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Structural Intearitu red

Procedia Structural Integrity 2 (2016) 517-524

www.elsevier.com/locate/procedia

# 21st European Conference on Fracture, ECF21, 20-24 June 2016, Catania, Italy

# The influence of metallurgical factors on corrosion fatigue strength of stainless steels

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### Abstract

Corrosion fatigue strength of stainless steels is controlled by tangled interaction among environmental, mechanical and metallurgical factors. In order to estimate corrosion fatigue strength it is indispensable to understand the role of an each influencing factor. The aim of this paper is to present briefly surveyed results on metallurgical factors on corrosion fatigue strength of stainless steels such as austenitic, martensitic and duplex stainless steels mainly based upon author's experimental results. The targeted dominant metallurgical factors focussed upon are chemical compositions, heat treatment, manufacturing process and microstructures.

The emphasis is placed upon effect of Molybdenum content on corrosion fatigue strength of austenitic stainless steels in 3%NaCl aqueous solution, tempering temperature on corrosion fatigue strength of 13% Chromium stainless steel in 3%NaCl aqueous solution and volume percent ferrite on corrosion fatigue strength of duplex stainless steel in potassium alum aqueous solution. The surface and fracture surface observation by optical and scanning electron microscopy revealed that corrosion pit formed at corrosion fatigue crack initiation area. In light of relatively smaller effect of corrosive environment on corrosion fatigue crack propagation rate it can be surmised that corrosion fatigue strength of stainless steels is governed by crack initiation process. It can be concluded that corrosion fatigue strength of stainless steels is strongly influenced by metallurgical factors such as chemical compositions, heat treatment, manufacturing process and microstructures.

The information obtained in this survey directly lead to prevention of corrosion fatigue failure in stainless steels made components, selection of stainless steels in corrosive environments and development of corrosion resistant stainless steels.

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Keywords: Corrosion fatigue, Stainless steels, Molybdenum content, Tempering temperature, Volume percent ferrite

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# 1. Introduction

Stainless steels are widely used as structural materials in various kinds of machine and plant. A lot of information on environmental degradation such as corrosion resistance and stress corrosion cracking under various kinds of environment has been accumulated so far. However information on corrosion fatigue strength of stainless steels seems not to be enough. Especially long term corrosion fatigue strength to estimate design stress of components under corrosive environments and corrosion fatigue crack initiation behavior to understand corrosion fatigue crack initiation mechanism are still unsolved problems.

It has been well recognized that corrosion fatigue strength of structural materials is controlled by tangled interaction among environmental, mechanical and metallurgical factors. Therefore it is indispensable to understand the role of each factor influencing on corrosion fatigue strength of stainless steels. In this paper it is focused upon the metallurgical factors to control corrosion fatigue strength of stainless steels. Dominant metallurgical factors to control corrosion fatigue strength of stainless steels are manufacturing processes, chemical compositions, heat treatment, microstructure and weld metal. In this paper it is reported on the briefly surveyed results on effect of chemical compositions, heat treatment, microstructure and manufacturing processes on corrosion fatigue strength of stainless steels on the basis of mainly author's experimental results.

