Influence of gadolinium on the microstructure and mechanical properties of steel and stainless steel

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Synopsis

Iron, in the form of steel and stainless steel, is the most commonly used metal in the world. Plain steels corrode and oxidize easily, while stainless steels exhibit improved corrosion and oxidation resistance. It has been found that rare earth metal (REM) additions, such as cerium and erbium, result in the improvement of the abovementioned properties in iron-containing compounds. Gadolinium is a REM, however, there is very little information available on the influence of gadolinium on the microstructure and mechanical properties of iron-containing compounds. Thus, the purpose of this research project was to determine the influence of gadolinium additions on the microstructure and mechanical properties of mild steel and 316 stainless steel.

Ten alloys were produced for the purposes of this research. Five of the alloys had a base composition of mild steel while the remaining five had base composition of 316 stainless steel. The alloys for each of the base composition contained gadolinium additions of 0.1, 0.5, 1.2, and 5 weight per cent. The as-cast and the cold-rolled alloys were analysed. The alloys responded well to the cold-rolling with the exception of the 5 weight per cent gadolinium mild steel and stainless steel alloys. These alloys were extremely brittle and underwent a significant amount of cracking during the cold rolling process.

A microstructural analysis of the alloys was conducted using a light optical microscope, while the chemical analysis of the alloys was conducted using energy dispersive x-ray spectroscopy (EDS). The resulting microstructures and EDS analyses revealed that the gadolinium displayed minimal solubility in the ferrite matrix of the mild steel alloys and minimal solubility in the austenite matrix of the stainless steel alloys. Instead the gadolinium formed as an interdendritic secondary phase in both alloys. EDS analysis revealed that the secondary phase in both alloys was gadolinium-rich. Vickers microhardness tests conducted on both alloys revealed that the alloys were composite-like, with a hard, brittle gadolinium-containing compound dispersed throughout a softer, more ductile matrix.

The corrosion resistance of the alloys was determined through potentiodynamic anodic polarization tests. Two solutions were used for the corrosion rate tests: a 0.5 weight per cent NaCl solution and a 0.5 M H_2SO_4 solution. The results from the mild steel alloys revealed that in both the solutions, the corrosion potentials and the corrosion resistance of the alloys increased with increasing gadolinium concentration up to 1 weight per cent. The corrosion rate test results from the stainless steel alloys revealed that the passivation current density and corrosion resistance of the alloys increased with increasing gadolinium concentration in both solutions. The oxidation resistances of the mild steel and stainless steel alloys were determined through the use of a Netzstch Simultaneous Thermal Analyser. For both the mild steel and the stainless steel alloys, it was found that the oxidation resistance of the alloys increased as the concentration of gadolinium increased when compared to the as-received mild steel and stainless steel samples. This could be due to a strongly adhering gadolinium oxide scale that formed on the surface of the alloys and resulted in the protection of the mild steel and the stainless steel.

Keywords

gadolinium, steel, alloys, microstructures, mechanical properties.

Introduction and project objectives

Steels and stainless steels are the most commonly used metals currently in the world. They are favoured in a wide area of applications due to their properties such as reasonable strength, ease of fabrication, and relatively low cost. Mild steels, however, corrode in many media, including most outdoor environments. They are also very susceptible to oxidation at high temperatures. As a result a large amount of the metal is lost, which is extremely undesirable and costly. Stainless steels do not corrode or oxidize as easily as ordinary mild steels. This is due to the fact that stainless steels contain chromium, which is absent in mild steels. Chromium is an active element which oxidizes readily to form a passive film of chromium oxide over the surface of the stainless steel component. If the passive film is uniform, stable, and self-repairing, which is often the case, it is able to provide protection to the stainless steel by preventing further surface corrosion or oxidation. This ensures that the metal's internal structure retains its integrity. Thus, stainless steels are employed when both the properties of steel and resistance to corrosion and oxidation are required.

Current advances in various areas of material science have led to the discovery that the addition of rare earth metals (REM) to iron-containing compounds, such as steels and stainless steels, has certain positive effects on the mechanical properties of the metals. These include increased resistance to pitting corrosion and a decrease in the preferential interface areas for the initiation of pitting corrosion in stainless steels[1]; a finer

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microstructure with fewer inclusions on the surface of the metal along with an increase in the micro-hardness of the metal as well as a significantly increased corrosion resistance of the iron-containing metal[2]; and the formation of a fine-grained oxide which contributes to scale plasticity, thus favouring improved scale adherence resulting in the improved oxidation resistance of the iron-containing metal[3]. These advances in field of REM additions to iron-containing metals led to the initiation of this project, which entailed the alloying of gadolinium (Gd) into two iron-containing metals i.e. mild steel and 316 stainless steel.

Gadolinium is a rare earth metal and has gained popularity in the field of nuclear science as it has the highest neutron-absorbing ability of any element. The metal, in the form of solutions of organic gadolinium complexes and gadolinium compounds, is also the most commonly used intravenous MRI contrast agent in medical magnetic resonance imaging. However, in terms of materials science, very little research has been conducted in order to determine and understand the effects of gadolinium additions on the fabrication, microstructure, and resultant mechanical and physical properties of mild steels, stainless steels, and other structural materials. Thus, the purpose of this project was to investigate the influence of gadolinium additions on the microstructure and mechanical properties of mild steel and stainless steel. This report describes the preliminary results of a test programme that was designed to assess the basic characteristics of mild steel and 316 austenitic stainless steel alloyed with gadolinium. The programme included an evaluation of the primary processing behaviour, microstructure, hardness (both micro- and macrohardness), corrosion characteristics, and high-temperature oxidation behaviour of the gadolinium-alloyed mild steel and gadolinium-alloyed stainless steel.

The project objectives are therefore to determine the influence of gadolinium on the:

➤ General microstructure
➤ Hardness
➤ Corrosion resistance
➤ Oxidation resistance of mild steel and 316 stainless steel.

Should the results of this test programme prove positive, this project is intended to provide a foundation for continued development and qualification of gadolinium-alloyed mild steel and stainless steel.

Literature review

Gadolinium and its properties

The element gadolinium (Gd) is a non-radioactive, metallic rare earth element which is characterized by its lustrous silvery–white appearance and slightly yellowish tint[4] (Figure 1). Its physical properties include malleability and ductility. Malleability is defined as a material's ability to deform under compressive stress. Ductility, a similar property, is defined as a solid material's ability to deform under tensile stress; this is often categorized by the material's ability to be stretched into a wire. Gadolinium is not usually found in nature as the free element, instead it is contained in minerals such as gadolite (Figure 1), monazite, and bastnasite. It has a melting point of

1.313°C, a boiling point of 3.000°C and its density is 7.87 g/cm3. At room temperature, gadolinium crystallizes in the hexagonal, close-packed alpha form. Upon heating to 1.235°C, alpha gadolinium transforms into the beta form, which has a body-centred cubic structure.

Naturally occurring gadolinium is composed of a mixture of six stable isotopes. Two of these isotopes, 155 Gd and 157 Gd, have excellent capture characteristics, which results in gadolinium having the highest neutron, absorbing ability of any element; however, these isotopes of gadolinium are only present naturally in low concentrations. As a result, gadolinium has a very fast burnout rate and only has limited use as a control rod material for nuclear reactors[5]. Gadolinium can also be combined with yttrium to form garnets that are used in microwave technology. The metal also has unusual superconductive properties, so when alloyed with iron, chromium, and other metals it is able to improve their workability.

