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Rapid Corrosion Test for Detecting Intermetallic Phases in Duplex Stainless Steels

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ABSTRACT

Recent examples of improperly heat-treated duplex fittings have created the need for rapid test methods for identification of sigma phase and other intermetallic phases. Several attempts have been made to simplify known methods in order to make them applicable for on-site testing. Yet metallographic examination is the only known technique that is reliable. It is sometimes combined with ferrite measurement for pre-screening. The possibilities of applying electrochemical techniques have been evaluated on duplex specimens representing different levels of sigma phase. The applied test methods include ASTM G150[1] for Critical Pitting Temperature (CPT) determination as well as simpler approaches for measuring the resistance against localized corrosion quickly. The preliminary results of the ongoing study are promising. Distinguishing between sensitized and non-sensitized duplex steel was obtained within few minutes by performing a potentiostatic test that may be suitable for on-site testing.

Key words: Duplex stainless steel, pitting corrosion resistance, electrochemical test, sigma phase, screening.

INTRODUCTION

Improperly heat-treated high-alloy stainless steels are occasionally encountered even though strict specifications and qualification tests are usually required for such grades. Recently, the delivery of sensitized duplex fittings for offshore production sent a shockwave through the business. The issue was realized quite late after a large number of components had been installed in several projects. In some cases, the excessive sigma phase content was not realized before the systems had been in service for 1-2 years. Authorities announced warnings addressing the problem including Petroleumstilsynet in Norway (PTIL) and Health and Safety Executive in UK (HSE)[2,3]. Consequently, large-scale efforts were made to identify the substandard components by using any available technique to locate and replace the affected components. On-site metallographic examination turned out to be the most reliable but also a quite laborious method. Even after this incident, the problem still occurs at times. Recently, we have seen several examples of 25Cr duplex piping (e.g. UNS S32750) and cast 6Mo components (e.g. UNS S31254) having significant sigma phase precipitation.

The presence of sigma phase in stainless steel is usually unacceptable due to its detrimental influence on corrosion and mechanical properties. Of main concern is the reduced fracture toughness, which is related to the hardness and brittleness of the sigma phase in itself and possibly also to the precipitation hardening effect of the phases foreign to the ferritic-austenitic matrix. Similarly, the corrosion resistance is affected by the depletion of chromium and molybdenum at the interface adjacent to the formed sigma phase.

This paper focuses on the possibility of establishing a rapid method that can evaluate the pitting corrosion resistance in chloride-containing environment in order to identify faulty components. The work is a continuation of the results presented earlier in a previous paper[4].

Numerous papers have been published about the impact on corrosion resistance, especially in relation to sigma phase formed during welding in which the low-temperature heat-affected zone (LTHAZ) is of particular concern. Without doubt, even small amounts of sigma phase influence the resistance against most corrosion forms such as pitting[5-12], sulphide stress corrosion cracking[7], intergranular corrosion[13-15] and hydrogen embrittlement[14]. Consequently, the standard criterion is that no sigma phase is allowed in produced duplex materials. There is at least one known example of failure in a seawater system that may be ascribed to sigma phase presence. However, small amounts of sigma phase or sigma phase formed at certain temperature intervals might be without influence in some applications. Fitness for purpose studies have in some cases demonstrated that up to 2.5 % sigma phase in super duplex welds may be accepted without compromising the corrosion properties[5,7,10].

Duplex welds and base materials for oil and gas installations are usually pre-qualified by using the ASTM G48 test for evaluating the pitting corrosion resistance in ferric chloride solution[16]. This test is an accelerated go/no-go test typically using a temperature criterion of 25 °C for 22Cr duplex and 35 or 40 °C for 25Cr duplex steel welds. Base materials are tested at higher temperatures. Our experience with this technique is that materials occasionally fail the test on a questionable basis due to impractical issues related to e.g. cut faces[17]. Earlier, we have consequently proposed an improved protocol for this test together with Det Norske Veritas (DNV)[18]. The ASTM G150[1] method for determining the CPT was applied as part of this study to obtain quantifiable data rapidly. Moreover, this test can be restricted to the surface intended for exposure, and the measured CPT can be directly correlated with literature data. The test showed good agreement between the measured CPT and the results of the G48 exposure tests.

In our previous study[4], the ASTM G150 method was applied on 22Cr duplex steel (UNS S31803) representing different levels of sigma phase obtained by heat treatment at 750 and 850 °C. As expected, sigma phase had a significant negative influence on the CPT. The same set of materials has been included in the present study to evaluate the possibility of establishing a rapid test method.

EXPERIMENTAL PROCEDURE

Materials

Model materials (D00-D08) were produced from the same 3 mm plate material of UNS S31803 duplex stainless steel. The chemical composition is shown in Table 1. The as-delivered material (D00) has a characteristic cold rolled microstructure with a volumetric ferrite content of 39.7 ± 4.8 % when measured according to ASTM E562[19].

