Ain Shams University
Faculty of Engineering
Design and Production Engineering Dept.

HEAT TREATMENT EFFECT ON THE CORROSION RESISTANCE OF SUPER DUPLEX STAINLESS STEEL

A Thesis
submitted in partial fulfilment of the requirements for the degree of PhD in Mechanical Engineering

By
Fady M. Moneeb Elsabbagh
B.Sc. Mechanical Engineering
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Supervised by
Prof. Dr. Mohamed Ahmed Taha
Dr. Rawia Mostafa Hamouda
Ain Shams University

EXAMINERS COMMITTEE

The undersigned certify that they have read and recommend to the Faculty of Engineering – Ain Shams University for accepting a thesis, entitled as "Investigation of Heat Treatment Effect on the Corrosion Resistance of Super Duplex Stainless Steel" (دراسة تأثير المعالجة الحرارية للصلب المقاوم للصدأ المزدوج البنية على مقاومة التآكل). Thesis is submitted by Fady Mohamed Moneeb El-Sabbagh, in partial fulfilment of requirement for the Doctor of Philosophy degree in Mechanical engineering.

Signature

1. Prof. Dr. Mohamed Ahmed Taha

   Department of Design and Production Engineering

   Faculty of Engineering, Ain Shams University, Egypt

2. Prof. Dr. Heinz Palkowski

   Institute of Metallurgy - Materials forming and Processing

   Clausthal University of Technology, Germany

3. Prof. Dr. Madiha Ahmed Shoeib

   Central Metallurgical Research and Development Institute, Egypt

STATEMENT

This thesis is submitted in the partial fulfilment of Doctor of Philosophy degree in Mechanical Engineering, Ain Shams University.

The author carried out the work included in this thesis, and no part of the thesis has been submitted for a degree or qualification in any other university.

Signature

Fady Mohamed Moneeb El-Sabbagh

Date:

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ABSTRACT

Stainless steels are exposed to elevated temperatures during welding, casting or high temperature services. These high temperatures cause the precipitation of several intermetallic phases leading to the deterioration of the mechanical and corrosion resistance properties of stainless steels. Each of the austenitic, ferritic and duplex stainless steel families has certain time/temperature precipitation range, which allows specific phases to precipitate in the material structure.

In this work, intermetallics precipitation in the super duplex stainless steel UNS S32760 is studied. For comparison purposes, UNS S32760 is compared against two other types of stainless steel, UNS S42900 and UNS N08367, representatives of the ferritic and the super austenitic stainless steel families. Due to their corrosion resistance, these three stainless steel grades have wide range of applications from the food to the seawater handling industries, where high corrosion resistant alloys are needed.

The purpose of this study is to identify the interrelation between the different intermetallic precipitates and the austenitic, ferritic and duplex structures of the three stainless steel grades. Also, to estimate the impact of these intermetallic precipitates on the mechanical and corrosion resistance properties of the stainless steel grades.

For these three stainless steel grades several heat treatments are conducted by isotehrmal holding for different holidng times before quenching in water. Further testing is carried out by investigating the microstructure, XRD, SEM, hardness, microhardness, Charpy impact toughness and corrosion testing, then compared against each other and against the unheated material properties.

SUMMARY

In this study, the effect of the secondary phase precipitation on super duplex stainless steel UNS S32760 is studied. For comparison purposes, two other grades of stainless steels namely UNS S42900 and UNS N08367 are also investigated. The three stainless steel grades represent the ferritic, austenitic, and duplex (austenitic-ferritic) stainless steel families. This is to understand the interrelation between the intermetallic precipitates and the crystal structure of the stainless steel grades.

Some grades of stainless steels have a superior corrosion resistance, which qualify them to be used in seawater handling applications. Seawater is considered as one of the most corrosive fluids on earth. The super duplex and super austenititc stainless steel grades are suitable for the seawater applications, meanwhile the ferritic grade is suitable for less corrosive environment, such as in food related industires.