Iron-gadolinium phase diagram

An alloy is a substance that has metallic properties and is comprised of two or more chemical elements, one of which must be a metal[6]. In the case of gadolinium alloyed with iron, both substances are metallic elements and they are therefore able to form a binary alloy system. Alloys may be homogeneous or inhomogeneous. From the phase diagram of the binary iron-gadolinium (Fe-Gd) system (Figure 2) it can be seen that the two metals are inhomogeneous, when alloyed, as many phases exist. It can also be seen that the two metals, Fe and Gd, are completely soluble in the liquid state but exhibit minimal solubility in the solid state. The phase diagram shows that the melting point of iron is 1.538°C while that of gadolinium is slightly lower at 1.313°C. Above the liquidus line, there is only a single-phase liquid solution, below the liquidus line solidification begins. The liquidus and solidus lines meet at the melting points of the two metals, and from the solidus lines it can be seen that alloys in this system never solidify crystals of pure Fe or pure Gd, but always a solid solution or a mixture of solid solutions. Table I provides a description of the important points displayed in the Fe-Gd phase diagram.

Gadolinium-alloyed microstructures

Understanding the microstructures which are usually obtained when gadolinium is alloyed with iron-containing compounds is very important as these microstructures, when used in conjunction with the Fe-Gd phase diagram, give an
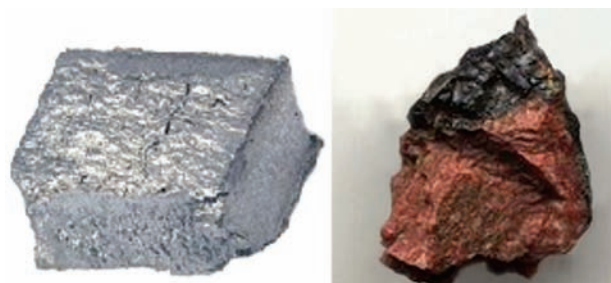

Figure 1—(a) Gadolinium metal in its pure solid state (b) The mineral gadolite[4]

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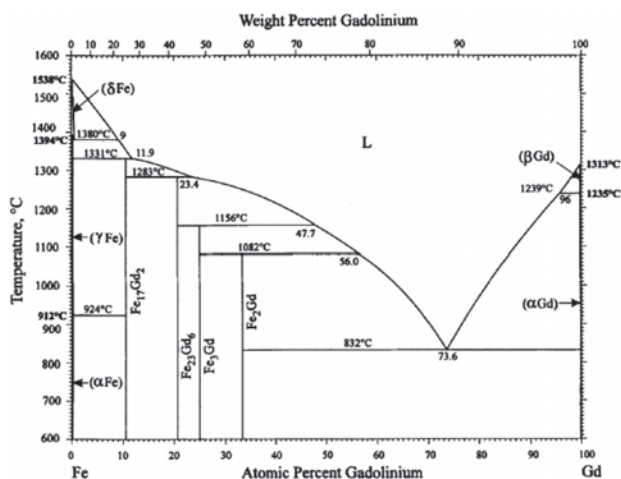
Figure 2—Fe-Gd binary phase diagram[7]

Table I

Description of important points on the Fe-Gd phase diagram[7]

Reaction	Composition (at% Fe)	Temperature (°C)	Reaction Type
$L \leftrightarrow \delta Fe$	100	1538	Melting
$\delta Fe \leftrightarrow \gamma Fe$	100	1394	Allotropic
$\gamma Fe \leftrightarrow \alpha Fe$	100	912	Allotropic
$\delta Fe \leftrightarrow L + \gamma Fe$	91	1380	Metatectic
$\gamma Fe + Fe_{17}Gd_2 \leftrightarrow \alpha Fe$	89.5	924	Peritectoid
$\beta Fe_{17}Gd_2 \leftrightarrow \alpha Fe_{17}Gd_2$	89.5	1215	Polymorphic
$L + \gamma Fe \leftrightarrow Fe_{17}Gd_2$	99.1	1331	Peritectic
$L + Fe_{17}Gd_2 \leftrightarrow Fe_{23}Gd_6$	89.5	1283	Peritectic
$L + Fe_{23}Gd_6 \leftrightarrow Fe_3Gd$	79.3	1156	Peritectic
$L + Fe_3Gd \leftrightarrow Fe_2Gd$	75	1082	Peritectic
$L \leftrightarrow Fe_{17}Gd_2 + \alpha Fe$	26.4	832	Eutectic
$L \leftrightarrow \beta Gd$	0	1313	Melting
$\beta Gd \leftrightarrow \alpha Gd$	0	1235	Allotropic

indication of which mild steel and 316 stainless steel gadolinium-alloyed microstructures can be expected. The mechanical properties of the gadolinium mild steel and stainless steel alloys will depend very strongly on these resulting microstructures and grain sizes.

In past research[8], gadolinium has also been added to boron-chromium-iron-containing compounds in order to determine the suitability of these alloys for advanced neutron absorbers for spent fuel applications. From the work done by Smolik *et al.*[8], it was found that only trace amounts of gadolinium dissolve in the matrix of the boron-chromium-iron-containing compounds, while the remainder formed as a gadolinium -rich interdendritic constituent with a preferred orientation dispersed throughout a matrix (Figure 3). It was also found that the amount of interdendritic constituent increased with increasing gadolinium concentration.

Experimental procedure

The test programme followed during this project was designed to determine the basic characteristics of

gadolinium-alloyed mild steel and gadolinium-alloyed 316 stainless steel. This programme included alloy fabrication, microstructural analysis, hardness testing, corrosion rate testing, and high-temperature oxidation rate testing. The duration of the test programme was 6 weeks.

Alloy fabrication

For the purposes of this project ten alloys were required. Five of the alloys were to have a base composition of mild steel while the remaining five alloys were to have a base composition of 316 stainless steel. Commercial sheet and plate stocks of sizes 30 cm x 30 cm, of both mild steel and 316 stainless steel, were provided. The gadolinium used was supplied by Aldrich Chemistry in the form of gadolinium chips which had a 99.9% metal basis. The target alloy compositions weight per cent for both the mild steel/Gd and 316 stainless steel/ Gd alloys, are provided in Table II. These samples were then taken to the Mintek laboratories, where they were alloyed in an argon-evacuated button arc furnace. Portions of the ten as-cast alloys were then cut off using an abrasive cut-off wheel. These as-cast samples underwent microstructural analysis and hardness testing. The remaining sections of the alloys were then cold-rolled down to 25% of the original thickness (2 cm) of the alloy. Rolled samples were then cut and these samples were used for microstructural analysis, hardness testing, corrosion rate testing, and high-temperature oxidation rate testing.