Identical specimens measuring 50x100 mm were cut from the plate material. The specimens were heat-treated at 750 or 850 °C for 5, 10, 20 or 60 minutes giving 8 levels of sigma phase formation (identified as D01-D08). The heat-treatment was followed by water quench. The volumetric content of sigma phase was determined by counting in accordance with ASTM E562.

In addition to the model materials, random duplex materials from our third party work have been included in the study, D09-D12 in Table 1. These materials have correct microstructure apart from the UNS S32750 duplex steel (D12) that contained significant amounts of sigma phase.

TABLE 1.
Composition of tested UNS S31803 and UNS S32750 materials (wt%).

Material ID	UNS	C	N	Si	Mn	P	S	Cr	Ni	Mo
D00-D08	S31803	0.021	0.167	1.49	0.025	0.025	0.001	21.9	5.8	2.99
D09	S31803	0.025	0.19	0.38	1.78	0.021	0.001	22.0	5.6	3.30
D10	S31803	0.017	0.15	0.41	0.86	0.023	0.001	22.0	6.1	3.34
D11	S32750	0.022	0.31	0.27	0.59	0.024	0.001	24	7.2	4.12
D12	S32750	0.025	n/a	0.41	0.84	0.020	0.011	24.0	6.7	3.55

ASTM G150

The test face of the specimen was wet-ground to #320 in sequential steps. Subsequently, the specimen was left for at least 20 hours in air before exposure. To avoid crevice corrosion, a flushed port cell with a specially formed flat gasket was used. The exposed surface area was 4.5 cm^2.

The critical pitting temperature (CPT) was obtained in double by performing a temperature ramp at fixed potential according to the ASTM G150 method. This implies polarization to +700 mV SCE in a solution of 1 M NaCl. The temperature was raised from 0 °C at a rate of 1 °C/min. CPT was read when the current exceeded 100 $\mu A/cm^2$.

Rapid Test

Portable equipment for electropolishing was modified to allow measurement directly on the surface. The equipment feeds the cell with fresh solution that was sometimes heated or cooled. The test set-up is illustrated in Figure 1. The exposed surface area was 0.8 cm^2.

Just before testing, the intended area for examination was wet-ground with #120 abrasive paper. An electrochemical test was then performed within few minutes. Potendynamic and potentiostatic techniques in different media were applied during initial testing. The chosen method implied measurement of open-circuit potential for 60 seconds followed by potentiostatic polarisation at +700 mV SCE for 120 seconds in 3 M NaCl solution at 25 °C.

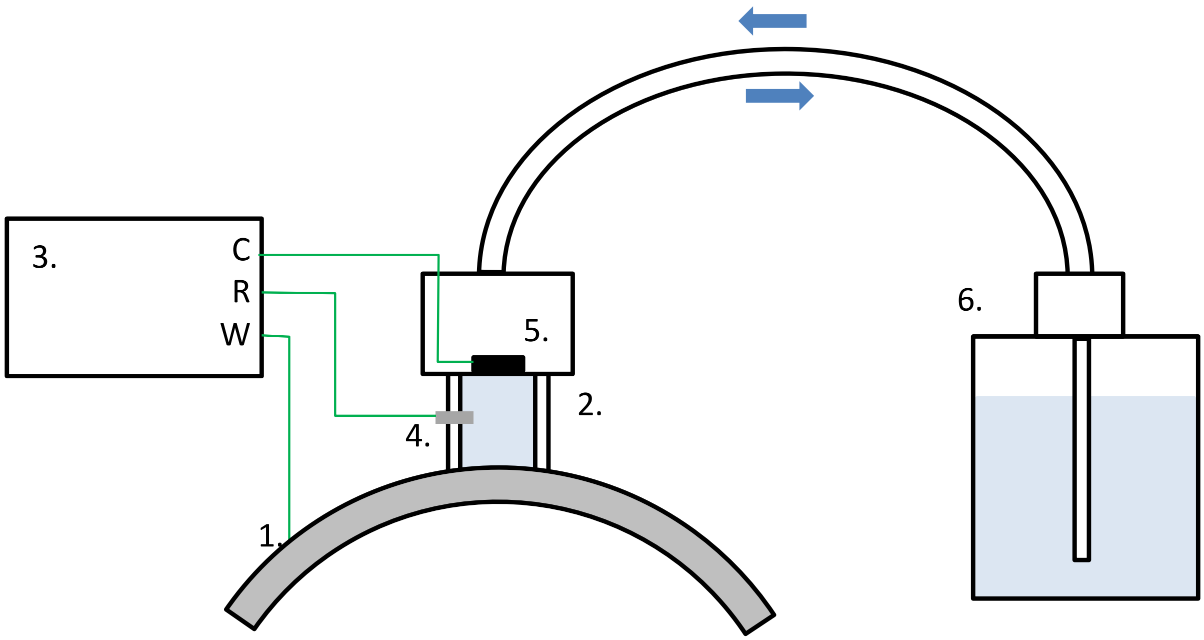

Figure 1: Set-up used for rapid testing. 1. specimen 2. cell (ID 10 mm) made from flexible rubber hose 3. potentiostat 4. silver/silver chloride reference electrode 5. counter electrode 6. pump.

