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Precipitation Processes in Creep-Resistant Austenitic Steels

Grzegorz Golański, Adam Zieliński and Hanna Purzyńska

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Abstract

Creep-resisting austenitic steels constitute a group of construction materials which can work in the conditions of creep for the temperature range from 550 to 700°C. The service of austenitic steels leads to the progressive degradation of their microstructure, which results in the changes of functional properties. The main mechanisms of degradation of the austenitic steel microstructure include the processes of matrix softening, the processes of precipitation and matrix depletion of the interstitial and substitution elements. Precipitation processes in austenitic steels are a very important indicator, which allows the advancement of microstructure degradation processes in these steels to be determined. Hence, the knowledge of the impact of individual secondary phases on the microstructure and properties of austenitic steels plays a very important role in diagnosing the components and equipment of the power boiler system and makes it possible to forecast the time of safe operation of systems made from these steels. Based on own studies and data from literature, this paper will present the characteristics of secondary phase precipitates occurring in creep-resistant austenitic steels during their operation at an elevated/high temperature. The effect of secondary precipitates on mechanical properties of these steels will be discussed too.

Keywords: creep-resistant austenitic steel, precipitation processes, mechanical properties, degradation of microstructure, matrix softening

1. Introduction

One of the ways to reduce air emissions of pollutants arising from combustion of solid fuel—hard coal or lignite in power units is to enhance steam parameters. By improving the efficiency of power units, higher steam parameters contribute to the reduction in emission



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Material	С	Si	Mn	Р	S	Cr	Ni	W	Со	Cu	Nb	Ν	В
TP347HFG	0.04-0.10	max 1.00	max 2.00	max 0.04	max 0.015	17.0-20.0	9.0–12.0	-	-	-	max 1.20 (10x C)	max 0.10	-
Super304H	0.07–0.13	max 0.30	max 1.00	max 0.04	max 0.01	17.0–19.0	7.5–10.5	_	_	2.5–3.5	0.30–0.60	0.05–0.12	0.001-0.010
HR3C	0.04-0.10	max 0.75	max 2.00	max 0.03	max 0.03	24.0-26.0	17.0–23.0	-	-	_	0.20-0.60	0.15–0.35	-
Sanicro 25	0.04–0.11	max 0.40	max 0.60	max 0.025	max 0.015	21.5–23.5	23.5–26.5	2.0-4.0	1.0–2.0	2.0-3.5	0.30–0.60	0.15–0.30	max0.008

 Table 1. Chemical composition of modern creep-resistant austenitic stainless steel, %mass.

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of pollutants. Higher requirements related to the enhancement of operating parameters of unit demands the use of new construction materials not only of adequate creep strength, but also with high resistance to corrosion and oxidation [1, 2].

Because of insufficient resistance to oxidation of 9%Cr martensitic steels and very unstable microstructure associated with the MX \rightarrow Z phase transition for 12%Cr martensitic steel, in plants operated at above 600°C, creep-resistant austenitic steels are used [3]. Compared to ferritic steels, the austenitic ones show higher heat and high-temperature creep resistance, however they have unfavourable physical properties, that is, higher thermal expansion coefficient and lower conductivity. The disadvantage of these steels is high price due to the content of expensive nickel in their chemical composition. Creep-resistant austenitic steels were developed by modification and optimisation of chemical composition of the classic 18/8-grade steels [4]. Nowadays, the (17–20%)Cr-(7–11%)Ni steels—TP347HFG and Super 304H and the (20–25%)Cr-(15–23%)Ni steels—HR3C are used in modern power boilers. The prospective steel Sanicro 25, classified as steel of the 25/23 type, is also in the phase of implementation to modern power units designed for work at the ultra-supercritical parameters of steam. Austenitic steels are intended for plant components working at above 600°C, and currently they are most often used for steam superheaters [2, 4–7]. The required chemical composition of the creep-resisting austenitic steels mentioned above is presented in **Table 1**.

In the as-received state, austenitic steels have austenitic structure with numerous annealing twins. Modern creep-resistant austenitic steels belong to the so-called stabilised steels, which mean they contain a strong carbide-forming element—niobium. Therefore, numerous randomly arranged primary NbC carbides with micrometric size are observed within the matrix of these steels. Sanicro 25 steel in the as-received condition may also include the primary Z phase (complex NbCrN nitride) precipitates. By binding carbon atoms, the primary NbC carbide precipitates reduce the processes of precipitation of $M_{23}C_6$ carbides at the grain boundaries. However, the niobium content in creep-resistant austenitic steels, in contrast to the "classic" austenitic steels, is limited below the level required for complete binding of carbon atoms [5, 7]. The metastable structure of austenitic steels will be subject to progressive evolution during service, and the main degradation mechanism includes the precipitation processes of secondary phases and changes in their morphology. Depending on steel grade and operating parameters, in the microstructure of austenitic steel, there may occur during long-term service the precipitation of carbides/nitrides: $M_{23}C_6$, MX, Z phase; intermetallic phases: σ , Laves, χ , complex silicide—G phase, as well as copper-rich precipitates— ε_c _Cu [5, 7–12].

This paper presents the characteristics of secondary phases occurring in modern creepresistant austenitic steels.

2. M₂₃C₆ carbide

In the majority of austenitic steels (without copper addition), chromium-rich $M_{23}C_6$ carbide is the first secondary precipitate that appears in the microstructure of these steels. The privileged locations of $M_{23}C_6$ carbide precipitation are grain boundaries (**Figure 1**) and, in the next place, incoherent and

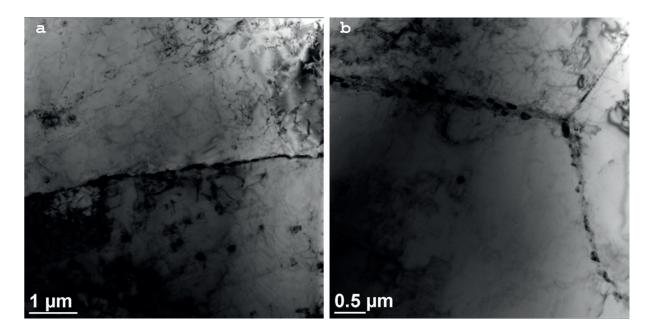


Figure 1. M₂₃C₆ carbide precipitates at the grain boundary in TP347HFG steel after service.

coherent twin boundaries [5, 8–10, 13]. Precipitation of $M_{23}C_6$ carbides at the grain boundaries in austenitic steels depends on the nature of the boundary. The privileged boundaries are those characterised by high degree of coincidence Σ or those with high misorientation angle Θ [9, 10].

