

Preliminary Study on Al₂O₃ Sol-Gel Coating for Corrosion Protection of Martensitic Stainless Steel in Artificial Geothermal Water

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ABSTRACT

Al₂O₃ coatings are often used as protective layers on steels against electrochemical and high-temperature corrosion because they are chemically inert and stable at elevated temperatures. This study presents preliminary work on the possibilities of using Al₂O₃ sol-gel coatings for corrosion protection of martensitic stainless steels in geothermal environments. Al₂O₃ sol-gel coatings were applied on UNS S42000, which is known to be susceptible to uniform and localized corrosion. The coated steel specimens were then tested in two types of artificial geothermal water, which simulate the geothermal fluids found in Sibayak (SBY), Indonesia, and North German Basin (NGB), Germany, respectively. SBY has pH 4 and 1.5 g/L of chloride ions, whereas NGB has a pH of 6 and 166 g/L of chloride ions. All experiments were carried out in autoclaves at 150 °C and 1 MPa under the deaerated condition. Evaluations were performed by investigating the surface profiles of both uncoated and coated steels before and after the corrosion test using a Laser Scanning Microscope (LSM) and Scanning Electron Microscope (SEM). Finally, Electrochemical Impedance Spectroscopy (EIS) was performed to compare the corrosion resistance of Al₂O₃ coated steels in SBY and NGB solutions. It was observed from the corrosion test that Al₂O₃ coatings are more suitable for use in geothermal water with a higher pH.

Key words: protective coating, sol-gel coating, geothermal, martensitic steel

INTRODUCTION

Geothermal energy is one of the most promising alternatives to fossil fuel due to its reliability and low CO₂ emission.¹ Despite being a prominent option in renewable energies, there are many challenges to build a durable and cost-efficient geothermal powerplant, such as corrosion and scaling. Geothermal water can be highly corrosive depending on the location and geographical history of a geothermal well. The corrosivity of geothermal water is influenced by its chemical and physical properties, such as dissolved salts and gas compositions, pH, temperature, pressure, and fluid flow.²⁻⁴ To overcome this challenge, geothermal wells should be built of corrosion-resistant materials or other lower alloyed steels coupled with corrosion protection measures, such as coatings and inhibitors.

Among developed coatings for high temperature and corrosive applications, Al₂O₃ coating is one of the most outstanding options due to its high thermal resistance, high corrosion resistance, and high wear resistance. Various methods have been used to coat Al₂O₃ on metallic materials, such as chemical vapor deposition (CVD)⁵, physical vapor deposition⁶, and sol-gel.⁷ Sol-gel coating is a versatile technique to prepare inorganic or hybrid coatings, which can be applied through different processes, such as dipping, spraying, or spinning. Al₂O₃ sol-gel coating has been proven to be successfully protective against corrosion due to the formation of a γ -Al₂O₃ layer on the metal surface via a heat treatment process.^{7, 8} Schulz et al. and Nofz et al. suggested that this type of coating is protective in high-temperature flue gas⁹ and NaCl-containing environment¹⁰, respectively. These findings further motivate another possible application, such as in a geothermal environment.

In this study, martensitic stainless steels UNS S42000 were used in the preliminary stage, including AISI 420 and AISI 420C, which have different carbon content. UNS S42000 has a wide range of applications for building different infrastructures, and it is relatively affordable among commercially available corrosion-resistant alloys for geothermal applications. However, in the geothermal environment, these steels are susceptible to localized corrosion.^{11, 12} Therefore, herein, an attempt has been made to coat Al₂O₃ on these materials to investigate the applicability of Al₂O₃ coatings in artificial geothermal water.

Based on the Pourbaix diagram of aluminum equilibrium at room temperature, aluminum is stable at a pH between 4 – 9, where a thin hydrated Al₂O₃ layer is formed and might protect the surface.¹³ However, it has been established that aluminum alloys are not recommended to be used for geothermal applications due to their susceptibility to catastrophic pitting corrosion.¹⁴ This is due to the fact that the native Al₂O₃ layer, formed as a result of an immediate reaction with air, might have defective structures. These defects can also be originated from the reaction between aluminum alloys and the environment, which results in severe pitting corrosion.¹⁵ Provided that the native Al₂O₃ layer might be stable in an aqueous medium with pH between 4 – 9 at room temperature, this preliminary study focuses on using Al₂O₃ sol-gel coating in aqueous media within the same range of pH at a higher temperature. Therefore, two representatives of acidic geothermal water were used, simulating Sibayak geothermal water (pH 4) and North German Basin (pH 6).

EXPERIMENTAL PROCEDURE

Substrate preparation

UNS S42000 was used in the preliminary stage. Their chemical compositions are described in Table 1, characterized by spark emission spectrometer (SPECTRO Analytical Instruments[†]). All testing specimens were prepared by grinding the surfaces using abrasive paper SiC from grade P120, P320, P600, to grade P1200. The ground specimens were then cleaned using bi-distilled water and ethanol thoroughly prior to the experiments. Specimens were prepared with a dimension of 27 mm x 10 mm x 5 mm. A hole with 3 mm diameter was drilled to enable the fixation of specimens in the autoclave using the PTFE band. For electrochemical tests, specimens were prepared with a dimension of 27 mm x 15 mm x 5 mm and fixed to Ni/Cr-based rods for a wiring purpose. To obtain an information about the surface roughness, surface profiles were measured for AISI 420 and AISI 420C prepared with P1200

grade SiC paper. Laser Scanning Microscope (LSM) Olympus LEXT OLS4100[†] was used to estimate the parameters of surface profiles, which was set to a magnification of 50 times.

