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Cyclic Polarization Studies on Clad and Thermal Sprayed Ni-Base Alloys In Synthetic Geothermal Brine

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ABSTRACT

Clad and thermal sprayed Ni-base alloys may offer potential savings in material costs for brine transportation and storage systems in geothermal applications. The electrochemical behaviour of wrought, clad and thermal sprayed alloys in synthetic geothermal brine was compared. Cyclic polarization curves were measured in order to examine corrosion characteristics. Initial tests were performed at room temperature on wrought and clad Inconel 625, Incoloy 825 and Hastelloy C276 and thermal sprayed Inconel 625. Clad and wrought Hastelloy C276 had similar behavior whereas the other alloys exhibited some differences. The thermal sprayed coatings also displayed changes in corrosion behavior from the wrought material due to porosity and oxidation.

Introduction

The chemistry of many geothermal brines and elevated service temperatures dictate that unprotected carbon or low alloy steels often have relatively short service life in geothermal power plants. Components that are prone to corrosion include turbine blades, nozzles and rotors, pipelines, vessels, condensers, condenser tubes, heat exchanger tubes, valves and well casing. The chemical aggressiveness of brines is largely attributed to the high concentrations of chloride ions in addition to dissolved gases such as H_2S, CO_2, CH_4 and NH_3. Since the exact chemistry of geothermal brine is site-specific and also time dependent, different materials have different rates of success. In general, it is frequently necessary to use corrosion resistant alloys (CRAs), protective coatings or non-metallic materials. Use of these materials increases the capital, operating and maintenance costs associated with generation of electricity from geothermal resources.

Life extension of existing equipment, service life prediction and optimization of currently available materials and technologies are important in reducing operation and maintenance-related materials costs. Examples of currently available materials that have potential for more extensive use in geothermal applications are CRAs clad or thermal sprayed on carbon steel. In particular, if more information on performance data, service life prediction and life cycle cost analysis were presented, then such materials could possibly be used with greater confidence.

Clad materials are used in various industries including chemical processing, oil, electronic, and automotive. Roll and explosive bonding are the primary methods for applying clad metals. Celant and Smith (1995) discussed the potential for clad CRAs in geothermal applications. Pipelines and vessels are potential candidates for use of clad alloys. Details on the cladding process and examples of applications are given by Smith and Celant (1998). Successful performance of clad components in the oil refinery industry is presented by Dobis and Chakravarti (1997). Although a clad alloy may be compositionally the same as a wrought material, some differences in corrosion behaviour may occur as a result of heat treatment, microstructural and surface finish effects.

Thermal sprayed coatings have also been used with success in aggressive environments (e.g., Moskowitz, 1993) particularly when the process used results in a dense material. The High Velocity Oxygen Fuel (HVOF) process is a system capable of producing such coatings. In the HVOF process, powdered feedstock particles are melted in combusted oxygen and fuel gas and propelled against the substrate at very high velocities. The resultant coatings are denser and contain fewer oxides than those produced by other thermal spray techniques such as electric arc and plasma. Despite the improvements, corrosion performance of thermal sprayed coatings is expected to differ from the equivalent wrought alloy because of oxidation during the spraying process, unmelted particles and coating porosity.

Predicting the performance of a material in a geothermal environment is a challenge owing to the complex brine chemistry, elevated temperature and flow conditions. Even with realistic exposure conditions, difficulties in predicting long-term corrosion performance by extrapolating results from short-term tests are encountered. For example, alloys that rely on passive films for corrosion protection may exhibit resistance over a short period of time and then undergo rapid pitting if the film breaks down. Other time dependent processes that affect corrosion rate include repassivation after pitting or formation of protective scales. Fundamental electrochemical tests under controlled conditions can be conducted and used to elucidate such important information on corrosion behaviour.