# 2. Effect of chemical compositions on corrosion fatigue strength of stainless steels

Very few papers on long term corrosion fatigue strength of stainless steels can be found. Plate bending corrosion fatigue tests were conducted for SUS304 and SUS316 in 3% NaCl aqueous solution up to over than 231 days (Hirakawa and Kitaura, 1981). Plane plate specimens with 6mm thick were used and the frequency was 0.5 Hz. Reduction of corrosion fatigue strength up to  $10^6$  cycles was 6% at most for both SUS304 and SUS316. The reduction rate in SUS304 gradually increased after  $2x10^6$  cycles and reached to 30% at  $10^7$  cycles. The sudden reduction of corrosion fatigue strength of SUS304 at  $7 \times 10^6$  cycles was attributed to corrosion pit initiation at the specimen surface. On the contrary the reduction rate in SUS316 was 6% up to  $2x10^6$  cycles and 0% even at  $10^7$ cycles. The smaller reduction rate of SUS316L than that of SUS304 in 0.9wt% sodium chloride aqueous solution was also reported (Otsuka et al., 2010). The reason of the smaller reduction rate of SUS316 and SUS316L strongly depends on about 2% Molybdenum content in chemical compositions of these stainless steels. Molybdenum effect on corrosion fatigue strength of austenitic stainless steels can also be recognized for various kinds of austenitic stainless steels in 3% NaCl aqueous solution (Ebara et al., 2011, 2012). Chemical compositions and mechanical properties of tested austenitic stainless steels are shown in Table1 and Table2 (Ebara, 2015), respectively. The dumbbell type specimens with minimum diameter of 3mm were used. The ultrasonic corrosion fatigue tests were very carefully conducted in 3% NaCl aqueous solution. Frequency was 20kHz and R(the ratio of minimum to maximum stress in the loading cycle) was -1. Because of the low thermal conductivity in austenitic stainless steels ultrasonic fatigue tests were very carefully conducted to prevent heating of the specimens during corrosion fatigue testing. The compressed air was blown into the center of dumbbell type specimens and the solution was circulated with a speed of 31/min. Intermittent testing with frequency of 110ms duty and 1100ms pause was also applied. Fig. 1 shows S-N diagrams of SUS 304 and SUS316 in air and in 3%NaCl aqueous solution. Corrosion fatigue strength of SUS304 at 10<sup>9</sup> cycles in 3% NaCl aqueous solution is 245MPa and is 15.5% lower than that in air. The reduction of corrosion fatigue strength of SUS316 at  $10^9$  cycles in 3% NaCl aqueous solution is 12% and the reduction rate is

Table1	Chemical con	positions	of austenitic	stainless :	steels (	mass %)	(Ebara 2015)	1
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Material	С	Si	Mn	Р	S	Ni	Cr	Mo	Nb	Ν
SUS304	0.005	0.44	0.87	0.025	0.005	8.15	18.15			
SUS304N2	0.004	0.81	0.082	0.029	0.001	7.55	19.45		0.09	0.2
SUS316	0.06	0.43	0.84	0.027	0.001	10.07	16.26	2.1		
NSSC250(Heat)	0.015	0.37	0.45	0.022	0.001	17.72	25.16	2.43		0.28
NSSC250(TMCP)	0.011	0.42	0.44	0.025	0.001	17.87	24.87	2.4		0.27
YUS270	0.08	0.46	0.46	0.02	0.01	18.9	19.9	6.16		

Table2. Mech	nanical properties of	austenitic stainless steels. (E	bara 2015)		
Material	0.2%Proofstress	Ultimate tensile strength	Elongation	Hardness	
	MPa	MPa	%	HB	
SUS304	274	653	61	156	
SUS304N2	442	766	50	213	
SUS316	269	590	63	136	
NSSC250(Heat)	375	745	56	177	
NSSC250(TMCP)	711	905	38	261	
YUS270	365	743	44	175	



Fig.1 S-N diagrams of SUS304 and SUS316 in air and in 3%NaCl aqueous solution. (Ebara et al., 2011)



Fig.2 S-N diagrams of YUS270 in air and in 3%NaCl aqueous solution. (Ebara et al.,2012)

Material	Reduction rate of giga-cycle corrosion fatigue strength of austenitic stainless steels in 3% NaCl aqueous solution,%		
SUS304	15.5		
SUS304N2	0		
SUS316	13.7		
NSSC250(HT)	12.1		
NSSC250(TMCP)	19.5		
YUS270	0		

