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*The structural stability of creep resistant  
austenitic steels SUPER 304H and Tp 347HFG*

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# 1 Introduction

General requirements to austenitic steel in the superheater application are corrosion resistance, exfoliation resistance and sufficient creep resistance. In literature ([1][2]) steels SUPER 304H and Tp 347HFG are categorized like suitable for this type of application.

Both SUPER 304H and Tp 347HFG are type 18/9 (18% chromium and 9% nickel) complexly alloyed creep resistant austenitic steels. The relatively high content of alloying elements leads to thermodynamic instability of those steels. The instability causes phase precipitations during the thermal exposition.

In literature [3] are listed conditions for precipitation of the brittle phases in austenitic steels according to their chemical composition. Steels SUPER 304H and Tp 347HFG meet the conditions. There is a possibility for precipitation of the brittle phases, which deteriorates steel mechanical properties. It was shown in literature [4], [5], [6] that precipitation of the brittle phases really occurs in those steels under the heat exposition.

Motivation for this thesis is to provide the information about creep resistant 18/9 steels group instability (especially by using group representatives Tp 347HFG and SUPER 304H) and its influence on the mechanical properties. Second motivation is to research how to influent precipitation rate by the modification of those steels chemical composition or by the manufacturing process.

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## 2 Theoretical part

### 2.1 The precipitates causing embrittlement in austenitic creep resistant steels

Embrittlement of the austenitic steels from group 18/9 is in general caused by precipitation of the intermetallic phase. Name of those precipitation groups is the sigma phase. The sigma phase precipitates in Fe-Cr system.

The sigma phase may precipitate in several variations, depending on the chemical composition of the steel. Fig. 1 illustrates different chemical composition of the sigma phase and its lattice parameters.

Alloy	Lattice parameter (Å)	Composition of phase (wt%)					Formula
		Fe	Cr	Ni	Mo	Si	
Fe-Cr	$a_0 = 8.799, c_0 = 4.544$						Fe-Cr
Fe-Mo	$a_0 = 9.188, c_0 = 4.812$						Fe-Mo
17Cr-11Ni-2Mo-0.4Ti	—		30	4.3	9	0.8	
17Cr-11Ni-0.9Mo-0.5Ti	—		33	4.5	5.4	0.7	
Type 316	$a_0 = 8.28 \sim 8.38, c_0 = 4.597 \sim 4.599$	55	29	5	11	—	$(\text{FeNi})_x(\text{CrMo})_y$
Type 316L	$a_0 = 9.21, c_0 = 4.78$						
20Cr-25-34Ni-6.5-8Mo	$a_0 = 8.87, c_0 = 4.61$	35/37	17/26	15/21	21/28	—	
25Cr-20Ni	—	40	46	9.4	—	3	

Fig. 1 *The sigma phase lattice parameters depending on the chemical composition [3]*

The precipitated volume fraction of sigma phase in various types of alloys is shown in Fig. 2. Graphs confirm that other alloying elements influence sigma phase precipitation rate. Category including the steels SUPER 304H and Tp 347HFG is austenitic complexly alloyed steels. The main word is complexly. Here is place to make model of sigma phase precipitation.

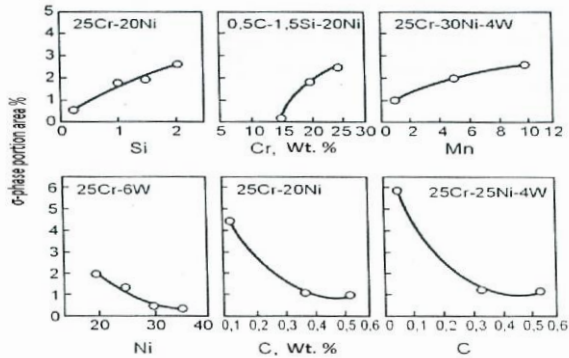


Fig. 2 The influence of Si, Cr, Mn, Ni and C content to sigma phase precipitation (annealing 1250°C and exposition 1000 hours/ 850°C) [7]

Fig. 2 summarized influence of alloying elements in high chromium and nickel austenitic steel. On the other hand, there is no information about influence of copper which is nowadays used like alloying element in complexly alloyed steels like SUPER 304H. That is missing information.

## 2.2 The specific austenitic steels from group 18/9 for USC power plants

### 2.2.1 The similarity and differences of both steels

Steel SUPER 304H is modern and more complex alloyed in comparison with Tp 347HFG. It is consistent with higher creep resistance of SUPER 304H in comparison with a Tp 347HFG. Both steels were created by continuously modifications of origin AISI 302 and are members of the stable austenitic steels group 18/9.

First difference is in content of base alloying elements (Cr and Ni). Influence of chromium and nickel alloying in binary system is presented in Fig. 3. Most interesting part is over 30 % of chromium where is sigma phase region. According to the information summarized in subchapter 2.1 sigma phase can precipitate under this chromium content during heat exposition. The sigma phase precipitation rate will be strongly dependant on carbon and chromium content (initial state of sigma phase precipitation). After beginning of precipitation, the precipitation rate will be driven by diffusivity of chromium, iron and nickel.