Finely dispersed $M_{23}C_6$ carbides precipitated at the grain boundaries in the initial stage of operation hinder the slip at the grain boundaries and thus contribute to the increase in creep resistance. These carbides also inhibit the migration of grain boundaries contributing to a delay in the matrix softening process (**Figure 2**). However, $M_{23}C_6$ carbides are characterised by fairly

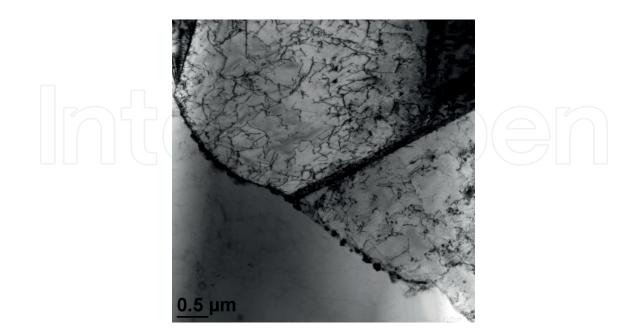


Figure 2. Impeding the grain migration by $M_{23}C_6$ carbides precipitated on the grain boundary-TP347HFG steel after service.

low thermal stability, which results in the increase in size of these precipitates (**Figure 1b**) and formation of the so-called continuous network of precipitates at the grain boundaries during service. The enthalpy of creation, which can be treated as a measure of the stability of precipitates, for the $Cr_{23}C_6$ and NbC carbides amounts to -25 and -55 kJ/mol, respectively, whereas for the NbN nitride, -125 kJ/mol [14].

The formation of the continuous network of $M_{23}C_6$ carbides at the grain boundaries and increase in their size during service results in the appearance of microareas with reduced chromium contents nearby the grain boundaries. This may result in the sensitisation of steel, that is, its increased susceptibility to intergranular corrosion. The chromium-depleted microareas constitute an anode in the corrosion process, which results in their oxidation. Such a type of corrosion is very dangerous because the process of destruction (oxidation) runs very fast throughout the material on the grain boundaries, leaving no visible traces on the steel surface. The effect of sensitization of the near-boundary areas of grains in the austenitic steel is also the disturbance in the material consistency, which can result in falling out of single grains, for example, influenced by the metallographic reagent (**Figure 3**).

Numerous precipitates at the grain boundaries have also a negative impact on ductility of austenitic steels (**Figure 4**) [9, 10, 13–17]. The precipitates of $M_{23}C_6$ carbides on the grain boundaries, for instance, in the case of HR3C steel, constitute to a very rapid decrease in ductility in a relatively short time and favour the brittle cracking with the intercrystalline mechanism (**Figure 5**) [17, 18].

The introduction of micro-addition of boron into the chemical composition of austenitic steel results in partial replacement of carbon atoms with the boron ones in $M_{23}C_6$ carbides. This causes the precipitation of $M_{23}(C, B)_6$ borocarbides in place of "pure" $M_{23}C_6$ carbides. Compared to $M_{23}C_6$ carbide, the $M_{23}(C, B)_6$ borocarbides are distinguished by higher thermal stability due to a better fit of the crystalline network of precipitates and matrix. As a consequence, the $M_{23}(C, B)_6$ borocarbides keep their finely dispersed form over a longer time during service. This results in reduction in the tendency towards the grain slip, and thus reduction in susceptibility of steel to intercrystalline cracking during creep [19, 20]. A similar favourable effect of micro-addition of boron on the increase in stability of $M_{23}C_6$ carbides was also observed in the 9–12% Cr high-chromium martensitic steels [21].

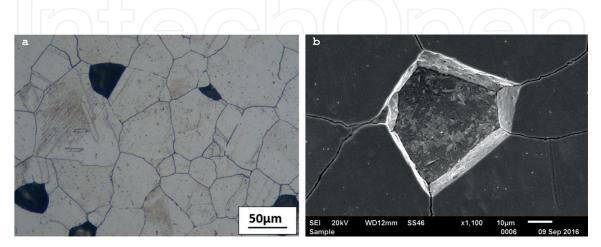


Figure 3. Austenite grains fallen out in HR3C steel after service [17].

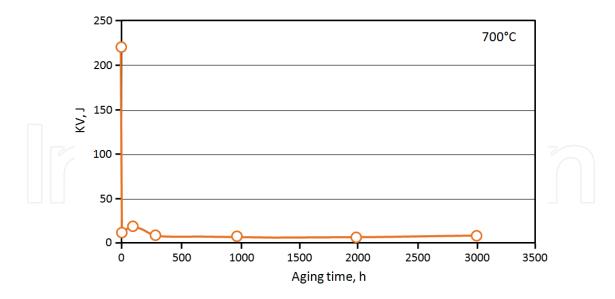


Figure 4. The impact energy changes with ageing time at 700°C in HR3C [7].

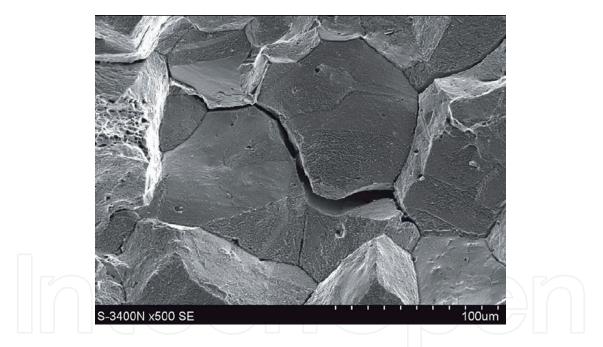


Figure 5. The intercrystalline mechanism of cracking with secondary cracks of HR3C steel after 1000 h of ageing at the temperature of 650°C [18].

