International Journal of Applied Research in Mechanical Engineering

Volume 2 | Issue 4

Article 1

April 2013

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Recommended Citation

SRINIVASA VADAYAR, K. and DEVAKI RANI, S. (2013) "HOT CORROSION BEHAVIOUR OF NICKEL BASED SUPERALLOYS," *International Journal of Applied Research in Mechanical Engineering*: Vol. 2: Iss. 4, Article 1.

DOI: 10.47893/IJARME.2013.1090

Available at: https://www.interscience.in/ijarme/vol2/iss4/1

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HOT CORROSION BEHAVIOUR OF NICKEL BASED SUPERALLOYS

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Abstract- High temperature corrosion of coated and uncoated IN738LC and uncoated CM247LC nickel based super alloys in chloride and vanadium environment were carried out. To create corrosive environment (i.e. chloride and vanadium environment) salts of required proportions of Na_2SO_4 , NaCl and V_2O_5 were applied on both sides of samples and loaded into the furnace at 700°C and 900°C. The weight changes were noted and SEM analysis was done to determine the surface morphology of hot corroded samples. Electron Dispersive Spectroscopy (EDS) was used to determine different elements present in corroded samples of CM247LC and IN738LC in chloride and vanadium environments at 700°C and 900°C. The present study revealed that CM247LC is more susceptible to hot corrosion than IN738LC due to varying amount of chromium and tungsten which is explained by degradation mechanism. Coated IN738LC has more life span than that of other samples.

Key words- Super alloys, Corrosion, SEM, EDS

1. INTRODUCTION

Super alloys are based on Group VIIIB elements and usually consist of various combinations of Fe, Ni, Co, and Cr, as well as lesser amounts of W, Mo, Ta, Nb, Ti, and Al. The term "super alloy" is applied to alloys which have outstanding high temperature strength properties. Super alloys are classified according to the main alloying elements in the composition, with the three base metals being nickel, cobalt, and iron. The entire super alloy family shares a common basic microstructure, which is a face-centered cubic (FCC) matrix with a number of dispersed secondary strengthening phases. In super alloys, both iron and cobalt are stabilized by the addition of nickel to retain FCC crystal structure throughout the gas turbine engine (GTE) application temperature range. Iron based super alloys contain major alloying elements are 9-38% Ni, 15-22% Cr, and 32-67% Fe. The major alloying elements in Cobalt based super alloys are up to 35% Ni, 19-30% Cr and 30-65% Co. The nickel based super alloys contain carefully balanced alloying additions of up to 27% Cr, up to 20% Co, 38-70% Ni, Al, Ti, and other elements [1]. Nickel based super alloys are used in a variety of applications, the majority of which involve corrosion resistance and/or heat resistance such as aircraft gas turbines, steam turbine power plants, medical applications, nuclear power systems, chemical and petrochemical industries [2]. There have been many developments to increase the temperature capability of these alloys with complex alloying additions and improvements in processing technology and alloy design methodology but in 24 years an increase of only ~100°C has been accomplished, with little scope for any further increases [3]. The need for increased application temperature arises because turbine engines are more efficient and provide greater thrust at higher temperature. This increased efficiency

means less fuel burned, reduced cost as well as reduced CO₂ emissions. The present study is specially associated with the hot corrosion of IN738LC and CM247LC nickel based super alloys. Hot corrosion is a high temperature analog of aqueous atmospheric corrosion. A thin film deposit on an alloy surface in a hot oxidizing gas causes accelerated corrosion kinetics. Recognition of the problem and a search toward a mechanistic understanding and engineering abatement were initiated in response to the severe corrosion attack of military gas turbines during the Viet Nam conflict. Initially, the researchers were misled by the observation of corrosion product sulfides beneath a fused film of sodium sulfate to denote the problem and mechanism as "sulfidation". Later, studies by Bornstein and DeCresente and Goebel and Pettit demonstrated that the principal corrosive environmental component was not a vapor species, but rather the contact of the fused salt with the surface [4,5]. This fused salt (sodium sulfate) exhibited an acid-base character which at the time was quite uncertain and undefined. The electrolytic nature of the fused salt film and its similarity to atmospheric corrosion led to the more proper naming of the problem as "hot corrosion". Degradation by high temperature oxidation, hot corrosion and erosion are the main failure modes of components in the hot sections of gas turbines, boilers, industrial waste incinerators, metallurgical furnaces, petrochemical installations etc. [6].

