High Temperature Oxidation and Carbon Nano Tubes-An Overview

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Abstract

Oxidation of metals and alloys took place when they are heated to elevated temperatures in air or highly oxidising environments. It is considered to be the most important high-temperature corrosion reaction as it is understood that oxidation reaction develop a protective oxide scale to resist various corrosion attacks. High temperature oxidation is a solid-gas chemical reaction that produces the oxide (s) of constituents within the solid. The rate of oxidation for metals and alloys increases with the increase in temperature and this further leads to the spalling of protective oxide layers. At elevated temperatures the oxide may also be liquid or volatile. And once the protective oxide layer is peeled off, more and more basic elements of the base alloy get oxidised to heal the scales. This phenomenon of breaking and healing of the scales will lead to the loss of basic elements from the metals and alloys rendering them unfit for a specific use. Further, for elevated-temperature service, use of superalloys and the effect of incorporation of Carbon Nano Tubes (CNTs) into various alloy powder coatings on the morphology of the coating surface and corrosion properties has been a topic of technology concern.

In this paper a review has been made of the recent studies on the phenomenon of high temperature oxidation of metals, alloys and superalloys and the incorporation of Carbon Nano Tubes into various alloy powder coatings.

Keywords

CNTs, High Temperature Oxidation, Superalloys, Corrosion

I. Introduction

Surface engineering is the range of technologies that modify the surface of a component to improve its performance characteristics whether it is wear & corrosion resistance or something else. The vast majority of engineering components fail as a direct consequence of a surface-initiated failure, be it fatigue, corrosion or wear. Coatings can be applied to surfaces to improve the surface characteristics over those of the bulk properties and are widely used in tribological applications. One of the foremost coating methods is thermal spraying [1].

Oxidation of metals and alloys took place when they are heated to elevated temperatures in air or highly oxidising environments. It is considered to be the most important high-temperature corrosion reaction as it is understood that oxidation reaction develops a protective oxide scale to resist various corrosion attacks. High temperature oxidation is a solid-gas chemical reaction that produces the oxide(s) of constituents within the solid. The rate of oxidation for metals and alloys increases with the increase in temperature and this further leads to the spalling of protective oxide layers [2].

The superalloys are frequently used in high temperature applications such as gas turbine and energy conversion systems etc. During operation, blades and vanes of gas turbine are subjected to high thermal stresses and mechanical loads. In addition, they are also attacked chemically by oxidation and/or high temperature corrosion [3]. According to Eliaz et al., [4], the superalloys at gas turbine engines serve most of the time in an oxidising environment. Therefore high temperature oxidation of superalloys has attracted the attention of many researchers in the past as well as in the recent times.

Nanotechnology nowadays is one of the most important trends in science, perceived as one of the key technologies of the present century. It has vast applications in industrial manufacturing processes, in the introduction of advance materials. In 1991, Sumio Iijima [5], reported the preparation of a new type of finite carbon structures. These carbon needles were made of coaxial graphitic tubes (up to about 50) ranging from 4 to 30 nm diameter, up to 1m in length and invariably closed at both ends (fig. 1, shows the electron micrographs of the microtubules of graphitic carbon obtained in this work) [6].

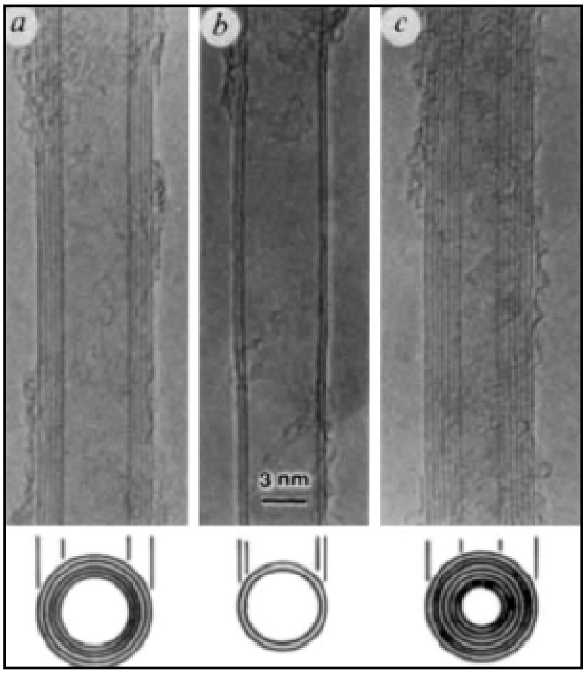

Fig. 1: Electron Micrographs of "Microtubules of Graphitic Carbon" Obtained in the First Report of CNTs. Parallel Dark Lines Correspond to the (0 0 2) Lattice Images of Graphite. A Cross-Section of Each Tubule is Illustrated. (a) Tube Consisting of Five Draphitic Sheets, Diameter 6.7 nm. (b) Two-Sheet Tube, Diameter 5.5 nm. (c) Sevensheet Tube, Diameter 6.5 nm, Which has the Smallest Hollow Diameter (2.2 nm)

Reprinted from with permission from Nature Publishing Group. [6].

