corrosion, tubing for transfer of molten salt within these systems is commonly fabricated from superalloys (N06625 and N06230 have been commonly utilized for nitrate salt systems). One recent study compared the life cycle cost of five materials (N06625, S31609, N06230, N08810 and N07740), considering the temperature dependence of tube material properties, elastic-plastic stresses/strains, and stress relaxation. The results indicated that N07740 shows the best lifetime and cost/power performance, for service in current systems employing nitrate salts for thermal energy storage.²

The high strength creep and fatigue properties of a material like N07740 expand the range of utilization for processes imposing high pressures and stress at high temperatures (as high as 825 deg. C). The alloy is allowed for ASME section I construction with code case 2702 (revision 6); a section VIII code case is also pending. A significant body of characterization work has been done for this material.^{3, 4, 5, 6}

Capitalizing upon the true potential of a material like N07740 requires consideration of systems ultimately operating at higher temperatures than the nitrate salt systems employed by current CSP technology. Recent research has explored the potential of using chloride salt systems to push TES systems to higher temperatures.^{7, 8, 9, 10} Utilization of such a salt system will likely require nickel-base alloys for corrosion resistance, but protective additives may still be required.

Heat transfer via the Alum cycle utilizing supercritical CO₂ with high-temperature, high-pressure systems has been the subject of much recent research. Corrosion behavior of a variety of alloys, including alloy N07740, has been studied by multiple laboratories illustrating that the material shows promise for service in this medium.^{12, 13, 14}

EXPERIMENTAL

Corrosion behavior of N06625, N06230 and N07740 alloys in SQM refined grade binary high temperature thermal storage nitrate salt consisting of 60 wt% NaNO_3 , 40 wt% KNO_3 , was investigated at a temperature of 600°C and durations of 1000, 2000, 3000 and 4000 hours by the University of Wisconsin Madison. EDM machined samples from seam welded 1 inch and 2-inch OD tubes of thickness 0.040" and 0.060" were exposed to the nitrate salt. A total of 2 samples of each alloy for each exposure time was conducted to allow some statistical reproducibility between samples for a total of 24 samples. The goal was to assess weight change of the samples and assess depth and scale of the corrosion on the seam weld and base metal. Additionally, salt samples were collected and the metal content in the salt was measured by ICP-MS analysis conducted at the Wisconsin state hygiene laboratory. Weight analysis was conducted on all samples after each exposure interval (1000, 2000, 3000, and 4000 hrs). Optical microscopy and SEM surface and cross-sectional analysis was conducted on one 1000-hour and one 4000-hour coupon of each alloy.

Samples were EDM cut into 0.5" wide by 0.75" long samples cut from the center portion of the tubes as shown in Figure 1. Each of the samples was then stamped with the alloy designation and the sample number to ensure proper determination of sample after testing. Samples dimensions were recorded for the thickness and surface area at several locations with a precision micrometer. The samples were then ultrasonically cleaned in acetone followed by water and ethanol and dried. The samples were then weighed on a precision Sartorius CP-14, six place balance to an accuracy of 0.002 mg a minimum of five times along with a NIST-certified 5 g sample. Each sample was photographed on the front and back side (see Figure 2) and then each of the two samples of the same alloy that would be exposed for the same time were connected with a nickel wire that was used to suspend the samples into the nitrate salt. Four sets of two samples for each of the different materials were connected to a 316 stainless steel lid that would sit on top of an alumina crucible as shown in Figure 3.

