A solution to the Embrittlement after Aging of HR3C

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Abstract. HR3C steel was widely used in superheaters and Reheaters of Million Power Unit because of its good anti-oxidation and corrosion performance and high endurance strength. With the increase of service time, HR3C steel showed obvious aging embrittlement, that is, in the early stage of service, the elongation at room temperature decreased to less than 10%, which posed a threat to the safe operation of units. Although the durable strength of S30432 steel was higher than that of HR3C steel at 600 ℃ ~700 ℃, the anti-oxidation and corrosion performance of S30432 steel was lower than that of HR3C steel because of the less Cr content of S30432 steel, which limited the application of S30432 steel. The research on the anti-oxidation and corrosion performance of S30432 steel was analyzed. The results showed that after surface modification such as shot peening and aluminizing, the anti-oxidation performance of S30432 steel was equivalent to that of HR3C steel. The plastic decline of S30432 steel after aging was analyzed. The results showed that the plasticity of S30432 steel would also decline in the early service, but the aging embrittlement was not obvious. Based on the above analysis, a method of replacing HR3C steel with surface modified S30432 steel was proposed to solve the aging embrittlement problem of HR3C steel.

Keywords: HR3C, embrittlement after aging, oxidation resistance, shot.

1. Introduction

In order to accommodate the increasing demand for power and the escalating pressure on environmental protection, significant advancements have been made in ultra-supercritical thermal power units with large capacity and high parameters. Consequently, their proportion has gradually increased. The enhancement of operational parameters has led to more stringent requirements being placed on the steel used for the high-temperature heating surfaces of boilers. Apart from requiring higher durable strength, the material should also exhibit excellent resistance to oxidation corrosion. The 18Cr-8Ni series (S30432, etc.) and 25Cr-20Ni series (HR3C, etc.) austenitic heat-resistant steels are extensively employed in the key high-temperature components (such as superheaters and reheaters) of 600℃ ultra-supercritical power station boilers in active service. Furthermore, it’s worth noting that the 25Cr-20Ni austenitic heat-resistant steel with higher content of Cr exhibits better oxidation corrosion resistance than the 18Cr-8Ni austenitic stainless steel. As a result, the 25Cr-20Ni HR3C steel is more extensively used in the final superheater and final reheater with the highest temperature.

However, HR3C steel has gradually revealed certain issues as the operation time of millions of units in China increases, which most being reflected in its obvious tendency of aging embrittlement, that is, the impact energy at room temperature will plunge to 10% of the original pipe after aging at 650℃/1000h, witnessing a decline of 90%[1-2]. The same scenario is also observed in the room temperature mechanical property test of the service pipe. The impact energy of the HR3C steel pipe in service for 5400h drops to 1/3 of the original pipe [3], while the impact energy of the HR3C steel pipe in service for 15000h falls to 1/10 of the original pipe [4]. The impact of HR3C tubes in service for 50000h at room temperature decreases to 4J from the original state of 201J, amounting to a reduction of 98%. In the meanwhile, the elongation after fracture plummets to less than 10%, and the impacted fracture exhibits a brittle behavior [5~9]. Relevant studies indicates that the primary reason for the marked decline in plasticity is the formation of $M_{23}C_6$ flakes along the grain boundary, which grow rapidly. Although the causes of the plasticity decline in HR3C have basically reached a consensus, there exists relatively few relevant studies on how to solve this problem. In the reference 10, it is suggests that the ratio of Ni-N content in HR3C steel has a discernible influence on the aging embrittlement performance.

Compared with TP304H steel, the strengthening elements Cu, Nb, N and B are added to S30432 steel, meanwhile the microstructure stability and high temperature performance of S30432 steel of it have been improved for the addition of Cu element. The durable strength of S30432 steel at 700℃ is 14.5% which superior than that of HR3C steel, and its durable strength at 750°C is marginally higher than that of HR3C steel [11]. Consequently, S30432 steel surpasses HR3C steel in terms of durable strength alone. However, the oxidation corrosion resistance of S30432 steel is inferior to that of HR3C steel, and its flue gas corrosion resistance is lower than that of TP347HFG steel [10]. Therefore, The materials which primarily used in the high-temperature sections of the final passing and final reheating of ultra-supercritical units is HR3C steel.

Furthermore, relevant research have identified that[12-15] though the plasticity of S30432 steel after service still exhibits a downward trend, it does not display an obvious aging embrittlement tendency Therefore, if the oxidation corrosion resistance of S30432 can be enhanced to equal or even surpass that of HR3C steel, S30432 steel could be considered a viable alternative to HR3C steel. This would mitigate the adverse effects of HR3C steel's aging embrittlement on the safe operation of the unit.