Unfortunately, several failures have occurred to these grades, when subjected to high temperature for prolonged periods of time, during fabrication (such as welding or casting processes) or during service at high temperatures. The reason for these failures was attributed to the precipitation of several secondary phases in the structure of the material when subjected to high temperatures for prolonged periods of time. The secondary phases have significant impact on the properties of the stainless steel, in which the corrosion resistance and material impact toughness are decreased.

This raises the need to study the relationship between the secondary precipitates and the different structures of the stainless steel materials. Also, this questions the suitability of these stainless steel grades to the severely corrosive seawater, with respect to the precipitated secondary phases in the structure.

In this study, Chapter 1 “1LITERATURE SURVEY” introduces the different families of stainless steels, the relations between the families, what are the alloying elements that drive to forming the stainless steel family, as well as the advantages and disadvantage of each family. Most of the disadvantages of the stainless steels are due to the precipitation of intermetallic phases, which drastically impact the mechanical and corrosion resistance properties of the stainless steels. This chapter illustrates the different types of intermetallic phases and the properties of each one.

Chapter 2 “PROBLEM DEFINITION AND PLAN OF WORK” presents the motive for this thesis based on previous field experiences that huge piping network had been failed due to seawater corrosion. The motive is to study the duplex stainless steel as a composite material composed of austenite and ferrite elements. This analogy was considered to study the effect of the constituent stainless steel family (i.e. austenite and ferrite) on the composite duplex stainless steel, from the toughness and corrosion perspectives. Then this chapter specifies the three stainless steel grades under study, which are UNS S32760, UNS N08367 and UNS S42900 representing the super duplex, super austenitic and ferritic stainless steel families respectively.

Chapter 3 “EXPERIMENTAL TECHNIQUES AND PROCEDURES” presents the testing plan for the stainless steel grades under study. The testing plan is briefed as identifying the incoming material, determining whether it needs for prior heat treatment (i.e. solution annealing), then isothermal heat treatment, and testing. The testing plan included optical microscopic investigation, scanning electron microscope (SEM), X-ray diffraction (XRD), microhardness, impact toughness and corrosion resistance testing.

Chapter 4 “RESULTS AND DISCUSSION (PHASE IDENTIFICATION)” presents a trial for identifying the precipitated phases, by using the test results of the optical microscopic investigation, SEM, XRD, and microhardness. This was conducted for each stainless steel grade under study.

In Chapter 5 “RESULTS AND DISCUSSION (MECHANICAL AND CORROSION)”, the results of the impact toughness and corrosion testing are presented and evaluated.

Then, Chapter 6 “MODELLING OF SDSS” proposes a model for considering the duplex stainless steel as a composite material composed of austenite and ferrite elements. Such model is a new approach to correlate between the properties of the duplex stainless steel with its primary phases (i.e. austenite and ferrite).

Finally, in Chapter 7 the conclusions are derived and summarized.

NOMENCLATURE

Al	Aluminium
C	Carbon
Cr	Chromium
CPT	Critical Pitting Potential
Cu	Copper
DSS	Duplex Stainless Steel
E_p	Pitting Potential
FSS	Ferritic Stainless Steel
LOM	Light Optical Microscope
MC	Metal Carbide
Mn	Manganese
Mo	Molybdenum
N	Nitrogen
Nb	Niobium
Ni	Nickel
PRE_N	Pitting Resistance Equivalent Number
ROM	Rule of Mixture
S	Sulphur
SASS	Super Austenitic Stainless Steel
SCC	Stress Corrosion Cracking
SDSS	Super Duplex Stainless Steel
$SDSS_A$	Austenitic part of the Super Duplex Stainless Steel
$SDSS_F$	Ferritic part of the Super Duplex Stainless Steel
Se	Selenium
SEM	Scanning Electron Microscope
Si	Silicon
SS	Stainless Steel
TEM	Transmission Electron Microscope
Ti	Titanium
UNS	Unified Numbering System
V	Vanadium
W	Tungsten
XRD	X-Ray Diffraction
α	Alpha (Ferrite-Phase)
δ	Delta (Ferrite-Phase)
γ	Gamma (Austenite-Phase)
χ	Chi
σ	Sigma
ε	Epsilon
π	Pi