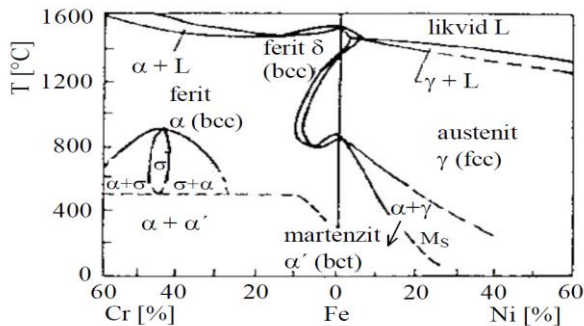


Fig. 3 *Double binary diagram Fe-Cr and Fe-Ni [8]*

The second difference in chemical composition is complex alloying for increasing steel creep resistance. For increasing SUPER 304H steel creep resistance is alloyed Cu, N, Al and B (boron increases mechanical properties too). Cu alloying into steel SUPER 304H may ensure nanoprecipitation of Cu coherent particles, which may slower creep processes. All of those alloying elements will influence sigma phase precipitation rate just by their content.



### 2.3 The austenitic 18/9 creep resistant steels structural stability

The information about heat exposition influence on the steel SUPER 304H is presented in [4][6][9][10]. In general influence of heat exposition on the austenitic steels is:

- Grain coarsing
- Slowly generating of corrosion layers
- The microstructure changes

Precipitation of the sigma phase for steel type Tp 347HFG after laboratory exposition up to 10 000 hours is present in [11]. The sigma phase microstructure in austenitic matrix of Tp 347HFG is shown in Fig. 4.

Presented results are very beneficial like information about sigma phase precipitation. On the other hand, exposition temperature is absolutely out of range suitable for those material applications.

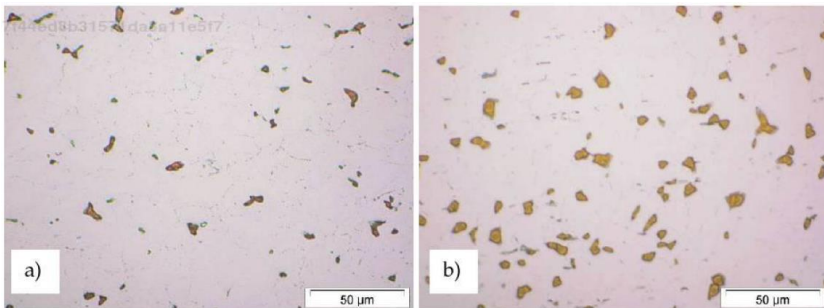


Fig. 4 *Sigma phase in 347HFG after a) 5 000 hours and b) 10 000 hours of aged 750°C [11]*

# 3 The thesis goals

As it was mentioned above both steels SUPER 304H and Tp 347HFG are structurally unstable under USC operation conditions. In general, there is just a little or no information about kinetics of the sigma phase precipitation in these types of steels. It gives a possible field for study of the structural stability of this type of steels. Moreover, precipitation is thermally activated and driven by historically described physical laws which give possibility for model modification for a small material group with similar chemical composition.

Set goals are:

- Describe sigma phase precipitation processes for steel SUPER 304H and perform their general mathematical description
- Model precipitation kinetics processes based on chemical composition and physical laws like modification of the steel Tp 347HFG
- Correlate model with measured particles after the long-term heat exposition for steel Tp 347HFG
- Find and describe the kinetic function of the sigma phase precipitation for the steel SUPER 304H

# 4 Methodology

## 4.1 Used experimental materials

Most of the performed experiments were done at the material SUPER 304H because of its availability. Specification of steel is listed in [12]. Material was supplied by the Sumitomo Metals. Steel SUPER 304H was supplied in the form of the seamless tubes with outer diameter 38 mm, wall thickness 6,3 mm and a tube length of 5700 mm [12]. Heat treatment made by producer (Sumitomo) was solution annealing under conditions 1150°C / 2 min. / cold by water quenched [12]. Samples were separated into two groups Not annealed (NA) and Annealed (A). Solution annealing was done under condition 1130°C / 15 min. / water cooling.

The heat number of supplied steel is F124139. Its chemical composition is summarized in Tab. 1. Supplied steel is in accordance with prescribed values by the standard ASME Case 2328-1.

