Research on the Application of Thermoelectric Potential Technology in Austenitic Heat-resistant Steel During Aging

Daijun Xiang¹, Junchi Ma¹, Yuwei Wang¹, Yu Zhang², Xiao Jin³, Yanfen Zhao³, Xuqiu Ren⁴, Xiancheng Zhang⁵, Xianxi Xia³, Baoyin Zhu³, Guodong Zhang³, *

¹China Energy Jiangsu Power Co., Ltd., Nanjing, Jiangsu province, 210017, PR China
²Jianbi Power Generation Co., Ltd., Zhenjiang, Jiangsu province, 212006, PR China
³Suzhou Nuclear Power Research Institute, Suzhou, Jiangsu Province, 215004, PR China
⁴Suzhou Hutian Electric Development Co., LTD, Suzhou, Jiangsu Province, 215004, PR China
⁵School of Mechanical and Power Engineering, East China University of Science and Technology, Shanghai, 200237, PR China

*Corresponding author: zhanggdln@163.com

Abstract. HR3C heat-resistant steel is an important material for ultra-supercritical units. The results of the current study show that HR3C heat resistant steel suffers from a significant short term reduction in impact power under long term high temperature conditions. In this paper, through the austenitic heat-resistant steel HR3C through a long time high-temperature aging heat treatment, the results show that after high-temperature aging HR3C significant characteristics of its grain boundaries precipitation of a large number of M23C6 phase, the austenite grains will be closely wrapped, is the main cause of the HR3C impact power found to be significantly reduced. In addition, the thermoelectric potential non-destructive testing technique can better characterise the changes in the characteristics of HR3C heat resistant steel during the long term thermal ageing process and has a greater engineering application in monitoring changes in the properties of HR3C materials, affecting the results of HR3C thermoelectric potential testing in relation to the second phase produced during its thermal ageing process.

Keywords: HR3C, aging, high temperature, microstructure, Thermoelectric Potential

1. Introduction

Improving the operational parameters of power plants increases the thermal efficiency of thermal power plants and aids in the resolution of the growing challenges of energy scarcity and pollution. The performance of the heat resistant steel materials utilized is critical to increasing the parameters. In the application of heat-resistant steel, special attention should be paid to its reliability and safety, long service caused by changes in the organization and performance of the pipe [1, 2]. Power station boilers with heat-resistant steel to work at high temperatures, high pressure, and steam flue gas corrosion in the long-term characteristics, especially for the boiler superheater and reheater, in the application of heat-resistant steel should pay special attention to its reliability and safety, long service caused by changes in
Changes in the organization may exacerbate the metal's high-temperature performance, compromising equipment safety, decreasing its life, and resulting in major mishaps such as pipe bursts. Heat-resistant steel for ultra-supercritical units must have high tensile and yield strength, excellent high-temperature endurance strength, creep resistance, good high-temperature organisational stability, and good processing properties to ensure that it can be used in boiler components for a long time, due to the harsh service conditions in boilers.

HR3C heat-resistant steel is a type of boiler superheater and reheater for the material's final parts. HR3C heat-resistant steel is based on the traditional 18-8 austenitic heat-resistant steel, with the proportion of Cr and Ni elements increased to improve the material's resistance to water vapour and flue gas oxidation performance. However, as the Cr content rises, the brittle phase's inclination to precipitate becomes more apparent. As a result, the Ni content is raised at the same time to stabilize the austenite structure while also suppressing the precipitation propensity of the phase. As a result, HR3C has good oxidation resistance and a robust austenitic structure, making it one of the most popular materials for ultra-supercritical boilers' tough steam and flue gas conditions. HR3C materials are also strengthened by limiting the C content and adding strong carbon and nitride forming elements Nb with a mass fraction of 0.20 percent to 0.60 percent and N with a mass fraction of 0.15 percent to 0.35 percent, using the precipitation of diffusely distributed, fine NbCrN phase and Nb-rich carbon and nitride as well as $M_{23}C_6$, resulting in HR3C materials that are significantly more durable.