Carbon Nanotubes (CNTs) are known to possess exceptional mechanical properties, very high thermal conductivity [7], high current carrying capacity [8]. Further studies made by researchers [9], revealed that the CNTs–Alloy powder composite coating, made on mild steel substrate, possesses higher resistance to corrosion (more than double, 42 hours as compared to 20 hours) when compared to pure alloy powder coating. Chen et al. [10], also reports that the metal surface possesses defects, cracks, gaps, crevices and micro holes. More over this micro hole behaves as active sites for dissolution of metal during corrosion. Nanoparticles i.e. CNTs can easily enter and fill these gaps and act as physical barrier to the corrosion process. Thus CNTs enhances the mechanical and tribiological behavior of composites.

II. Oxidation of Metals and Alloys

Oxidation of metal is reaction between a metal and oxygen gas and the total chemical equation is considered as,

$$aM + \frac{b}{2}O_2 \rightarrow M_aO_b$$

It may seem to be the simplest chemical reaction. However, the reaction mechanisms may prove to be more complex, as the reaction path and oxidation behaviour of a metal depend on a variety of factors.

The initial step in the metal-oxygen reaction involves the adsorption of gas on the metal surface. As the reaction proceeds, oxygen may dissolve in the metal, resulting in the formation of oxide on the surface either as a film or as separate oxide nuclei. Both the adsorption and the initial oxide formation are functions of surface orientation, crystal defects at the surface, surface preparation and impurities in both the metal and the gas [11].

The surface oxide then separates the metal and the gas. When a compact film covers the surface, the reaction may proceed only through a solid-state diffusion of the reactants through the film. Metals may also form porous oxide scales which as such do not serve as a solid-state diffusion barrier between the reactants. In such cases the reaction may be limited by processes occurring at phase boundaries. Further, at high temperatures, the oxide may also be liquid or volatile [11].

Ni is one of the base metals in several of today's superalloys. Haugsrud [12], revisited the high-temperature oxidation of Ni with an extensive review and conducted experiments to study the oxidation behaviour of Ni in the range of 500-1300^{0}C and oxygen pressure from 1X10^{-4} to 1 atm. The oxidation followed a parabolic rate law at 1100^{0}C and the rate was found to be governed by outward lattice diffusion of Ni via either singly or doubly charged Ni vacancies. At lower temperatures the oxidation mechanism has been reported to be more complex and contradictions are found in the literature. Short circuit mechanisms of both Ni and oxygen are of importance, where the influence of oxygen transport increases with decreasing temperature. Further he concluded that the mechanism of oxygen entering is not fully clear, but since the oxygen diffusivity in NiO is too slow to account for the inward growth, oxygen is assumed to penetrate the scale as gaseous species.

The effects of thin surface applied Y_2O_3, Al_2O_3 and Cr_2O_3 coatings or films on the selective oxidation of chromium for Ni-15Cr and Ni-10Cr alloys in air at 1000^{0}C have been studied by Yedong and Stott [13]. The oxide films were deposited by an electrochemical method. They observed the establishment of chromia scale which was promoted effectively by the presence of an Y_2O_3 film on Ni-15Cr and at least locally on Ni-10Cr. In comparison with the cases of surface deposited Al_2O_3 and Cr_2O_3 oxide films, the additional beneficial effect of the Y_2O_3 film in maintaining the selective oxidation of chromium reportedly attributed to its ability to improve the mechanical integrity and adhesion of the chromium scale.

Bittel et al. [14], studied the oxidation of 304 L stainless steel in steam and in air in the temperature range of 1000 to 1375^{0}C and found that the oxidation by steam was fast as compared to that by air. The diffusion through Fe-Ni-Cr spinel layer was suggested as the parabolic rate controlling process in case of oxidation by steam. Whereas, in case of oxidation by air the formation of Cr_2O_3 was reflected as a reason for slow oxidation.

Further oxidation behaviour of three grades of austenitic stainless steel (AISI-316, -321 and -304) in dry air with and without superficially applied CeO_2 was investigated by Seal et al [15]. The linear heating rate employed was 6 K min^{-1} up to maximum temperature of 1423 K (1150^{0}C) and the isothermal holding temperature was 1273 K (1000^{0}C). In the bare condition 321-grade steel was reported to exhibit best performance whereas in the presence of coatings the performance of 316 and 321 grades was identical. Roy et al [16] have also studied the role of the similar type of coatings on AISI 347 and reported identical results.

III. Oxidation of Superalloys

Since superalloys are frequently considered for use at elevated temperatures under oxidising environments such as in gas turbines and energy generation systems, it is pertinent to discuss the oxidation of the superalloys. 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 aluminium or chromium to develop oxidation resistance [17]. Further Pettit and Meier [17] 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 aluminium or chromium in the superalloys.

Further, according to Chatterjee et al. [18], the mixed oxides of the general composition AB2O4 (A and B represent two metallic components) have often been identified as oxidation products of Fe-, Ni- and Co- based alloys. The most important properties of these compounds with respect to oxidation resistance are the diffusion coefficients of the cations and anions, which are usually much smaller than in their parent oxides.