RESULTS

Microstructure

The performed heat treatments of the model materials generated sigma phase contents between 0 and 28 % as can be seen in Table 2. From the micrographs in Figures 2 and 3, it appears that the sigma phase is formed mainly in the ferrite phase. The sigma phase appears as an orange and sharp-edged phase when etched with NaOH. The sigma phase is formed at the austenite-ferrite boundary and grows in to the grey ferrite phase. Generally, treatment at 850 °C gives larger and coarser sigma phase precipitates that those observed at 750 °C. Heat treatment at 750 °C for 5 and 10 minutes did not generate any detectable sigma phase.

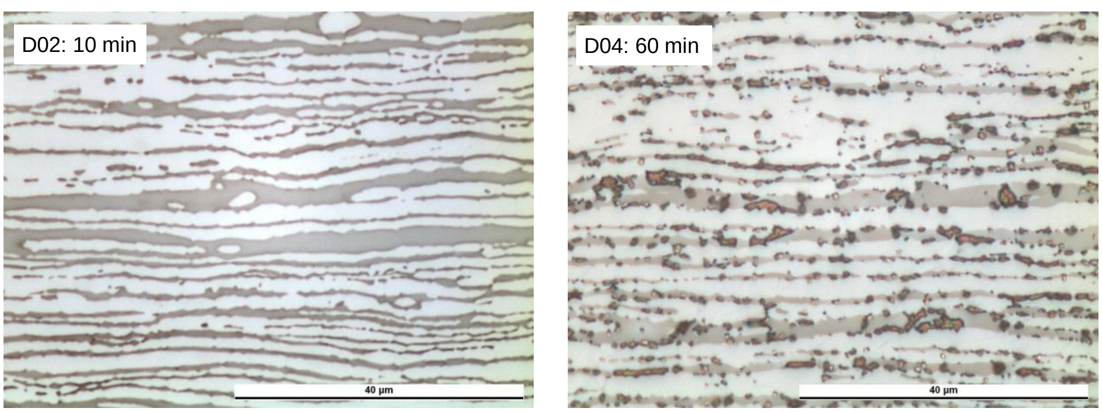

Figure 2: Microstructure of UNS S31803 stainless steel heat-treated at 750 °C for 10 and 60 minutes. Electrolytically etched with NaOH.

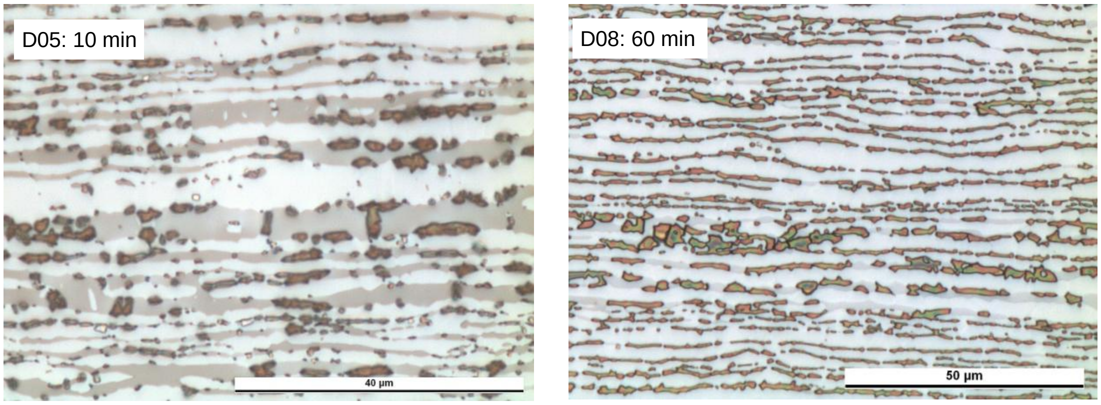

Figure 3: Microstructure of UNS S31803 stainless steel heat-treated at 850 °C for 10 and 60 minutes. Electrolytically etched with NaOH.

Besides the model materials, a discarded tube sample of UNS S32750 (D12) was included in the study along with healthy reference materials. As shown in Figure 4, the microstructure of D12 shows excessive sigma phase precipitation.