Table.3 Reduction rate of giga-cycle corrosion fatigue strength of austenitic stainless steels. (Ebara 2015)

lower than that of SUS304.This fact is well correlated to the above mentioned long term plate bending corrosion fatigue testing results of SUS304 and SUS316 tested at 0.5Hz in 3%NaCl aqueous solution (Hirakawa and Kitaura,1981). The lower reduction rate of corrosion fatigue strength in SUS316 than that in SUS304 is deeply related to Molybdenum content in SUS316.The reduction rate of giga-cycle corrosion fatigue strength of various kinds of austenitic stainless steels are summarized in Table3(Ebara,2015). It can be evaluated that reduction rate of giga-cycle corrosion fatigue strength of austenitic stainless steels is relatively low with less than 20%. The effect of Molybdenum content on corrosion fatigue strength of NSSC250(TMCP) is not observed well, however it effectively reduced the reduction rate of corrosion fatigue strength of NSSC250(HT). As shown in Fig.2 corrosion fatigue strength of YUS270 was just a little influenced by 3% NaCl aqueous solution at higher stress amplitude over than 350MPa, however the giga-cycle corrosion fatigue strength was not influenced by 3% NaCl aqueous solution. Thus it can be concluded that Molybdenum in austenitic stainless steel is effective to improve corrosion fatigue strength of 3% NaCl aqueous solution. The higher the Molybdenum content, the lower the influence of 3% NaCl aqueous solution is. Nitrogen is also effective chemical composition to improve corrosion fatigue strength of SUS304N2 in 3% NaCl aqueous solution.

Corrosion fatigue crack of austenitic stainless steels in 3%NaCl aqueous solution is not straight and is associated with very small corrosion pits on specimen surface. Fig.3a) shows the typical corrosion fatigue crack with very small corrosion pits observed on NSSC250 (HT). On the contrast fatigue crack in air is almost straight and without corrosion pit as shown in Fig.3b) (Ebara et al.,2011). It has been well documented that Molybdenum likewise



Fig.3 Fatigue crack observed on specimen surface of NSSC250(HT). (Ebara et al.,2011) a) 3% NaCl aqueous solution,260MPa,3.8x10<sup>6</sup>cycles b) air, 320MPa, 5.5x10<sup>6</sup> cycles

Chromium and Nickel increases pitting resistance of stainless steels (Fontana and Greene,1967). Nitrogen also improve pitting resistance of austenitic stainless steels (Gavriljuk and Berns,1999). It can be concluded that Molybdenum and Nitrogen retard corrosion pit initiation in corrosion fatigue crack initiation process of austenitic stainless steels. Molybdenum effect on corrosion fatigue strength was also reported on 13% Chromium martensitic stainless steel (Schmitt-Thomas et al.,1976). Corrosion fatigue life of 13% Chromium stainless steel with 1% Molybdenum increased more than 10 times than that of 13% Chromium stainless steel without Molybdenum under stress amplitude of 250MPa with mean stress of 350MPa in 27% NaCl aqueous solution. The reason is attributed to passivation accelerated by stable protective film formed on specimen surface of 13% Chromium stainless steel. The influence of NaCl aqueous solution on duplex stainless steel with 3.27% Molybdenum was not observed at 2.5x10<sup>7</sup> cycles (comparable to 577 days) after plate bending long term corrosion fatigue test with frequency of 0.5Hz (Hirakawa and Kitauta,1980).It was also reported that reduction of giga-cycle corrosion fatigue strength of duplex stainless steel was only 12.5% in the results of ultrasonic corrosion fatigue test with frequency of 20kHz (Ebara and Miyoshi,2014).It is also reported that corrosion fatigue strength of 13% Chromium cast steel(ASTM CA15) can be improved by adding 11.91% Molybdenum in severe paper mill environment (Kurusu et al.,1984).