HR3C has much better creep resistance than other heat-resistant steels of the same type. In the results of previous studies, it is found that $M_{23}C_6$ phase is easy to precipitate in HR3C under long-term high temperature conditions. During operation, HR3C has much better creep resistance than other heat-resistant steels of the same type. In the results of previous studies, it is found that $M_{23}C_6$ phase is easy to precipitate in HR3C under long-term high temperature conditions. The results reveal that the outstanding mechanical properties of HR3C at high temperatures are due to the nanoscale Z-phase precipitated at high temperatures. However, the $M_{23}C_6$ phase precipitated at the grain boundaries of HR3C under high temperature conditions is the main cause of the decrease in impact power of HR3C, and the main component of this $M_{23}C_6$ phase is $Cr_23C_6$, which can easily precipitate in austenitic heat-resistant steel under high temperature conditions.

The only way to characterize the current performance test for this considerable loss in impact power is to use destructive sampling for impact power testing, which can be harmful to the unit's integrity. On the other hand, welding faults produced by replacing new tubes pose a hidden threat to the unit's stability, so it's critical to look into a non-destructive testing technique that's appropriate for HR3C impact power testing.

When studying the precipitation behavior of Mo-containing precipitated phases in steel, Marc H. et al. discovered that the change in Thermoelectric Potential (TEP) correlated well with the change in hardness value of the material, and further studies discovered a correlation between the change in TEP value at hot room temperature and the presence of precipitated phases such as $M_{23}C_6$. The TEP has risen. The findings suggest that the TEP approach is useful for determining the evolution of precipitated phases like $M_{23}C_6$ in heat-resistant steels as they aged.

The preliminary research on the evolution process of the microstructure of HR3C, the force, and the application of corresponding testing technology is carried out in this thesis, and the microstructure-mechanical properties-nondestructive testing technology is established through the thermal aging test of HR3C heat-resistant steel at high temperature for different time lengths. The two's collaboration provides ideas and proposals for developing real-time online monitoring and detection technology for heat-resistant steels like HR3C.

**2. Experimental**

In the present work, the new material for this study is commercially HR3C (25Cr-20Ni-Nb-N) heat-resistant steel produced by Japan's Sumitomo Metals, and the supplied heat treatment state is solid solution. The standard compositional range of HR3C alloy is shown in Table 1, together with the composition of the of the studied steel analyzed by infrared spectrometer (ICP-AES).
To model the evolution of the material's microstructure and its influence on mechanical characteristics under high temperature circumstances, the austenitic stainless steel HR3C was subjected to thermal aging studies at temperatures close to service temperature (650°C). The specific heat treatment process is as follows: after the heating furnace temperature reaches 650°C, the sample is loaded into the furnace, and the experiment of various durations is carried out, after the aging time reaches the required time, take out the sample and cool it to room temperature in a refrigerator. The resilience of heat-resistant steel can be studied using a long-term aging test. The aging temperature in this study is 650°C, which is the design temperature of an ultra-supercritical unit, and the aging times are 500 hours, 1000 hours, 3000 hours, 5000 hours, and 8000 hours. After age, the samples are subjected to a microstructure study and a hot spot potential test.

A 10 mm × 10 mm × 3 mm sample was taken from the HR3C tube in new and serviced material, then the simples were ground to a 2000 mesh size using different types of sandpaper. Subsequently, electrolytic polishing was carried out with perchloric acid alcohol solution (10% vol perchloric acid) under temperature conditions. The polishing voltage was 20 V and the polishing time was 15–20 s. The microstructure of the samples was observed using SEM and BSE (TESCAN MIRA3 LMH). To get appropriate microstructure information, SEM equipment was utilized to observe the fracture morphology of HR3C samples with various ageing periods.