Microstructural and chemical analysis

The microstructural analysis of the alloys was conducted through the use of a light optical microscope, while the chemical analysis was performed using a JEOL JSM- 5800LV scanning electron microscope using energy-dispersive X-ray
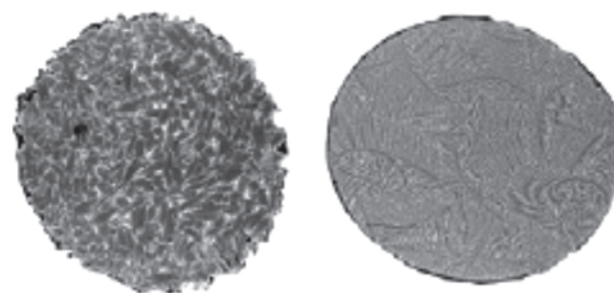

Figure 3—Microstructures of boron-chromium-iron containing compounds alloyed with (A)1 & (B)8 wt% Gd Smolik *etal.*[8]

Table II

Target mild steel and stainless steel alloy compositions (wt%)

Metal	C	Mn	P	S	Gd
Reference mild steel	0.37	0.60	0.04	0.045	0
Gd/mild steel alloy	0.37	0.60	0.04	0.045	0.1, 0.5, 1, 2, 5
Metal	**C**	**Mo**	**Ni**	**Cr**	**Gd**
Reference 316 SS	0.08	2.5	12	17	0
Gd/ SS alloy	0.08	2.5	12	17	0.1, 0.5, 1, 2, 5

spectroscopy (EDS). These analyses were conducted in order to determine the general microstructure and chemical composition of the alloys respectively. The as-cast alloys and a sample from each of the cold-rolled alloys were hot-mounted using a clear Clarofast resin and an Opal 410 mounting press. The rolled and as-cast hot-mounted alloys were manually ground using 80pp grit paper prior to being placed in the automatic grinder and polisher which ground the alloys using 220, 600, and 1200 pp plates and polished the samples using 3 μm and 1 μm plates. The mild steel alloys were etched by suspending them in Nital (3 volume per cent nitric acid (HNO₃) and 97 volume per cent ethanol) for 5 seconds. The 316 stainless steel alloys were electrolytically etched using an etchant which consisted of 40 volume per cent nitric acid and 60 volume per cent distilled water, for 8 seconds. An accelerating voltage of 20 kV was used for the EDS analyses. The K X-ray lines were used to analyse for Fe, Ni, Cr, Mn, and Si, while the L lines were used for Gd and Mo during the EDS analyses.

Hardness tests

The microhardness of the samples was determined using a FM-700 Vickers microhardness tester with a load of 300 grams-force applied for 10 seconds. Five indentations were made across the surfaces of the samples to determine whether each phase in the microstructure of the alloys displayed a different hardness. The macrohardness tests were performed using a Leco V-100-A2 Vickers hardness tester with a load of 5 kg which indented the samples for 8 seconds. The hardness measurement obtained was an average of at least 5 indentations.

Corrosion rate tests

The corrosion rate test work was conducted on all the rolled alloys except the 5 weight per cent gadolinium alloys, as these alloys underwent significant cracking during the cold-rolling process, which rendered them unsuitable for the corrosion tests. A potentiodynamic anodic polarization test was performed on the remaining alloys using a Nova Potentiostat. The alloys were individually connected to plastic-insulated copper wire using aluminium tape and were then cold-mounted. The potentiodynamic anodic polarization tests were conducted at constant temperature (25°C) at varying pH values. Thus two solutions with two different pH values were required. The first solution used was a 0.5 weight per cent sodium chloride (NaCl) solution with a pH of 7.25, and the second solution was a 0.5 M sulphuric acid (H₂SO₄) solution with a pH of 0.85. The reference electrode that was used was an Ag/AgCl electrode submerged in a 3 M KCl solution, while the counter-electrode used was made of graphite.

High-temperature oxidation rate tests

The high-temperature oxidation rate (HTOR) tests were conducted in order to determine the oxidation resistance of the mild steel and stainless steel alloys. For the purposes of this test 10–15 mg of the rolled alloys were cut, placed in alumina crucibles, and tested. HTOR tests were carried out through the use of a Netzsch STA 429 CD Simultaneous Thermal Analyser (STA). The STA was able to conduct a

thermal gravimetric analysis (TGA) of the alloys. TGA measures the mass loss/mass gained by the samples as a function of temperature. The reference crucible in each of these tests ran empty, and the settings used for each test are provided in Table III. Due to the time required to conduct each test, it was decided that only samples of the 0.5 per cent and 2 per cent gadolinium mild steel and 316 stainless steels alloys, as well as control samples of the as-received mild steel and 316 stainless steels, would undergo the HTOR tests.

Experimental results and discussion

Microstructural and chemical analysis

Gadolinium mild steel alloys

Energy dispersive X-ray spectroscopy (EDS) allows one to determine the overall composition of an alloy as well as conduct chemical analysis on localized regions within an alloy. Thus, EDS analyses were conducted on the mild steel alloys using an average of 5 points. From the EDS analysis of the mild steel alloys, provided in Table IV, it can be seen that the overall composition of most of the mild steel alloys differed slightly from that of the target alloy gadolinium compositions. Many factors may have caused these discrepancies, one of which may have been that the magnification used during the EDS analysis was too high and therefore the points selected were not representative of the whole alloy. Another factor may have been that segregation may have occurred in the alloys, since the alloys underwent no subsequent heat treatment and the regions in which gadolinium was not very rich could have been selected during the EDS analysis, and thus the discrepancies seen were actually indications of segregation. The final factor may be that an average of only 5 points were selected during the EDS analysis, which may have been insufficient. Usually 5–10 points should be selected when conducting an overall EDS analysis of an alloy, as this will ensure that the composition obtained is as representative of the alloy as possible.

The microstructures obtained for the 5 weight per cent gadolinium mild steel alloy are shown in Figure 4. All of the mild steel alloys microstructures were found to display a similar microstructure to that of the 5 weight per cent gadolinium mild steel alloy. These microstructures consisted of a light matrix and a darker interdendritic constituent deposited at the grain boundaries of the matrix within each of the alloys. The interdendritic constituent in each of the mild steel alloys, however, was found to increase as the concentration of gadolinium increased. Upon comparison of the gadolinium mild steel alloys microstructures, it could be seen

Table III

Thermogravimetric analysis temperature settings

Parameter	Value
Starting temperature	20°C
End temperature	1200°C
Heat rate	10 K/min (Kelvin)
Acquisition rate	10 points/min

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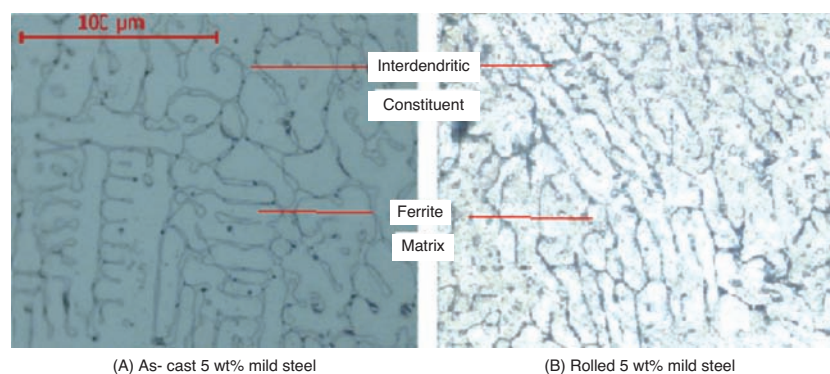(A) As- cast 5 wt% mild steel   (B) Rolled 5 wt% mild steel

Figure 4—Photomicrographs (500x) of the as-cast and rolled 5 wt% gadolinium-alloyed mild steel

that the grain sizes varied throughout the microstructures, with small grains dispersed throughout large grains. A grain-refining effect was also observed as the concentration of gadolinium increased in the alloys. Thus, the grains within the 5 weight per cent alloy were much finer and more uniform in size in comparison to that of the lower concentration gadolinium mild steel alloys.

Examinations of the Fe-Gd phase diagram indicated that the solubility of gadolinium in iron is minimal, and therefore Gd-rich compounds were expected to form. The EDS analysis of the interdendritic constituent within the mild steel alloys, shown in Figure 5, revealed that the darker interdendritic constituent (region 1) was found to be gadolinium-rich with a maximum gadolinium concentration of 27.1 weight per cent recorded for the interdendritic constituents within the 5 weight per cent mild steel alloy (Figure 5). The dispersion of the gadolinium phase, however, was not uniform; instead, it was sparsely distributed throughout the alloys. The matrix in each of the alloys (region 2, Figure 5), contained no dissolved gadolinium, but it had a composition similar to that of ferrite.

