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Research Progress on High-temperature Oxidation of Austenitic Stainless Steel for Ultra-superCritical Boilers

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Abstract. In this paper, four typical austenitic heat-resistant steels (TP304H steel, TP347H steel, Super304H steel and HR3C steel) are taken as examples to review the research progress of high-temperature oxidation of austenitic stainless steel for ultra-supercritical unit boilers, and the mechanism and protective measures of high-temperature oxidation of austenitic stainless steel are discussed, so as to provide references for material improvement and safe use of unit boilers.

1. Introduction

In recent years, with the rising demand for electricity, efficiency and reduce the pollution of coal-fired power plant put forward higher requirements, improve the parameters of power plant boiler is a kind of effective method to solve the problem, the development of the ultra-supercritical unit becomes the hotspot technology development at home and abroad [1-2]. The ultra-supercritical unit is a boiler whose parameters are raised to a steam temperature not less than 593°C or a steam pressure not less than 31 MPa [3-4]. The improvement of the parameters can increase the thermal efficiency of thermal power plant to 48%, and reduce the coal consumption per kilowatt-hour of power supply to 256g [5-6]. The improvement of boiler parameters of the unit also greatly improves the material performance requirements of the key parts, namely the "four tubes" of the boiler (superheater tube, reheater tube, water-cooled wall tube and economizer tube) [7-8].Austenitic stainless steel has become the preferred material for ultra-supercritical unit boiler steel due to its excellent high-temperature strength, high-temperature endurance strength and high-temperature oxidation resistance [9-10].Austenitic stainless steel has been in service for a long time in high-temperature and high-pressure environment. Oxidation of pipe wall and peeling off of oxide skin have always been the key to the service life of materials, which has attracted a large number of researchers to study the high-temperature oxidation of austenitic stainless steel [11-12].

In this paper, the main austenitic stainless steel as the object, the research status and protection mechanism of high temperature oxidation of different kinds of austenitic stainless steel were reviewed, and the existing problems of high temperature oxidation resistance of austenitic stainless steel were discussed, in order to provide reference for the improvement of materials and anti-oxidation protection in the future.

2. High Temperature Oxidation of Austenitic Stainless Steel for Ultra-supercritical Boiler

2.1. TP304H Stainless Steel

TP304H steel belongs to type 18-8 chromium-nickel austenite heat-resistant steel, which has good bending and welding properties, high durable strength, corrosion resistance and microstructure stability. The maximum service temperature of the material can reach 650°C, and the maximum oxidation resistance temperature can reach 850°C [13-14].

TP304H steel were studied at 560°C, 590°C and 620°C temperature oxidation behaviour by Ming-li Xu in Xian university of technology [15], it is found that TP304H steel oxidation kinetics equation follow $\Delta m = KTZ$ parabolic law, test temperature material does not appear in the process of oxidation layer peeling situation, at the same time, the study found that the TP304H steel surface oxide growth way is: first generate granular oxide surface, and then generate crystal in oxide on the surface of objects, these crystals lateral growth form continuous oxide film layer, crystalline oxide grew up further, started the longitudinal grew up, small holes formed between crystalline oxide, with the extension of time, the crystalline oxide continue to grow up, the hole between the disappear, then on the crystalline oxide generated a lot of whisker. And with the increase of oxidation temperature, this growth process is faster.TP304H inner wall oxide is composed of two layers of oxide, the outer layer oxide is loose, the outer layer oxide is Fe_2O_3, the inner layer oxide is dense, and the inner layer is composed of (Fe, Cr) spinel oxide and NiO. The interface between the inner and outer oxides corresponds to the original metal surface.