1.1 Coating of Super Alloys:

Super alloy products that are subjected to high working temperatures and corrosive atmosphere (such as high pressure turbine region of jet engines) are coated with various kinds of coatings to increase life period and efficiency of the component. Different coating techniques are Air plasma spray (APS), Low pressure plasma spray (LPPS), Electron beam physical vapor deposition (EBPVD), High Velocity Oxygen Fuel (HVOF) spraying. Extensive work has been carried out by I. Gurrappa on hot corrosion of nickel based super alloys as engine components and turbine materials [7-10]. He not only did work on hot corrosion mechanism but also predicted the life of materials in service and also developed various coatings to prevent / control hot corrosion. Hot corrosion resistant MCrAIY based bond coating containing 18%Cr, 22%Co, 12%Al and 0.5%Y has been developed for use in gas turbine engines where the hot corrosion is a major problem. The developed coating exhibits maximum life in both sodium chloride and vanadium containing environments.

2. EXPERIMENTAL WORK:

The hot corrosion experiments were conducted on IN738 LC and CM 247 LC nickel based super alloys and their chemical composition is presented in Tables 1 and 2. MCrAIY coated IN738LC samples have also been evaluated for their hot corrosion resistance with a view to compare with uncoated alloys.

2.1 Specimen Preparation:

The specimens of IN738LC and CM 247LC with a diameter of 15mm and thickness 3 mm cut by using BUEHLER ISOCUT, which has a wafering blade (diamond metal bonded). Then they were polished up to 800 emery paper in the sequence 320, 400, 600, 800 and then washed with water and acetone subsequently. The samples were weighed before and after hot corrosion by electronic weighing machine. Table 1: Chemical Composition of

Co	Cr	Al	Si	С	Fe	W
8.59	16.08	3.43	0.18	0.11	0.5	2.67
Та	Nb	Ti	Mn	Cu	Ni	
1.75	0.90	3.38	0.03	0.03	Bal	

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Table 2: Chemical Composition of CM 247 LC Super Alloy (Wt %).

С	Cr	Co	W	Mo	Та
0.07	8.1	9.2	9.5	0.5	3.2
Al	Ti	Hf	В	Zr	Ni
5.6	0.7	1.4	0.015	0.015	Bal

2.2 Hot Corrosion:

The hot corrosion experiments were carried out in chloride and vanadium environments at 700°C and 900°C for the coated and uncoated IN738LC and uncoated CM 247 LC samples. Once the furnace attains the required temperature and stabilizes, the boat was carefully loaded into the furnace. The specimens were allowed to expose at that temperature for a period of 3 hrs initially and later on a cycle of 20 hrs, was continued till all samples are corroded.

On completion of the time the samples were unloaded from the furnace and were allowed to cool in the air. The samples are washed with luke warm water to remove the salt layer adhering it, allowed to dry and were weighed again. This sequence of applying salt, loading, unloading, cleaning is employed for various exposure times. The surface morphology of the corroded samples were studied by using SEM. Electron Dispersive Spectroscopy (EDS) was used to determine different elements present in corroded samples of CM247LC and IN738LC in chloride and vanadium environments at 700°C and 900°C.

3. RESULTS AND DISCUSSION:

It is clear from the Fig.1 that CM 247LC is more susceptible to hot corrosion than IN 738 LC because of varying alloying elements and also seen that the corrosion attack is more in chloride environment than in vanadium environment at 900°C. Fig. 2 shows the weight change as a function of exposure time for the CM 247LC in chloride and vanadium environments (a) at 900°C (b) at 700°C. It can be observed that the weight change is rapid with time of exposure in chloride environment than in vanadium environment in both cases.



Fig.1: Hot corroded CM 247LC and IN 738 LC super alloys in chloride and vanadium environment at 900°C



International Journal of Applied Research in Mechanical Engineering (IJARME) ISSN: 2231-5950, Vol-2, Iss-4





CM 247LC in chloride and vanadium environments (a) at 900°C (b) at 700°C.

From the Fig. 3 (a) it can be observed that the weight change is small till 120 hrs and then suddenly decreases with time of exposure in chloride environment while in vanadium environment the weight change remains constant with time of exposure and in Fig. 3 (b) it can be seen that the weight change behavior is similar up to 160 hrs in both the environments. However, weight increases suddenly after 200 hrs and then decreases rapidly followed by constant weight change in vanadium environment.



Fig. 3: Weight change as a function of exposure time for the IN 738 LC in chloride and vanadium environments (a) at 900°C and (b) at 700°C.





Fig. 4: Weight change as a function of exposure time for the coated IN 738 LC in chloride and vanadium environments(a) at 900°C and (b) at 700°C.