*Tab. 1 Chemical composition of supplied steel SUPER 304H [12]*

	C	Si	Mn	P	S	Cu	Cr	Ni	Nb	B	N	Al
Min. (ASME Case 2328-1)	0,07	-	-	-	-	2,50	17,0	7,5	0,30	0,001	0,05	0,003
Max. (ASME Case 2328-1)	0,13	0,30	1,00	0,04	0,01	3,50	19,0	10,5	0,60	0,010	0,12	0,030
Heat No. F124139	0,08	0,25	0,81	0,003	0	3,07	18,3	9,0	0,49	0,004	0,11	0,005

### 4.2 The laboratory isothermally ageing

For reaching of the degraded state of the austenitic steels SUPER 304H and Tp 347HFG laboratory isothermal ageing without special protective atmosphere was used. Used temperatures were 650, 675 and 700°C. Those temperatures were selected like slightly higher in comparison with operation parameters of USC power plant, because of the degradation processes acceleration. Time of isothermal ageing was up to  $2,45 \times 10^4$  hours.

### 4.3 Applied experimental methods for material description

Part of the thesis focused on the characterisation of structural changes is crucial for reaching the thesis goals. The sigma phase quantification is based on colour (selective) etching and optical microscopy. Before quantification of the sigma phase it was necessary to confirm this phase by more sophisticated methods. For the phase identification TEM, SEM, EBSD were used. Chemical analysis of the sigma phase and its near surrounding of austenitic matrix were measured by EDS method.

# 5 Experimental part

## 5.1 The electron microscopy

### 5.1.1 The sigma phase particles identification

Results from precipitation investigation of SUPER 304H samples after long term laboratory exposition (20 000 hours) were published in [13]. Precipitated sigma phase is marked at the base of chromium detection in Fig. 5.

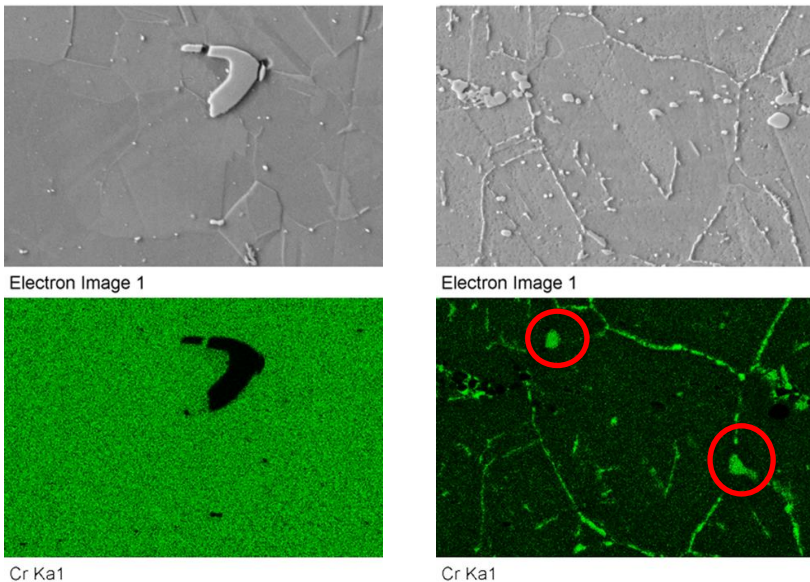


Fig. 5 *Microstructure and Cr map of base material (left) and aged by 20000 hours (right) [13]*

The cross-section of  $\sigma$ -phase obtained by FIB technique used for TEM-foils preparation enabled more detailed investigation of  $\sigma$ -phase situated on the

boundaries. Fig. 6 shows the distribution of Cr (green colour), Nb (dark blue) and Cu (magenta) around the grain boundaries. It can be seen that colonies of relatively fine  $\sigma$ -phases (mean size  $\sim 300$  nm) were formed along the grain boundaries which are covered by large Cr and Nb carbides.

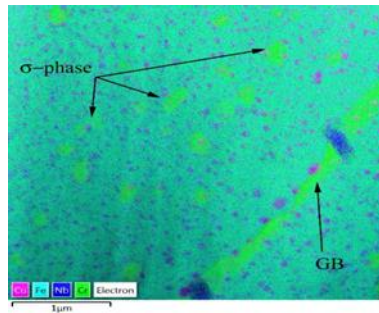


Fig. 6 *Distribution of elements around austenitic grain boundary [14]*

Measured chemical composition of sigma phase is summarized in Tab. 2. Fig. 7 summarises the sigma phase lattice parameters and chemical composition variation. Chemical composition match with theoretical. For absolute accuracy identification it is necessary to perform atomic diffraction of the phase or to use the EBSD method.