Gadolinium stainless steel alloys

EDS analyses were conducted on the stainless steel alloys using an average of 5 points. From this the overall composition of the stainless steel alloys could be determined (Table V). From the EDS analysis it could be seen that the overall composition of all the alloys differed from that of the target alloy gadolinium compositions. The same factors discussed for the mild steel alloys previously may have caused these discrepancies observed. Further EDS analysis of each stainless steel alloy (Figure 6) showed that the gadolinium did not disperse uniformly throughout the stainless steel alloys. Instead, the gadolinium partitioned to certain regions throughout the alloys (region 2 and 3, Figure 6), forming as an interdendritic constituent throughout the matrix of the alloys (region 1, Figure 6). These interdentric constituents were found by the EDS analyses to be gadolinium-rich. From the regions of the matrix (region 1, Figure 6) selected during the EDS analyses, it was found that the matrix of the stainless steel alloys contained no dissolved gadolinium, but had a composition similar to that of austenite. This is to be expected when alloying elements with minimal solubility in iron are added to 316 stainless steel.

Table IV

EDS analysis showing overall composition of the mild steel alloys (wt %)

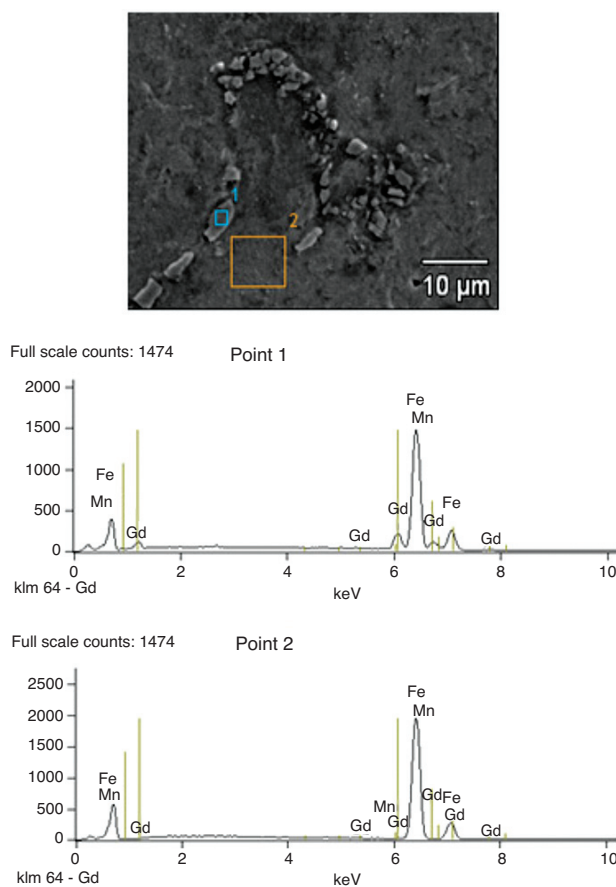| Alloy	C	Mn	Gd
0.1 Gd/steel	0.3	0.2	0.1
0.5 Gd/steel	0.3	0.6	0.4
1 Gd/steel	0.2	0.2	0.9
2 Gd/steel	0.4	0.1	1.6
5 Gd/steel	0.4	0.5	3

Figure 5—EDS analysis of the two phases within the 1 wt% gadolinium mild steel alloy

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The microstructures obtained for the 5 weight per cent gadolinium stainless steel alloy are shown in Figure 7. All of the stainless steel alloys microstructures were found to display a similar microstructure to that of the 5 weight per cent gadolinium stainless steel alloy. The interdendritic gadolinium-rich constituents were seen to be deposited at the grain boundaries of the stainless steel alloys, and the amount of interdendritic constituent was found to increase as the concentration of gadolinium increased in each of the alloys. The partitioning of the gadolinium in the alloys could be caused by the segregation during cooling of the as-cast stainless steel alloys after they had been formed in the button arc furnace. However, the partitioning should be expected, irrespective of segregation which may have taken place, as gadolinium displays only minimal solubility in iron according to the Fe-Gd phase diagram.

Hardness tests

Gadolinium mild steel alloys

The microhardness tests conducted across the surfaces of both the as-cast and the rolled mild steel alloys revealed a range of hardness throughout the surface of the alloys. Thus, it was clear that the two constituents within the microstructure of the alloy displayed different hardnesses. Due to the fact that a greater amount of the interdendritic constituent was deposited at the grain boundaries of the 5 weight per cent mild steel alloy, the hardness of both the matrix and the interdendritic constituent could be determined. The hardness of each phase, taken as an average

of five points for each phase, is provided in Table VI. From these results in can be seen that the mild steel alloys were composite-like, with a hard interdendritic constituent dispersed throughout a soft, ductile ferritic matrix.

The bulk hardnesses of the as-cast and rolled gadolinium mild steel alloys are represented in Figure 8. It can be seen that the as-cast 0.1, 0.5, 2, and 5 weight per cent gadolinium-alloyed mild steel samples all had a bulk hardness above that of the as-received mild steel sample (zero weight per cent gadolinium). The as-cast 1 weight per cent gadolinium mild steel alloy, however, had a bulk hardness considerably lower than that of the as-received mild

Figure 6—EDS analysis of the two phases within the 5 wt% gadolinium stainless steel alloy

Table V

EDS analysis showing overall composition of the stainless steel alloys (wt %)

Alloy	C	Cr	Ni	Mo	Gd
0.1 Gd/SS	1.7	21.2	10.3	2.1	0.2
0.5 Gd/SS	3.8	15.8	9.2	1.2	0.3
1 Gd/SS	4.0	16.2	9.5	1.6	0.8
2 Gd/SS	2.0	15.6	8.6	1.6	1.5
5 Gd/SS	1.1	20.1	10.0	2.3	3.6

Interdendritic Constituent

Austenite Matrix

(A) As-Cast 5 wt% Gd-316 SS

(B) Rolled 5 wt% Gd-316 SS

Figure 7—Photomicrographs of the rolled and As-cast 5 wt% gadolinium stainless steel alloy

steel. The bulk hardness values of the rolled gadolinium mild steel alloys were all higher than that of the as-received mild steel. Another feature of Figure 8 is the fact that the bulk hardnesses of the rolled gadolinium mild steel alloys were all significantly higher than that of the as-cast gadolinium mild steel alloys. This was due to the cold working that took place during the rolling process, which resulted in the deformation of the mild steel alloys below their recrystallization temperature.

A consequence of the cold-working process was a strain-hardening effect. This caused the number of dislocations in the alloys to increase, which in turn resulted in the strengthening of the alloys i.e. increased hardness, while the shape of the alloys was changed. It was found, however, that the concentration of Gd did not have an influence of the amount of strain hardening that took place. From the hardness trends displayed in Figure 8, it could be seen that the as-cast and rolled alloys exhibited the same trends except for the rolled 5 weight per cent gadolinium mild steel alloy. This deviation from the trend was attributed to the cracks that occurred on the surface of the rolled alloy during the indentation process. From the work done by Quinn *et al.*[9], it was found that cracked surfaces affect the hardness values obtained as indentations made on a cracked surface are larger than indentations made on an uncracked surface. Thus, it can be assumed that the cracks on the 5 weight per cent mild steel alloy influenced the hardness values obtained after each indentation, as the cracks caused the diagonals of the indentations to be slightly larger than they would be on an uncracked surface. These larger indentations therefore resulted in lower hardness measurements obtained for the 5 weight per cent gadolinium mild steel alloys.

