

# High Temperature Oxidation/ Corrosion and Degradation Mechanisms of Superalloys—Review

Subhash Kamal<sup>1</sup> and Chennupati Vijya Kumar<sup>2</sup>

<sup>1</sup>School of Engineering & Technology (ASET), Sharda University, Uttar Pradesh, Greater Noida–201 303, U.P., India

<sup>2</sup>SSIT, B. Gagaram (V), Sathupally-Khammam, Andhra Pradesh, India  
E-mail: <sup>1</sup>subhashkamal@gmail.com

**Abstract**—High temperature oxidation represents the most deleterious forms of surface degradation, which can lead to the loss of mechanical strength and catastrophic failure of structural and engineering components. They are routinely encountered in superalloys used in land based turbine and aero engines, which operate in high temperature and corrosive environments. Due to extensive application of the superalloys in land-based and aero gas turbine engines, the high temperature oxidation behaviour of superalloys has been the subject of intense investigation for the past several years. Most of the studies have focused on the mechanism of oxidation such as oxide scale growth behaviour of materials based on short-term tests. An understanding of long term high temperature oxidation behaviour of superalloys is extremely important for the industrial applications.

**Keywords:** Superalloys, Oxidation, Mechanism, High temperature

## INTRODUCTION

In India, the corrosion losses will be around Rs. 1 lakh crore per annum. Around 80 per cent of the unscheduled shutdowns and breakdowns in industries are due to corrosion and process fouling. Out of the total loss due to corrosion, 25 per cent of loss can be easily saved with pro-active approach and protecting the system by applying protective coatings (Madhu Chittora, 2008). In today's gas turbines, the emphasis is on saving energy and reducing the amounts of pollutants emitted. This can be attained only by designing alloys with higher melting points and the capability to retain mechanical integrity at increased temperatures. The development of nickel-based superalloys has reached its limit, as the alloys are operating at critical temperatures close to their melting points. Further increase in the operating temperatures will result in dissolution of the strengthening phases and even melting. It has been estimated that the cost of corrosion to U.S. households, businesses, and government agencies exceeds \$400 billion dollars per year.

Increased temperatures have an adverse effect on the corrosion of the alloys (Maledi, 2006). Early age gas turbines were developed after the 1940s, and were designed to operate at 700 °C. Improvements in metallurgical processes, blade cooling techniques and application of coatings allowed for increased working temperatures (Eliaz et al., 2002). Coatings made a greater contribution towards increased operating temperatures and protection against environmental degradation (Stringer, 1987; Gurrappa, 2003).

Unacceptable corrosion rates have occurred when bio-fuel fired boiler has been operated with steam temperature of 530°C (Salmenoja et al., 1996). However, these lower steam temperatures drastically decrease the efficiency of electricity production. On the other

hand, in order to meet the demand for more electricity, the operating temperature and pressure of pulverized coal-fired boilers have to be increased (Blum, 1997). Among high temperature alloys, the promising alloys are “superalloys” namely Nickel, Cobalt and Iron based superalloys, which show high temperature mechanical properties and moderate resistance to hot corrosion.

## HIGH TEMPERATURE OXIDATION/ CORROSION

Oxidation is an environmental phenomenon in which metals and alloys (and other materials) exposed to oxygen or oxygen-containing gases at elevated temperatures convert some or all of the metallic elements to their oxides. The oxide can form as a protective scale if it remains adherent, and reduces further oxidation, or may continually spall off, exposing fresh metal. The latter case results in progressive metal loss. Additionally, internal oxidation may also occur. The technological implications of oxidation lie in the loss of load-bearing capability of the original metal or alloy component, eventually resulting in component failure. Resistance to oxidation at high temperatures is a requisite for superalloys whether used in the coated or uncoated conditions. Therefore, a better understanding of the superalloy oxidation and how it is influenced by the alloy characteristics and exposure conditions are essential for effective design and application of superalloys.

## Oxidation of Superalloys

Giggins and Pettit, (1971) reported the oxidation mechanism of Ni-Cr-Al alloys in Fig. 1, the results obtained by them are as follows. In the beginning, for any alloys, the rapid uptake of oxygen, converts the surface layer of the alloy into an oxide, as illustrated in Fig.1 (a), this layer is predominantly Ni (Cr, Al)<sub>2</sub>O<sub>4</sub>