In the research reported in this paper, cyclic polarization studies were conducted as a first step towards comparing the corrosion characteristics of wrought, clad and thermal sprayed Ni-base alloys in synthetic geothermal brine. Initially, tests were performed at room temperature to determine whether there were any significant differences in behaviour. Specifically, the pitting and protection (repassivation) potentials, extent of passivity and passive current density were of interest. The pitting potential is designated as the potential at which a steep increase in anodic current is measured after the constant current density passive region in the polarization curve. Formation of stable pits occurs at potentials more noble than the pitting potential. The protection potential is where the reverse scan on a cyclic polarization curve intersects with the forward scan. Pits grow at potentials noble to the protection potential. The more electropositive these potentials, the more corrosion resistant the material. It is recognized that the corrosion behavior will change at higher temperatures and with actual brine. The tests conducted represent basic analysis prior to evaluation under more realistic conditions.

Experimental

The wrought and clad materials tested were Inconel 625, Incoloy 825 and Hastelloy C276. The compositions of the wrought materials are given in Table 1. The thermal sprayed coating was applied to carbon steel and the feedstock powder had a composition similar to Inconel 625. The coatings were produced using the HVOF process described above and the thicknesses were 13 and 22 mils. The clad materials were supplied as roll bonded plate on carbon steel substrates. The wrought alloys had a 120 grit finish. Clad materials were cleaned in isopropanol and tested in as-received surface condition. The electrolyte used was synthetic hypersaline brine with composition given in Table 2. The pH of the brine was 4.15. No dissolved gases were used to date.

Table 1. Chemical composition of wrought alloys.

	Chemical Composition (%)		
	Inconel 625	Incoloy 825	Hastelloy C276
Al	0.13	0.10	-
C	0.015	0.01	0.002
Co	0.04	-	1.97
Cr	21.55	22.80	15.91
Cu	-	1.70	-
Fe	1.71	26.42	5.82
Mn	0.03	0.39	0.51
Mo	8.75	3.30	16.08
Nb	3.37	-	-
Ni	64.00	44.19	60.00
P	0.004	-	0.007
S	0.004	0.001	0.003
Si	0.10	0.12	0.02
Ti	0.19	0.97	-
V	-	-	0.14
W	-	-	3.54

Table 2. Composition of synthetic brine.

Component	Concentration (g/l)
NaCl	58
$CaCl_2$	25
KCl	15
$MnCl_2.4H_2O$	1.46
$SrCl_2.6H_2O$	0.72
$FeCl_2$	1.0
$ZnCl_2$	0.37
H_3BO_3	0.33
$BaCl_2.2H_2O$	0.15

Cyclic polarization curves were measured to compare the propensity for pitting corrosion. A computer controlled Versastat II potentiostat (EG&G Instruments) was used. Samples were mounted in an EG&G flat cell and had an exposed area of 1 cm^2. The reference electrode was Ag/AgCl and the counter electrode was platinum mesh. Samples were conditioned for one hour in brine and the open circuit potential was monitored. After one hour a potential 200 mV negative from the open circuit potential was applied. The potentiodynamic scan then proceeded in the positive direction at a rate of 1 mV/s until a current density of approximately 5 mA/cm^2 was reached at which point the scan was reversed. Three curves were measured for each material. Tests were performed at 21 °C and under aerated conditions as a first step in comparing the materials. It is recognized that geothermal brines are much hotter than this temperature and the effect of temperature on corrosion characteristics is part of an ongoing study.

Results and Discussion

In the interests of clarity only one curve for each tested material is reported. However, it is noted that some variability in corrosion behaviour was observed and this is consistent with the stochastic nature of localized corrosion. The selected curves are indicative of general trends. The curves tended to lack distinct "classical" features such as primary passivation, pitting and repassivation potentials owing to the high chloride content of the electrolyte. Figure 1 depicts the cyclic polarization curves for the wrought alloys in brine. Inconel 625 had the highest corrosion potential and lowest corrosion current density thereby

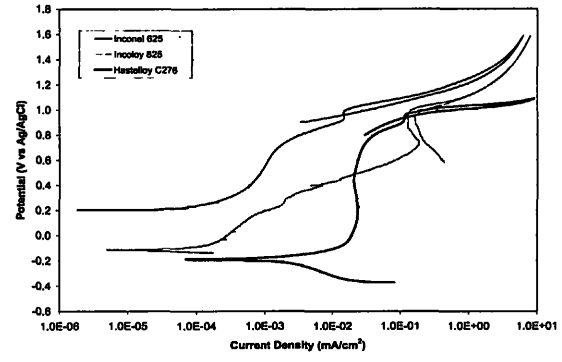

Figure 1. Cyclic polarization curves for wrought alloys.