#### 3. Effect of heat treatment on corrosion fatigue strength of stainless steels

The tensile properties and fracture toughness of 13% Chromium stainless steel is controlled by heat treatment. Tensile strength, 0.2% offset yield strength and hardness are not influenced by austenitizing temperature. Elongation, reduction of area and Charpy impact energy is just a little decreased in higher austenitizing temperature. On the contrast tensile properties and fracture toughness of 13% Chromium stainless steel is influenced by tempering temperature. At higher tempering temperature tensile strength, 0.2% offset proof stress and hardness decreases, while elongation, reduction of area and Charpy impact value increases. Therefore fatigue strength in air decreases with increasing of tempering temperature. Fig.4 shows rotating bending fatigue test results of 13 % Chromium stainless in air and in 3% NaCl aqueous solution. Plain round bar specimen with minimum diameter of 7 mm was used and frequency was 60Hz (Ishii et al.,1982). Fatigue limit of 13% Chromium stainless steel tempered at 750,600 and 450°C was 400,520 and 700MPa, respectively. The higher the tempering temperature, the lower the fatigue limit was. However, corrosion fatigue strength of 13% Chromium stainless steel at 10<sup>8</sup> cycles tempered at 750,600 and 450°C was 130, 20 and 200MPa, respectively. It is apparent that corrosion fatigue strength tempered at 600°C was the smallest and the reduction rate was 99.6%. Crack propagation tests were also conducted in air and 3%NaCl aqueous solution. The round center notched plate specimen was used and the frequency was 30Hz. In air the da/dN



Fig.4 Influence of tempering temperature on rotating bending fatigue strength of 13% Chromium stainless steel in air and in 3%NaCl aqueous solution. (Ishii et al.,1982)

of the 750°C tempered specimen was almost same as that of the 600°C tempered specimen and was faster than that of the 450°C tempered specimen. In 3% NaCl aqueous solution the da/dN of all tempered specimens was lower than those in air for  $\Delta$  K's below 18MPa · m<sup>1/2</sup>. Crack propagation rate of 13% Chromium stainless steel specimen tempered at 750°C in air and in 3%NaCl aqueous solution is shown in Fig.5. From these experimental results it can be concluded that corrosion fatigue strength of 13% Chromium stainless steel is strongly influenced by tempering temperature through crack initiation process. Based on the long term corrosion fatigue experiments it was concluded that in the environment containing NaCl fatigue crack initiated at corrosion pits and propagated intergranular (Ebara et al. 1978). In this investigation corrosion fatigue crack initiated from corrosion pit at specimens tempered at  $600^{\circ}$ C and 750°C. The corrosion pits observed on the specimen tempered at 750°C were 10 to 20 $\mu$ m, while extremely large corrosion pits with 100 to 400 $\mu$ m were observed on specimens tempered at 600<sup>o</sup>C. Furthermore the martensite lath structure was observed at depth of corrosion pits. This phenomenon support that the microstructure of the  $600^{\circ}$ C tempered 13% Chromium stainless steel is particularly easy to attacked by 3%NaCL aqueous solution. Tempering temperature effect on corrosion fatigue strength was also recognized on turbine blade 17-4PH stainless steel. Plate bending corrosion fatigue tests were conducted on 17-4Ph stainless steels with tempering temperature in the range of 538 to 677°C after solution treated condition (1038°C for 0.5hr.,air cool) with various tempering temperature in 6 wt% FeCl<sub>3</sub> aqueous solution (B.V.Syrett et al., 1982). Tapered plate specimens with 5mm thick were used and frequency was 12Hz. In air fatigue strength of the specimen tempered at  $538^{\circ}$ C was just 40MPa higher than that of the specimen tempered at 649°C. However, in 6 wt% FeCl<sub>3</sub> aqueous solution, corrosion fatigue strength of the specimen tempered at  $649^{\circ}$ C was 80MPa higher than that of the specimen tempered at  $538^{\circ}$ C. The reason of the corrosion fatigue strength increase in tempering temperature was not clarified yet. Numerous corrosion pits were observed on all tested specimens, however no significant differences could be detected in the size or the number of pits on the tested specimens. Corrosion fatigue strength of 17-4PH stainless steel depends on its melting processes.



 Fig.5 Effect of 3% NaCl aqueous solution on crack propagation rate of 13% Chromium stainless steel tempered at 750 °C. (Ishii et al.,1982) Heat treatment H: Austeniitization,970°C ,1hr Oil quench, Temper 750°C ,3hrs,Air cool

Corrosion fatigue tests in city water were carried out on various heat treated (H1075, H1025 and H900) 17-PH stainless steels which were manufactured by three different melting processes such as air, double and triple melting process (Hasegawa et al., 1992). Tempering temperature of H1075, H1025 and H900 is 580°C, 550°C and 480°C, respectively. The triple melted 1075 showed the highest value of corrosion fatigue strength, followed by the double melted and air melted specimens in the descending order. The result may be connected with the maximum size of inclusions in the specimen. Corrosion fatigue strength of triple melted specimens with H1025 showed the highest value of corrosion fatigue strength. Corrosion fatigue strength with H1075 was equivalent to that with H900.