3. MX precipitate

The MX secondary phases in austenitic steels are developed by carbide formers such as titanium, niobium, or hafnium. The MX precipitates in austenitic steels are ones of the most advantageous secondary phases [9, 10, 22, 23]. In austenitic steels, the MX precipitates have two main objectives:

- binding carbon atoms and preventing the precipitation of chromium-rich carbides at the grain boundaries and
- precipitation hardening of austenitic steels.

In the microstructure of niobium-stabilised austenitic steels, the presence of two types of MX (MC) precipitates is observed:

- large primary carbides of micrometric size (Figure 6) and
- finely dispersed secondary precipitates of nanometric size (Figure 7).

In addition to binding of carbon atoms, the NbC primary carbide precipitates effectively inhibit the grain growth during heat (thermomechanical) treatment. However, the NbC primary carbides should be treated as disadvantageous precipitates because the nucleation and growth of creep cracks may occur at their carbide/matrix interface.

The NbC primary carbides are characterised by very high stability: no increase in their size was observed even after 70,000 h ageing at 700°C. The NbX secondary precipitates occur during service within the grains, mainly at dislocations and stacking fault areas [9, 22, 24]. These precipitates form very effective barriers to free displacement of dislocations, pin and inhibit the possible motion of dislocations (**Figure 7**) and, in spite of their low volume fraction, have very strong effect on steel hardening. The effect of MC and $M_{23}C_6$ carbides on creep strength of the 18Cr10NiTiNb steel at 650°C can be illustrated with the following formula (1) [25]:

$$R_{z/650/10\ 000} = 21.5 \text{ x (C as MC)} + 6 \text{ x (C as M}_{23} \text{ C}_{6}) + 85.32 \text{ (MPa)}$$
(1)

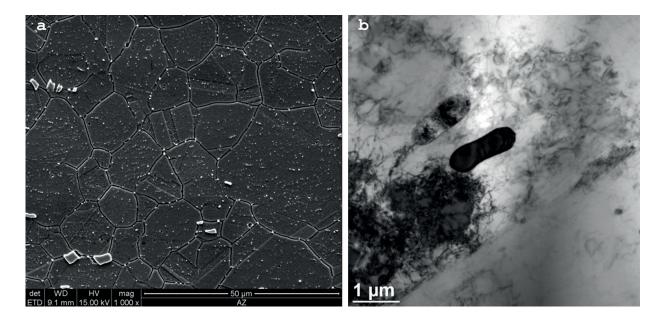


Figure 6. The NbC primary precipitates in TP347HFG steel.

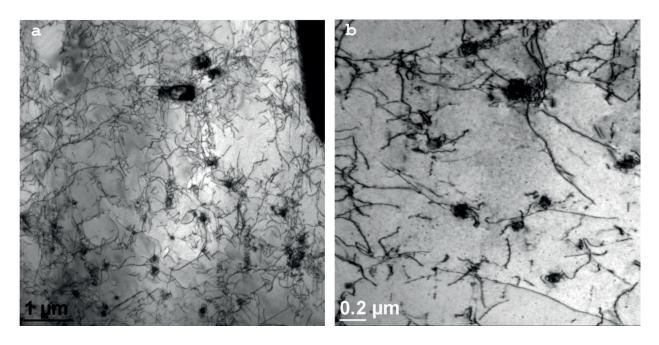


Figure 7. The NbX secondary precipitates in TP347HFG steel (a) and their interaction with dislocations (b).

The MX secondary precipitates are also characterised by high thermal stability up to approx. 700°C, which results in a very slow increase in size of these precipitates during long-term service. The MX precipitates binding the atoms of nitrogen can also cause the growth of the steel susceptibility to pitting corrosion [26].

4. ε_Cu precipitate

In austenitic steels containing a copper addition in their chemical composition, for example, Super 304H or Sanicro 25, one of the main hardening mechanisms that occur during service is the precipitation hardening with ε _Cu copper-rich particles (**Figure 8**).

The ε _Cu particles can also dissolve the atoms of iron, chromium and nickel, and their contents in a precipitate that depends on the temperature and time. These precipitates at the initial stage of service/ageing are the precipitates rich in iron, chromium and nickel, and the content of copper in the particle does not exceed 20% then (**Figure 8**). As the time passes, the precipitates get rich in copper and after around 500 h of ageing at the temperature of 650°C they constitute around 90% of copper [7, 27, 28]. Precipitation of these particles takes place very quickly. In Super 304H steel, the precipitates of this type and of approx. 2 nm were revealed only after 1 h of ageing at 650°C [7, 27, 29]. In spite of their low volume fraction (approx. 3%), finely dispersed ε _Cu precipitates (whose density in Super 304H steel after ageing at 650°C for 10,000 h was 0.38 × 10⁴ m⁻² and average particle diameter was 35 nm) represent a very effective barrier to free displacement of dislocations. The calculated shear stress for these coherent precipitates is approx. 37 MPa [26]. These precipitates are also characterised by quite high stability (**Figure 9**). The Cu-rich phase is growing during 650°C long time ageing till 10,000 h, but the growth rate

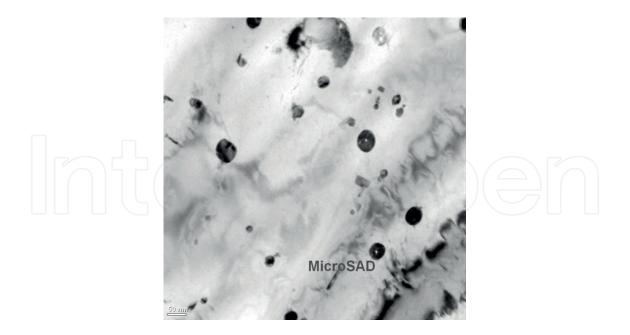


Figure 8. The ε_Cu precipitates in aged Super 304H steel.

is very slow. The average size of Cu-rich phase still keeps about 34 nm at 650°C ageing for 10,000 h [7]. This is mainly due to low energy at the ε _Cu precipitate/matrix interface, which is approx. 0.017 J/m², and the fact that these precipitates are coherent with the matrix.