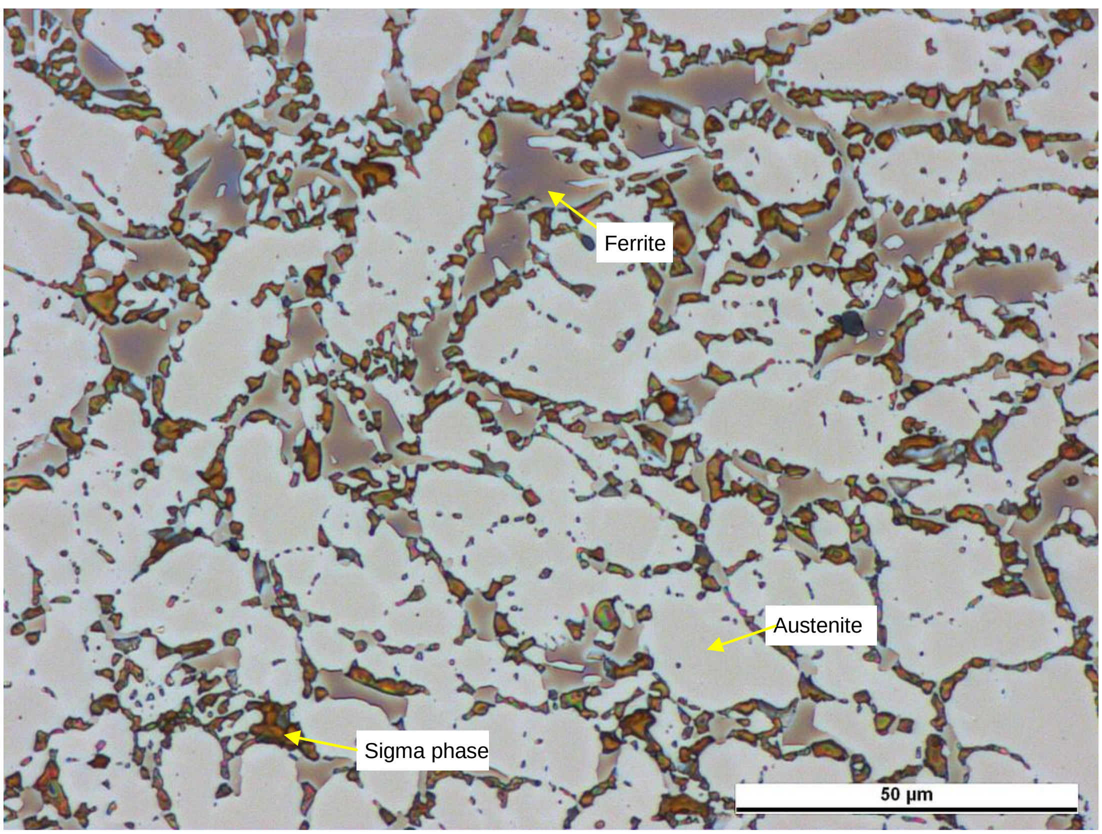

Figure 4: Microstructure of UNS S32750 steel (D12) showing excessive sigma phase precipitation. Electrolytically etched with NaOH.

Critical Pitting Temperature

Table 2 compares the obtained CPT values. The effect of sigma phase on CPT is evident. At sigma phase contents in the range of 2 to 6 % there is a significant drop in the measured CPT. Furthermore, it appears that the same amounts of sigma phase obtained at the two different temperatures affect the CPT differently. The effect is stronger for materials heat-treated at the low temperature of 750 °C. This correlates well with the fact that diffusion takes place at slower rate causing steeper concentration gradients in the region up to the sigma phase precipitates.

TABLE 2.
Sigma phase content and Critical Pitting Temperatures (CPT) determined by using ASTM G150 for duplex UNS S31803 with different heat treatments[4].

ID	Heat treatment Temp.	Time	Sigma phase* Vol. frac., %	Critical Pitting Temperature, °C n1	n2	Average
D00	SA - as delivered		0 ± 0.0	51	52	52
D01	750 °C	5 min, WQ	0 ± 0.0	53	48	51
D02		10 min, WQ	0 ± 0.0	49	46	48
D03		20 min, WQ	5.7 ± 1.6	30	33	32
D04		60 min, WQ	18.9 ± 3.3	22	23	23
D05	850 °C	5 min, WQ	1.9 ± 1.1	49	45	47
D06		10 min, WQ	14.7 ± 4.1	40	32	36
D07		20 min, WQ	20.7 ± 3.5	28	27	28
D08		60 min, WQ	27.5 ± 3.8	27	26	27

SA solution annealed, WQ water quenched. *) Determined acc. to ASTM E562, 16 grid points, 30 fields