Alloy	Lattice parameter (Å)	Composition of phase (wt%)					Formula
		Fe	Cr	Ni	Mo	Si	
Fe-Cr	$a_0 = 8.799, c_0 = 4.544$						Fe-Cr
Fe-Mo	$a_0 = 9.188, c_0 = 4.812$						Fe-Mo
17Cr-11Ni-2Mo-0.4Ti	—		30	4.3	9	0.8	
17Cr-11Ni-0.9Mo-0.5Ti	—		33	4.5	5.4	0.7	
Type 316	$a_0 = 8.28 \sim 8.38, c_0 = 4.597 \sim 4.599$	55	29	5	11	—	$(\text{FeNi})_x(\text{CrMo})_y$
Type 316L	$a_0 = 9.21, c_0 = 4.78$						
20Cr-25-34Ni-6.5-8Mo	$a_0 = 8.87, c_0 = 4.61$	35/37	17/26	15/21	21/28	—	
25Cr-20Ni	—	40	46	9.4	—	3	

Fig. 7 *Lattice parameters and chemical composition of the sigma phase [3]*

Tab. 2 Chemical composition of sigma-phase – State after 15 000 hours of ageing [15]

Point analysis of chemical composition of sigma-phase (wt.%)	
Fe	53,1
Cr	40,8
Ni	3,2
Mo	2,2
Si	0,8

The kikutchi lines obtained from transmission diffraction (Fig. 8a) were compared with a theoretical model for sigma-phase. Conformity with the theoretical model is shown in Fig. 8b. [15]

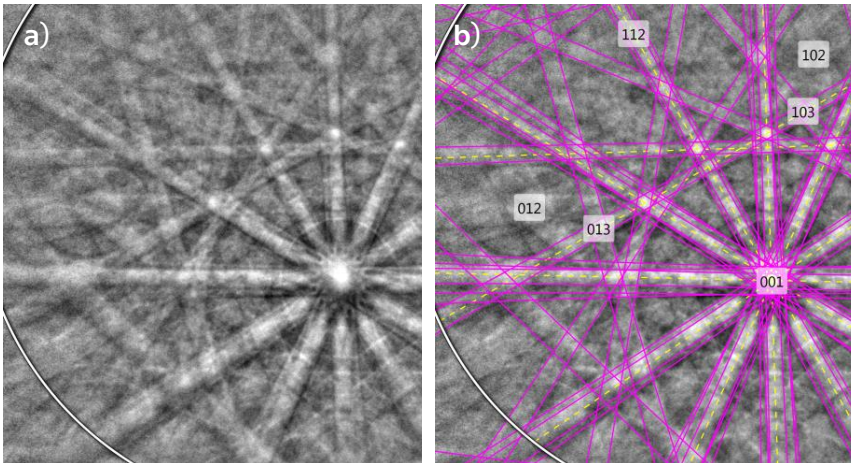


Fig. 8 Kikutchi lines obtained in the analysis of sigma phase in the steel Super 304H a) measured lines b) conformity with the theoretical model [15]

## 5.1.2 The correlation between the electron and the optical microscopy

The chemical composition of the sigma phase and SUPER 304H steel matrix measured on the correlation sample is presented by Fig. 9, chemical composition results by Tab. 3. Ratio of chromium and iron for Spectrum 1 confirms the sigma phase.

Tab. 3 Chemical measurement results for Fig. 9

Spectrum	Cr	Fe	Ni	Cu	Nb
Spectrum 1	36.29	56.27	3.33		
Spectrum 2	18.84	66.95	8.80	4.54	0.15

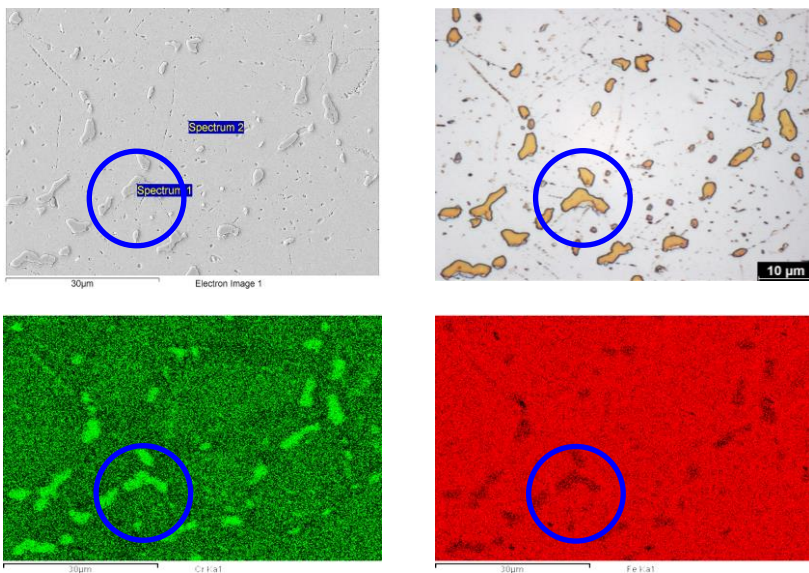


Fig. 9 Comparative image for sigma phase verification for optical microscopy



Image (Fig. 9) shows direct comparison between the electron microscope image, measured chromium and iron maps and the optical microscope image. The blue circles added to Fig. 9 connect one of the sigma phases visualised by different methods.

Results documented by Fig. 9 give possibility to use optical microscopy for the sigma phase quantification.