This translates into slow growth of the copper-rich phase particles during the service and has a positive impact on the maintenance of high properties over a long time of service, especially that the volume fraction of the copper-rich precipitates grows with the time of ageing (**Figure 10**).

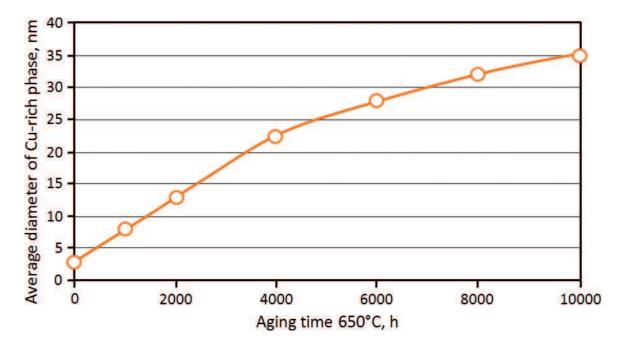


Figure 9. The effect of the time of Super304H ageing at 650°C on increase in the volume of ε_Cu precipitates [7].

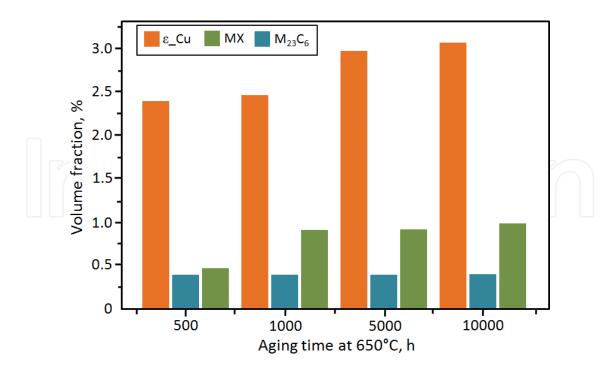


Figure 10. The precipitates volume fraction in Super304H at 650°C with ageing time [7].

However, the precipitation of ϵ _Cu particles has a destabilising effect on the passive layer and reduces the corrosion resistance of the steel.

5. Z phase

The NbCrN (Z phase) precipitate is privilegedly precipitated in austenitic steels with high niobium and nitrogen contents, mainly at the grain boundaries and inside the grains (**Figure 11**). In Sanicro 25 steel, both the primary and secondary Z phase precipitates are observed. In contrast to 9–12% Cr martensitic steels, the Z phase precipitated in austenitic steels has a positive impact on mechanical properties. NbCrN precipitates are characterised by high thermodynamic stability up to approx. 700°C, which results in a slow increase in the size of these precipitates. Finely dispersed NbCrN particles precipitated inside the grains cause precipitation hardening, thus contributing to the increase in creep strength [7, 9, 10, 30, 31] (**Figure 11**).

The calculated value of stress required for dislocation to bypass the precipitate with Orowan mechanism for the Z phase in Sanicro 25 steel at 700°C after 4265 h creep with average precipitate diameter of approx. 14 nm and volume fraction of 0.014 amounts to 118.7 MPa. And after 12,920 h creep at 700°C, with average diameter of Z phase secondary particles of approx. 18 nm and their volume fraction in Sanicro 25 steel amounting to 0.016, it is 105.7 MPa. For comparison, the estimated value of the stress after 4265 h creep at 700°C for ε _Cu particles in Sanicro 25 steel was 44.6 MPa [31].

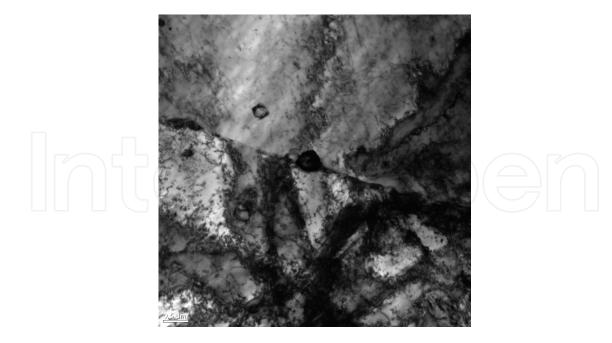


Figure 11. The Z phase precipitation at the grain boundary in Super 304H steel.

6. σ phase

The σ phase in austenitic steels is a secondary intermetallic phase which precipitates mainly at the grain boundaries, and the particularly privileged locations are the contact point of three grain boundaries and delta ferrite precipitates (**Figure 12**). The σ phase precipitation at the grain boundaries may be accompanied by dissolution of M₂₃C₆ carbides in the matrix



Figure 12. The σ phase precipitation at the contact point of three grain boundaries in T321H steel after long-term service.

[9, 10, 31–34]. The precipitation of σ phase in austenitic steels is much slower than that of $M_{23}C_6$ carbides, which results mainly from the factors such as (1) diffusion of substitution elements, for example, chromium, takes place slowly in austenite, (2) σ phase precipitates in austenite are incoherent with the matrix, (3) solubility of carbon and nitrogen in austenite is low, hence the privileged precipitation processes is the formation of carbides and/or nitrides [9, 11, 33–36]. In addition to chromium, other ferrite formers also create favourable conditions for σ phase precipitation. Particularly strong effect is shown by stabilising elements (carbide formers), that is, titanium and niobium. In austenitic steels with higher titanium and niobium contents, the σ phase is formed much easier due to the fact that carbon and/or nitrogen atoms are bound into MX precipitates. The rate and temperature of the σ phase precipitation in austenitic steel grow with the increase in chromium content in alloy (Figure 13). Also silicon shows as intensive effect on the acceleration of the σ phase precipitation process as carbide formers. The increase in the content of silicon, as an element which enhances heat resistance of austenitic steels from 0.17 to 0.76% wt, may intensify the precipitation of the σ phase and its volume fracture increases from 6 to 22%. The element that has a strong effect on delay in the σ phase precipitation is carbon, which forms $M_{23}C_6$ carbides and thus decreases chromium content in the matrix [9, 10, 32, 37].