The reasons for the hardness trends observed for the as-cast and rolled mild steel alloys were investigated. A possible cause for the increased hardness of the 0.1 weight per cent mild steel alloy could be solid-solution strengthening. However, from the Fe-Gd phase diagram it can be seen that the solubility of gadolinium in iron is minimal. Due to the low concentration of gadolinium in the 0.1 weight per cent mild steel alloy, it was possible for a small amount of the gadolinium to dissolve into the ferrite matrix at some regions in the alloy. This could have resulted in solid-solution strengthening of the matrix. If the solubility of a material is exceeded by adding too much alloying element a second phase forms. This was the case with all the mild steel alloys, as the solubility of gadolinium in iron was extremely low. The increase in the amount of the second phase which formed resulted in the increased hardness values observed for the 2 and 5 weight per cent mild steel alloys.

The boundaries between the two phases present in the alloys is known as an interphase interface. At this interface the atomic arrangement was not perfect. Thus, the boundary and atomic arrangements interfered with slip/movement of the dislocations. This resulted in the increased hardness, and is known as dispersion strengthening. The higher hardness of the 5 weight per cent mild steel alloy compared to the 2 weight per cent alloy was due to the fact that the 5 weight per cent mild steel alloy formed more of the second phase. The increased hardness of the 2 and 5 weight per cent mild steel alloys, compared to the other mild steel alloys, could also be attributed to the more refined grains that were observed in these alloys. A more refined grain structure will result in improved mechanical properties, one of them being increased hardness.

Gadolinium stainless steel alloys

Microhardness tests were conducted across the surface of both the rolled and the as-cast stainless steel alloys revealed that the different phases within the alloys exhibit different hardness values, with one phase being considerably harder than the other. Due to the fact that a greater amount of the interdendritic constituent was deposited at the grain boundaries of the 5 weight per cent stainless steel alloy, the hardness of both the matrix and the interdendritic constituent could be determined. The hardness of each phase, taken as an average of five points for each phase, is provided in Table VII. From these results it can be seen that the stainless steel alloys consisted of a hard, brittle gadolinium phase dispersed throughout a relatively soft, ductile austenitic matrix. Another observation was the expected fact that the microhardness of the rolled alloys was much greater than that of the as-cast alloys. This was due to strain-hardening caused during the cold-rolling process.

The bulk hardness values of the as-cast and rolled gadolinium stainless steel alloys are represented in Figure 9. It can be seen that the as-cast 0.5, 1, and 5 weight per cent gadolinium stainless steel alloys all had hardness values above that of the reference as-received stainless steel sample. The as-cast 0.1 and the 2 weight per cent gadolinium stainless steel alloys, however, exhibited hardness values below that of the as-received stainless steel. The hardness values of the rolled gadolinium stainless steels alloys were all

Table VI

Microhardness of the as-cast and rolled 5 wt% gadolinium mild steel alloy

Phase	As-cast 5 wt % mild steel (HV)	Rolled 5 wt % mild steel (HV)
Interdendritic constituent	159.7	401.5
Matrix	119.4	263.05

Figure 8—Macrohardness of the as-cast and rolled gadolinium mild steel alloys

significantly greater than that of the as-received stainless steel and the as-cast stainless steel alloys due to the strain hardening that took place. However, once again the concentration of gadolinium did not influence the amount of strain-hardening. The rolled stainless steel alloys were found to display the same hardness trend as the as-cast stainless steel alloys.

From the results in Figure 9 it can be seen that the rolled stainless steel alloys displayed an increasing trend in hardness for the 0.1 to 1 weight per cent gadolinium stainless steel rolled alloys, while the bulk hardness of the 2 weight per cent gadolinium stainless steel alloy once again decreased. The only discrepancy between the trends of the as-cast and rolled hardness values of the stainless steel alloys was the bulk hardness of the rolled 5 weight per cent stainless steel alloy, which was much lower than to be expected. This discrepancy was attributed to the cracks that formed on the surface of the alloy during the indentation process, which resulted in an inaccurately low hardness being obtained. The reasons for the hardness trends observed for the as-cast and rolled stainless steel alloys were investigated, and were found to be the same as those mention for the gadolinium mild steel alloys as discussed earlier.

Corrosion rate tests

Gadolinium mild steel alloys

The corrosion rate of the as-received mild steel in the 0.5 weight per cent sodium chloride solution was 0.151 mm/a as shown in Figure 10. This was much higher than the corrosion rates of the 0.1 to 1 weight per cent gadolinium mild steel alloys. From the corrosion rates test results it was found that the corrosion rates decreased as the concentration of Gd increased up to 1 weight per cent, as seen in Figure 10. From Figure 10, it can also be seen that the 2 weight per cent mild steel alloy exhibited the highest corrosion rate when compared to the other mild steel alloys, and an even higher corrosion rate than that of the as-received mild steel. The corrosion rate of the 2 weight per cent mild steel alloy was 0.185 mm/a which was 18 per cent greater than that of the as-received mild steel. From the anodic polarization curves of the alloys it was found that the corrosion potential of the mild steel alloys increased as the concentration of gadolinium increased up to 1 weight per cent when compared to the as-received mild steel, as shown in Figure 11. The polarization curve of the 2 weight per cent mild steel alloy revealed that the corrosion potential of that alloy was the lowest compared to the other mild steel alloys as well as the as-received mild steel. A more positive corrosion potential causes a metal to be more thermodynamically stable, thereby resulting in improved corrosion resistance

The corrosion rate of the as-received mild steel in the 0.5 M sulphuric acid solution was 11.80 mm/a. This was much higher than that of the 0.1 to 2 weight per cent gadolinium mild steel alloys. From Figure 12 it can be seen that the corrosion rate of the gadolinium mild steel alloys decreased as the concentration of gadolinium increased up to 1 weight per cent. Upon increasing the gadolinium concentration to 2 weight per cent, the corrosion rate increased. However, the rate of corrosion of the 2 weight per cent alloy

was still lower than that of the as-received mild steel sample. The polarization curves shown in Figure 13 illustrate the fact that the mild steel alloys all displayed the same anodic polarization trend as that of the as-received mild steel sample when tested in the sulphuric acid solution. The differences in the polarization curves indicate the corrosion potentials of each of the mild steel alloys and the as-received mild steel. On comparison of the corrosion potentials it can be seen that the corrosion potentials of the gadolinium mild steel alloys were not much greater than that of the as-received mild steel. However, it is clear that as the concentration of gadolinium increased (up to 1 wt%) the corrosion potential of the mild steel alloys increased slightly. The 2 weight per cent mild steel alloy, however, exhibited the lowest corrosion potential of all the alloys and the as-received mild steel in the sulphuric acid solution.