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CHAPTER I

1 LITERATURE SURVEY

Stainless steels are alloys exhibiting passive surface layers that can prevent substrate layers from further reaction with the environment. That passive layers are made of chromium oxide, which is formed by the reaction between oxygen in the environment and the alloying chromium in the material. The chromium content should be at least 10.5 wt.% [1]）.

1.1 Families of Stainless Steels

Stainless steels are commonly classified according to their crystalline structure into five families: martensitic, ferritic, austenitic, duplex (ferritic-austenitic), and precipitation-hardening stainless steels. The martensitic and ferritic stainless steels have body-centred cubic (BCC) crystal structure. However, the martensitic stainless steel has a distorted BCC structure. The austenitic family has face-centred cubic (FCC) structure. The duplex stainless steel consists of an even mixture of the austenitic and ferritic phases.

1.1.1 Ferritic Stainless Steels

As per [1], the BCC ferritic stainless steels have a chromium content in the range of 10.5-30 wt.%. Some grades may contain molybdenum, silicon, aluminium, titanium, and niobium to present particular characteristics. Sulphur or Selenium may be added, as in the case of the austenitic grades, to improve machinability. The ferritic alloys are ferromagnetic. They can have good ductility and formability, but high-temperature strengths are relatively poor compared to the austenitic grades. Impact toughness is limited at low temperatures, such as -40 down to -50°C, below which the material becomes brittle as for common structural carbon steel grades.

In the Fe-Cr phase diagram shown in Figure 1-1, the ferritic steel compositions are on the right of the austenite (γ) loop. Because the carbon content found in commercial steels shifts the γ-phase boundary to higher chromium contents, the addition of strong ferritizining elements becomes necessary in order to prevent the formation of austenite.

