Aging precipitation behavior of $\sigma$ phase in 22Cr15Ni3.5Cu austenitic stainless steel

Pengcheng Che$^{1,3,a}$*, Fengjun Wang$^{1,b}$, Xindong Li$^{2,e}$, Min Xie$^{1,d}$, Yuzhe Liu$^{2,e}$, Yi Cheng$^{2,f}$

$^1$Harbin-electric power generation equipment national engineering research center CO., LTD., Harbin, 150028, China
$^2$State Key Laboratory of Efficient and Clean Coal-Fired Utility Boilers, Harbin Boiler Company Limited, Harbin, 150046, China
$^3$Harbin Institute of Technology, Harbin, 150000, China

*Corresponding author: aemail: chepc@harbin-electric.com,
bemail: 1195276279@qq.com, cemail: cpc1990cpc@163.com
demail: xiemin@harbin-electric.com, eemail: 1219478289@qq.com,
femail: chengyi@hbc.com.cn

Abstract: $\sigma$ phase is one of the main precipitates affecting the toughness of austenitic stainless steel, V-notch impact test, SEM, EDS and TEM analysis were conducted on the newly developed 22Cr15Ni3.5Cu stainless steel after 650°C aging. Precipitation mechanism of $\sigma$ phase and its effect on the toughness of the material were analyzed. The test results show that toughness of the material decreases to 25.6 J after 300h aging, $\sigma$ phase started to precipitate along the grain boundary after 500h aging, and in the crystal after 1000h aging. The precipitation spacing is about 100 nm, forming a gradually increasing size from crystal to grain boundary. As the precipitation time 500h of $\sigma$ phase was later than the critical aging time of ductile brittle transition, it can be inferred from the test result that $\sigma$ phase is not the main precipitation phase affecting the toughness of 22Cr15Ni3.5Cu.

1 Introduction

During high temperature service of austenitic stainless steel for superheater in the boiler, due to the precipitation of M$_2$3C$_6$ phase and $\sigma$ phase along the grain boundaries[1]. This phenomenon led to the rapid reduction of toughness after short-term aging, which called aging embrittlement[2]. It came to be important to analyze the influence of the two phases on toughness of the material, it provided theoretical support for steel composition design and improvement of properties in the long run[3]. 650°C aging were conducted on the samples ranging from 0h to 5000h, and then processed to 10×7.5×55mm for V-notch impact test according to ASME standard[4].

2 Effect of high temperature aging on toughness of 22Cr15Ni3.5CuNbN

Charpy V-notch impact test was conducted on 22Cr15Ni3.5CuNbN sample both at delivery condition and aging condition respectively. Impact absorbed energy value and lateral expansion at each aging point are shown in Table 1, the changing trend is shown in Figure 1. It can be seen that the two value decreased gradually with the increasing aging time. The impact absorption energy value reduced from 176J at delivery condition to 13.6J when aging for 5000h, and the lateral expansion reduced from 2.6mm to 0.2mm. Both of the two properties decreased significantly at the initial 100h, and then remained stable.
Table 1 Impact test properties after aging

| Aging time (h) | 0   | 50  | 100 | 200 | 300  | 500  | 1000 | 3000 | 5000 |
|---------------|-----|-----|-----|-----|------|------|------|------|------|
| Impact absorption energy /J | 176 | 96  | 32.8| 28.3| 25.6 | 22.3 | 19.1 | 14.2 | 13.6 |
| Lateral expansion /mm      | 2.6 | 2.3 | 1.2 | 1.07| 0.94 | 0.88 | 0.86 | 0.45 | 0.2  |

Fig. 1 Impact absorbed energy and lateral expansion value after aging

3. Microscopic analysis of σ phase

As shown in Fig. 2, through SEM analysis, σ phase cannot be seen at the grain boundary or in the crystal in delivery condition or during aging to 3000h. As shown in Fig. 2(e) and Fig. 2(f), when aging for 5000h, σ phase was found at the grain boundary as linear shape. The phase were paralleled in the crystal, with a length of about 100 nm. In the process of transition from crystal to grain boundary, the length of precipitates increased obviously. As shown in Fig. 3(a) and Fig. 3(b), EDS analysis results showed that composition of the phase is (Fe, Ni) x (Mo) y, it is σ phase which can be commonly observed in austenitic stainless steel [5].