The effect of chemical composition on susceptibility of the specific steel to σ phase precipitation is shown by the following formula (2) [39]:

$$Cr_{eq} = Cr + 0.31Mn + 1.76Mo + 0.97W + 2.02V + 1.58Si + 2.4Ti + 1.76Nb + 1.22Ta - 0.226Ni - 0.177Co$$
(2)

In the event when chromium equivalent Cr_{eq} is higher by 17–18% of the weight, the steel shows a strong tendency to σ phase precipitation.

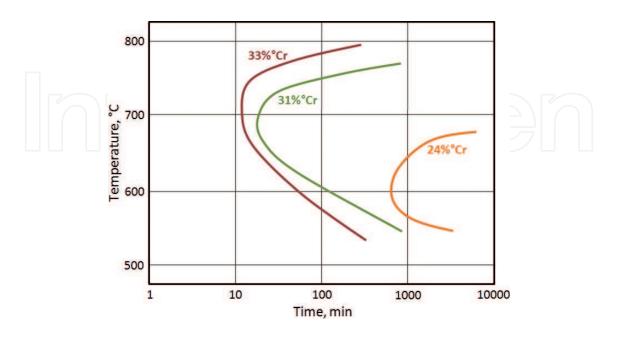


Figure 13. The effect of chromium content on the incubation period of σ phase precipitation [38].

The tendency for the σ phase to precipitate in the austenitic steel can also be shown with the dependency (3) based on the model of positive holes [33]:

$$N_{v} = 0.66\% \text{Ni} + 2.66\% \text{Fe} + 4.66\% (\text{Cr} + \text{Mo}) + 5.6\% \text{Nb} + 6.66\% \text{Si} + 7.66\% \text{Al}$$
 (3)

In the case when the value N_v is bigger than the number 2.52, there is a tendency for the σ phase to precipitate in the alloy.

The σ phase precipitation in austenitic steels at the grain boundaries is a very unfavourable phenomenon as it increases the brittleness of steel and its susceptibility to sensitisation and pitting corrosion. The σ phase has also a negative effect on the plastic properties determined in static tensile test, that is, elongation and reduction in area. The effect of the σ phase on creep strength of austenitic steels is ambiguous. In the initial stage of precipitation, the finely dispersed σ phase precipitates may have, due to precipitation hardening, a positive impact on the increase in creep resistance. However, other researchers show its negative role [11, 32, 34, 37, 40].

7. Laves phase

The intermetallic Laves phase (Fe₂Nb, Fe₂Ti, Fe₂Mo) precipitates in austenitic steel at above 600°C. The privileged locations of the Laves phase precipitation are grain boundaries and, in the second place, the interior of grains. The Laves phase is a more efficient and stable precipitate than $M_{23}C_6$ carbide, it coagulates more slowly at above 600°C, and its effect on steel properties depends on the fraction of its volume at the grain boundary. Higher surface fraction of the Laves phase at the grain boundaries affects the increase in creep resistance of austenitic steels. The Laves phase inhibits dislocation slip at the grain boundaries, and thus results in the increase in creep resistance while reducing the elongation. At the same time, the Laves phase precipitates at the grain boundaries have an adverse effect on ductility of austenitic steels and their high-temperature strength properties determined in static tensile test. The finely dispersed Laves phase particles precipitated inside the grains have a positive impact on creep and fatigue strength. The effect of the Laves phase precipitated inside the grains on steel properties depends on its size and volume fraction. The coagulation of the Laves phase during service results in disappearance of this effect [9, 10, 31, 41–44].

8. G phase

The G phase is a complex silicide with general formula of $A_{16}D_6Si$ where A – nickel, D – niobium or titanium (e.g. Ni₁₆Nb₆Si₇; Ni₁₆Ti₆Si₇; (Ni, Fe, Cr)₁₆(Nb, Ti)₆Si₇). The G phase precipitates in titanium or niobium-stabilised austenitic steels after long-term service. Like most secondary phases precipitating in austenitic steels during service, the G phase is located at the grain boundaries (**Figure 14**) [9, 10, 32, 44, 45]. The G phase is formed in austenitic steels due to the *in situ* transition of primary NbC carbides and/or enrichment of $M_{23}C_6$ carbides in silicon. The *in situ* NbC carbide \rightarrow G phase transition takes place as a result of enrichment due to NbC diffusion into

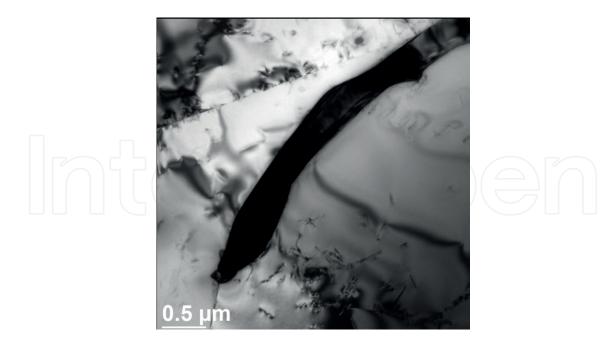


Figure 14. The G phase precipitation at the grain boundaries in T321H steel after long-term service.

nickel and silicon atoms. The rate of transition—G phase formation depends strongly on silicon content in steel. Higher silicon contents result in reduction in the time of G phase incubation [9, 15].

The effect of the G phase on properties of austenitic steels is ambiguous. The G phase precipitated at the grain boundaries has a positive impact on elongation in creep test and delays the second-ary recrystallisation processes by inhibiting the migration of grain boundaries [9, 10, 15, 44–47].