suggesting the best corrosion resistance. However, Hastelloy C276 seems to exhibit passivity in the form of approximately constant current density between 0.10 and 0.70 V vs. Ag/AgCl. Pitting appears to commence after this region in that the current density steeply increases around 0.75 V vs. Ag/AgCl. The peaks around 0.92 to 0.95 V vs. Ag/AgCl in the Inconel 625 and Hastelloy C276 curves are probably associated with dissolution of chromium oxide film.

Wrought and clad Inconel 625 and Incoloy 825 are compared in Figures 2 and 3, respectively. In both cases the clad material had a more active corrosion potential and higher corrosion current density. The clad Incoloy 825 (Figure 3) had an apparent passive region starting at a potential around 0.3 V vs. Ag/AgCl and the spikes in the curve suggest metastable pitting activity. Wrought and clad Hastelloy C276 are compared in Figure 4. The cyclic polarization curves and pertinent features are similar. Passivity is evident with possible metastable pitting, particularly for the clad material. Also, the clad material had a lower passive current density.

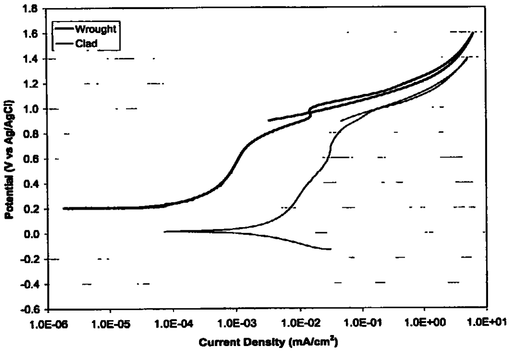

Figure 2. Cyclic polarization curves for wrought and clad Inconel 625.

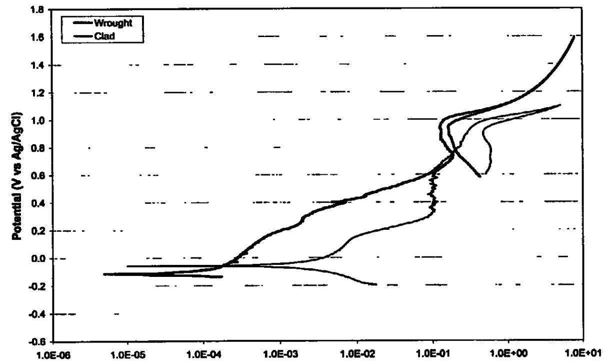

Figure 3. Cyclic polarization curves for wrought and clad Incoloy 825.

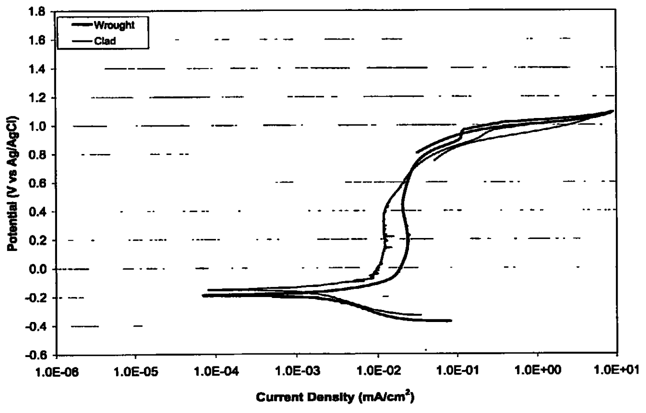

Figure 4. Cyclic polarization curves for wrought and clad Hastelloy C276.