#### 3. Effect of microstructure on corrosion fatigue strength of stainless steels

It has been well recognized that austenite-ferrite duplex stainless steels have been extensively applied to suctionpress roll working under white water environment. The higher corrosion fatigue strength of duplex stainless steels than that of martensitic cast steel such as CA15 is attributed to austenitic-ferritic duplex microstructures. Rotating bending corrosion fatigue tests of duplex stainless steels with different vol. percent ferrite were conducted in potassium alum aqueous solution with pH value of 3.5 at  $40^{\circ}$ C (Ebara et al.,1981). These stainless steels were prepared by different melting processes such as air and vacuum oxygen decarburization (VOD) melt. Fig.6 shows fatigue strength at  $10^{7}$  cycles in air and corrosion fatigue strength at  $10^{8}$  cycles in potassium alum aqueous solution at  $40^{\circ}$ C as a function of volume percent ferrite. The fatigue strength of VOD melted specimens is higher than that of the air melted specimens. The higher the volume percent ferrite the higher the fatigue strength at  $10^{7}$  cycles in air is. This inclination has already been reported on IN744 duplex stainless steel (Hayden and Floreen,1978). The higher the volume percent ferrite the higher the fatigue strength decreases after reaching to the maximum fatigue strength at volume percent ferrite of 57%. Corrosion fatigue strength of VOD melt specimens is about 20 % higher than that of the air melted specimens. Compared to air melted steel small ferrite phase is dispersed in microstructure of VOD melted steel with higher cooling rate. Structure dependent transgranular fracture surfaces were observed on crack propagation area of corrosion fatigue fracture surfaces of duplex stainless steel.



Fig.6 Dependence of fatigue limit in air and corrosion fatigue strength in potassium alum aqueous solution on volume fraction of ferrite. (Ebara et.al., 1981)

Therefore it can be concluded that corrosion fatigue strength of duplex stainless steels is strongly dependent on microstructure. For duplex stainless steels such as VK-A171 and VK-A172 there was no marked difference in crack propagation rates between the air and the white water environments (Kelly et al., 1975). Therefore corrosion fatigue strength of duplex stainless steels is controlled by crack initiation process.Corrosion fatigue crack initiation process depends on kind of steels. In white water environment corrosion fatigue crack of Vk-A171 and VK-A271 initiate at persistent slip band in austenite, while corrosion fatigue crack of IN744 initiate at phase boundary of austenite and ferrite. It can be mentioned that electrochemically accelerated crack initiation at persistent slip band reduce the resistance to persistent slip band formation brought about an interaction between white water and the near surface dislocation structure (Moskovitz and Pelloux,1978). The higher the volume percent ferrite the higher the corrosion fatigue strength of air and VOD melted specimens is. The similar inclination was also observed on duplex stainless steel for suction-press roll in felt cleaning solution with pH3.5 at 40<sup>o</sup>C (Kurusu et al.1984).In this experiment the highest corrosion fatigue strength was gained at volume percent ferrite of 50.Corrosion fatigue crack initiate at corrosion pit. Corrosion fatigue strength is affected by size of inclusion and cleanliness of steels.

## 4. Concluding remarks

A brief survey was conducted to investigate effect of metallurgical factors on corrosion fatigue strength of stainless steels mainly based upon author's experimental results. It was revealed that metallurgical factors contribute to corrosion fatigue strength improvement are Molybdenum content for austenitic stainless steel, tempering temperature for 13% Chromium stainless steel and volume percent ferrite for duplex stainless steel. These metallurgical factors strongly involved in corrosion pit formation at corrosion fatigue crack initiation process. Further investigation on corrosion pit initiation is recommended more in detail.

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