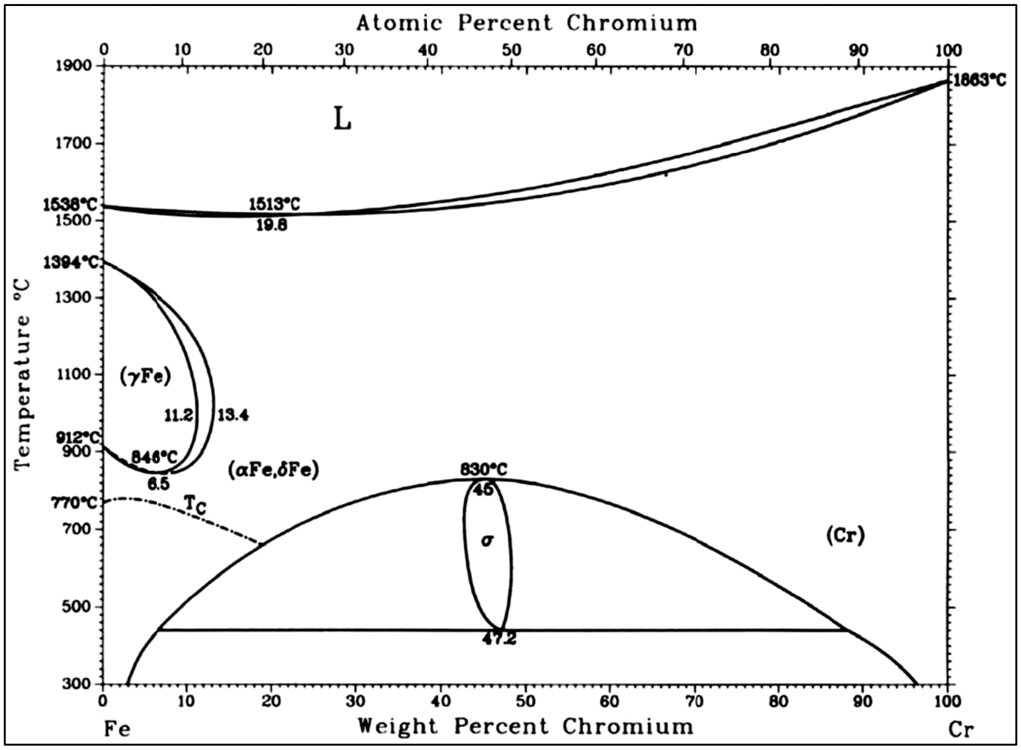

Figure 1-1 Binary Fe-Cr equilibrium phase diagram [1]

Ferritic stainless steels are designated by the AISI as 4XX series.

There are essentially three generations of ferritic stainless steels. First ferritic stainless steel generation has carbon content that is not very low, so that chromium content needs to be high. The prototype alloy is type 430 stainless steel, typically containing 0.12 wt.% maximum of carbon and 17% chromium. The second generation of ferritic stainless steels has lower carbon and low nitrogen contents, to which a stabilizer is added to tie up whatever carbon and/or nitrogen is present. The prototype of this second generation is type 409, typically 0.04C-11Cr-0.5Ti. The titanium ties up both carbon and nitrogen, leaving all of the chromium free. With titanium being ferrite stabilizer, the alloy is ferritic at all temperatures. The third generation of ferritic stainless steels has carbon and nitrogen contents of 0.02% or less, and stabilizers, such as titanium and/or niobium are often added to tie up any free interstitials. The prototype alloy is type 444 (18Cr-2Mo) [1].

The chemical compositions of the common ferritic stainless steel grades are shown in Table 1-1:

Table 1-1 Chemical composition of ferritic stainless steel grades (wt.%) [2]

UNS	Type	C	Mn	P	S	Si	Cr	Ni	Mo	N	Others
S40500	405	0.08	1.0	0.04	0.03	1.0	11.5-14.5	0.6	-	-	Al 0.1-0.3
S42900	429	0.12	1.0	0.04	0.03	1.0	14.0-16.0	-	-	-	-
S43000	430	0.12	1.0	0.04	0.03	1.0	16.0-18.0	0.75	-	-	-
S44400	444	0.025	1.0	0.04	0.03	1.0	17.5-19.5	1.0	1.75-2.5	0.035	Ti+Cb 0.02 + 4 (C+N) min.; 0.8 max.

Mechanical properties of the above grades are shown in Table 1-2:

Table 1-2 Mechanical properties of ferritic stainless steel grades [2]

UNS	Type	Tensile strength, Min. (MPa)	Yield strength, Min. (MPa)	Elongation in 50mm, Min. (%)	Hardness, Max. (HBN)
S40500	405	415	170	20	179
S42900	429	450	205	22	183
S43000	430	450	205	22	183
S44400	444	690	485	15	293

1.1.2 Austenitic Stainless Steels

Austenitic stainless steels have a face-centred cubic (FCC) structure that is attained through the liberal use of austenitizing elements such as nickel, manganese, and nitrogen. The most famous austenite stabilizer is nickel, see Figure 1-2. These steels are essentially nonmagnetic in the annealed condition and can be hardened only by cold working. They usually possess excellent cryogenic properties and good high-temperature strength. Their chromium content generally varies from 16 to 26 wt.%; nickel up to about 35%; and manganese up to 15% [1].

AISI designates the austenitic stainless steels stabilised with nickel as 3XX, meanwhile the manganese stabilised austenitics as 2XX. The 3XX types contain larger amounts of Ni and up to 2% of Mn, Mo, Cu, Si, Al and Ti. Nb may be added to avail characteristics such as halide (e.g. flourides and chlorides) pitting resistance and oxidation resistance. The 2XX series steels