3. Results and discussion

3.1. Microstructure of HR3C heat-resistant steel before aging

Figure 1 illustrates the morphology of the HR3C sample after electropolishing without age treatment. Figure 1(a) shows a SEM image of the same location, whereas Figure 1(b) shows a BSE image of the same area. The austenite grain condition in the unaged heat-treated sample exhibits no visible deformation, and some of the grains have straight twin borders, indicating that the material has been thoroughly heat-treated during the preparation process, as shown in Figure 1. In addition, an unevenly distributed second phase can be seen in the initial HR3C material. This second phase is dispersed both in the grain boundart and inside the grain, as can be seen more intuitively in the BSE snapshot. BSE images are found to provide clear advantages in assessing HR3C with a second-phase structure. As a
result, BSE images are frequently used in the follow-up examination of vascular tissue anatomy. This second phase, which looks white in the BSE photograph, is the Nb-rich phase that is not dissolved throughout the material manufacturing, according to earlier research findings. Although the particle size of this second phase is relatively large, the quantity of precipitated phases produced by HR3C under high temperature conditions is significantly smaller, hence the impact on the material's characteristics is restricted.

3.2. Microstructure of HR3C heat-resistant steel after aging

HR3C is an austenitic heat-resistant steel that is developed for use in ultra-supercritical units at high temperatures and pressures. The intended service temperature is around 650°C, and the construction is quite stable at ambient temperature. The chemical elements in HR3C heat-resistant steel do not migrate rapidly enough to form compound precipitation at room temperature, but at high temperatures, the diffusion rate of alloying elements in the matrix increases, making it easier to precipitate with C and other elements inside the material [19]. Affect the HR3C's high-temperature mechanical qualities, and hence the safety of the unit's operation. Under high temperature settings, a considerable amount of alloying elements added to the metal will precipitate several sorts of second phases, including both strengthening and weakening phases, or the impact of the same phase will alter with time. In general, the second phase particles found inside metal crystal grains can efficiently stop dislocations from moving. The finer the second phase particles are, the more dispersed they are, and the narrower their spacing, the stronger the effect. Because HR3C alloy contains a significant number of alloying elements, it produces a wide range of precipitation phases when heated to high temperatures. Precipitation strengthening is the main strengthening mechanism of austenitic heat-resistant steel HR3C in the strengthening mechanism of austenitic heat-resistant steel.

![Microstructure of HR3C with different aging time](image)

*Fig 2.* Microstructure of HR3C with different aging time: (a) 0h; (b) 500h; (c) 1000h; (d) 3000h; (e) 5000h; (f) 8000h
Fig. 3 show the microstructure of HR3C after aged for different time. Fig.3 (a) is the BSE view of sample before aging, a minor quantity of second phase is randomly distributed in the image, with a size of less than 1 micron, and the majority of these second phases are in the crystal grains, with no visible second phase particles at the grain boundaries. A BSE photograph of HR3C after 500 hours of aging is shown in Fig.3 (b). The image shows that several second-phase particles emerge on the grain boundaries in addition to the white Nb-rich phase scattered inside the grains. The gray particles near the grain boundary are M23C6 phase, which is the primary cause of the decrease in impact energy following HR3C high temperature aging.

A BSE photo of HR3C after 1000 hours of aging is shown in Fig.3 (c). The image shows that after 1000 hours of aging, there are still a considerable number of gray precipitates scattered on the grain boundaries of the sample, as opposed to 500 hours of aging. The sample size has greatly expanded. Furthermore, there is an evident second phase structure at the top of the sample's twin boundary under the corresponding conditions, but the second phase structure is nearly imperceptible on the twin boundary's two parallel surfaces. The BSE photo of HR3C after 3000 hours of age is shown in Fig.3 (d). The second dispersed distribution may be seen inside the grains next to the big-angle grain boundary, in addition to the visible precipitation phase on the big-angle grain boundary. The phase structure is observable in the grains far away from the large-angle grain boundary, but the small second term amount is nearly imperceptible. The BSE photo of HR3C after 5000 hours of aging is shown in Fig.3 (e). There is a little quantity of white second phase inside the crystal grains, in addition to the typical large-angle second phase precipitation on the large-angle grain boundary. This is the second white phase. The phase is a remnant of the original sample's Nb-rich phase. The Nb-rich phase does not change in size as the service duration grows in general. The BSE photo of HR3C after 8000 hours is shown in Fig.3 (f). The figure shows that when HR3C heat-resistant steel is subjected to long-term high-temperature thermal aging, a considerable number of precipitates form on the large-angle grain boundaries. This is supported by literature. The key explanation for the quick drop of HR3C shock is determined to be the second phase that forms under these high temperature conditions.