and NiO. However, the exact composition of this layer varies with starting composition of the alloy, a significant amount of  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  would be present on alloy surface with sufficiently high Cr or Al contents. As the reaction continues, diffusional processes in the alloys begin to affect the oxidation reaction. Since the oxygen activity required to oxidise Cr and Al in the alloy is less than that established over the alloy by NiO or spinel in the external oxide scale, it moves in to the alloy and precipitate  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  (Fig.1b). The activity of oxygen requires to oxidise the Al in the alloy is smaller than that required for oxidising of the Cr. Thus, the particles of  $\text{Al}_2\text{O}_3$  extended deeper in to the alloy than the particles of  $\text{Cr}_2\text{O}_3$ . The diffusion of Cr and Al from the interior of the alloy results in the precipitation of additional  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in the subscale zone afterwards, and a continuous layer of  $\text{Cr}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3$  scales are formed beneath the external oxide layer (Fig.1c). The formation of continuous, duplex layer of oxide further reduces the flux of the oxygen in to the alloy since it establishes a low oxygen activity over the alloy. For the  $\text{Cr}_2\text{O}_3$ -former alloys (Group I), the flux of oxygen from the duplex scale in to the alloy is still sufficient to oxidise the Al internally but not the Cr, therefore Cr diffuses from the alloy through the duplex scale to form  $\text{Cr}_2\text{O}_3$  above the duplex scale (Fig.1d). In the case of the  $\text{Al}_2\text{O}_3$ -former alloys (Group II), the volume fraction of precipitated  $\text{Al}_2\text{O}_3$  is sufficient to form a continuous layer beneath the duplex zone as shown in Fig.1e. Steady state conditions are reached when the  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  layer becomes continuous and the oxidation reaction is controlled by transport through the  $\text{Al}_2\text{O}_3$  scale (Giggins and Pettit, 1971). Superalloys are now widely used in a variety of applications at temperatures ranging from 923 to 1373 K in aggressive atmospheres such as the combustion products of fuel and air, high temperature catalytic reactors etc. (Jena, 1984). In order to function satisfactorily in such a severe environment, superalloys must possess properties such as outstanding high temperature strength, creep and fatigue resistance, excellent ductility, good impact resistance and adequate resistance to hot-corrosion (Jena, 1984). Superalloys are used extensively in oxidizing environments; for example, as disks in turbine engines. The superalloys have been developed to achieve oxidation resistance by utilising the concept of selective oxidation. The selective oxidation approach to obtain oxidation resistance in superalloys consists of oxidising essentially only one element in the superalloy and relying upon this element's oxide for protection. For effective protection, it is anticipated that the oxide should cover the whole surface of the alloy and it must be an oxide through which the diffusion of the reactants takes place at comparatively slow rate. Nickel-, cobalt- and iron-base superalloys make use of the selective oxidation of the aluminum or chromium to develop oxidation resistance (Pettit and Meier, 1985). Further,

Pettit and Meier (1985) have reported that the selective oxidation processes are affected by a number of factors such as alloy composition, alloy surface conditions, gas environment and cracking of the oxide scale. Cyclic oxidation conditions whereby the oxide scales crack and spall, as well as certain phases present in the superalloys, both affect the capability to selectively oxidise aluminum or chromium in the superalloys. For example, Co- and Fe-based superalloys cannot be made to contain enough aluminum to permit them to be alumina formers as it will have detrimental effect on their mechanical properties. Therefore, the Co- and Fe-base superalloys have to rely on the chromia scales for oxidation resistance. Consequently the oxidation resistance of Co- and Fe-base superalloys is inferior to that of Ni-base superalloys. Furthermore, even when considering the Ni-base superalloys that are chromia formers, as degradation begins i.e. the chromia scales are damaged, the less protective oxides formed on the Ni-base alloys contain significant amount of nickel oxide as compared to cobalt and iron oxides on the cobalt and iron-base superalloys, respectively. Since nickel oxides are more protective than cobalt and iron oxides, the oxidation resistance drop-off is more abrupt in the case of the Co- and Fe-base superalloys. Further, the oxidation resistance of the Co- and Fe-base superalloys usually increases with the chromium concentrations and the oxidation resistance of the alloys with less than about 20% chromium is comparatively poor (Pettit and Meier, 1985).

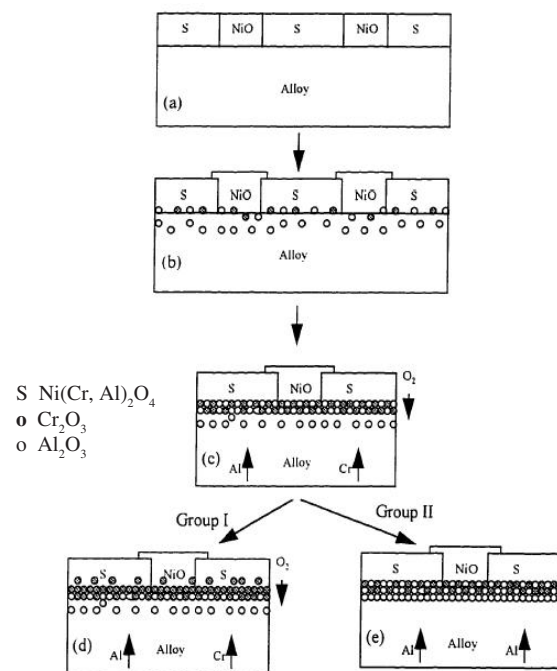


Fig. 1: Schematic Diagram Illustrating the Oxidation Mechanisms for Ni-Cr-Al Alloys (Giggins, *et al.*, 1971)

The superalloys exhibit outstanding strength and surface stability at temperature up to 85% of their melting points. Usually the superalloys are used at temperatures above 540 oC (Metal Handbook, 1990). However, compared with steels, corrosion resistance of the superalloys is relatively less known (Smith et al., 1999; Castello et al. 2000). The superalloys are broadly classified as nickel-, cobalt- and iron-based alloys.