2. Structure and performance changes of S30432 after service

The materials which be used in the final superheater and the final reheater of the million units should possess sufficient endurance strength and excellent organizational stability. It had been reported[12-15] that the microstructural changes of S30432 steel after prolonged service or aging primarily manifest as the precipitation of rich-Cu and MX phases within the crystal, as well as the precipitation of $M_{23}C_6$ along grain boundaries. On the other hand, these changes in properties were mainly characterized by an increase in strength and a decrease in plasticity. It could be found that the precipitated phases within the crystal would have a contribution to precipitation strengthening, which finally promoted the increase of strength and hardness. In addition, it was worth noting that a decline in plasticity could be found for the precipitation of $M_{23}C_6$ at the grain boundary which had a weakening effect on the grain boundaries. In this regard, S30432 steel exhibited similar characteristics to HR3C steel. However, the rate of $M_{23}C_6$ precipitation along grain boundaries in S30432 steel was lower compared to HR3C steel, resulting in a lesser decline in plasticity. Reference 13 revealed that no significant coarse grain boundary precipitates could be observed within the metallographic structure of S30432 steel at 650℃ under a stress level of 190MPa for a duration of 16364.1 hours. Moreover, this sample exhibited a post-fracture elongation value of 23.2%.

Pan[14] conducted research on microstructural and property changes occurring in aged S30432 steel using an aging temperature of 650℃ with maximum aging time set at 3000 hours. It was observed that during early stages (within first 1000 hours) of aging process, both elongation and impact toughness values rapidly decreased after tensile fracture at room temperature, however, their rate declined gradually over time until reaching stability levels at last. After undergoing an aging period lasting for 3000 hours, S30432 demonstrated an elongation value exceeding 35% at room temperature alongside impact toughness surpassing 90J/cm^2 with impact work greater than or equal to 72J, which indicated that S30432 steel could sustain good plasticity even after extended periods of aging treatment. The results indicated that the elongation and impact toughness of S30432 after tensile fracture at room temperature decreased rapidly in the early stage of aging (within 1000h), and the decline rate slowed down at last. Therefore, it can be concluded that the aging embrittlement tendency of S30432 steel is lower than that of HR3C steel.

Zhao et al.[15] investigated the microstructural and mechanical property changes of S30432 superheater tubes after 10,000 hours of service. It was reported that the grain growth could be observed on the outer wall and a decrease in room temperature elongation following service. In the meanwhile, the original tube had an elongation at room temperature of 61%, while the fire side exhibited elongations of 53% and 46.8% after 10,000 hours of service, indicating a significant reduction by 23.2%.

3. A comparison of the oxidation corrosion resistance of S30432 and HR3C

The oxidation corrosion resistance of HR3C steel was better than that of S30432 steel for the more content of Cr in HR3C steel. As clearly in reference 10, the steam oxidation resistance and smoke corrosion resistance for both steels was compared and it was obtained that under steam oxidation conditions at 650℃×1000h, HR3C steel displayed an oxide layer thickness below 2.5μm whereas S30432 steel exhibited a thickness of approximately one order magnitude higher at 18μm. Similarly, under smoke corrosion conditions at 650℃×20h, it was found that the weight loss for HR3C steel was measured to be 12mg/cm^2 while that for S30432 steel was 35mg/cm^2, which resulted in three times greater weight loss for S30432 steel compared to HR3C.

Li [16] conducted a comparative study on the corrosion resistance between HR3C steel and S30432 steel at temperatures of 650℃，700℃ and 750℃ by simulating flue gas environment using sulfate coating method with weight gain used as an indicator for characterizing corrosion resistance. The longest test duration lasted 200 hours. The experiment result revealed that the weight gain for S30432 steel twice exceeded that of HR3C steel at 650°C/200h.

Wang et al.[17] investigated the flue gas corrosion resistance of HR3C steel and S30432 steel at 700°C using a coating synthetic coal ash method to simulate flue gas environment. The longest test duration lasted 2000 hours. After completion of corrosion processes, the corroded products were cleaned clearly and the corrosion resistance was characterized by the weight reduction of the sample. Based on the discussion, it could be inferred that the corrosion resistance ratio between HR3C steel and S30432 steel exhibited superiority in favor of HR3C steel.