The fracture morphology of HR3C samples under various aging time circumstances is shown in Figure 4. A huge number of dimples can be visible at the fracture of the first sample, as can be shown in the image. The dimples are the perfect size and depth, with clear ductile fracture features, indicating that the initial sample's fracture performance is improved. Due to the M23C6 on the grain boundary, there are only a few very shallow dimple morphologies at the fracture when the ageing period reaches 500 hours. This is directly related to the evolution of the precipitated phase on the grain boundary in the heat-resistant steel at this time. The phases coarsen and form a typical belt-like structure of precipitated
phases throughout time. The grain boundary has a characteristic belt-like structure that appears as a little depression on the impact fracture. When the aging time reaches 1000 hours or more, there are almost no dimples left, and the material's impact performance is at its lowest.

The above impact fracture's morphological alterations suggest that the evolution of the second phase on the grain boundary is directly related to the change in impact energy. The form and distribution of the M23C6 phase on the grain boundary are primarily responsible for the shift in impact energy. The M23C6 phase on the grain boundary has precipitated and joined in a continuous chain shape during the first 500 hours of age, accompanied by the development of portion of the M23C6 phase. Cracks benefit from the continuous distribution of the M23C6 phase and the grain boundary. The spread of the alloy causes the alloy to become brittle, reducing the toughness of the heat-resistant steel substantially.

### 3.3. TEP value of HR3C heat-resistant steel after aging

The TEP value of HR3C heat-resistant steel changed over time during the 650°C long-aging process, as shown in Figure 5. As can be seen in the graph, the TEP value decreases as the aging time increases. The TEP value reduces significantly in the first 500 hours, from approximately 3.5 to 3.4, which is equivalent to 8000 hours of high temperature aging. The TEP gradually declined during this process, and the final TEP value. TEP is influenced by a variety of circumstances, according to prior research findings. TEP is affected by the quantity of components, the number of dislocations, and the number of second phase precipitation (particularly M23C6). Since the initial simple of HR3C heat-resistant steel is fully annealed, there will not be a high number of defects such as dislocations induced by deformation and other processes in the grains during the long-term aging test of austenitic heat-resistant steel. Furthermore, the chemical makeup has remained relatively unchanged. The precipitation phase, particularly the amount of M23C6 on the grain border, is the only difference. TEP is a non-destructive testing technique that detects changes in the valence state of the Cr element. On the grain border, M23C6 consists mostly of Cr23C6. As a result, the precipitation of a considerable amount of M23C6 on the grain boundary is identical to the precipitation of Cr23C6, resulting in a bigger TEP result. The true cause for the switch.

### 4. Conclusions

In this paper, a new austenitic heat-resistant steel HR3C aged for about 8000h are studied. A lot of SEM and Non-destructive testing work are carried out in order to find the evolution of microstructure and precipitates in HR3C steel under aging, and the TEP test results of HR3C heat-resistant steel after long-term thermal aging are obtained. The conclusions shows as follow:
1. HR3C heat resistant steel produces a large amount of M$_{23}$C$_6$ phase at the grain boundaries during long thermal ageing, and this precipitated phase forms a tight chain structure at the grain boundaries, resulting in a significant reduction in the material's impact power, and the fracture morphology shows obvious intergranular fracture characteristics.

2. The thermoelectric potential non-destructive measurement technique can better characterize changes in the properties of HR3C heat resistant steel during the long-term thermal ageing process, and has a greater engineering application in monitoring changes in the properties of HR3C materials, affecting the results of HR3C thermoelectric potential measurement in relation to the second phase produced during it.

Acknowledgements
This work was supported by the Guangdong Major Project of Basic and Applied Basic Research(NO 2019B030302011).