Hongfei Feng [16] studied the double-layer structure of TP304H steel oxide film and found that the inner layer contained Cr elements and the outer layer only contained oxygen and Fe elements. Moreover, continuous holes were often formed on the interface between the inner and outer layers. The growth mechanism of the outer oxide layer is as follows: firstly, granular oxide is generated on the surface; then, it grows into continuous crystalline oxide layer; then, the grains grow vertically and pores appear; then, as the grains grow horizontally, the pores disappear and the oxide film continues to thicken. The growth process of inner layer is as follows: due to the presence of Cr in inner layer, Cr rich band will be generated in the growth process, which can effectively reduce the growth rate of oxide layer. However, due to the slow diffusion of Cr elements in the grain, it is difficult to form a continuous Cr rich belt, and the oxide layer can continue to grow beyond the Cr rich belt, and often forms a Cr rich black spot. Due to the rapid diffusion of Cr element, continuous and dense Cr-rich layer is often formed at the grain boundary, so it is difficult for the grain boundary to be oxidized, and finally, long and narrow white unoxidized gap or closed nickel-rich region is often formed.

Xingeng Li [17] and others studied shot peening in TP304H steel high temperature steam oxidation behavior of function, the results show that the surface peening deformation can effectively slow oxidation kinetics in 0.5 MPa shot peening intensity and improve the effect of antioxidant properties under the condition of 730°C, the best surface oxidation film grains are refined, Cr in membrane relative concentration increased significantly, oxide film phase composition by pure Fe and Fe, Cr mixed oxide into Cr_2O_3.It is concluded that the treatment of surface shot peening increases the concentration of dislocation, vacancy and other defects in the surface area of the alloy, improves the nucleation density in the early oxidation stage, provides a large number of short circuit diffusion channels for Cr, and reduces the critical concentration of selective oxidation of Cr. The short-circuit diffusion of Cr on the surface layer of matrix ensures the diffusion flux of the stable growth of Cr_2O_3 film, thus inhibiting the formation of Fe oxide.

2.2. TP347H Stainless Steel

TP347H steel is a niobium stable chromium-nickel austenite heat-resistant steel with high thermal strength and intergranular corrosion resistance, good oxidation resistance and good elbow and welding performance [18-19].

Dongbin Wei [20] and others using home-made lab under 800°C high temperature steam oxidation device of TP347H steel tube sample simulation test and high temperature steam oxidation, TP347H steel high temperature steam oxidation organization and composition were studied, and the results show that the TP347H steel at 800°C water vapor oxidation kinetics follows the laws of parabola, the oxide film of test samples by scanning electron microscopy (SEM) and energy spectrum analysis showed that the structure of the oxide film is divided into inside and outside two layer, in the outer layer, oxygen content gradually reduce from outside to inside, Fe content gradually reduce from the inside out; The outer oxide film only contains trace Cr and Ni elements, while Cr elements in the inner layer are enriched at the interface between matrix and inner layer, while Ni elements in the inner layer show correlation dilution.

Yanming Chen [21] and others, using analog device designed steam oxidation experiments under 700°C for 1.5, 2 and 4 h 4 oxidation experiment was carried out at different times of the early stage of TP347H steel oxidation behavior research, the results showed that under 700°C, TP347H fast oxidation, surface covered by tiny particles completely first, then give birth to many island structure, and on the island structure will grow small whisker. EDS and Raman results show that the oxide layer consists of inner and outer layers, which are mainly composed of Cr_2O_3, NiO, Fe Cr_2O_4 and Fe Cr_2O_4.

Qiang Ma et al. [22] studied the high-temperature vapor oxidation layer after 5000h operation of TP347H tube in the screen superheater of 600MW supercritical unit. The results showed that the volatilization of $CrO_2(OH)_2$ led to the formation of Fe oxide on the outer layer, and the formation of $FeCr_2O_4$ inner layer could effectively slow down the process of vapor oxidation, and the thickness of oxide layer would remain unchanged after entering the steady state oxidation stage. At the same time, the vapor oxidation resistance of TP347H was improved with the decrease of grain size.

2.3. Super304H stainless Steel

Super304H steel is improved and developed on the basis of TP304H steel. By adding Cu to form Cu rich phase, creep fracture strength of the material is greatly improved. By adding Nb and N elements in the composite, high-temperature strength and durability of the material are further improved [23-24]. Xuedong Li and et al. [25] studied the high-temperature steam oxidation behavior of Super304H steel, and the results showed that the oxidation rate of Super304H steel was close to a straight line at 400°C, while the oxidation rate was closer to a parabola when it was higher than 400°C. Super304H steel oxide film has a double-layer structure, and the outer oxide film particles are thick and loose, mainly composed of Fe_3O_4, while the inner oxide film particles are small and compact, mainly $FeCr_2O_4$.