### **5.2 The optical microscopy**

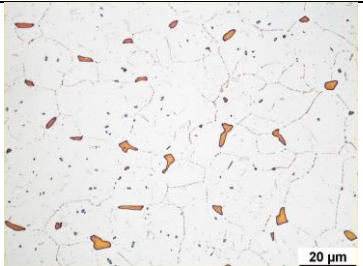
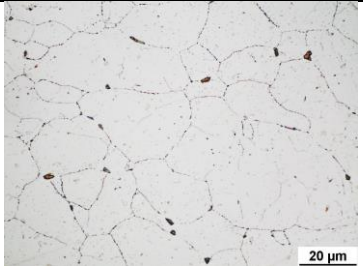
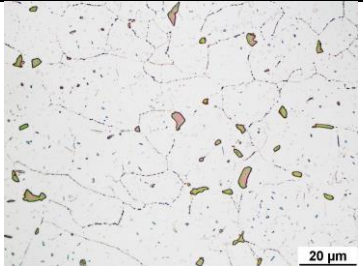
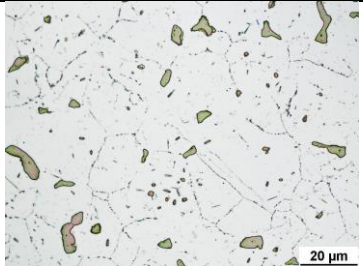
The optical microscopy is used for the sigma phase precipitation description and its quantification. Subchapters deal with precipitation morphology and then with quantitative description of the sigma phase precipitation.

#### **5.2.1 Evolving of the sigma phase morphology during aging for steel SUPER 304H**

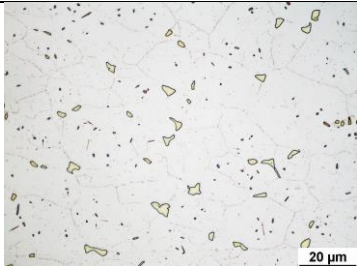
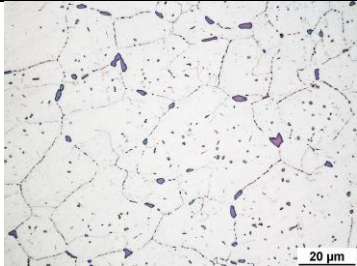
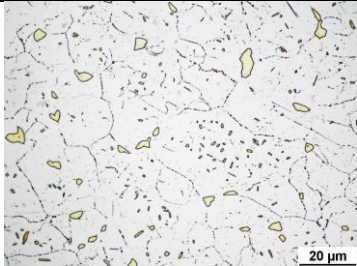

Not annealed (NA) state samples are summarised by figures from Fig. 10 to Fig. 17.

For each of sample figures are added LMP value. Higher LMP value means higher degradation state.

**5 Experimental part**

Temperature	650 °C	675 °C	700 °C
Aging time  12000 hours	X	 <p data-bbox="783 488 1086 546">Fig. 10 LMP 23589 NA (3)</p>	X
15000 hours	 <p data-bbox="400 852 703 910">Fig. 11 LMP 23057 NA (1)</p>	 <p data-bbox="783 852 1086 910">Fig. 12 LMP 23681 NA (4)</p>	 <p data-bbox="1166 852 1469 910">Fig. 13 LMP 24305 NA (7)</p>

## 5 Experimental part

Temperature	650 °C	675 °C	700 °C
Aging time  20000 hours	X	 <p data-bbox="780 488 1082 546">Fig. 14 LMP 23800 NA (5)</p>	X
24500 hours	 <p data-bbox="397 852 699 910">Fig. 15 LMP 23253 NA (2)</p>	 <p data-bbox="780 852 1082 910">Fig. 16 LMP 23883 NA (6)</p>	 <p data-bbox="1163 852 1465 910">Fig. 17 LMP 24513 NA (8)</p>

### 5.2.2 Evolving of the precipitation kinetics

Separately plotted sigma phase portion area for state NA is shown in Fig. 18. Exponential growth of dependence is marked into graphs by green lines. Mathematical description of exponential growth for state NA which describes precipitation of the sigma phase summarised Eq. (1). The precipitation rate equation obtained like the time derivation of the sigma portion area presents Eq. (2). Used range of LMP covers the whole planned lifetime of power plant.

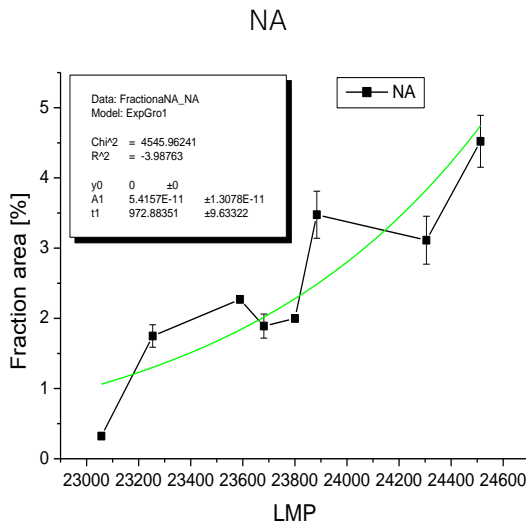


Fig. 18 Evolving of the sigma phase fraction area to LMP for NA state

$$\text{Fraction area} = 5,42 * 10^{-11} * e^{\left(\frac{LMP}{972,88}\right)} \quad \text{Eq. (1)}$$

$$\text{Precipitation rate} = 5,57 * 10^{-14} * e^{\left(\frac{LMP}{972,88}\right)} \quad \text{Eq. (2)}$$