Table VII

Microhardness of the as-cast and rolled 5 wt% gadolinium stainless steel alloy

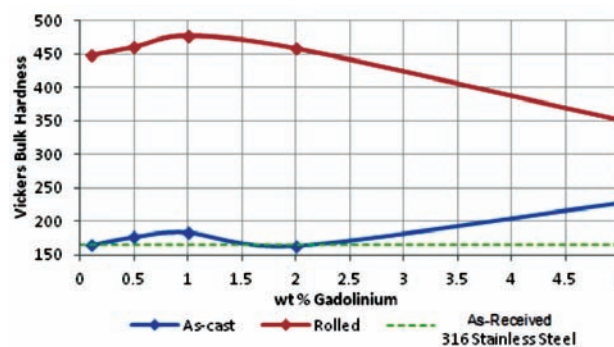| Phase	As-cast 5 wt % mild steel (HV)	Rolled 5 wt % mild steel (HV)
Interdendritic constituent	158	205
Matrix	132	182

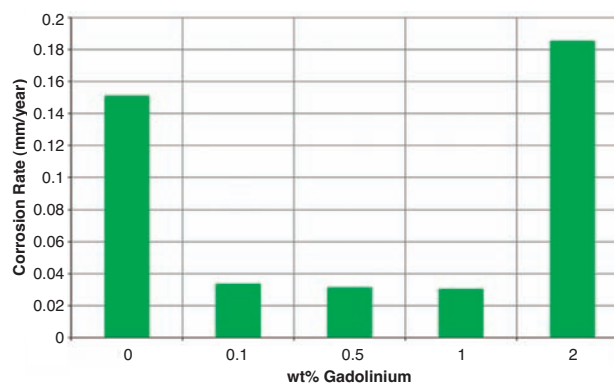Figure 9—Macrohardness of the as-cast and rolled gadolinium stainless steel alloys

Figure 10—Corrosion rate of gadolinium mild steel alloys in 0.5 wt% NaCl solution

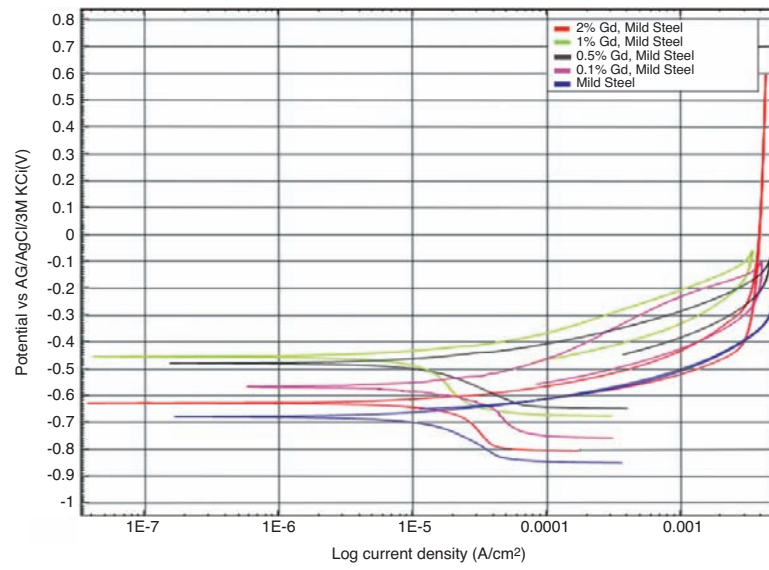# Influence of gadolinium on the microstructure and mechanical properties of steel

Figure 11—Comparison of polarization curves obtained for the gadolinium mild steel alloys in 0.5 wt% NaCl solution
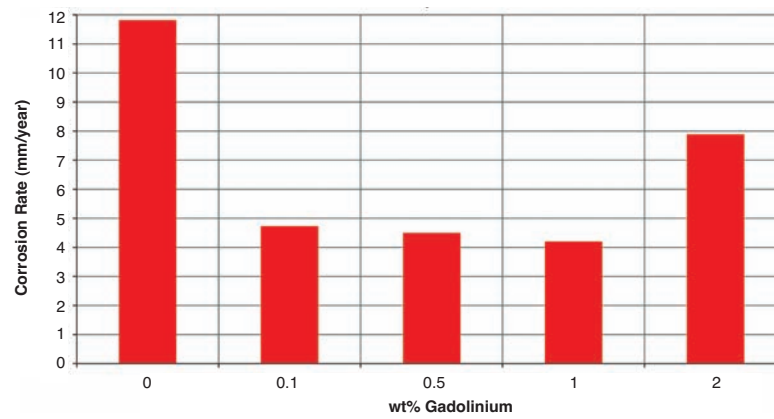

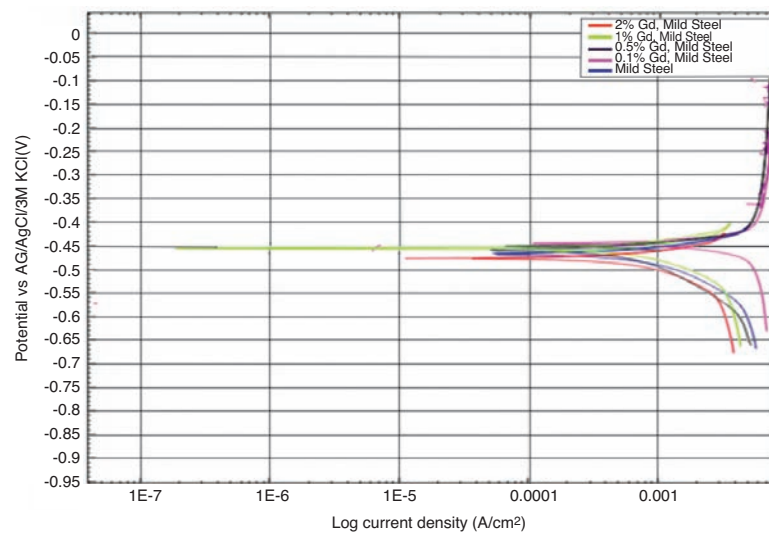**Figure 12—Corrosion rate of gadolinium mild steel alloys in 0.5 M H_2SO_4 solution**

Figure 13—Comparison of polarization curves obtained for the gadolinium mild steel alloys in 0.5 M H_2SO_4 solution

Influence of gadolinium on the microstructure and mechanical properties of steel

Thus, it was clear that a gadolinium addition of up to 1 weight per cent had a positive effect on the corrosion potential of the mild steel alloys in both solutions, while a gadolinium addition of up to 2 weight per cent had a negative effect, and therefore adversely affected the corrosion resistance. The decreased corrosion potential and increased corrosion rate of the 2 weight per cent mild steel alloy led to the assumption that a gadolinium addition threshold exists between 1 and 2 weight per cent. This threshold, once exceeded, would result in the gadolinium causing deleterious properties in the mild steel, such as decreased corrosion resistance. These adverse results could be due to the excess gadolinium, which may have caused graphite to form from the carbon present in the mild steel.

Graphitization results in deleterious properties in steel. It is for this reason that alloying elements are usually added in very small proportions to mild steel in order to prevent the onset of graphite formation. Further test work is required in order to determine the gadolinium addition threshold in mild steels, and whether above this gadolinium threshold the gadolinium behaves as a graphite-forming element. From the polarization curves shown in Figure 13 it is clear that the mild steel alloys did not undergo passivation, thus the cause of the increased corrosion resistance in displayed by the mild steel alloys up to 1 weight per cent was attributed to the increased corrosion potentials obtained with increasing gadolinium concentrations in both solutions. These increased corrosion potentials increased the thermodynamic stability of the alloys.

Gadolinium stainless steel alloys

The corrosion rates for each stainless steel alloy in the 0.5 weight per cent sodium chloride solution are represented in Figure 14. It can be seen that the corrosion rate of the as-received stainless steel in the sodium chloride solution was 0.00054 mm/a. It can also be seen that the corrosion rates of the stainless steel alloys decreased as the gadolinium concentration increased from 0.1 weight per cent to 2 weight per cent gadolinium, with a much lower corrosion rate being observed at 2 weight per cent compared to the as-received stainless steel. Similar corrosion rate results were found for the gadolinium stainless steel alloys in the 0.5 M sulphuric acid solution, as shown in Figure 15. It can be seen that the corrosion rate of the as-received stainless steel in the sulphuric acid solution was 0.042 mm/a, which is higher than that of the 0.1 to 2 weight per cent stainless steel alloys.