References
[1] Y. Fang, Precipitation in advanced heat-resistant austenitic steel HR3C, Dalian University of Technology, 2010.
[2] C.Y. Chi, H.Y. Yu, X.S. Xie. Advanced austenitic heatresistant steels for ultra-supercritical(USC) fossil power plants. In: Morales EV Dr., editor. Advanced austenitic heat-resistant steels for ultra-supercritical (USC) fossil power plants. Shanghai, (2011)171–200.
[3] B. Wang, Z. C. Liu, S. C. Cheng, et al. Microstructure Evolution and Mechanical Properties of HR3C Steel during Long-term Aging at High Temperature. Journal of Iron and Steel Research, International 21 (2014) 765-773.
[4] I. A, O. H, S. H, I. M, Long term creep properties and microstructure of SUPER304H, TP347HFG and HR3C, Energy Materials 2 (2007) 199-206.
[5] Z. Zhang, Z. Hu, H. Tu, S. Schmauder, G. Wu, Microstructure evolution in HR3C austenitic steel during long-term creep at 650°C, Materials Science and Engineering: A 681 (2017) 74-84.
[6] M. Farooq.Strengthening and degradation mechanisms in austenitic stainless steels at elevated temperature. PhD Dissertation]. Royal Institute of technology,2013.
[7] Zhihong Peng, Wen Ren, Chao Yang, et al. Relationship between the evolution of phase parameters of grain boundary M23C6 and embrittlement of HR3C super-heater tubes in service. Acta Metallurgica Sinica 51 (2015) 1325-1332.
[8] B. Peng, H. Zhang, J. Hong, et al. Effect of aging on the impact toughness of 25Cr–20Ni–Nb–N steel, Materials Science and Engineering: A 527(7-8) (2010) 1957-1961.
[9] Wang Hui, Zhao Jie, Yang Zhi, et al. Study on σ phase precipitation of HR3C steel used in ultracritical boiler, Acta Metallurgica Sinica 51 (2015) 920-924.
[10] A. Zielinski. Ausenitic steels for boiler elements in USC power plants. Journal of Achievements in Materials and Manufacturing Engineering. 57(2)(2013) 68-75.
[11] J. Z. Wang, Z. D. Liu, H. S. Bao, et al. Effect of Ageing at 700 °C on Microstructure and Mechanical Properties of S31042 Heat Resistant Steel, Journal of Iron and Steel Research International 20(4) (2013) 54-58.
[12] Y. Yang, L. Zhu, Q. Wang, et al. Microstructural evolution and the effect on hardness and plasticity of S31042 heat-resistant steel during creep, Materials Science and Engineering: A 608 (2014) 164-173.
[13] Y. Zhou, Y. Liu, X. Zhou, et al. Precipitation and hot deformation behavior of austenitic heat-resistant steels: A review, Journal of Materials Science & Technology 33(12) (2017) 1448-1456.
[14] W. Bin, Investigation on Optimization of Microstructure and Mechanical Properties of S31042 Austenitic Heat-resistant steel, Northeastern University, Shen Yang, 2013.
[15] M. Houzé, X. Kleber, F. Fouquet, M. Delnondedieu, Study of molybdenum precipitation in steels using thermoelectric power measurement, Scripta Materialia 51(12) (2004) 1171-1176.
[16] F.G. Caballero, A. García-Junceda, C. Capdevila, C.G. de Andrés, Precipitation of M23C6 carbides: thermoelectric power measurements, Scripta Materialia 52(6) (2005) 501-505.

[17] Y.D. Park, Analysis of Microstructure Using Thermoelectric Diagnostics for Non-Destructive Evaluation of Materials, AIP Conference Proceedings, 2005, pp. 1308-1315.

[18] M. Perez, C. Sidoroff, A. Vincent, C. Esnouf, Microstructural evolution of martensitic 100Cr6 bearing steel during tempering: From thermoelectric power measurements to the prediction of dimensional changes, Acta Materialia 57(11) (2009) 3170-3181.

[19] J.S. Pan, M.B. Tian, J.M. Tong, Material Science and Foundation, Tsinghua Univeristy Press, Beijing, 2011.