

Numerical simulation of precipitates evolution during solidification and ageing of Super 304H steel

Roman Kuziak, Adam Zieliński, Hanna Purzyńska, Łukasz Poloczek

Lukasiewicz Research Network Upper Silesian Institute of technology,

Karola Miarki Street 12-14, 44-100 Gliwice

roman.kuziak@git.lukasiewicz.gov.pl,

adam.zieliński@git.lukasiewicz.gov.pl,

hanna.purzyńska@git.lukasiewicz.gov.pl,

lukasz.poloczek@git.lukasiewicz.gov.pl

Keywords: Super 304H austenitic steel, precipitation processes, Calphad method, numerical simulations

1. Introduction

Super 304H austenitic heat-resistant steels is widely used in ultra-supercritical boilers, mainly in superheater and reheater tubes, due to favorable combination of creep and oxidation resistance at high temperatures [1]. The chemical composition of Super 304H austenitic steel is given in Table 1. The microstructural evolution and mechanical properties of the Super304H steel during exposure to high temperatures have attracted considerable research attention. Zieliński [1] revealed that the precipitation of Cu-rich disperse particles inside grains during aging at 650°C and 700°C, effectively improved the strength of the Super 304H steel. The same effect was related to the precipitation of M23C6 carbide on grain boundaries. The addition of Nb is intended to increase the strength of the steel through the precipitation of Nb(C,N) particles. Moreover, the presence of both Nb and N can also cause the precipitation of fine Z₂ Phase (NbCrN) what also could contribute to the strength of the Super 304H steel during creep [2]. Other phases that have been identified in this steel in service or during creep tests include sigma [1,3], M23C6 [1,4] and (Cr, V)₂N [5].

Table 1. Chemical composition (wt.%) of Super H304H austenitic steel

C	Si	Mn	P	S	Cu	Cr	Ni	Nb	B	N	Al
0.09	0.20	0.80	0.003	0.001	2.99	18.40	8.80	0.48	0.004	0.11	0.006

The aim of the investigation presented in this paper is to gain understanding of the precipitation processes occurring in Super 304H austenitic steel using the Calphad method [6].

2. Methodology

The investigation was performed in reference to the ageing experiments performed on Super 304H samples, described in [1]. Prior to ageing, the samples were solution treated at 1000°C for 1 hour, followed by water cooling. The ageing was performed at 700°C during 10 000, 20 000, 30 000 and 50 000 hours. Thermodynamic and kinetic modelling was performed, respectively, using ThermoCalc and TC-PRISMA software. In the TC-PRISMA software a physics-based

The project is co-financed by funds from the state budget, granted by the Minister of Science as part of the Excellent Science II Program, project no. KONF/SP/0109/2024/02, subsidy amount 67 870 PLN.



Ministry of Science and Higher Education
Republic of Poland



Republic
of Poland

approach was implemented based upon the Langer-Schwartz theory and its development and numerical implementation in the Kampmann-Wagner (numerical) approach [7-9]. Both programs take advantage of the CALPHAD method. The calculations presented in this paper were performed using ThermoCalc software (v. 2023a) and database TCFE11.

The microstructure investigation was carried out using Joel JSM 6610LV scanning electron microscope (SEM). The precipitations were identified using TITAN 80-300 transmission electron microscope (TEM). The Metilo program was used for the assessment of the precipitates size which was defined as mean equivalent diameter.

3. Results

3.1. Results of the equilibrium calculations

The calculated volume fractions of phases that can form under equilibrium conditions, as function of temperature, are shown in Figure 1. The detailed description of the phases is given in Table 2.

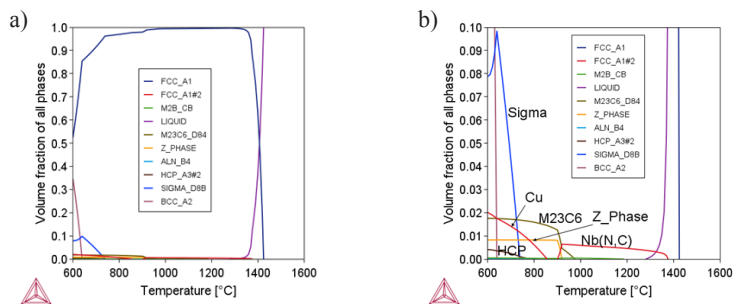


Figure 1. The fraction of equilibrium phases as function of temperature

Table 2. Temperature range of the equilibrium secondary phases occurrence

Predicted phase	Temperature range [°C]
FCC A1/Austenite	1 424.4
FCC_A1#2/Nb(N,C)	1 373.3
$M_{23}C_6$ _D84	973.3
Z_Phase	919.5
ϵ Cu	847.5
Sigma_D8B	736.7
HCP_A3#2/Cr ₂ N	763.4
M ₂ B_CB	1 163.1
AlN_B4	814.4
BCC_A2	638.7

One can see that the first formed element during the steel solidification is carbonitride Nb(C,N). The phases that can form under service conditions include: $M_{23}C_6$ carbide, Z_Phase, ϵ _Cu, Sigma phase and Cr₂N nitride. The results of the thermodynamic calculations are in a good agreement with the experimental observations [1].