Pettit and Meier (1985) opined that during isothermal oxidation of Ni-base superalloys,  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  scales are expected to be formed. Where as, under cyclic conditions, depletion of chromium and aluminum leads to the formation of NiO scale, some alloys move toward the NiO scale formation much more rapidly than others. They further concluded that the application of aluminide coatings to two nickel based superalloys B-1900 and Mar M200 makes them remain in alumina scale formation range for even longer times than obtained for the uncoated. The time over which nickel base superalloys can maintain protective, external scales of alumina or chromia is affected by temperature, the gas environment and alloy composition. Superalloys contains a number of significant alloying elements in addition to Cr and Al, including Mn, Ti, Si, and the refractory elements, Mo, W, Ta, Zr, and Hf. In many cases, these elements exert significant influence on the oxidation resistance of  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  forming alloy. Some alloying elements are beneficial and some are deleterious to superalloy oxidation resistance depending upon their amount and working condition. A number of studies have been carried out on the effect of their additions on the oxidation behaviour of different alloys. Smialek et al. (1987) has given an extensive review of this behaviour.

Levy et al (1989) reported studies on the cyclic oxidation resistance of three single-crystal nickel base superalloys and DS Mar M 200 at 1093 °C using a tube furnace and burner rig. The same ranking of the alloys was reported in both tests with the single-crystal superalloys having better oxidation resistance than the directionally solidified alloy DS Mar M 200. They further opined that tube furnace tests can be used in place of burner-rig tests to rank alloys. Oxidation tests at 900°C using the tube furnace produced a ranking of the alloys consistent with the 1093 °C results.

Kamal et al(2009) has conducted high temperature oxidation studies on bare and D-gun coated  $\text{Cr}_3\text{C}_2$ -NiCr coating on two Ni- and one Fe- based superalloys at 900° C, Weight gain/unit area ( $\text{mg}/\text{cm}^2$ ) vs. number of cycles plots for the bare as well as detonation-gun-sprayed  $\text{Cr}_3\text{C}_2$ -NiCr-coated superalloys (Superni 75, Superni 718 and Superfer 800H) oxidized at 900 °C in air up to 100 cycles are shown in Fig. 2. They have concluded that a saving in overall cumulative weight gain for  $\text{Cr}_3\text{C}_2$ -NiCr

coated superni 75, superni 718 and superfer 800H with respect to the bare alloys are of the order of 37.3, 26.3 and 19.6%, respectively.

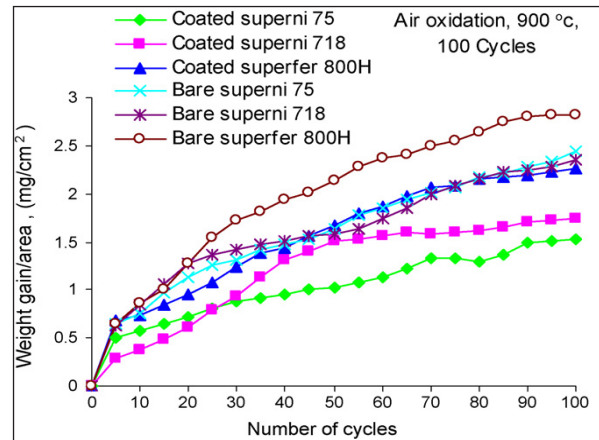


Fig. 2: (Weight gain/area)<sup>2</sup> Vs. Number of Cycles Plot for  $\text{Cr}_3\text{C}_2$ -NiCr-coated and Bare Superalloys Subjected to Cyclic Oxidation in air for 100 Cycles at 900°C. Kamal et al (2009)

## CONCLUSION

The use of Ni-, Fe- and Co- based superalloys by virtue of their excellent high temperature properties coupled with corrosion resistance, have been widely used as gas turbine engine components, boilers, etc and many more applications are still to be explored, where these alloys may have remarkable potential. Although the superalloys have sufficient mechanical strength for such high temperature applications, yet they are prone to degradation by high temperature oxidation/corrosion during long term exposures. Therefore, the superalloys need to be protected, however the protection system must be practical, reliable and economically viable. A mathematical model needs to be developed to simulate the actual industrial environmental conditions for predicting the corrosive behaviour and life of the coatings.

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