### 5.2.3 V notch pendulum testing

Because of probable sigma-phase assisted embrittlement of exposed steels, the impact strength measurements with reduced width (5 mm) of the specimens with V notch were carried out. Experimental material was isothermally aged at 675 °C for 20 000 hours. Results are summarized in Tab. 4. As can be seen, applied dissolving annealing and/or isothermal ageing (E-NA and E-A states) have strong deteriorating influence on absorbed energy KV 300/5. Similar situation can be observed for steel SUPER 304H. Base material fracture surface (Fig. 19) is ductile with no marks of brittle fracture. Fracture surface after exposition (Fig. 20) is mostly brittle. This change is caused by the sigma phase precipitation.

*Tab. 4 Results of impact testing of SUPER 304 [16]*

Steel	SUPER 304H	
State	KV 300/5 [J]	The sigma phase area fraction [%]
BM	44.7 ± 1.0	0.0
E-NA	11.4 ± 0.4	2.6
E-A	11.5 ± 0.3	2.8

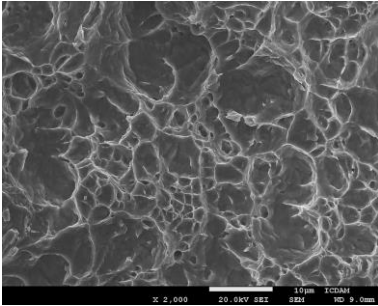


Fig. 19 *Ductile fracture surface of as-received SUPER 304H steel*

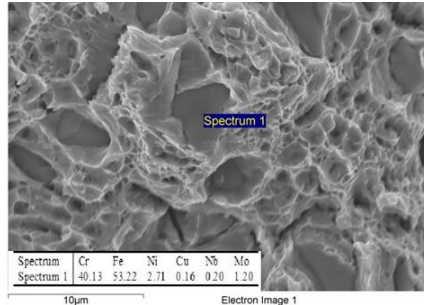


Fig. 20 *Sigma phase with its chemical composition (Spectrum 1) on fracture surface of SUPER 304H steel [16]*

Phase analysis, higher magnification, TEM diffraction patterns, and EDX analysis were used to identify secondary phases located on the fracture surfaces, as illustrated in Fig. 20. The analyses of those particles are implemented into the figures. The measured chemical composition is in accordance with nominal sigma phase chemical composition.

On the basis of microstructure results it can be suggested that a drop of impact strength after long-term ageing is significantly influenced by  $\sigma$ -phase formation.

## **6 Discussion of experimental results**

### **6.1 The sigma phase verification and extension for optical microscopy quantification**

The sigma phase identification was based on combination of four methods. Measurement of chemical composition via SEM EDS detector, TEM microscope include STEM mode for taking pictures and chemical composition measurement, correlation of Kikuchi lines and EBSD method were used. All of the previous named methods confirm precipitation of the sigma phases in microstructure of steel SUPER 304H.

Application of optical microscopy and colour etching require verification between electron and optical microscope. The verification is summarised in the subchapter 5.1.2. Fig. 9 compared image made by electron microscope to image from optical microscopy with EDS method measured chemical maps. The verification confirms possibility of usage of the optical microscope and colour etching (Fig. 9).

### **6.2 The sigma phase precipitation morphology**

Process of the sigma phase precipitation is documented by Fig. 10 - Fig. 17 for NA state. Each of used characteristic images was randomly chosen from

## **6 Discussion of experimental results**

about two hundred of images made for definite combination of exposed time and temperature.

No sigma phase precipitation was documented for original state (without any exposition). This result means that the sigma phase precipitation is induced by heat exposition of experimental material. Used combination of exposed temperatures and times covered through LMP whole power plant lifetime.

The sigma phase precipitation begins at triple points. During continuous thermal exposition precipitation continuous at triple point and also starts along boundaries of austenitic grains.

Particles get coarser with longer heat exposure. Dominant direction of coarsening is along austenitic matrix grain boundaries. Particles precipitated at the triple points get into the shape of a triangle. Others precipitating on the grain boundaries are elongating in direction of grain boundary. Coarsening perpendicular to grain boundary is slower.

Last part of the precipitation process is precipitation of the sigma phase inside the austenitic grains. Precipitation starts like spheroid particles which continuously elongated into the final elliptic shape.

In general, it is possible to state that precipitation of the sigma phase is a continuous process which decreases free enthalpy of system and it is possible to quantify and model it.