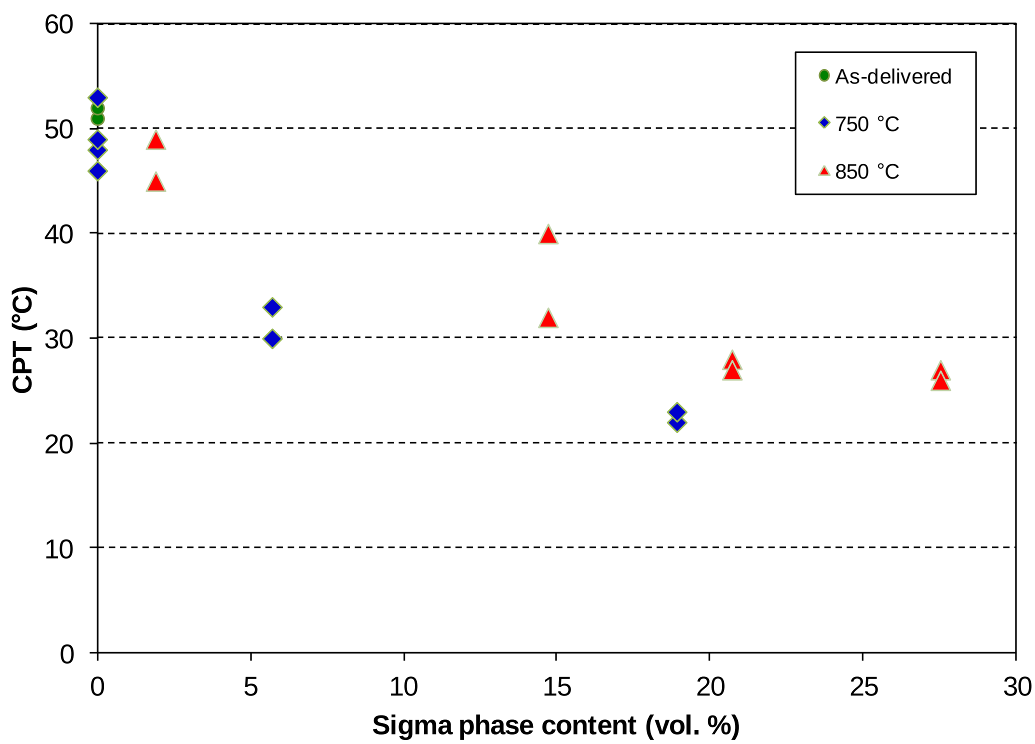

Figure 5: Influence of sigma phase content on CPT of UNS S31803 heat-treated at 750 and 850 °C.

Rapid Testing of Model Materials

The model materials tested by the ASTM G150 technique were subjected to rapid testing using the portable set-up. After initial grinding of the surface, the test was completed in 3 minutes. Figures 6 and 7 show the obtained current curves during the potentiostatic test. The test is evaluated by the curve trend and the final current density after 120 seconds. Table 3 correlates the obtained results with the CPT and sigma phase content.

The materials heat-treated at 750 °C fall into two groups. The solution annealed material (D00) shows the desired trend, i.e. decreasing current that indicates passive behavior. Heat-treated materials without any detectable sigma phase (D01 & D02) show the same tendency. This also correlates well with the measured CPT. The materials having more than 5.7 % sigma phase show an increasing curve trend and a high final current, which indicates poor resistance.

The materials heat-treated at 850 °C show similar characteristics. The material containing 1.9 % sigma phase (D05) behaves as a passive material with properties comparable to those of the solution-annealed material. Higher amounts of sigma phase are revealed by a considerable increase in current. As a whole, the results correlate well with the CPT measurements.