From the Fig. 4 (a) it can be observed that the weight change is same in both the environments up to 40 hrs and then suddenly increases followed by rapid decrease after 60 hrs., subsequently the weight change is zig zag in nature with time and in Fig. 4 (b) it can be observed that the weight change behavior is similar in both the environments through the exposure period i.e. zig zag nature.It is important to mention that chromium is the most effective alloying element for improving the hot corrosion resistance of super alloys. In order to obtain good resistance to hot corrosion, a minimum of 15wt % chromium is often needed in nickel based super alloy. Among the IN 738LC and CM 247LC super alloys, CM 247 LC was corroded severely indicating that this super alloy is highly susceptible to hot corrosion due to high amounts of tungsten and less amount of chromium which can be explained by the following degradation mechanism.

3.1 Degradation Mechanism:

Tungsten which is the alloying element added along with other alloying elements in order to obtain high temperature strength characteristics of the super alloys, forms acidic tungsten oxide (WO₃) due to which fluxing of protective oxide scales such as alumina and chromic oxide takes place very easily.

This type of acidic fluxing is self-sustaining because WO_3 forms continuously that cause faster degradation of super alloys under marine environmental conditions at elevated temperatures. The degradation mechanism is explained in two steps such as (a) the tungsten present in the new super alloys reacts with the oxide ions present in the environment and forms tungsten ion : $WO_3 + O_2^- = WO_4$ and (b) As a result, the oxide ion activity of the environment decreases to a level where acidic fluxing reaction with the protective alumina and chromic oxide can occur: $Al_2O_3 = Al_{3^+} + O_{2^-}Cr_2O_3 = Cr_{3^+} + O_{2^-}A similar reaction mechanism occurs if the super alloys contain other refractory elements like vanadium and molybdenum.$

3.2 Scanning Electron Microscope:

From the Fig. 5 (a) a large crack is observed in chloride environment and a star shaped crack is observed in vanadium environment [Fig. 5 (b)].

From the Fig. 6 (a) a small crack was observed in chloride environment and no crack was observed in vanadium environment [Fig. 6 (b)].

From the Fig. 7 (a) multiple cracks were observed in chloride environment and wavy cracks were observed in vanadium environment [Fig. 7 (b)]





Fig .5: Surface morphology of CM247LC (a) in chloride environment (b) in vanadium environment at 900°C





Fig. 6: Surface morphology of IN 738LC (a) in chloride environment (b) in vanadium environment at 900°C



International Journal of Applied Research in Mechanical Engineering (IJARME) ISSN: 2231 -5950, Vol-2, Iss-4



Fig.7: Surface morphology of coated IN 738LC in (a) chloride environment and (b) vanadium environment at 900°C

3.3 Electron Dispersive Spectroscopy (EDS):

Table 3 shows the electron dispersive spectroscopy data of hot corroded CM247LC super alloy in vanadium environment at 900°C. It shows higher amounts of Ni, O, Co, Na, W and lower amounts of Cr, Al, S, V.

Element	O K	Na K	Al K	WK	S K
Wt. %	15.66	4.65	2.92	4.36	1.54
Element	VK	Cr K	Co K	Ni K	
Wt. %	0.65	3.16	6.32	60.73	

Table 3: EDS data of hot corroded CM247LC super alloy in vanadium environment at 900°C

Element	OK	Na K	Al K	WK	S K
Wt. %	15.66	4.65	2.92	4.36	1.54
Element	VK	Cr K	Co K	Ni K	
Wt. %	0.65	3.16	6.32	60.73	

Table 4 shows the electron dispersive spectroscopy data of hot corroded IN738LC super alloy in chloride environment at 900°C.It shows higher amounts of O, Na, Ni, S and lower amounts of Co, Cr, Al, Ti.

Table 4: E.D.S. data of hot corroded IN738LC super alloy in chloride environment at 900°C

4. CONCLUSIONS

Systematic hot corrosion experiments were conducted on nickel based super alloys IN738LC and CM247LC. CM 247LC is highly corroded due to less amount of chromium and high amount of tungsten. Larger cracks are observed in CM 247LC than in IN738LC. In vanadium environment less number of cracks and sometimes no crack was observed compared to chloride environment and in coated samples multiple cracks were observed. Life time of coated MCrAlY IN738LC is more than that of uncoated sample. The EDS data of hot corroded CM247LC super alloy in vanadium environment at 900°C shows higher amounts of Ni, O, Co, Na, W and lower amounts of Cr, Al, S, V. Incase of hot corroded IN738LC super alloy in chloride environment at 900°C, EDS data shows higher amounts of O, Na, Ni, S and lower amounts of Co, Cr, Al, Ti.

ACKNOWLEDGEMENTS:

The Authors are thankful to Director, DMRL for permitting to carryout the experimental work at DMRL. We are also thankful to MBG for carrying out SEM. We are grateful to Registrar, JNTUH University, Hyderabad for his constant support and encouragement.

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