The polarization curves for the stainless steel alloys in both solutions (Figure 16 and Figure 17) indicate that all the stainless steel alloys exhibited a lower passivation current density than that of the as-received stainless steel in the sodium chloride solution. The significance of a lower passivation current density is that the alloys were able to passivate at a lower current density than the stainless steel. Therefore, they were able to form a protective layer much sooner than un-alloyed 316 stainless steel. The results also show that the gadolinium stainless steel alloys exhibited a higher corrosion potential than that of the as-received stainless steel when tested in both solutions. All the stainless steel alloys displayed increasing corrosion potentials with

increasing gadolinium concentration i.e. from 0.1 to 2 weight per cent gadolinium. These results show that increasing the gadolinium concentration in the stainless steel alloys resulted in an increase in the corrosion potential of the alloy. At higher corrosion potentials a metal is said to be more thermodynamically stable. Thus, the gadolinium additions caused the stainless steel to be more thermodynamically stable, and this stability increased with increasing gadolinium concentration.

Similarly it was shown that the corrosion rates of all the alloys decreased as the concentration of gadolinium increased. Increasing gadolinium additions result in passivation of the stainless steel, and this is the cause of the increased corrosion resistance. This could be due to a layer of gadolinium oxide which may have formed on the surface of the alloys. The passive layer is assumed to be gadolinium oxide, as gadolinium oxide has the most negative enthalpy of formation when compared to all the oxides that could form in the stainless steel alloys, including chromium oxide. Gadolinium is therefore the most active element and the most likely to oxidize first. Since the corrosion rate of the as-received stainless steel was higher than that of all the stainless steel alloys, this suggest that gadolinium oxide, or a combination of gadolinium and chromium oxide, is more effective in protecting the stainless steel from corrosion than the chromium oxide layer that formed on the as-received stainless steel. Another conclusion that could be drawn from the sodium chloride corrosion rate tests on the stainless steel
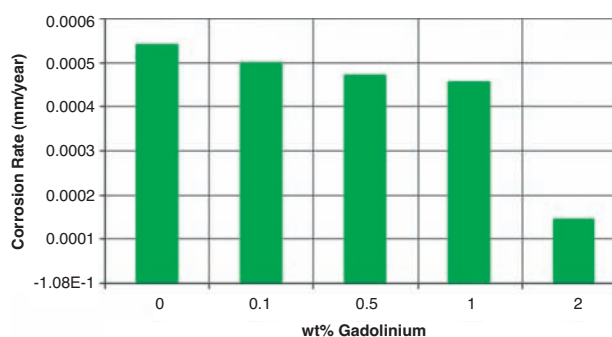

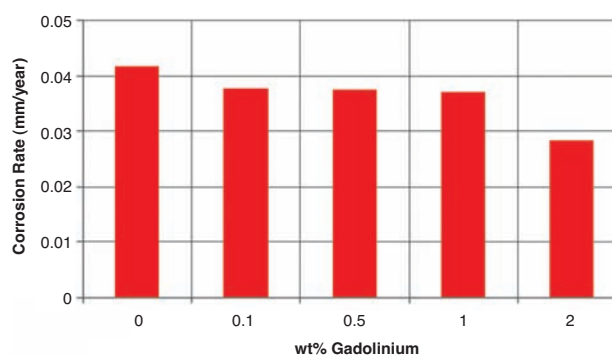Figure 14—Corrosion rate of gadolinium stainless steel alloys in 0.5 wt% NaCl solution

Figure 15—Corrosion rate of gadolinium stainless steel alloys in 0.5 M H$_2$SO$_4$ solution

Influence of gadolinium on the microstructure and mechanical properties of steel
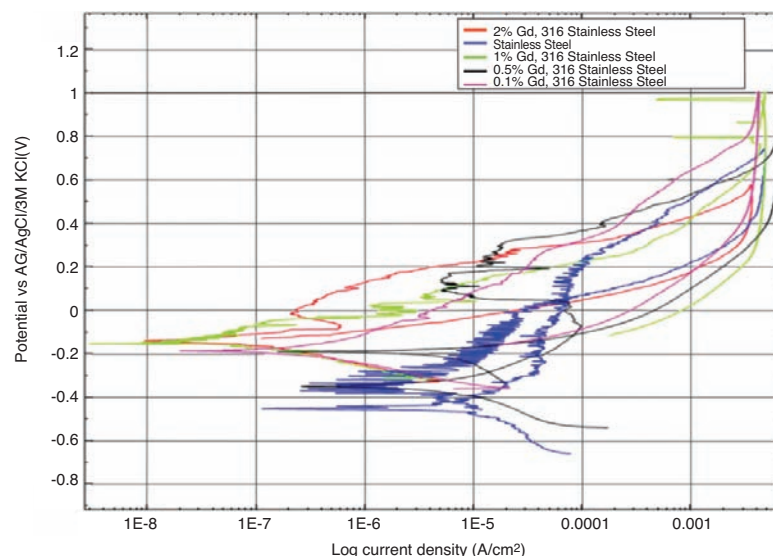
Figure 16—Comparison of polarization curves obtained for the gadolinium stainless steel alloys in 0.5 wt% NaCl solution
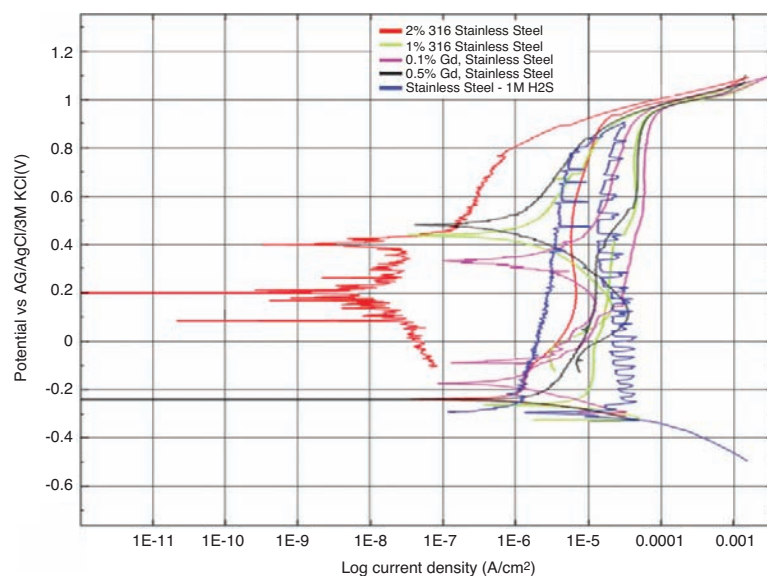

Figure 17—Comparison of polarization curves obtained for the gadolinium stainless steel alloys in 0.5 M H_2SO_4 solution

alloys is that the gadolinium or gadolinium/chromium oxide layers formed were uniform, continuous, tenacious, and self-repairing. This is supported by the fact that, although the alloys underwent passivation, they did not display any pitting corrosion, which meant that the passive oxide film did not break down in either of the solutions.