Table 1: Chemical composition of AISI 420 and AISI 420C in wt.% using spark emission spectroscopy

Materials	Fe	Mn	Cu	C	Cr	Si	Ni	Al	S
AISI 420	85.7	0.39	0.03	0.23	12.95	0.45	0.12	0.008	0.001
AISI 420C	84.4	0.51	0.06	0.49	13.29	0.48	0.48	0.011	0.004

Materials	P	Sn	Ti	V	Mo	Co	Pb	Nb
AISI 420	0.016	0.004	0.004	0.067	0.03	0.02	0.001	<0.005
AISI 420C	0.022	0.006	0.005	0.039	0.13	0.02	0.002	0.013

Coating application

Al₂O₃ coating was applied by the sol-gel method, as described by Nofz et al.⁷ A sol was prepared by Boehmite (Sasol) stirred in ethanol at room temperature for 20 minutes. Polyvinylbutyral type PVB B76 (Butvar) was dissolved in ethanol and added as a binder. A small amount of isopropanol was also added to improve the solubility of the binder in the solution. The sol was then ultrasonicated for 5-10 minutes in a water-bath cooled with ice to achieve a good homogenization with small particle size. The final sol contained 15 wt% boehmite and 45 mg PVG per gram sol. The resulting boehmite-sol is Newtonian, with the shear rate range between 1 and 500 s⁻¹. The corresponding viscosity is 20 mPa s.

To apply the alumina coating on the substrate, the specimens were dipped into the boehmite-sol for 20 s and withdrawn with a speed of 170 mm/min to produce a homogeneous film on the surface. The specimens were then dried in an oven at 120 °C for 5 minutes. The specimens were then heat-treated by heating up the furnace from room temperature to 500 °C with a heating rate of 10 °C/minute. This heat treatment was continued by tempering the specimens inside a muffle furnace at a constant temperature of 500 °C for 2 hours to transform the sol-gel coating from boehmite sol to alumina. The furnace was then switched off to cool down the specimens.

Coating optimization

Coating thickness was optimized by varying the dipping process 1 to 3 times, followed by tempering at 600 °C. To reveal the coating performance based on the optimized parameters, short exposure tests were performed, and the adhesion of coatings was evaluated. The evaluation includes an identification of coating delamination using visual observation and LSM. The specimens with intact coatings were further tested in different types of artificial geothermal water to investigate the coating suitability and limitation in geothermal applications.

Electrolytes

Electrolytes used in the experiments were artificial geothermal waters produced in the laboratory to simulate the composition of a realistic geothermal brine found in Sibayak, Indonesia (SBY)¹⁶ and a North German Basin (NGB) geothermal brine (Table 2).

Table 2: Ions content (in g/L) of artificial geothermal water produced in a laboratory at room temperature.

Solution	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	Sr ²⁺
SBY, pH = 4	1.5	0.02	0.015	0.2	-	0.25	0.6	-	-
NGB, pH = 6	166	0.05	-	56.5	0.5	3.1	38.7	0.2	1.55

Exposure Test

Exposure tests were conducted to reveal the performance of coated and uncoated steels in the artificial geothermal water. For each experiment, three to four identical specimens were placed in a 1-L autoclave containing 500 ml of Argon-saturated artificial geothermal water. The autoclave is equipped with a glass vessel to avoid contamination. The autoclaves were kept in the climate chamber for 1, 5, or 7 days at 150 °C with a total pressure of 1 MPa. Masses of specimens were measured before and after the experiments, and the photos of surfaces were taken to evaluate the specimens visually. The surfaces of specimens were analyzed using LSM before and after the exposure tests. In addition, SEM (LEO Gemini 1530VP[†]), with an accelerating voltage of 15 kV and low vacuum pressure, was used to further analyze the morphology of corrosion products and coatings.

Electrochemical Test

Electrochemical tests were carried out at 150 °C using a standard three-electrode system connected to Gamry[†] Potentiostat. The working electrode was either the coated or uncoated AISI 420; the counter electrode was a Ti/TiO₂ mesh electrode, and the reference electrode was a specialized Ag/AgCl for high-temperature application (Cormet Oy[†], Finland). Each tested specimen was attached to a Ni/Cr-based rod for a contact purpose and fixed to the autoclave to perform an electrochemical test. A glass vessel was placed inside the autoclave to avoid contamination. For each test, 500 ml of artificial geothermal water was used and deaerated using Ar gas for at least 30 minutes. Initial Argon partial pressure of 500 kPa was used at room temperature, which resulted in a total pressure of 1 MPa at 150 °C. Electrochemical Impedance Spectroscopy (EIS) was performed after 1 hour of immersion at 150 °C. All electrochemical data were analyzed using Gamry Echem Analyst[†] to further understand the corrosion resistance of each specimen.

RESULTS

Experimental results are discussed to evaluate the optimization of coating application, the resulting coating quality and the suitability of Al₂O₃ coatings for a geothermal application.

Identification of Suitable Substrates

For a coating application, surface preparation is the most important step to remove all the loose materials on the surface, including chemically bonded oxide or scale, to provide the best adhesion between substrate and coating.¹⁷ The adhesion between coating and substrate can be achieved by mechanical, chemical, or polar interaction.¹⁷ Hence, different surface pretreatment techniques have been used to optimize the adhesion¹⁸, e.g., grinding, sand-blasting, shot peening, pre-oxidation, and phosphating. To have a smoother coating and a definite thickness, surfaces should have less roughness than the coating thickness. Based on previous research, the acquired Al₂O₃ sol-gel coating thickness after the first dipping is approximately 1 μm.¹⁹ Therefore, the goal is to choose the