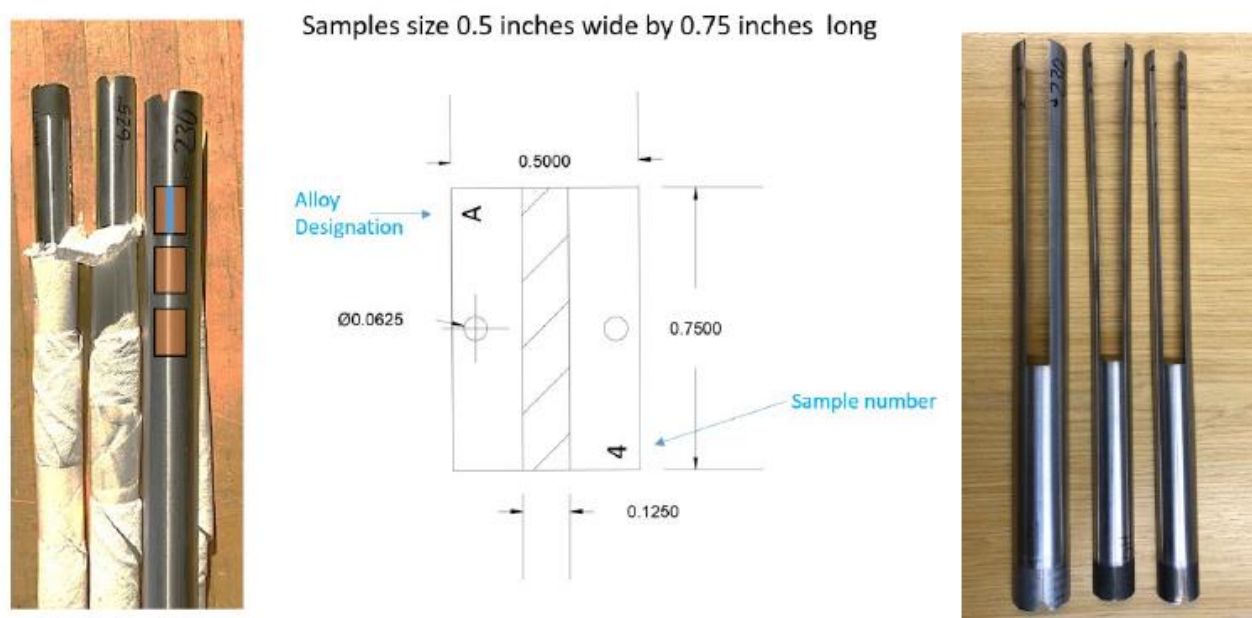


Figure 1. Schematic of samples cut from tubes with the weld located near the center of the sample. The far right image shows the raw material after EDM cutting.

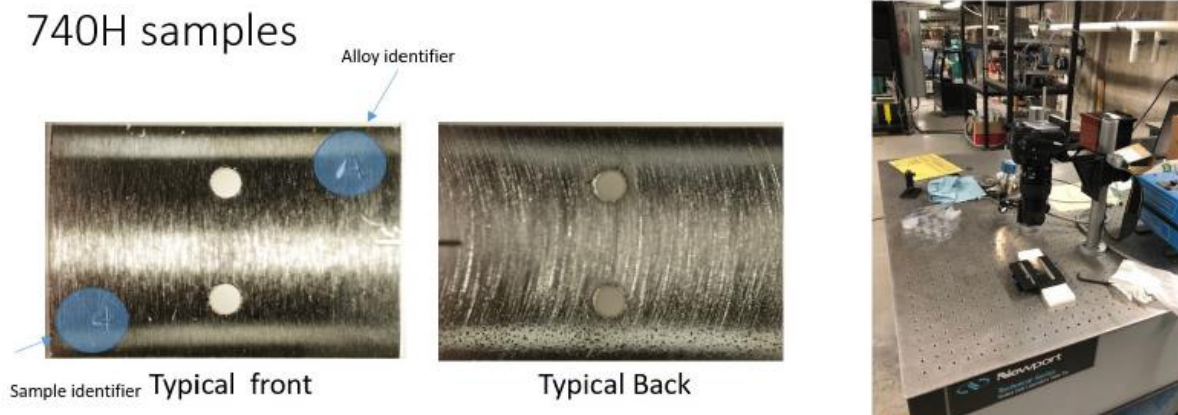


Figure 2. Example of photographs taken for each sample.