High-temperature oxidation rate tests

Gadolinium mild steel alloys

Thermal gravimetric analyses (TGA) were conducted on the alloys and the as-received mild steel sample in order to determine the change in mass as a function of temperature. The results from the TGA are illustrated in Figure 18. It can

be seen that the as-received mild steel sample underwent a significant amount of oxidation after a temperature of 800°C was exceeded. Once the maximum temperature of the STA test was reached (1200°C) the total mass increase of the mild steel sample was found to be 9.17 per cent. However, both the gadolinium mild steel alloys did not undergo a significant amount of oxidation, even once the maximum temperature of the STA test was reached. The 0.5 weight per cent, mild steel alloy experienced a total mass increase of 0.55 per cent while the 2 weight per cent alloy experienced a total mass increase of 0.51 per cent.

From the results obtained from the TGA analysis for the mild steel alloys, it is clear that gadolinium additions to the mild steel resulted in a decrease in the amount of oxidation.
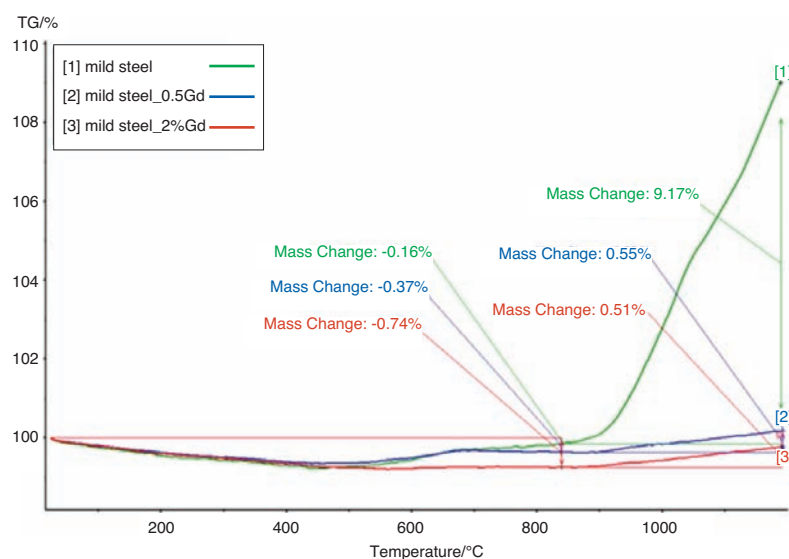
Figure 18—Mass change vs. temperature for the mild steel alloys
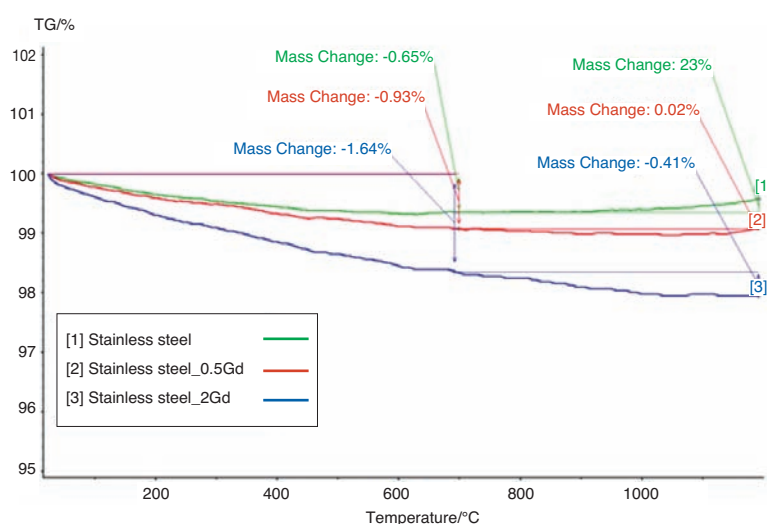

Figure 19—Mass change vs. temperature for the stainless steel alloys

It is also clear that the oxidation resistance of the mild steel increased with increasing gadolinium concentrations. This is assumed to be due to the formation of gadolinium oxide on the surface of the mild steel. Gadolinium oxide has the most negative heat of formation of all the elements present in the mild steel, and as a result is very active. This activity caused the gadolinium to oxidize much faster than any of the other elements present. Samanta *et al.*[3] found that rare earth metal additions to iron-containing compounds resulted in the formation of a fine-grained oxide, which contributed to scale plasticity thus favouring improved scale adherence. Thus, it is assumed that if gadolinium oxide was formed, it would form as a strongly adhering scale on the surface of the mild steel, and this would explain the significant oxidation resistance exhibited by the mild steel alloys. Once the

gadolinium oxide scale was formed, it would proceed to grow at a very slow rate,[10] therefore it would not penetrate into the mild steel. It is assumed that as the concentration of gadolinium increased the amount of oxide scale formed increased, therefore, the underlying mild steel would be better protected, and this resulted in the increased oxidation resistance exhibited by the 2 weight per cent mild steel alloy compared to the 0.5 weight per cent mild steel alloy.

Gadolinium stainless steel alloys

The results from the TGA on the gadolinium stainless stell alloys are illustrated in Figure 19. It can be seen that the stainless steel sample did not undergo a significant amount of oxidation. The total change in mass of the stainless steel

sample on completion of the STA test was 0.23 per cent. Both the gadolinium stainless steel alloys experienced an even lower change in mass on completion of the STA test. The 0.5 weight per cent stainless steel alloy experienced a mass change of 0.02 per cent, while the 2 weight per cent stainless steel alloy experienced a mass change of – 0.41 per cent (mass loss).

From these results it can be concluded that gadolinium additions to stainless steel resulted in a decrease in the amount of oxidation experienced by the stainless steel. It is also clear that the oxidation resistance of the stainless steel increased with increasing gadolinium concentration. The reason for the increase in the oxidation resistance of the stainless steel was assumed to be the formation of gadolinium oxide a on the surface of the stainless steel, as in the case of the gadolinium mild steel alloy.

Conclusion

The objectives of this project were met, as it was found that gadolinium additions to both mild steel and 316 stainless steel enhanced the mechanical properties in terms of improved hardness, improved corrosion resistance, and improved oxidation resistance. The general microstructures of the mild steel and stainless steel alloys that were obtained displayed a gadolinium-rich interdendritic constituent with a preferred orientation dispersed throughout the alloys. The alloys had a microstructure which was composite-like. Since the results of this project have proved to be positive, they are intended to serve as a foundation for the further development of the gadolinium mild steel and stainless steel alloys.

Recommendations

1. The effect of rolling on the etching process should be investigated further, along with an investigation to determine more suitable etchants that could be used for the gadolinium mild steel alloys
2. The same test programme as that followed in this project should be conducted on as-cast alloys which are subjected to hot-rolling or which have undergone subsequent heat treatments in order to homogenize the structure of the alloys
3. Characterization of the size, distribution, and indentity of the gadolinium-containing phases should be conducted, as these factors play a defining role in the mechanical properties of the alloys
4. Alloys with closer increments of gadolinium concentrations should be fabricated and tested in order to determine the gadolinium addition thresholds of the alloys
5. Further EDS analyses, on at least 10 points, should be conducted in order to determine the exact composition of the alloys. If the actual compositions still differ from that of the target compositions, care should be taken in the fabrication stage in order to ensure the correct amounts of gadolinium are added to the as-received mild steel and stainless steel
6. The other mechanical properties of the mild steel and stainless steel alloys i.e. tensile and impact strength should be investigated

7. The oxide layer formed on the mild steel and stainless steel during the high-temperature oxidation rate tests should be analysed in order to determine whether the layer consists of purely gadolinium oxide or a combination of oxides
8. The passive layer formed on the stainless steel alloys during the anodic polarization tests should undergo chemical analysis in order to determine whether the layer consists of purely gadolinium oxide or a combination of oxides.

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