The finely dispersed G phase precipitates at the grain boundaries have also a positive impact on creep resistance of austenitic steels during service at around 750°C. Nevertheless, like any precipitate at the grain boundary, the G phase has also a negative impact on steel ductility. The scale of this negative impact is affected by the amount and size of precipitates at the boundary. The formation of the G phase is accompanied by matrix depletion of nickel, which affects the increase in instability of the matrix and has a negative impact on corrosion resistance. The matrix depletion of nickel also results in the increase in susceptibility to σ phase precipitation in these steels [9, 10, 15, 45–47].

9. χ phase

The intermetallic χ phase precipitates mainly in high-nitrogen steels with addition of molybdenum. Similarly to $M_{23}C_6$ carbides, the privileged locations of the χ phase precipitation are primarily the grain boundaries, and further the incoherent and coherent twin boundaries as well as the dislocations within the grains. In the initial stage of precipitation and growth at the grain boundaries, the dispersive χ phase has a positive impact on creep resistance of austenitic steels as these precipitates hinder slip at the grain boundaries. The increase in size of the χ phase precipitated at the grain boundaries during service has an adverse impact on ductility, which is related to reduction in impact strength. The χ phase precipitated at the grain boundaries in austenitic steel increases the susceptibility of the alloy to intercrystalline cracking. These precipitates also result in steel sensitisation. The χ phase precipitates at the boundaries have a negative impact on creep strength of the steel too. The individual effect of the χ phase on performance properties of austenitic steels is difficult to define, because this phase occurs together with the σ phase in the microstructure. In austenitic steels operating at above 700°C, the χ phase may be transformed into the intermetallic σ phase according to the following diagram [9, 10, 32, 48].

The effect of the secondary phases precipitating in creep-resistant austenitic steels during service on their performance properties is summarised in **Table 2**.

Phase	Location	Positive effect	Negative effect			
M ₂₃ C ₆ carbides	Grain boundaries, incoherent and coherent twin boundaries, inside the grain	 Finely dispersed carbides precipitated at the grain boundaries increase creep resistance; Inhibition of secondary recrystallisation 	✓ Increase in embrittlement✓ Sensitisation of steel			
MX precipitates	Inside the grains at dislocations	 Precipitation hardening Increase in hardness and strength properties Increase in creep strength 	✓ At the MX primary precipitate/ matrix interface, there may occur the nucleation and growth of creep cracking			
Z phase (NbCrN)	Inside the grains at dislocations	 Precipitation hardening Increase in hardness and strength properties Increase in creep strength 	✓ Disappearance of MX precipitates			
σ phase	Grain boundaries, incoherent twin boundaries, inside the grain	-	 ✓ Increase in embrittlement ✓ Sensitisation of steel ✓ Deteriorates strength and plastic properties ✓ Reduces temporary creep strength 			
G phase	Grain boundaries	 Increases the value of elongation at creep Delays secondary recrystallisation 	 Reduces temporary creep strength Results in decrease in corrosion resistance 			
Laves phase	Grain boundaries	Increases creep resistanceIncreases fatigue strength	 Reduces elongation Deteriorates ductility Deteriorates high-temperature strength properties 			
X phase	Grain boundaries, incoherent twin boundaries, inside the grain	• Hinders slip at the grain boundaries—increases creep strength	✓ Sensitisation of steel✓ Increase in embrittlement			
ε_Cu	Inside the grain	 Precipitation hardening Increase in strength properties and creep resistance 	✓ Reduction in corrosion resistance			

Table 2. The effect of secondary phase precipitates on properties of austenitic steels.

10. Summary

The paper describes the influence of particular precipitates on the microstructure and functional properties of creep-resisting austenitic steels. The structure of austenitic steels in the supersaturated state is a non-equilibrium structure which will undergo gradual degradation during the service at elevated temperature, which will further influence the decrease in mechanical properties and corrosion resistance/ oxidation resistance of these materials. The precipitation processes running during the service of austenitic steels are the basic mechanism having a very significant effect on the functional properties of these steels. The type of precipitates and their volume fraction depends on the chemical composition of the given steel, the solubility limit of carbon and alloy elements in the matrix, and the service history (temperature, time, pressure, number and sort of shutdowns, etc.). The main factor influencing the precipitation processes for a given sequence of precipitation of secondary phases during the service is the temperature of work. Precipitations in austenitic steels can be divided in terms of their influence on the microstructure and functional properties into the favourable ones, including nitrides/carbonitrides NbX, Z phase and ECu precipitates, and the harmful ones, including σ , χ and G phases. However, the influence of M₂₃C₆ carbides and Laves phase on the properties of austenitic steels depends on their morphology.

Particularly dangerous precipitates in austenitic steels are the ones precipitating on the grain boundaries, σ phase and $M_{23}C_6$ carbides. Therefore, the growth of stability of $M_{23}C_6$ carbides and the delay or even inhibition of precipitation of the σ phase, or using the strengthening with intermetalic phases seem to be the main directions of further development of the creepresisting austenitic steels.

Author details

Grzegorz Golański1*, Adam Zieliński2 and Hanna Purzyńska2

*Address all correspondence to: grisza@wip.pcz.pl

1 Institute of Materials Engineering, Czestochowa University of Technology, Czestochowa, Poland

2 Institute for Ferrous Metallurgy, Gliwice, Poland

References

[1] Viswanathan R, Henry JF, Tanzosh JM, Stanko G, Shingledecker J, Vitalis B, Purget R. US program on materials technology for ultra-supercritical coal power plants. Journal of Materials Engineering and Performance. 2005;14:281-292. DOI: doi.org/10.1361/ 10599490524039