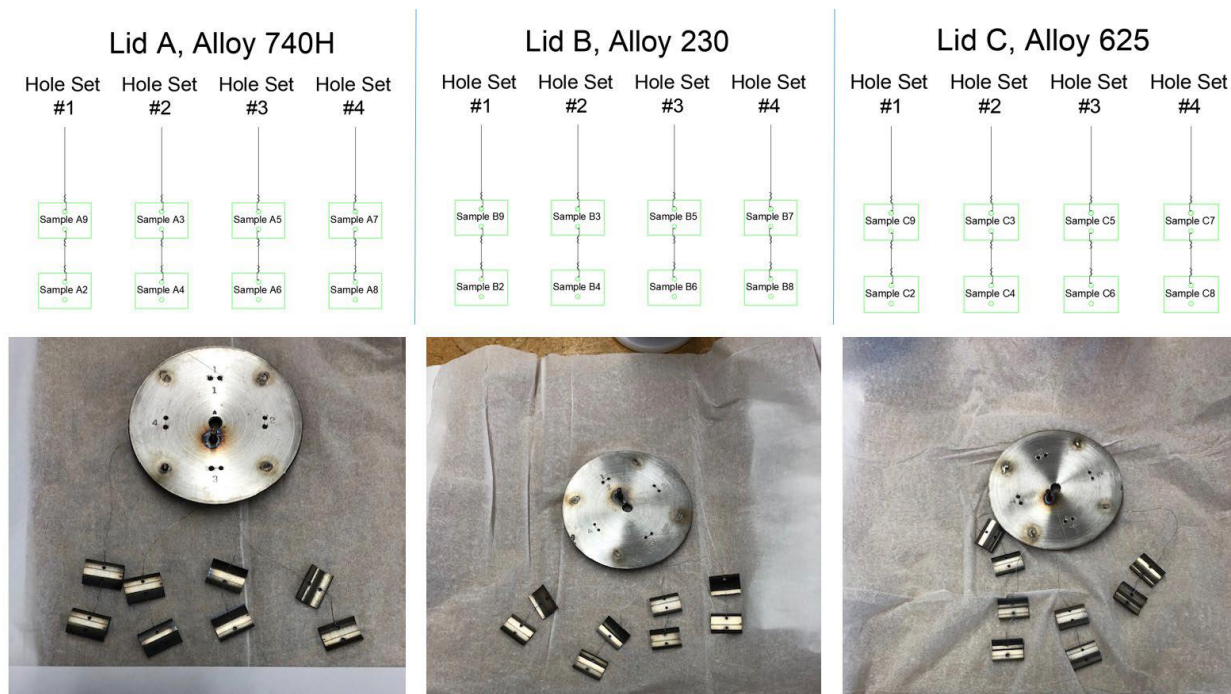


Figure 3. Four sets of two samples of each material connected to a separate lid which was placed on top of an alumina crucible filled with nitrate salt mixture. After each 1000-hour duration two of the samples were removed and the remaining sample inserted back into the salt.

The corrosion testing facility consisted of 3 independent alumina crucibles set into a 316 stainless steel container that was heated on the outside with a high temperature tape heater and controlled with a PID temperature controller. The stainless vessel that contained the alumina crucibles was insulated with a microtherm pourable insulation surrounding the vessel. Each crucible was instrumented with its own quartz

coated thermocouple to monitor the temperature of each of the crucibles independently for the PID temperature controller.

The nitrate salt mixture was made from SQM refined grade NaNO_3 and KNO_3 prills. The amount of each salt was carefully measured for each crucible such that when melted the samples would be significantly under the salt level and there was sufficient salt to take multiple samples during the course of testing. Figure 4 shows the sample arrangement in each crucible.

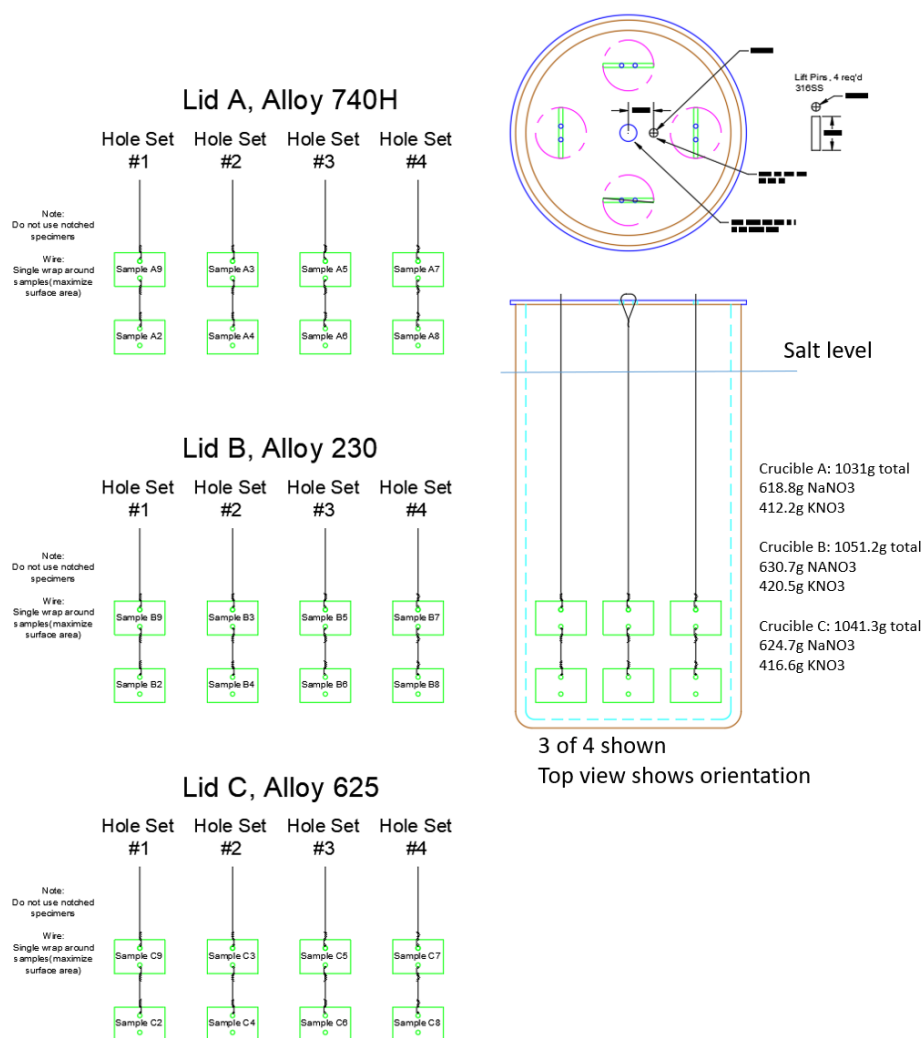


Figure 4. Layout of samples and salt fill in alumina crucibles.