Levy et al [19], has reported studies on the cyclic oxidation resistance of three single-crystal nickel base superalloys and DS Mar M 200 at 1093^{0}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^{0}C using the tube furnace produced a ranking of the alloys consistent with that produced by tests at1093^{0}C.

Another comparison of the oxidation kinetics of four commercial heat-resisting alloys namely Hastelloy C-4, SS 304L, Incoloy 800H and Incoloy 825 in air from 600 to 1200^{0}C has been presented by Hussain et al [20]. Hastelloy C-4 was found to be the most resistant to oxidation for temperatures upto 1000^{0}C following a cubic-rate law. SS 304L was reported to be oxidised in the form of stratified nodules of two distinct layers, which grow in opposite directions at the metal-oxide interface irrespective of time and temperature of oxidation. Incoloy 800H and Incoloy 825 showed similar kinetics, following parabolic-rate law at 1000^{0}C and 1200^{0}C. They also observed the deleterious effect of Mo on the oxidation resistance of Incoloy 825.

The oxidation behaviour of a single-crystal Ni-base superalloy has been studied using discontinuous thermogravimetric analysis and prolonged exposure in air at 800 and 900^{0}C by Li et al [3], and over the temperature range from 1000–1150°C by Li et al [21]. They observed that the mass gain at 900^{0}C was lower than that at 800^{0}C due to the formation of a protective inner α-Al_2O_3 layer at 900^{0}C. The scale formed at 900^{0}C was found to be more uniform than that formed at 800^{0}C, which consisted of several layers: an NiO outer layer, spinel-rich sublayer, a $CrTaO_4$-rich layer and an α-Al_2O_3 inner layer. Where as in the temperature range of 1000–1150°C, the outer NiO layer was observed to be replaced by an outer layer of spinel, a sublayer of mainly α-Al_2O_3, with unchanged composition of inner layers of the scale. Further, no internal oxides or nitrides were observed below the inner α-Al_2O_3 layer after 1000 hr at 1000°C, and after 200 hr at 1100 and 1150°C.

IV. Studies of CNTs Incorporated Alloy Powders Coatings

Experimental work made by Keshri et al. [22], showed that thermal spray processes provides the possibility of developing coatings of Al_2O_3–1.5 wt.% CNT on AISI 1020 steel. An increase of 15% in the microhardness value, 24% in relative fracture toughness was observed with the addition of 1.5 wt.% CNT in the reference coating (coating with Al_2O_3 powder without CNTs). Furhter Balani et al. [23], reported an improvement of 49 times in the sliding wear resistance by the addition of 8 wt.% CNT to Al_2O_3. Such improvement was attributed to a uniform dispersion of nanotubes, CNT bridging between the splats and enhanced densification by CNTs.

Experimental results of the study made by Praveen et al. [9], revealed that the CNTs–Zn composite coating, made on mild steel substrate, possesses higher resistance to corrosion (more than double, 42 hours as compared to 20 hours, during salt spray corrosion testing) when compared to pure zinc coating. CNTs inclusion reduces the porous nature of pure zinc coating. Corrosion behavior of metal deposits containing nano particles reports that the incorporation of CNTs in the deposits improved the corrosion resistance.

Experimental results of the study made by Chen et al. [10], revealed that the corrosion resistance for the CNTs– Ni coating was seven times and three times as compared to the bare and pure Ni coated samples. CNTs were embedded deeply in the nickel grains, reinforcing the nickel layer, and filled in crevices, gaps and micron holes [9]. CNTs act as inert physical barriers to the initiation and development of defect corrosion, modifying the microstructure of the nickel layer and hence improving the corrosion resistance of the coating.

V. Conclusion

Since oxygen is present in most of the high temperature environments, oxidation is the most important form of high temperature corrosion. Most materials experience oxidation if subjected to air or to environments containing sufficient oxygen at a high temperature. It is noticed that oxidation resistance depends mainly on the capability of the alloys to form and maintain a protective oxide of Cr_2O_3, Al_2O_3 or SiO_2 with low rates of growth. This scale acts as a barrier between the bare alloy and the environment consequently limiting the corrosive attack. Furthermore, upto to about 950^{0}C, alloys relying upon a Cr_2O_3 oxide layer can be utilised, whereas at higher temperatures, alloys capable of forming the more stable Al_2O_3 are preferably employed since the Cr_2O_3 tends to convert to volatile CrO_3 beyond 950^{0}C. CNTs possess exceptional mechanical, thermal and electrical properties and are showing enhanced corrosion resistance when made a composite with alloy powder coatings as compared to the pure alloy powder coating.

Further it has been observed from the literature that although considerable insight has been accumulated on mechanisms of high temperature oxidation, from both engineering and more fundamental studies, reaction mechanisms are often not fully understood. Degradation by the high temperature oxidation is one of the main failure modes of hot-section components in the gas turbines and boiler tubes, so an understanding of the oxidation is very necessary for superalloys and CNTs may be proved very successful in controlling corrosion.

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