- [2] Di Gianfrancesco A. The fossil fuel power plants technology. In: Di Gianfrancesco A, editor. Materials for Ultra-supercritical and Advanced Ultra-supercritical Power Plants. Cambridge: Woodhead Publishing; 2017. p. 1-49
- [3] Danielsen HK, Hald J. Influence of Z-phase on long-term creep stability of martensitic 9 to 12%Cr steels. VGB PowerTech. 2009;5:68-73
- [4] Mayer K–H, Masuyama F. The development of creep-resistant steels. In: Abe F, Kern T-U, Viswanathan R, editors. Creep Resistant Steels. Cambridge: Woodhead and Maney Publishing; 2008. p. 15-77
- [5] Zieliński A, Dobrzański J, Purzyńska H, Golański G. Properties, structure and creep resistance of austenitic steel Super304H. Materials Testing. 2015;57:859-865. DOI: doi. org/10.3139/120.110791
- [6] Plaut RL, Herrera C, Escriba DM, Rios PR, Padilha AF. A short review on wrought austenitic stainless steels at high temperatures: processing, microstructure, properties and performance. Materials Research. 2007;10:453-460. DOI: dx.doi.org/10.1590/ S1516-14392007000400021
- [7] Chi Ch YH, Xie X. Advanced austenitic heat-resistant steels for ultra-super-critical (USC) fossil power plants. In: Morales EV, editor. Alloy steel—Properties and Use. Rijeka: InTech Publ; 2011. p. 171-201
- [8] Golański G, Lis AK, Słania J, Zieliński A. Microstructural aspect of long term service of the austenitic TP347HFG stainless steel. Archives of Metallurgy and Materials. 2015;60:2091-2094
- [9] Sourmail T. Precipitation in creep resistant austenitic stainless steel. Materials Science and Technology 2001;14:1-14. DOI: dx.doi.org/10.1179/026708301101508972
- [10] Padilha AF, Rios PR. Decomposition of austenite in austenitic stainless steels. ISIJ International. 2002;42:325-337. DOI: doi.org/10.2355/isijinternational.42.325
- [11] Lai JKL. A review of precipitation behaviour in AISI Type 316 stainless steel. Materials Science and Engineering. 1983;**61**:101-109. DOI: doi.org/10.1016/0025-5416(83)90191-X
- [12] Ayer R, Klein CF, Marzinsky CN. Instabilities in stabilized austenitic stainless steels. Metallurgical Transactions. 1992;23A:2455-2467. DOI: 10.1007/BF02658049
- [13] Kaneko K, Futunaga T, Yamada K, Nakada N, Kikuchi M, Saghi Z, Barnad JS, Midgley PA. Formation of M₂₃C₆-type precipitates and chromium-depleted zone in austenite stain-less steel. Scripta Materialia. 2011;65:509-512. DOI: doi.org/10.1016/j.scriptamat.2011.06.010
- [14] Pickering FB. Historical development and microstructure of high chromium ferritic steels for high temperature applications. In: Strang A, Grooch DJ, editors. Microstructural Development and Stability in High Chromium Ferritic Power Plant Steel. Cambridge: The Institute of Materials; 1997. p. 1-20

- [15] Wang B, Liu D, S-Ch C, Ch-M L, Wang JZ. Microstructure evolution and mechanical properties of HR3C steel during long-term aging at high temperature. Journal of Iron and Steel Research, International. 2014;21:765-773. DOI: doi.org/10.1016/S1006-706X(14)60139-4
- [16] Saucedo-Munoz ML, Lopez-Hirata VM, Avila-Davila EO, Melo-Maximo DV. Evaluation of toughness deteriotation by an electrochemical method in an isothermally-aged N-containing austenitic stainless steel. Materials Characterization. 2009;60:119-124. DOI: doi.org/10.1016/j.matchar.2008.07.007
- [17] Golański G, Kolan C, Zieliński A, Klimaszewska K, Merda A, Sroka M, Kłosowicz J. Microstructure and mechanical properties of HR3C steel after service. Archives of Materials Science and Engineering. 2016;81:62-67
- [18] Zieliński A, Sroka M, Hernas A, Kremzer M. The effect of long-term impact of elevated temperature on changes in microstructure nad mechanical properties of HR3C steel. Archives of Metallurgy and Materials. 2016;61:761-766. DOI: doi.org/10.1515/amm-2016-0129
- [19] Laha K, Kyono J, Sasaki T, Kishimoto S, Shinya N. Improved creep strength and creep ductility of type 347 austenitic stainless steel through the self-healing effect of boron for creep cavitation. Metallurgical and Materials Transactions A. 2005;36A:399-409. DOI: 10.1007/s11661-005-0311-0
- [20] Laha K, Kyono J, Kishimoto S, Shinya N. Beneficial effect of B segregation on creep cavitation in a type 347 austenitic stainless steel. Scripta Materialia. 2005;52:675-678. DOI: doi.org/10.1016/j.scriptamat.2004.11.016
- [21] Abe F. New martensitic steels. In: Di Gianfrancesco A, editor. Materials for Ultra-Supercritical and Advanced Ultra-Supercritical Power Plants. Cambridge: Woodhead Publishing; 2017. p. 323-374
- [22] Erneman J, Schwind M, Andrén H-O, Nilsson J-O, Wilson A, Ágren J. The evolution of primary and secondary niobium carbonitrides in AISI 347 stainless steel during manufacturing and long-term ageing. Acta Materialia. 2006;54:67-76. DOI: doi.org/10.1016/j. actamat.2005.08.028
- [23] Solenthaler C, Ramesh M, Uggowitzer PJ, Spolenak R. Precipitation strengthening of Nb-stabilized TP347 austenitic steels by a dispersion of secondary Nb(C,N) formed upon a short-term hardening heat treatment. Materials Science and Engineering: A. 2015;647A:294-302. DOI: doi.org/10.1016/j.msea.2015.09.028
- [24] Zhou Y-H, Ch-X L, Liu Y-C, Guo Q-Y, Li H-J. Coarsening behavior of MX carbonitrides in type 347H heat-resistant austenitic steel during thermal aging. International Journal of Minerals, Metallurgy, and Materials. 2016;23:283-293. DOI: 10.1007/s12613-016-1237-9
- [25] Minami Y, Kimura H. Effect of M₂₃C₆ and MC carbides on the creep rupture strength of 18%Cr-10%Ni-Ti-Nb steel. Transactions of the Iron and Steel Institute of Japan. 1989;27:299-301. DOI: 10.2355/isijinternational1966.27.299
- [26] Bai G, Lu S, Li D, Li Y. Influence of niobium and solution treatment temperature on pitting corrosion behaviour of stabilised austenitic stainless steel. Corrosion Science. 2016;105:111-124. DOI: doi.org/10.1016/j.corsci.2016.03.009