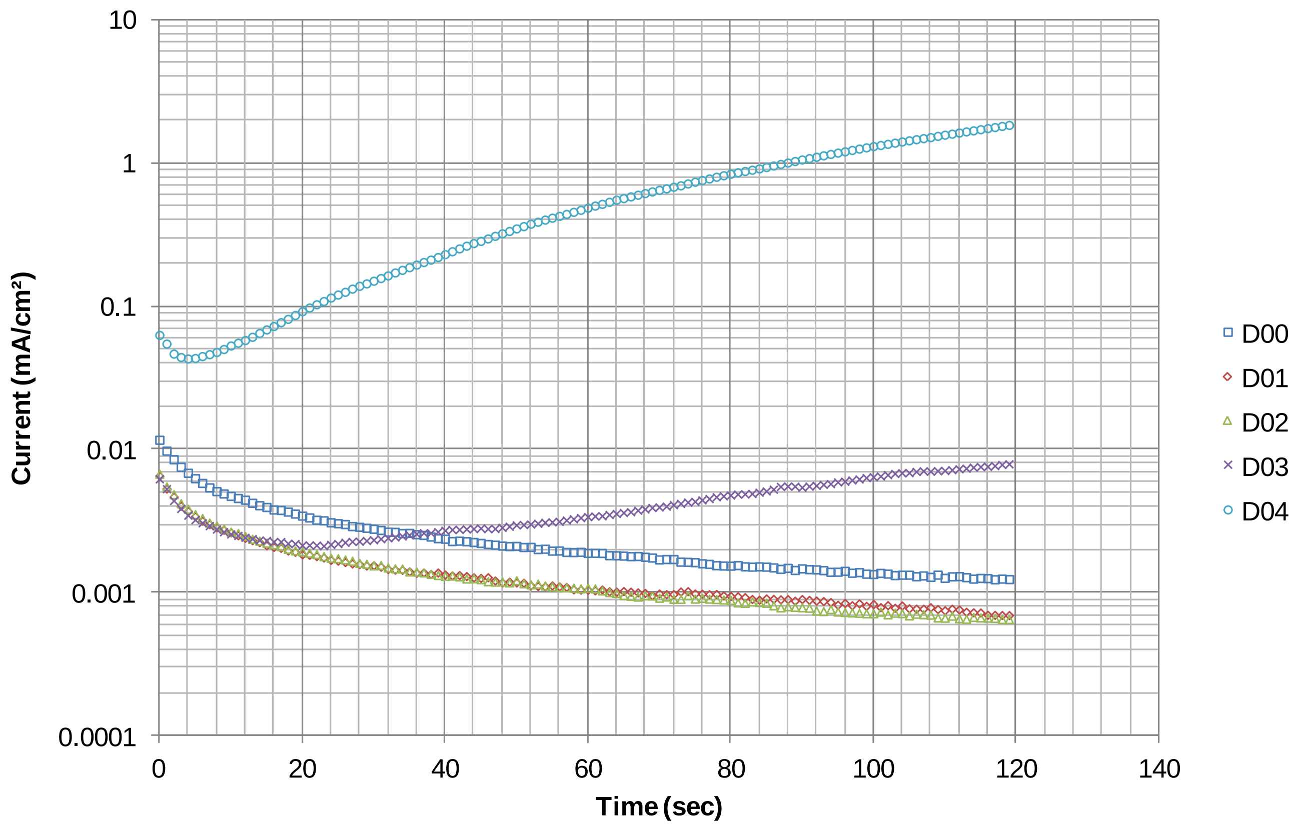

Figure 6: Development in corrosion current at 700 mV SCE and 25 °C when testing UNS S31803 stainless steel heat-treated at 750 °C for 10 and 60 minutes.

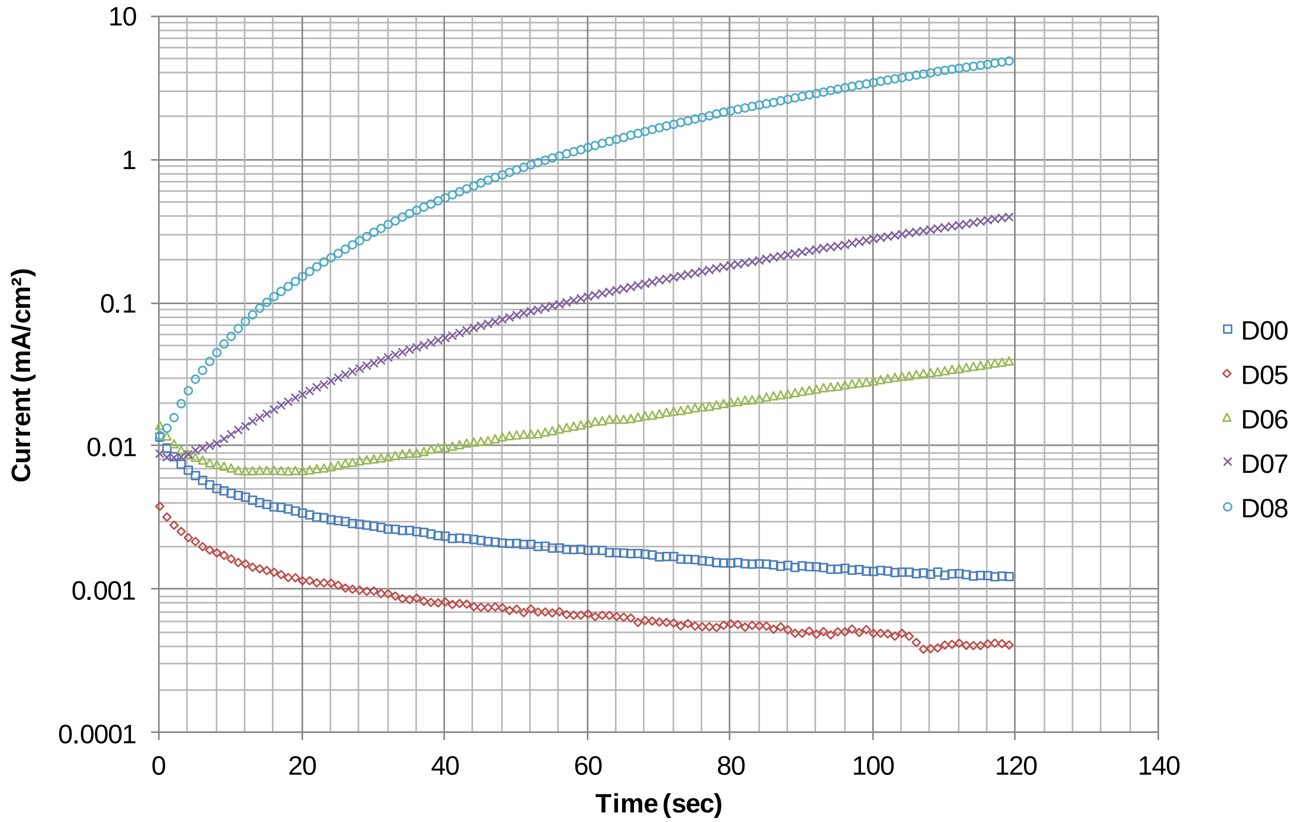

Figure 7: Development in corrosion current at 700 mV SCE and 25 °C when testing UNS S31803 stainless steel heat-treated at 850 °C for 10 and 60 minutes.

TABLE 3.
Sigma phase content and response in rapid testing at 25 °C correlated with CPT obtained with ASTM G150 for duplex UNS S31803 with different heat treatments.