Fig. 2 SEM morphology of σ phase at 0h-5000h aging
(a)0h; (b)500h; (c)1000h; (d)3000h; (e) 5000h-1; (f) 5000h-2
As its fine size, and the gradually coarsening of M₂₃C₆ along the grain boundary with aging time, σ precipitate would be covered by band-like M₂₃C₆ and hard to be observed through SEM. Therefore, it is necessary for σ phase to be observed by transmission electron microscope test (TEM) further[6].

As shown in Fig.4(a)-(c), there was no obvious strip-like phase precipitated within 300h aging. As shown in Fig.4(d), fine and parallel strip precipitates were observed in the crystal when aging for 500h, with a length of 90nm and a spacing of 100nm. The phases were in the initial stage of nucleation. At the same time, phases along the the grain boundary were also precipitated with similar morphology but coarsened in size.

As shown in Fig. 4(g)-(i), it is found that there was no obvious change in length and spacing of σ phase during 3000h aging, but width of the phases were coarsening. The parallel phase has no fixed size and fixed orientation relative to the grain boundary. At the same time, the growth of σ phase also caused the particle size and precipitation density of copper rich phase increasing significantly. Diameter of copper rich phase can even reach 20 μm and segregation formed obviously.

According to the research of M₂₃C₆ in 22Cr15Ni3.5CuNbN stainless steel, the critical aging time of ductile brittle transition is 300h, while the initial precipitation aging time of σ phase is about 500h. Obviously, when σ phase precipitated, the impact absorbed energy value of V-notch test had already been at a low condition and remained stable. Therefore, σ phase is a kind of intergranular embrittlement phase, it has no obvious effect on the changing toughness of 22Cr15Ni3.5CuNbN stainless steel during high temperature service. Length of σ phase in the crystal is about 100nm, the length of σ phase near the grain boundary is about 900nm, average spacing in the crystal is about 100nm, and average spacing along the grain boundary is about 150nm. As the grain boundary belongs to defects theoretically, structure fluctuation would cause elements segregation and abnormal growth of precipitates. With the decrease of the distance from the grain boundary, size gradually increases and reaches the maximum value at the grain boundary. This phenomena indicates that the nucleation and growth rate of σ phase at the grain boundary is higher than that in intracrystalline. As shown in Fig.5 is the changing trend of σ phase during the transition from crystal to grain boundary. At the same time, σ phase precipitated in the crystal in parallel and short line shape, and didn’t coarsen and lengthen obviously with the increasing aging time. Therefore, the dispersed phase can pin dislocations and strengthen the matrix in the crystal.
4. conclusion
The components of \( \sigma \) phase in 22Cr15Ni3.5CuNbN stainless steel is \((\mathrm{Fe, Ni})_x (\mathrm{MO})_y\), the threshold aging time of precipitation and growth is 500h. \( \sigma \) phase precipitated in intracrystal is in a parallel and short structure, the phases at the grain boundary has a parallel strip structure. \( \sigma \) phase can pin dislocations, the matrix strength can be improved by pinning effect, size of \( \sigma \) phase increases with the decreasing distance
from the grain boundary, and the precipitation time of 500h is later than the critical aging time of ductile brittle transition (200h-300h), so it is a kind of intergranular embrittlement phase, but not the main reason for the decrease of toughness.

References

[1] R. Jones, V. Randle, G. Owen, Carbide precipitation and grain boundary plane selection in overaged type 316 austenitic stainless steel, Mat. Sci. Eng. A-Struct. 496 (2008) 256-261.
[2] Che Pengcheng et al. Effect of Aging on the Toughness of Heat-Resistant 22Cr-15Ni-4Cu Austenitic Steel[J]. Journal of Physics: Conference Series, 2021, 1965(1)
[3] P. Yan, Effect of normalizing temperature on the strength of 9Cr–3W–3Co martensitic heat resistant steel, Mat. Sci. Eng. A-Struct. 597 (2014) 148-156.
[4] C. J. Thomas, Environmentally assisted crack growth in a martensitic stainless steel, Mat. Sci. Eng. A-Struct. 78 (1986) 55-63.
[5] X. F. Wang, W. Chen, Influence of Isothermal Aging on the Embrittlement of 00Cr25Ni7Mo4N Super Duplex Stainless Steel, Steel. Res. Int. 80 (2009) 779-784.
[6] E. A. Trillo, L. E. Murr, A TEM investigation of M23C6 carbide precipitation behaviour on varying grain boundary misorientations in 304 stainless steels, J. Mater. Sci. 33 (1998) 1263-1271.