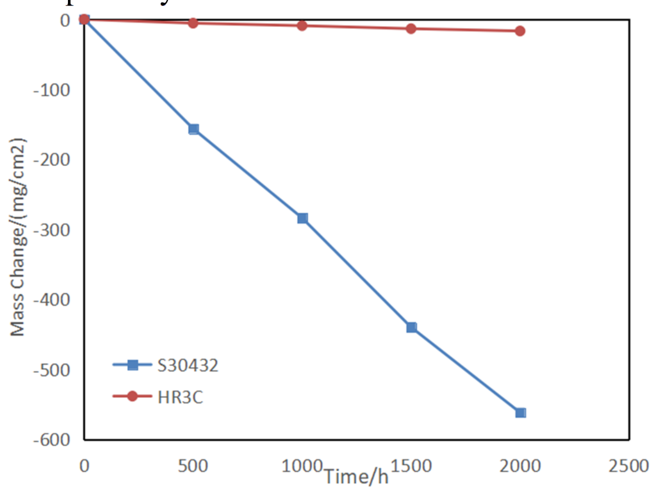

Fig.1 Corrosion kinetic curves of the S30432 and HR3C coated with synthetic coal ash in simulated atmosphere of 700 ℃

4. Effect of shot peening on steam oxidation resistance of S30432

The surface strengthening technology of shot peening had been applied to enhance the steam oxidation resistance of TP347H and TP304H superheater. By inducing compressive stress on the surface of austenitic steel pipe and promoting surface martensitic transformation, shot peening could effectively improve the steam oxidation resistance of austenitic stainless steel pipe [18].

In a study conducted by Yue et al.[19], the oxidation behavior of S30432 steel with and without shot peening treatment was investigated in water vapor at 650℃. It was found that shot peening reduced the oxidation rate of S30432 steel by one order of magnitude, resulting in finer oxide particles and an oxide layer approximately 3% compared to non-shot peened pipes. What's more, shot peening increased the Cr content on the tube wall's surface and induced martensitic phase transformation in the outermost layer, altering the composition of the oxide layer and significantly increasing its Cr oxide content. After shot peening, the Cr content in the surface oxide layer reached 36.3%, preventing further formation of oxides and thereby improving steam oxidation resistance. Wang et al.[18] confirmed that corrosion resistance is primarily influenced by Cr content and it could be speculated that smoke corrosion resistance for S30432 steel would greatly benefit from shot peening.

Zhao et al.[20] conducted 1,000-hour steam oxidation tests on both shot blasted and unshot blasted S30432 steel at temperatures ranging from 670℃ to 790℃ respectively. The results demonstrated that shot peening treatment has a positive influence on reducing its oxidation rate for one order of magnitude which significantly enhanced steam oxidation resistance for S30432 steel. This phenomenon was consistent with the research of Yue et al.[19].

Wang et al. [21] performed steam oxidation tests on both shot blasted and unshot blasted S30432 at 650℃ and the results demonstrated that the S30432 with shot peening treatment exhibits improved oxidation resistance within 600 hours. In addition, it was also observed that the weight of the oxide layer had no significantly increase and its thickness was approximately one-tenth compared to that without shot peening. Conversely, both the weight and thickness of the oxide layer on S30432 increased over time without shot peening. It was well known that the surface oxide layer of unshot blasted S30432 steel exhibited non-uniformity with local chromium content ranging from 29.69% to 2.17% (both mass fractions), while the surface oxide layer of shot-peened S30432 steel displayed uniformity with a chromium content of 44.26% (both mass fractions). According to the research of Wang et al. [18], it could be speculated that smoke corrosion resistance in S30432 steel will be significantly enhanced through shot peening treatment for that corrosion resistance was primarily associated with chromium content.

For further understanding the efficacy of shot peening process, Ge et al. [22] investigated the oxidation behavior of shot blasted and non-shot blasted S30432 steel under supercritical steam conditions at 635℃/25MPa. The findings revealed that after 3000 hours, the inner wall oxide layer thickness in non-shot blasted S30432 was more than three times greater than that in shot-blasted samples. Additionally, while the inner wall oxide layer in unshot-blasted S30432 exhibited a layered structure prone to detachment, it appeared thin and lacked obvious stratification phenomena when subjected to shot blasting treatment.

What's more, Yang et al.[23] conducted steam oxidation experiments on TP347HFG as well as inner wall-shot-peened samples of S30432 and TP347H at temperatures reaching 650℃ under pressures up to 27MPa. After observing million-unit service durations totaling approximately 72,000 hours for high-temperature reheater tubes made from both materials (S30432 and HR3C), it was found that inner wall-shot-peened TP347H and S30432 exhibits more excellent than TP347HFG.

The effect of heat treatment on the steam oxidation resistance of shot peening S30432 steel was investigated by Wang et al.[24]. The results indicated that there were no significant changes in the appearance of the shot peening layer during heat treatment at temperatures ranging from 730 to 800℃. Furthermore, the study on oxidation behavior at 620℃/(90%H2O+10%Ar) revealed that heat treatment had no noticeable impact on steam oxidation resistance.

Liu et al.[25] examined the stability of the shot peening layer in S30432 steel through various heat treatments. Hardness and metallography analyses were conducted to evaluate the condition of the shot peening layer. It was found that within a temperature range of 740 to 770℃, the shot peening layer maintained its ability to transport Cr element effectively towards the outer surface without significant changes in appearance. However, degradation of the shot peening layer began after heat treatment above 800℃, and it completely disappeared when subjected to temperatures exceeding 1000℃.