ID	Heat treatment		Sigma phase	ASTM G150 CPT, °C	Rapid test at 700 mV SCE	
	Temp.	Time	Vol. frac., %	Average	Final current μA/cm^2	Tendency
D00	SA - as delivered		0 ± 0.0	52	1.24	Decreasing
D01	750 °C	5 min, WQ	0 ± 0.0	51	0.70	Decreasing
D02		10 min, WQ	0 ± 0.0	48	0.65	Decreasing
D03		20 min, WQ	5.7 ± 1.6	32	7.9	Increasing
D04		60 min, WQ	18.9 ± 3.3	23	1840	Increasing
D05	850 °C	5 min, WQ	1.9 ± 1.1	47	0.41	Decreasing
D06		10 min, WQ	14.7 ± 4.1	36	40	Increasing
D07		20 min, WQ	20.7 ± 3.5	28	402	Increasing
D08		60 min, WQ	27.5 ± 3.8	27	4920	Increasing

The model materials were also tested at different temperatures to simulate alternating conditions that may be encountered when doing on-site examination. Testing at 40 °C was able to distinguish the materials in the same manner as demonstrated above. At 10 and 60 °C, respectively, all materials showed either passive or active behavior without the possibility of distinguishing the materials.

Rapid Testing of Additional Materials

A selection of UNS S31803 and UNS S32750 duplex stainless steels obtained during our third party work was tested with the established technique at 25 °C. Three of those (D09-D11) are standard duplex materials without any suspicion of defects. The last material (D12) represents UNS S32750 duplex tubing that originates from a pharmaceutical plant. As a consequence of severe sigma phase precipitation (Figure 4), the tube fractured longitudinally during pressure testing due to low impact toughness. This material is clearly identified from the results of the tests shown in Figure 8. The healthy materials show stable behavior, which is seen by the decreasing trend in current.

Additional testing of UNS S32750 and UNS S31254 steels having lower sigma phase content did not provide reliable distinguishing between the materials. Consequently, the current test conditions are only capable of detecting extreme cases among the high-alloy grades.

