

## Computational Modelling of Chromium Steel in High Temperature Applications

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**ABSTRACT:** Modern martensitic 9-12% Cr steels are alloys with excellent mechanical properties even at elevated temperatures. The high temperature strength of these materials is inevitably related to their complex microstructure. Due to diffusional processes however, this microstructure changes during high temperature service, which leads to a decrease in strength. This work was aimed at modeling the 9-12% Cr steels with tailor-made microstructures for applications such as fossil fuel fired power plants, internal combustion engines etc. The investigations concentrated in the design and characterization of heat resistant steels for applications in high oxidizing atmospheres. A microstructure-property link is formulated with focus on the precipitate and solid solution hardening effect. For different heat treatments, the numerical results are compared with other samples. The numerical simulation showed excellent agreement in the case when all operative strengthening mechanisms are duly considered. The experimental results can be reproduced in a comprehensive and consistent manner by the numerical simulations using the software as MatCalc and ThermoCalc. From the result of the simulation, the observed phases after creep ( $M_{23}C_6$  carbides, V-MX and Nb-MX particles and Laves phase) are in good agreement with the MatCalc and ThermoCalc calculations except for the Z-phase phase. The volume fraction of precipitated  $M_{23}C_6$  carbides is directly related to the carbon content of the alloys.

**KEYWORDS:** Modelling, 9-12% Cr steels, mechanical properties, elevated temperatures, microstructure.

### 1 INTRODUCTION

Power plants, gas turbine, automobile engines were built using heat resistant steels grades. This type of steel is characterized by a low price but still acceptable oxidation resistance and good mechanical properties at elevated temperatures [1]. The high strength of these steels originates from their complex austenite microstructure with high dislocation density, fine sub-grain structure and dense distribution of different types of precipitates [2].

Typical operating parameters for steels used in the manufacture of power plants undergo severe conditions during service life. But this is especially so for steels where the service life is many decades. The degree of reliability demanded of heat resistant steels is therefore extraordinary especially 9-12% Cr steel, and must represent one of the highest achievements of technology [3]. Their safe service life means high investment and production utilization and savings. That is why; such a high attention is paid to the monitoring and surveillance of their service. During service life of heat resistant steels there is gradual degradation in the micro-structure of the steel and this way some decrease of properties conditions. Although these materials show excellent mechanical properties in the initial stage of service, after long term application at elevated temperatures, a change of these properties can be observed. Due to the on-going diffusion processes, substructure coarsening with simultaneously growth, coarsening and sometimes dissolution of precipitate populations can be observed. Heat resistance in steel is dependents on its creep strength. The microstructure of 9-12% Cr steel grades in the initial state with the common heat treatment of the used products (normalizing annealing followed by tempering) is not really the equilibrium state of the steel [4]. This leads to a remarkable change in the mechanical properties, which represents the main limiting factor in the temperature applicability of the material and, thus, in the efficiency increase of the whole thermal applications in which they are used. Any thermal or mechanical influences are changing the microstructure in the direction

to a higher level of equilibrium. Coagulation and coarsening of precipitates, carbides transformation, additional precipitation, and the evacuation of alloying elements from the matrix, are supposed to be the most detrimental processes. Embrittlement, weakening of the micro structure and the final creep failure can be the result. The degree and intensity of creep degradation depend on both, in service conditions (temperature, stress, and environment) and exposition time [5]. It is very important to study and know the time dependence of the performance of steel in service conditions and this way survey the possibilities of service life increase [6].

The aim of this project is to carryout computational modelling of 9-12% Cr steel for high temperature applications.

## 2 MATERIALS AND METHOD

### 2.1 MODELLING OF 9-12% CR STEEL

In the present section, modelling of heat resistant steel based on the creep strength, which has been developed and implemented in the software MatCalc, is introduced and basic formulations to determine the strengthening contribution of precipitates as well as the solid solution hardening effect in multi-component alloys are developed [7]. The most essential input parameters on the strengthening models, which is the inter-particle distance  $\lambda$ , are discussed and a general superposition rule for different strengthening mechanism is stated.

### 2.2 HEAT TRANSFER

Heat transfer is the science that seeks to predict the energy transfer that may take place between material bodies as a result of a temperature difference, since heat resistance steels applications involves temperature changes, this makes heat transfer being taken into account. The three mode of heat transfer are conduction, convection and radiation.