3.2. Simulation of the solidification process with Scheil module

The results of the calculations presented in section 3.1 relate to the thermodynamic equilibrium. Therefore in the next stage, the simulation of the solidification process was performed using non-equilibrium Scheil [10] model that is incorporated in the ThermoCalc program. The simulation was performed assuming back diffusion phenomenon for C and N. The assumed cooling rate during the solidification was 1°C/s. The results of the simulation are presented in Figure 2 and Figure 3. The following phase transformations sequence was predicted during cooling from the liquid phase:

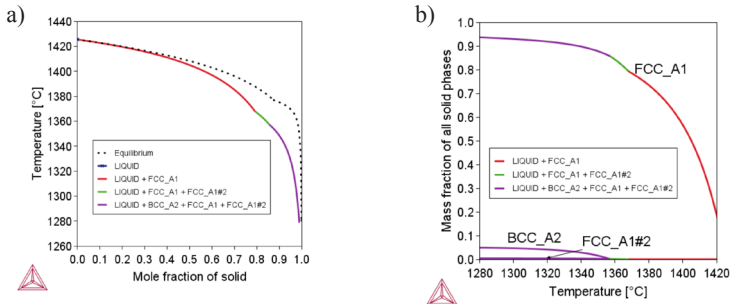


Figure 2. Scheil simulation of the solidification process: (a) mole fraction of solid phase; (b) volume fraction of phases formed during the solidification

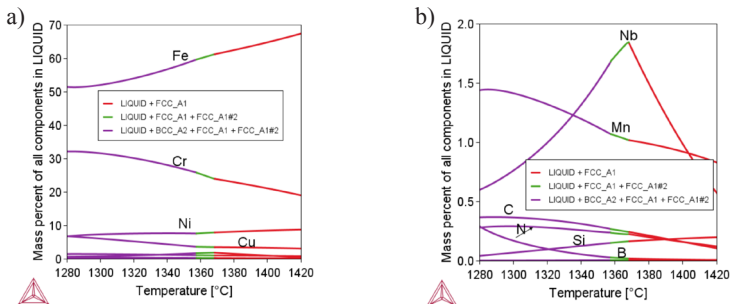


Figure 3. Segregation of elements into inter-dendritic liquid phase during the solidification process

From Figure 3, one can see that non-equilibrium solidification leads to a substantial increase of Cr in the liquid phase, resulting in the δ ferrite formation although the content of this phase is low. The formation of δ ferrite was observed in welds of Super 304H steel [11].

3.3. Simulation of the kinetics of the precipitation process

The simulation of the kinetics of the precipitation reaction is a very advanced process, since it requires adjustment of many model coefficients. For the sake of illustration, here the precipitation process of sigma phase is considered. The precipitation of this phase has a substantial impact on the mechanical properties of Super 304H steel [1]. Figure 4 presents the sigma phase particles in the sample of Super 304H steel.

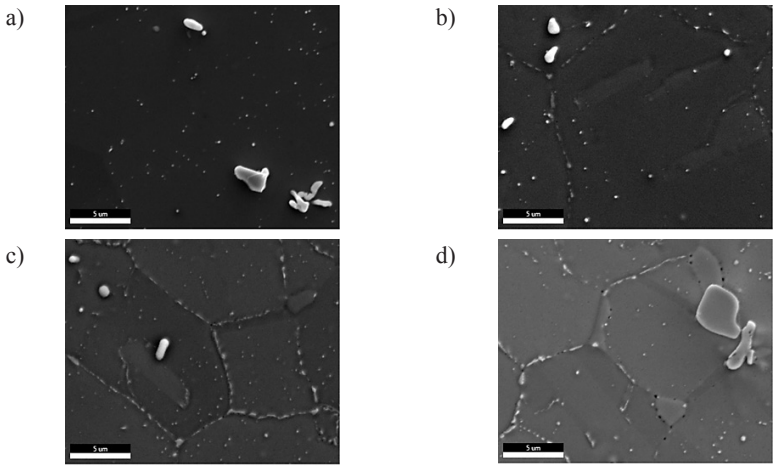


Figure 4. Precipitates of sigma phase in Super 304H steel: a) initial state, b) 10 000 h, c) 30 000 h, d) 50 000 h

Interfacial energy (precipitate/matrix) is the most important parameter used in the precipitation kinetics simulations. For the sake of illustration, precipitation of Following [12] the value of this parameter 0.032 J/m^2 was assumed.