Two of the curves obtained for the thermal sprayed Inconel 625 are shown in Figure 5. The results are similar for the 13 and 22 mil thick coatings. The thicker coating had a more noble corrosion potential. The curves suggest active corrosion behavior of the coatings and there are dissolution peaks at 0.10 to 0.12 and 0.60 V vs. Ag/AgCl. The corrosion potentials for the thermal sprayed Inconel 625 were more active than the wrought and clad material, whereas the corrosion current density was lower. Figure 6 is an example of the microstructure of the thermal sprayed coating. The porosity of the coating is evident.

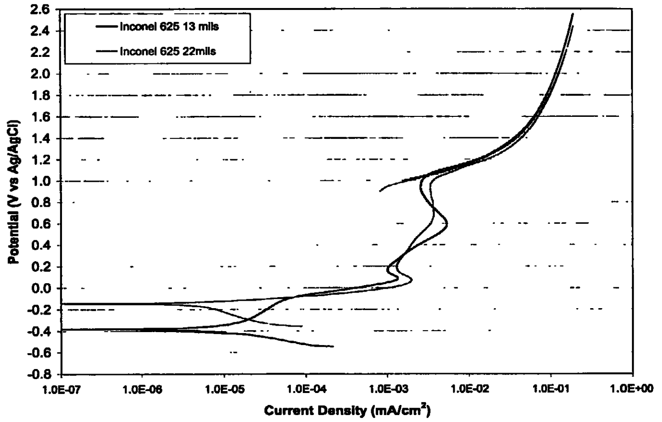

Figure 5. Cyclic polarization curves for thermal sprayed Inconel 625.

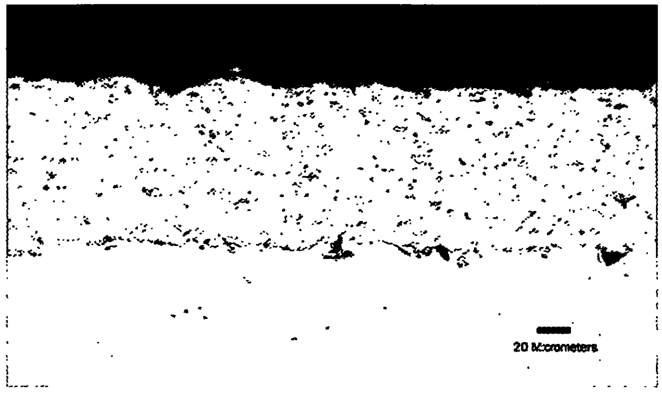

Figure 6. Microstructure of 13 mil thick thermal sprayed Inconel 625.

It is expected that pitting susceptibility of will increase with increasing brine temperature and chloride concentration. Scale formation will also play a role in corrosion phenomenon and this was not addressed. Given the limitations and simplistic nature of cyclic polarization studies, the results indicate that the wrought and clad alloys simultaneously have similarities and subtle differences in electrochemical behaviour for the temperature and synthetic brine composition tested. Of the materials tested, wrought Inconel 625 gave the best performance based on corrosion potential and corrosion current density. Clad and wrought Hastelloy C276 have very similar behavior and exhibit clear passivity. Future research will examine the corrosion resistance of clad Ni-base alloys in more realistic geothermal environments and study the role of microstructure on performance. Repassivation characteristics, stochastics of pitting, scale-corrosion interactions and in-situ performance are of particular interest. Thermal sprayed Hastelloy C276 and other Ni-base alloys will also be considered.

Conclusions

The cyclic polarization technique enabled comparison of the corrosion characteristics of wrought, clad and thermal sprayed Ni-base alloys. Initial tests were performed under ambient temperature and pressure conditions in synthetic brine as a first step in evaluation. Distinct features such as primary passivation, pitting and repassivation potentials tended to be absent in the cyclic polarization curves. Corrosion potentials, corrosion current densities and the general form of the curves were compared. Some slight differences in behaviour of clad and wrought Inconel 625 and Incoloy 825 were determined whereas the two versions of Hastelloy C276 were similar in performance. Whether the observed differences will significantly affect corrosion resistance and mechanisms under operating conditions in a geothermal system needs to be investigated further.

Acknowledgements

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