### 2.3 CONDUCTION HEAT TRANSFER

When a temperature gradient exists in a body, experience has shown that there is an energy transfer from the high-temperature region to the low-temperature region. We say that the energy is transferred by conduction and that the heat-transfer rate per unit area is proportional to the normal temperature gradient [8].

$$\frac{q_x}{A} = \frac{\partial T}{\partial x} \tag{1}$$

When the proportionality constant is inserted,

$$q_x = -KA \frac{\partial T}{\partial x} \tag{2}$$

Where  $q_x$  is the heat-transfer rate and  $\partial T/\partial x$  is the temperature gradient in the direction of the heat flow. The positive constant  $k$  is called the thermal conductivity of the material, and the minus sign is inserted so that the second principle of thermodynamics will be satisfied; i.e., heat must flow downhill on the temperature scale.

$$-KA \frac{\partial T}{\partial x} + \dot{q}A dx = \rho cA \frac{dT}{d\tau} dx - A \left[ K \frac{\partial T}{\partial x} + \frac{\partial}{\partial x} k \left( \frac{\partial T}{\partial x} \right) dx \right] \tag{3}$$

This is the one-dimensional heat-conduction equation. To treat more than one-dimensional heat flow, we need consider only the heat conducted in and out of a unit volume in all three coordinate directions

$$q_x + q_y + q_z + q_{gen} = q_{x+dx} + q_{y+dy} + q_{z+dz} + \frac{dE}{d\tau} \tag{4}$$

and the energy quantities are given by

$$q_x = -K dy dz \frac{\partial T}{\partial x} \tag{5}$$

$$q_{x+dx} = - \left[ K \frac{\partial T}{\partial x} + \frac{\partial}{\partial x} k \left( \frac{\partial T}{\partial x} \right) dx \right] dy dz \tag{6}$$

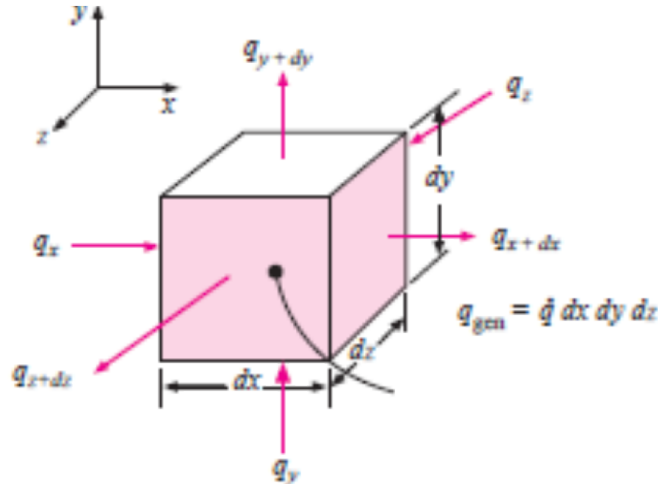
$$q_y = -K dx dz \frac{\partial T}{\partial y} \tag{7}$$

$$q_{y+dy} = - \left[ K \frac{\partial T}{\partial y} + \frac{\partial}{\partial y} k \left( \frac{\partial T}{\partial x} \right) dx \right] dx dz \quad 8$$

$$q_z = -K dx dy \frac{\partial T}{\partial z} \quad 9$$

$$q_{z+dz} = - \left[ K \frac{\partial T}{\partial z} + \frac{\partial}{\partial z} k \left( \frac{\partial T}{\partial z} \right) dx \right] dx dy \quad 10$$

$$q_{gen} = \rho c dx dy dz \frac{dT}{d\tau} \quad 11$$



so that the general three-dimensional heat-conduction equation is

$$\frac{\partial}{\partial x} k \left( \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} k \left( \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} k \left( \frac{\partial T}{\partial z} \right) + \dot{q} = \rho c \frac{dT}{d\tau} \quad 12$$

For constant thermal conductivity, the above equation is written

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} + \frac{\dot{q}}{k} = \frac{1}{\alpha} \frac{dT}{d\tau} \quad 13$$

where the quantity  $\alpha = k/\rho c$  is called the thermal diffusivity of the material. The larger the value of  $\alpha$ , the faster heat will diffuse through the material. This may be seen by examining the quantities that make up  $\alpha$ . A high value of  $\alpha$  could result either from a high value of thermal conductivity, which would indicate a rapid energy-transfer rate, or from a low value of the thermal heat capacity  $\rho c$ . A low value of the heat capacity would mean that less of the energy moving through the material would be absorbed and used to raise the temperature of the material; thus more energy would be available for further transfer. Thermal diffusivity  $\alpha$  has units of square meters per second.