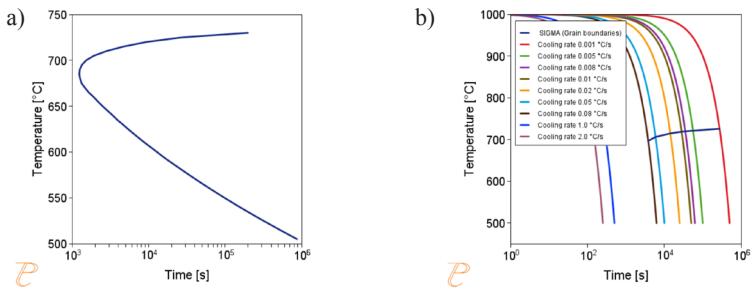


Figure 5. TTT – (a) and CCT – (b) diagrams for the precipitation of sigma phase

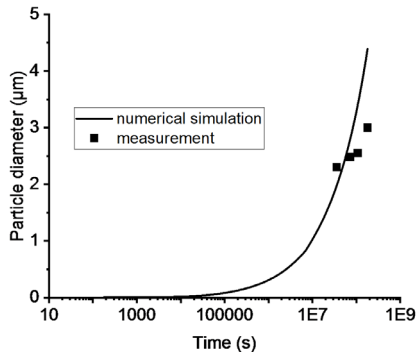


Figure 6. Comparison of the measured values of the mean value of sigma phase equivalent diameter with the results of the numerical simulations

Figure 5 presents the results of the TTT and CCT diagrams calculations. The TTT diagram (Figure 5a) shows that the sigma phase precipitation starts at the lowest time (incubation period) at approximately 690°C. Since the reaction is diffusion controlled, lowering temperature causes extension of the time for the start of precipitation process. This also causes the suppression of the process as the cooling rates following solution treatment are greater than 0.1°C/s (Figure 5b).

Figure 6 presents the results of the calculations of the variation of mean particle diameter changes as function of time. The results of the mean particle diameter are also included in this figure.

The results of the calculation presented in Figure 6 suggest that the precipitation reaction did not reach equilibrium even at the longest ageing time. It should be noted that the results of the simulation compare fairly well with result of the measurement.

4. Conclusions

- 1) The application of CALPHAD method enabled obtaining a concise and accurate description of the precipitation processes occurring in Super 304H steel. The obtained results are in a very good agreement with the results of the investigations presented in technical literature.
- 2) The adjusted precipitation kinetics model, implemented in PRISMA program, can be used for the prediction of the evolution of precipitates at times beyond these applied in the laboratory experiments.
- 3) The thermodynamic calculations also can be used to modify the chemical composition of Super 304H steel to obtain new functional capabilities.

References

1. Zieliński A., *Trwałość eksploatacyjna żarowytrzymałych stali o osnowie austenitycznej*, Monografia, GIT, 2021.
2. Golański G, Zieliński A, Purzyńska H, *Precipitation Processes in Creep-Resistant Austenitic Steels*, <http://dx.doi.org/10.5772/intechopen.70941>.
3. M. Jesenský, *Structure stability and weldability of stainless steels*, Ph.D. Thesis, MTF STU, Trnava, Slovakia; 2006.
4. Padilha AF, Escriba DM, Materna-Morris E, Rieth M, Klimenkov M, Precipitation in AISI 316L(N) during creep tests at 550 and 600 °C up to 10 years, *J Nucl Mater* 2007;362:132–8.
5. Cheng-yu Chia, n, Hong-yaoYub, Jian-xinDongb, Wen-qingLiuc, Shi-changChengd, Zheng-dong Liud, Xi-shanXieb, *The precipitation strengthening behavior of Cu-rich phase in Nb contained advanced Fe–Cr–Ni type austenitic heat resistant steel for USC power plant application*, *Progress in Natural Science: Materials International* 2012;22(3):175–185.
6. Lukas HL, Fries SG, Bo Sundman, *Computational thermodynamics – The CALPHAD method*, 2007.
7. Langer J, Schwartz K, *Kinetics of nucleation in near-critical fluids*, *Physical Review A* 21 (1980).
8. Kampmann R, Wagner R, *Decomposition of alloys: the early stages*, [in:] *Proc. 2nd Acta-Scripta Metall. Conf.*, Pergamon, Oxford, 1984, pp. 91–103.
9. Wagner R, Kampmann, Voorhees PW, *Homogeneous second-phase precipitation*, *Materials science and technology*, [in:] *Phase Transformations in Materials*, ed. by Gernot Kostorz, p. 948 Wiley-VCH (2001).
10. Siedlecki J, Szopa R, Wojciechowska W, *Numerical simulation of solidification process using the Scheil model*, *Scientific Research of the Institute of Mathematics and Computer Science*, 2007, Volume 6, Issue 1, pages 253-260.
11. Kumar MV, Balasubramanian V, Rao AG, *Effect of filler addition on solidification behaviour and hot tensile properties ofGTA-welded tube joints of Super 304H austenitic stainless steel*, *International Journal of Mechanical and Materials Engineering* (2015), DOI 10.1186/s40712-015-0051-x
12. Shunyi L. *Precipitation behaviour of the super austenitic stainless steel SANICRO® 35 and the effect on impact toughness and pitting corrosion resistance*, Degree Project in Materials Science and Engineering, Stockholm, Sweden, 2022.