- [27] Ou P, Xing H, Wang XL, Sun J. Tensile yield behavior and precipitation strengthening mechanism in Super304H steel. Materials Science and Engineering: A. 2014;600A:171-175. DOI: doi.org/10.1016/j.msea.2014.01.085
- [28] Chi C-Y, Yu H-Y, Dong J-X, Xie X-S, Chen X-F, Lin F. Strengthening effect of Cu-rich phase precipitation in 18Cr9Ni3CuNbN austenitic heat-resisting steel. Acta Metallurgica Sinica (English Letters). 2011;24:141-147
- [29] Yu H, Chi C. Precipitation behavior of Cu-rich phase in 18Cr9Ni3CuNbN austenitic heatresistant steel at early aging state. Chinese Journal of Materials Research. 2015;**29**:195-200
- [30] Yang Y, Zhu L, Wang Q, Zhu C. Microstructural evolution and the effect on hardness and plasticity of S31042 heat-resistant steel during creep. Materials Science and Engineering: A. 2014;608A:164-173. DOI: doi.org/10.1016/j.msea.2014.04.073
- [31] Zhou R, Zhu L, Liu Y, Lu Z, Chen L, Ma H. Microstructural evolution and the effect on hardeness of Sanicro 25 welded joint base metal after creep at 973K. Journal of Materials Science. 2017;52:6161-6172. DOI: 10.1007/s10853-017-0758-6
- [32] Lo HK, Shek CH, Lai JKL. Recent developments in stainless steels. Materials Science and Engineering: A. 2009;65R:39-104. DOI: doi.org/10.1016/j.mser.2009.03.001
- [33] Hsieh Ch-Ch WW. Overview of intermetallic sigma (σ) phase precipitation in stainless steels. International Scholary Research Network732471. 2012:1-16
- [34] West D, Hulance J, Higginson RL, Wilcox GD. σ-phase precipitation in 347HFG stainless steel. Materials Science Technology. 2013;29:835-842. DOI: dx.doi.org/10.1179/17432847 12Y.0000000100
- [35] Padilha AF, Escriba DM, Materna-Morris E, Rieth M, Klimenkov M. Precipitation in AISI 316(N) during creep tests at 550 and 600°C up to 10 years. Journal of Nuclear Materials. 2007;362:132-138. DOI: doi.org/10.1016/j.jnucmat.2006.12.027
- [36] Shwind M, Källqvist J, Nilsson J-O, Ågren J, Andrén H-O. σ-Phase precipitation in stabilized austenitic stainless steels. Acta Materialia. 2000;48:2473-2481. DOI: doi.org/10.1016/ S1359-6454(00)00069-0
- [37] Lin D-Y, TCh C, Liu GL. Effect of Si contents of the growth behavior of σ phase in SUS 309L stainless steels. Scripta Materialia. 2003;43:855-860. DOI: doi.org/10.1016/ S1359-6462(03)00481-0
- [38] Blicharski M. Materials Technology. Steel. Warsaw: WNT; 2013 (in Polish)
- [39] Barnard P. Austenitic steel grades for boilers in ultra-supercritical power plants. In: Di Gianfrancesco A, editor. Materials for ultra-supercritical and advanced ultra-supercritical power plants. Cambridge: Woodhead Publishing; 2017. p. 99-119
- [40] Strutt AJ, Vecchio KS. Simultaneous oxidation and sigma-phase formation in a stainless steel. Metallurgical and Materials Transactions A. 1999;30A:355-362. DOI: 10.1007/ s11661-999-0324-1

- [41] Kestenbach H-J, Bueno LO. Effect of Fe₂Nb precipitation on the creep properties of niobium-bearing austenitic stainless steels. Materials Science and Engineering: A. 1984;66: 19-23. DOI: doi.org/10.1016/0025-5416(84)90157-5
- [42] Chen SW, Zhang C, Xia ZX, Ishikawa H, Yang ZG. Precipitation behavior of Fe₂Nb Laves phase on grain boundaries in austenitic heat resistant steels. Materials Science and Engineering: A. 2014;615A:183-188. DOI: doi.org/10.1016/j.msea.2014.07.104
- [43] Spiegel M, Schraven P. New austenitic steels for the advanced USC power plants. In: Di Gianfrancesco A, editor. Materials for Ultra-Supercritical and Advanced Ultra-Supercritical Power Plants. Cambridge: Woodhead Publishing; 2017. p. 375-390
- [44] Powell DJ, Pilington R, Miller DA. The precipitation characteristics of 20% Cr/25% Ni-Nb stabilised stainless steel. Acta Metallurgica. 1988;36:713-724. DOI: doi.org/10.1016/ 0001-6160(88)90105-8
- [45] Ibañez RAP, de Almeida Soares GD, de Ameila LH, May IL. Effects of Si content on the microstructure of modified-HP austenitic steels. Materials Characterization 1993;30:243-249. DOI: doi.org/10.1016/1044-5803(93)90071-3
- [46] Ecob RC, Lobb RC, Kohler VL. The formation of G-phase in 20/25 Nb stainless steel AGR fuel cladding alloy and its effect on creep properties. Journal of Materials Science. 1987;22:2867-2880. DOI: doi.org/10.1007/BF01086484
- [47] Wang J-Z, Liu Z-D, Bao H-S, Cheng SC. Evolution of precipitates of S31042 heat resistant steel during 700°C ageing. Journal of Iron and Steel Research, International. 2013;20:113-121. DOI: doi.org/10.1016/S1006-706X(13)60186-7
- [48] Anburaj J, Mohamed Nazirudeen SS, Narayanan R, Anandavel B, Chandrasekar A. Ageing of forged superaustenitic stainless steel: precipitate phases and mechanical properties. Materials Science and Engineering: A. 2012;535A:99-107. DOI: doi.org/10.1016/ j.msea.2011.12.048