Dongsheng Li and et al. [26] studied the high-temperature oxidation resistance of Super304H austenitic stainless steel by weighing method, SEM, XRD et al. It is found that the oxidation kinetics curves of the two stainless steels follow the parabolic law. Super304HS has a better oxidation resistance than Super304H, and Super304H oxidized 100 at 900°C H, the oxide film obvious loss. The method of using scanning electron microscopy (SEM), X-ray diffraction (XRD) on Super304H stainless steel on the surface of the oxide film morphology and structure were studied, the results show that at 700°C and 800°C, the two materials of oxide film, are $FeCr_2O_4$ Cr_2O_3 and small amounts of spinel structure, Super304H oxidation product of steel at 900 ℃ is mainly composed of Cr_2O_3, Fe_2O_3 and spinel $FeCr_2O_4$ Super304HS at 900°C of oxide film is mainly composed of Cr_2O_3 and spinel $FeCr_2O_4$.

Ming Le [27] studied the influence of surface modification technology on Super304H steam oxidation behavior, and the research results showed that :(1) surface modification methods, such as shot peening and aluminizing, could significantly improve the anti-steam oxidation ability of Super304H.When Super304H carried out steam oxidation in water vapor with dissolved oxygen concentration of 10ppb, its oxidation kinetics curve tended to be linear, and the oxidation film was mainly single-layer Cr_20_3.When the surface shot peening samples were oxidized in the water vapor environment with dissolved oxygen concentration of 10ppb, the oxidation kinetics curve was parabolic and the oxide film was monolayer Cr_2O_3.When the surface aluminizing sample was oxidized in the water vapor environment with dissolved oxygen concentration of 10ppb, its oxidation kinetics curve was parabolic and the oxide film was single layer $A1_2O_3$.(2) with the increase of steam temperature,Super304H oxide film gradually changed from single layer to double layer structure. The oxidation behavior of surface shot peening samples and surface aluminizing samples was not affected by temperature. (3) Dissolved oxygen concentration plays an important role in the oxidation weight gain, the morphology and composition of the oxide film of Super304H samples. When the concentration of dissolved oxygen in the steam rose to 5ppm, the oxide scale of Super304H sample developed a large-scale peeling after 500h of steam oxidation. The anti-vapor oxidation capacity of the surface shot peening samples was less affected by the concentration of dissolved oxygen. With high concentration of dissolved oxygen, the parabolic rate constant of the surface shot peening samples increased, and the oxidation activation energy increased. The vapor oxidation resistance of surface aluminized samples was not affected by the concentration of dissolved oxygen. Under the condition of high dissolved oxygen concentration, the parabolic rate constant of the surface shot peening sample increases and the oxidation activation energy increases.

Jiangbin Wang [28] studied the oxidation characteristics of Super304H stainless steel. Based on the supercritical water experiment platform, experiments were carried out in supercritical water environment with different temperatures and dissolved oxygen for Super304H austenitic steel. Through the analysis of oxidation weight gain, oxide surface morphology, oxide cross section EDS analysis figure and XRD. The effects of temperature and dissolved oxygen on the growth rate and microstructure of oxide film were investigated. It was found that the oxidation rate increased with the increase of temperature and dissolved oxygen. The oxide film is a typical three-layer structure. The outer layer is rich in iron, the inner layer is rich in chromium, and the inner layer is diffused. With the increase of temperature and dissolved oxygen, the amount of holes in the outer oxide film increased gradually. In the early stage of oxidation, nodular oxides will form, and with the increase of temperature and time, these nodular oxides will eventually completely cover the metal surface. The oxides formed in the absence of oxygen are mainly Fe_3O_4 and $(Fe, Cr)_3O_4$.Fe_2O_3 is formed in the outermost layer of the environment containing 2000ppb dissolved oxygen. In this paper, the stress factors leading to the flaking of the oxide film are analysed, and the two kinds of wedge-type flaking and buckling flaking under tensile stress are explained. It is also discussed that the temperature fluctuation and the thickness change of oxide film have significant influence on the spalling.