Besides, S30432 steel without shot peening will form an oxide film primarily composed of Cr in the surface layer initially under steam oxidation conditions. It was well known that an Fe oxide film would be formed instead when diffusion of Cr was insufficient within this surface layer. And due to a much lower diffusion rate compared to oxidation rate, an outer loose porous iron-rich oxide film and an inner dense Fe-Cr spinel phase were developed within this oxide layer structure. This loose oxide layer tends to easily detach from the material's surface. After shot peening, the Cr content of the surface layer was much higher than that of the substrate material, and it could be found that numerous grain boundaries and dislocation defects were formed in the surface layer to act as a fast channel for element diffusion, which accelerated element diffusion significantly. Consequently, a Cr-based oxide film which formed within this modified surface layer effectively inhibiting further material oxidation while greatly enhancing its overal

5. Effect of aluminizing on resistance of S30432 to steam oxidation

Aluminizing was a surface treatment technology commonly used for carbon steel which could significantly enhance the corrosion resistance of steel by applying an aluminum coating on its surface. Yang et al. [26] employed the slurry aluminizing method to prepare an aluminum diffusion coating on S30432 and investigated its structure and oxidation resistance. The results revealed a dense continuous Al_2O_3 film had been formed on the aluminized surface of S30432 and there was a remarkable improvement in oxidation resistance with almost no weight gain observed after subjecting it to steam oxidation at 650°C for 1000 hours.

Le et al.[27] compared the oxidation resistance of unmodified S30432 steel with shot peened and aluminized S30432 steel under test conditions of 650°C for up to 1000 hours. It was observed that untreated S30432 steel exhibited oxide layer detachment starting from 500 hours, while shot peened S30432 steel had an oxide layer primarily composed of flake-rich chromium oxide with a thickness around 3μm, in contrast, only one aluminum oxide layer formed in aluminized steel. Based on the above, the order of oxidation resistance from high to low was as follows: aluminized > shot peening > untreated.

6. Comprehensive discussion

Compared with HR3C steel, S30432 steel displayed no obvious aging embrittlement tendencies and possessed higher durable strength but lower oxidation resistance than HR3C steel below 750°C. If the surface modification technology can greatly enhance the oxidation resistance of S30432, it may be possible to replace HR3C steel with S30432 to address the aging embrittlement issue associated with HR3C steel.

In addition, the shot peening process can alter the structure of the surface oxide layer of S30432 steel, resulting in the formation of a chromium-rich oxide layer on its surface. This Cr-rich oxide layer enhances the oxidation resistance of S30432 steel to a level equal to or even surpassing that of HR3C steel. Based on Wang et al.'s study [17], it was also speculated that shot peening can improve the smoke corrosion resistance of S30432 steel as smoke corrosion resistance is primarily influenced by the chromium content. Additionally, aluminizing treatment creates a dense aluminum oxide layer on the surface of S30432 steel, effectively isolating contact between iron (Fe), chromium (Cr) and oxygen, and thereby further enhancing its oxidation resistance. However, due to its complex nature, aluminizing treatment may introduce new challenges for subsequent welding processes.

Currently, research efforts focused on shot peening mainly concentrated on improving oxidation resistance within the inner wall of S30432 steel pipes. However, there were limited experimental studies investigating whether shot peening could enhance smoke corrosion resistance. According to the investigation of Wang et al. [18], one key factor influencing smoke corrosion resistance was the chromium content in the surface layer and shot peening had been shown to promote the formation of a Cr-rich oxide layer on this surface layer of S30432 steel. Therefore, based on principles governing corrosion prevention measures, it could be inferred that shot peening may also had an effect on improving smoke corrosion resistance in S30432 steel.

7. Summary

1)Both shot peening and aluminizing treatments could significantly enhance oxidation resistance in S30432 steel, among which shot peening could improve the oxidation resistance of S30432 steel by an order of magnitude, basically equivalent to the oxidation resistance of HR3C. And it was also found that the oxidation resistance of S30432 steel after aluminizing was better than that of shot peening treatment. Based on these aspects, substituting HR3C steel with S30432 steel proved an effective way in addressing aging embrittlement issues associated with HR3C steel.

2)The research on shot peening for improving the oxidation resistance of S30432 steel pipe has mainly focused on the inner wall with limited experimental studies conducted on whether it can enhance the smoke corrosion resistance of the outer wall. Based on corrosion prevention principles, it was worth noting that shot peening could also improve the smoke corrosion resistance of S30432 steel.

3)Additionally, further investigation was needed to assess its long-term oxidation corrosion resistance during service processes for the test time of the steam oxidation resistance is short, which longest test time reached 2000h.

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