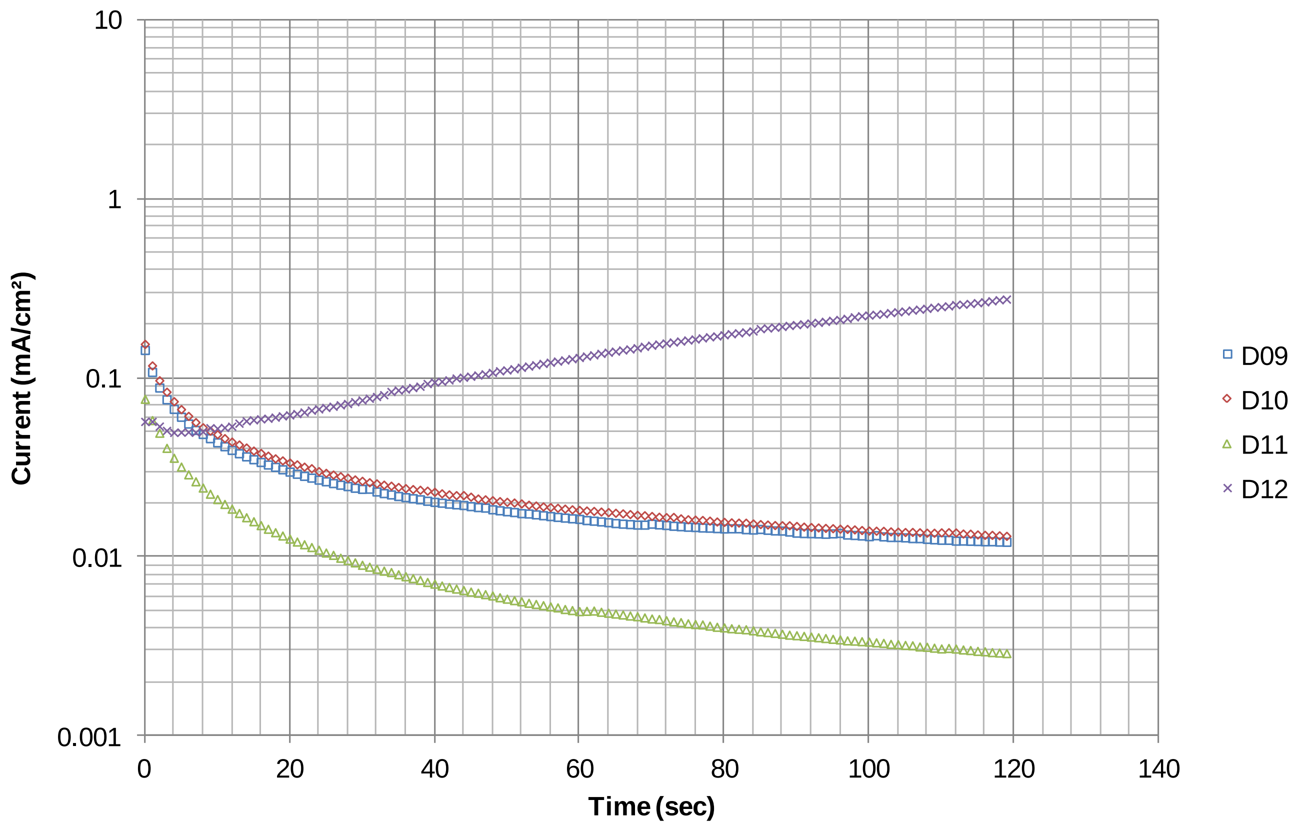

Figure 8: Development in corrosion current at 700 mV SCE at 25 °C when testing duplex stainless steels. D12 contains sigma phase while the other materials are considered healthy.

DISCUSSION

The established technique for rapid testing of UNS S31803 duplex stainless steel provides reasonable distinguishing between healthy and sensitized materials. This view is supported by the good correlation with CPTs obtained by using the ASTM G150 technique. It has also been demonstrated that the test is capable of identifying sigma phase in other product forms than the model plate material.

The test temperature is a crucial parameter. Testing at different temperatures showed consistent results at 25 and 40 °C. At lower or higher temperatures, all materials showed the same behavior without any possibility of distinguishing the materials. This effect is somewhat expected, because the test can only differentiate materials as long as the test temperature is between the CPT of the best and worst material.

Other test methods were examined on the model materials before deciding for the potentiostatic technique. Potentiodynamic technique for detecting the pitting potential and electrochemical potentiodynamic reactivation (EPR) were evaluated. Both techniques were incapable of providing reliable test results within few minutes. The use of mild chloride solutions rather than aggressive acids was also a motive for pursuing the simpler potentiostatic approach. Unless the material is sensitized, the imprint of the corrosion test is hardly detectable and insignificant. Consequently, the test can be considered as nondestructive and suitable for on-site evaluation.

The potentiostatic technique has also been applied to higher alloyed materials, such as UNS S32750 duplex and UNS S31254 steels. In one case, excessive sigma phase precipitation in UNS S32750 duplex could be identified by the technique, but distinguishing was not obtained in high-alloy grades having lower sigma phase content. In order to obtain this, the test parameters need to be modified to represent more aggressive conditions. Efforts are currently being made to define such test conditions.

Several attempts have been made by other groups to find a suitable field inspection method to detect intermetallic precipitates. One study[20] reviewed several NDT-methods. It turned out that on-site microscopy was the most reliable, while ferrite scope measurements (or eddy current) were only applicable for pre-screening. Our preliminary tests using eddy current technique led to the same conclusion, although we see possibilities of improvement. If sigma phase is present in duplex stainless steels, the electromagnetic properties are changed. The ferrite is ferromagnetic while austenite and sigma phase are paramagnetic. Thus, an increase of the sigma phase volume fraction and the resulting decrease of the ferrite phase volume fraction render the material behavior more paramagnetic[21].

We have used eddy current technique to perform examination of pipe sections with significant variations in impact strength. The examination revealed that there is a good correlation between the presence of sigma phase and low impact strength values. When the examination is made as relative measurements within the same batch, the eddy current technique provides a good resolution of the sigma phase volume fraction in the range above 1 %. Even though the impact strength may be severely affected below this level, we find the eddy current technique useful for screening in some situations. It may even provide greater resolution than the potentiostatic technique, but when testing unknown materials from many different batches, the potentiostatic technique appears to be a better choice for screening purposes.

CONCLUSIONS

A series of UNS S31803 duplex specimens representing different levels of sigma phase were tested using both the ASTM G150 method to determine CPT and the newly established technique based on rapid potentiostatic testing. The intention of the study was to develop a test suitable for rapid on-site testing. The following conclusions can be made from the study:

- Sigma phase has a significant negative influence on the CPT, and for same amount sigma phase, the effect is stronger for materials heat-treated at 750 °C in comparison to 850 °C.

- Potentiostatic testing at 700 mV SCE in 3M NaCl at 25 °C is capable of identifying materials having sigma phase precipitation within few minutes. The results are consistent with those obtained by CPT testing.

- In both methods (CPT and potentiostatic), the negative influence on corrosion resistance is observed at sigma phase contents above 2 to 6 % depending on the heat treatment history of the material.

- The rapid potentiostatic test shows consistent results at temperatures from 25 to 40 °C. Testing at 10 and 60 °C caused passive or active behavior, respectively, without any possibility of distinguishing the materials.

- Within the shown application window, the potentiostatic test can be used for rapid screening of 22Cr duplex as an alternative or supplement to on-site metallography. Since the mechanical properties may be affected at sigma phase contents lower than the detection limit of the corrosion test, it cannot fully replace other tests.

- Possibly, the potentiostatic test may be used for screening high-alloy stainless steels (25Cr and 6Mo), too. In one case, excessive sigma phase could be detected for UNS S32750 duplex, but the technique requires better distinguishing by adapting suitable test conditions.

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