### 6.3 The precipitation kinetics curves

Description of the sigma phase precipitation was based on quantification of the sigma phase in various states of degradation conditions. LMP parameter was used for possibility of combination of the degradation description. Used raw data were obtained from quantification of about 2150 images of SUPER 304H steel microstructure. That gave very broad datasheet which is definitely representative for those processes.

The sigma phase precipitation and its growth are driven by diffusion processes [3]. Obtained results are in accordance with this fact. Description of the precipitation process is like all nature processes exponentially. Equations (Eq. (1), Eq. (2)) which describe the sigma phase precipitation confirm that long term precipitation of the sigma phase is not involved by the pre-exposition solution annealing.

The sigma phase is highly brittle intermetallic particle [3]. If we consider triple points precipitation and those particles accelerate coarsening it will strongly influence mechanical properties. Precipitates will affect crack propagation and probably formation of the creep cavity. Describe precipitates and identify their position is necessary for decaying about those problems.

### 6.4 Influence of the precipitation to the mechanical properties

Pendulum testing of exposed samples from the steel SUPER 304H declined from the original value of

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## 6 Discussion of experimental results

44,7 J to 11,4 J after 20 000 hours of exposition at 675°C. That is a drop by approximately 75%. The drop by 75% is significant and there must be a reason for such a change. The sigma phase was documented by electron microscope on the fracture surfaces of experimental samples.

Results about decreasing of mechanical properties support the need for this thesis because there is no information about precipitation processes for the steel SUPER 304H.

### 6.5 The modelling and achieved results comparison

The sigma phase precipitation modelling for the steel Tp 347HFG is based on similarity with the steel SUPER 304H. The similarity means near base chemical composition, similarity in high fine grain size and stable austenitic microstructure. Those assumptions provide possibility to apply modification through physical laws which describe chemical components diffusion for the sigma phase precipitation modelling. Slight difference in chemical composition will cause difference of the sigma phase precipitation rate.

The sigma phase precipitation process is dependent on the time and concentration of chromium, iron and nickel. Description of the chemical elements transition in solid is provided by Fick laws. Mathematical equation of the second Fick law (Eq. (3) [17]) describes time and distance dependence of difunding chemical element.

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## 6 Discussion of experimental results

$$\frac{\partial c_k}{\partial \tau} = D_{kl} \frac{\partial^2 c_k}{\partial z^2} \quad \text{Eq. (3)}$$

$C_k$  means chemical element concentration,  $\tau$  – time,  $D_{kl}$  diffusion coefficient and  $z$  describes distance in case of 1D diffusion.

For solution of equation it is necessary to define diffusivity for each of the three elements (chromium, iron, nickel). Diffusivity calculation function is summarized by Eq. (4) [18].

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right) \quad \text{Eq. (4)}$$

Activation energies  $Q_d$  and diffusion coefficients  $D_0$  published by [19] for austenitic steel matrix is summarized in Tab. 5.

*Tab. 5 Diffusivity calculation coefficients [19]*

In Fe <sub>v</sub>	$D_0$ [cm <sup>2</sup> s <sup>-1</sup> ]	$Q_d$ [kJmol <sup>-1</sup> ]
Cr	10,8	291,8
Ni	0,77	280,5
Fe	4,085	311,1

General solution of concentration system difference describes Eq. (5).

$$c = (c_0 - c_1) \operatorname{erf}\left[\frac{x}{2(D\tau)^{1/2}}\right] + c_1 \quad \text{Eq. (5)}$$

Coefficients represent time (especially LMP) dependant chemical elements movement which influencing the sigma phase precipitation was calculated by numerical solution of Eq. (5). Calculated

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## 6 Discussion of experimental results

coefficient for steel SUPER 304H are summarised in Tab. 6 and for steel Tp 347HFG in Tab. 7.

*Tab. 6 Calculated coefficient for steel SUPER 304H*

SUPER 304H				
Temperature/time	LMP	Coefficient		
[K/Hours]	-	Cr	Ni	Fe
923,15/10000	22894	-8,33E-10	4,18E-09	3,38E-10
948,15/10000	23514	-1,38E-09	6,77E-09	5,77E-10
973,15/10000	24134	-2,21E-09	1,07E-08	9,57E-10

*Tab. 7 Calculated coefficient for steel Tp 347HFG*

Tp 347HFG				
Temperature/time	LMP	Coefficient		
[K/Hours]	-	Cr	Ni	Fe
923,15/10000	22802	-8,39E-10	3,23E-09	3,17E-10
948,15/10000	23419	-1,38E-09	5,23E-09	5,40E-10
973,15/10000	24037	-2,23E-09	8,27E-09	8,97E-10

Calculated coefficients represent influence of chemical composition and C constant (for LMP parameter calculation). Precipitation rate curve (Fig. 18) can be modified by those coefficients for Tp 347HFG application.