2.4. HR3C Stainless Steel

HR3C steel is a new type of austenitic heat-resistant steel developed by composite addition of Nb and N alloy elements on the basis of TP310, with high high-temperature strength and excellent comprehensive performance [29-30].

Zhen Yang and et al. [31] studied the high-temperature oxidation behavior of HR3C in air and water vapor at 750°C, and the results showed that continuous $(Cr, Mn)_2O_3$ films were formed on the surface of HR3C in two atmospheres. The oxidation kinetics of HR3C alloy in static air presents a piecewise parabola law. The existence of water vapor makes the $(Cr, Mn)_2O_3$ film rupture advance and greatly accelerate the oxidation of the alloy, which leads to the overall deviation of the oxidation kinetics of HR3C in the pure water vapor from the parabolic law. (Cr, Mn) the rupture of $(Cr, Mn)_2O_3$ film is the result of the combined action of the cavity in the interface between the film and the matrix and the growth stress inside the membrane, which makes the bare metal matrix react directly with the high-temperature air or water vapor to form Fe_3O_4 tumour.

Tong Lee-ying [32] huaneng yuhuan power plant are analyzed, at the end of the operation of a 5400 h and 23400 h HR3C level reheater tube steam side oxide layer of micro structure, morphology and distribution pattern of the elements of the results found that with the deepening of the oxidation, lateral HR3C steam oxide layer by layer structure developed into four layers structure, the poor Cr in the base metal near the oxide layer is the growth of the oxide layer shortcut.

3. High-temperature Oxidation Mechanism and Protection of Austenitic Stainless Steel for Ultra-supercritical Boiler

3.1. Oxidation Mechanism

Yamin Huang and et al. [33] studied the oxidation failure mechanism of austenitic stainless steel at ultra-high temperature, and the results showed that: the oxide film on the surface of stainless steel has a multi-film structure, and the oxidation environment and element distribution and diffusion at the interface between matrix and oxide layer have an important impact on the structure and performance of the oxide film. The failure behavior of the oxide film is mainly manifested by the generation of cracks in the oxide layer and the spalling of the non-dense oxide layer. Hong Xu and et al. [34] studied the regrowth and spalling behavior of oxide on the surface of austenitic heat-resistant steel. The results showed that iron ions were diffused outwards through complex fe-cr oxide to form the oxide outer layer dominated by iron oxide. When the outer oxide layer grows to a certain extent, local spalling occurs due to the size difference between the inner and outer oxide film oxide particles.

3.2. Protective Measures
The steam oxidation resistance and oxide stripping performance of steel should be considered in the design. Internal shot peening can produce crushed austenite grains and a large number of slip bands near the inner surface of the steel tube. In addition, due to the surface defects of shot peening, the nucleation density and growth rate of chromium oxide are increased, which is conducive to the formation of a single Cr_2O_3 film. During shot peening, we should pay attention to the strength of shot peening. Too low strength will lead to the diffusion and enrichment of chromium and no significant change in the nucleation rate of oxide. If the strength is too high, it will promote the diffusion of chromium as well as accelerate the diffusion of iron and oxygen ions. Both of them will cause the failure to form a single Cr_2O_3 film on the inner wall of the steel tube [35].

The grain size of the material can be controlled by controlling the amount of rolling deformation and the final solid solution treatment in the manufacturing process of the raw material. The larger the degree of cold deformation of the material, the finer the grain size will be, and the better its oxidation resistance will be. Therefore, the grain size should be refined as far as possible in the manufacturing process under the condition that other properties meet the requirements [36].

4. Summarize
High temperature oxidation of austenitic stainless steel has always been a hot topic in the industry. However, with the increasing of temperature, the oxidation of austenitic stainless steel becomes an inevitable problem, and there are many factors affecting the oxidation. Although there are a lot of researches on oxidation of austenitic stainless steel, there are always difficulties in this problem. The in-depth study of materials is of great significance to the development of materials science and engineering practice, and is also the focus of attention in the future.

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