Transformation methodology is based on removal influence of the SUPER 304H chemical composition to precipitation rate and then adding influence of Tp 347HFG chemical composition. Representation of the

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## 6 Discussion of experimental results

two-step modification is summarised by coefficient ratio listed in Tab. 8.

*Tab. 8 Calculated specific coefficients ration*

SUPER304H/Tp 347HFG coefficient				
Temperature/time	Element			
[K/Hours]	Cr	Ni	Fe	Average
923,15/10000	1,00675	0,77374	0,93710	0,90586
948,15/10000	1,00611	0,77326	0,93652	0,90530
973,15/10000	1,00669	0,77370	0,93708	0,90582

### 6.5.1 Tp 347HFG precipitation rate transformation verification

Verification was based on comparison between the recalculated fraction area for Tp 347HFG and the measured fraction area on the Tp 347HFG samples after isothermal aging of 700°C for 10 000 hours. The measured fraction area was 2,82%.

The calculated SUPER 304H fraction area is 3,24% for combination of exposition 700°C for 10 000 hours.

The corelated fraction area for steel Tp 347HFG by average value of coefficients listed in Tab. 8 is summarises in Tab. 9.

*Tab. 9 Calculated and measured results comparison*

SUPER 304H	Tp 347HFG	Tp 347HFG
Calculated	Calculated	Measured
3,24	2,94	2,82

Verification was done by comparison of Tp 347HFG measured and calculated values. Difference between calculated and measured values is 4,08 %. That confirms applicability of coefficient modification methodology.

### **6.6 The practical application of the thesis results**

#### **6.6.1 The degradation prediction**

The power plant operation conditions are not stable. There are many unstable states like heat fluxes during operation. Another non-stable state occurs during the power plant starts up and cooling down. Those operation conditions instabilities cause hardly predictable influence on degradation of the superheaters.

The precipitation model can be used inverse. It means that input will be distribution and size of particles and output temperature of exposition. Inverse model type in combination with the creep data of the steel can give information about remaining lifetime.

#### **6.6.2 The state of degradation**

Under the operation condition (heat and pressure long-term exposition) austenitic creep resistant steels change mechanical properties. The steels microstructure changes cause degradation. Many factors like grain coarsening, precipitation of particles and cavity formation act a role in the degradation

process. The model based on physically confirmed equation and information obtained from examination of real exposed material can give the answer to the question „How fast?“.

Respectively the model can give information about precipitation process. State of precipitation can be compared with the mechanical properties changes.

### **6.6.3 Information for future production of the next steels generation**

In general designing of the new special alloys is based on historical knowledge and theoretical based information. It leads to designing of special alloys with superior properties, which are tested just in short time examinations. Commercial distribution of the new material starts just after confirmation of materials requirement by short time tests.

The main problem is that short time testing can't predict changes of the material properties caused by medium-term or long-term exposition. Microstructural changes, precipitation or decrease of hardening effects can occur. Those changes may cause just small changes in case of mechanical or technology properties. In worse case changes will be more relevant.

One of the possible applications of modelling of the precipitation processes can be during testing period of a new material. Structural stability or changes in the microstructure can be predicted by modelling.

# 7 Summary

## 7.1 Meet the thesis goal

- Describe sigma phase precipitation processes for steel SUPER 304H and perform their general mathematical description

The precipitation processes were described through the sigma phase fraction area. Mathematical description of the sigma phase precipitation was made by exponential growth function.

- Model precipitation kinetics processes based on chemical composition and physical laws like modification of the steel Tp 347HFG

The sigma phase modelling was based on measured values for SUPER 304H and modification coefficients. Modification coefficients were calculated according Fick laws and Larson-Miller construction. Through application of modification coefficients (which describe chemical composition and LMP differences) sigma phase fraction area for steel Tp 347HFG was calculated.

- Correlate model with measured particles after the long-term heat exposition for steel Tp 347HFG

Correlation was performed for available degraded samples of Tp 3247HFG after exposition 700°C for



10000 hours. Difference between calculated values (based on coefficient modification) and real measured sigma phase fraction area was 4,08 %. This difference confirms applicability of coefficient modification methodology.

- *Find and describe the kinetic function of the sigma phase precipitation for the steel SUPER 304H*

The sigma phase kinetic function was described like time derivation of the fraction area exponential growth function.

### **7.2 The main conclusion description**

This thesis confirms high structural instability of the steel SUPER 304H and a similarity with the steel TP 347HFG. The sigma phase kinetics description was performed by exponential growth type equations.

Description of the fraction area was based on the sigma phase measurements in various degraded states of the steel SUPER 304H summarised by LMP parameter. This approach is based on examination of various degradation time and temperature combinations. Accelerated precipitation processes are obtained by this set of expositions.

At the bases of this function modification for steel Tp 347HFG based on differences in chemical composition and LMP constant was performed. This result confirms possibility for extending of those results for creep resistant complex alloyed steels group 18/9.

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The author's publications since 2014 to 2018 are summarised by this chapter.

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