In the derivations above, the expression for the derivative at  $x+dx$  has been written in the form of a Taylor-series expansion with only the first two terms of the series employed for the development

**Steady state one dimension heat flow (no heat generation):**

$$\frac{d^2 T}{dx^2} = 0 \quad 14$$

**Steady-state one-dimensional heat flow with heat sources:**

$$\frac{d^2 T}{dx^2} + \frac{\dot{q}}{k} = 0 \quad 15$$

**Two-dimensional steady-state conduction without heat sources:**

$$\frac{d^2 T}{dx^2} + \frac{d^2 T}{dy^2} = 0 \quad 16$$

### Convection heat transfer

$$Q = hA (T_w - T_\infty) \quad 17$$

Here the heat-transfer rate is related to the overall temperature difference between the wall and fluid and the surface area A. The quantity h is called the convection heat-transfer coefficient, and the above equation is the defining equation. An analytical calculation of h may be made for some systems. For complex situations it must be determined experimentally

## 2.4 RADIATION HEAT TRANSFER

In contrast to the mechanisms of conduction and convection, where energy transfer through a material medium is involved, heat may also be transferred through regions where a perfect vacuum exists. The mechanism in this case is electromagnetic radiation. Limiting the discussion to electromagnetic radiation that is propagated as a result of a temperature difference; this is called thermal radiation.

Thermodynamic considerations show that an ideal thermal radiator, or blackbody, will emit energy at a rate proportional to the fourth power of the absolute temperature of the body and directly proportional to its surface area. Thus

$$q_{\text{emitted}} = \sigma AT^4 \quad 18$$

Where  $\sigma$  is the proportionality constant and is called the Stefan-Boltzmann constant with the value of  $5.669 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$ . The above equation is called the Stefan-Boltzmann law of thermal radiation, and it applies only to blackbodies. It is important to note that this equation is valid only for thermal radiation; other types of electromagnetic radiation may not be treated so simply.

The net radiant exchange between two surfaces will be proportional to the difference in absolute temperatures to the fourth power; i.e.,

$$\frac{q_{\text{net exchange}}}{A} \propto \sigma(T_1^4 - T_2^4)$$

In addition, we must take into account the fact that not all the radiation leaving one surface will reach the other surface since electromagnetic radiation travels in straight lines and some will be lost to the surroundings.

We therefore introduce two new factors in Equation (1-9) to take into account both situations, so that

$$q = F_\epsilon F_G A \sigma (T_1^4 - T_2^4) \quad 19$$

where  $F_\epsilon$  is the emissivity function, and  $F_G$  is the geometric "view factor" function.

## 2.5 MODELLING OF 12%CR STEEL FOR HEAT RESISTANCE

The design of the novel 12% Cr alloys is based on previous work of the Sauthoff et al

In a first step, calculations were carried based on MatCalc out for a reference alloy of composition 12% Cr, 0.2% Si, 0.2% V, 0.1% C and 0.05% N to determine the influence of the main alloy elements on the austenite stability and on the Laves phase formation.

### 2.5.1 INFLUENCE OF CO AND W ON MICROSTRUCTURE FORMATION

High contents of Co were intentionally used in order to stabilize the austenitic field, Co shows a high solubility in the ferrite and low solubility in the precipitates, and hence Co remains in the matrix as a solid solution. As an example, the influence of Co on the austenite stability of the reference alloy calculated by MatCalc is shown in Fig. 4-1. A single-phase austenite field above 1055°C is found for high Co contents above 1% (in order to avoid the formation of  $\alpha$ -ferrite in the reference alloy).

#### 2.5.1.1 INFLUENCE OF W CONTENT

W is well known to increase the high temperature strength via solid solution hardening, suppressing the recovery of the martensitic matrix and increasing the stability of the precipitates by decreasing the self-diffusion rate. W is the most potent Laves phase former and for this reason it is interesting to determine the necessary amount of W in the reference alloy in order to form Laves phase at the temperature of interest (650°C). In Fig. 4-2 it can be seen that the Laves phase precipitates

for more than 1% W at 650°C. The amount of W is restricted to 5.5% in order to obtain single-phase austenite field at temperatures above 1085°C, avoiding the formation of  $\delta$ -ferrite which decreases the creep strength. In the phase field of interest, also ferrite and  $M_{23}C_6$  carbides are observed. The  $M_{23}C_6$  precipitate is of the type  $(Cr, W, Fe)_{23}C_6$  whereas the Laves phase is of the type  $Fe_2W$ . [10]

The calculations also predicted a stable Z-Phase of the type CrVN, what is indeed expected due to the high amount of Cr in the alloy [9]. A high Cr content increases the driving force for the precipitation of the Z-Phase, which is more stable compared to VMX carbonitride in 12% Cr alloys. The elemental composition of 12% Cr Steel is contained in Table 1.

**Table 1: Chemical composition of 12% Cr Steel**

Fe	Cr	Mn	Ta	W	Cu	V	C	Al	B	N	Si	Co
Bal	12.30	0.70	0.17	3.50	1.0	0.022	0.15	0.028	0.30	0.07	0.45	2.58

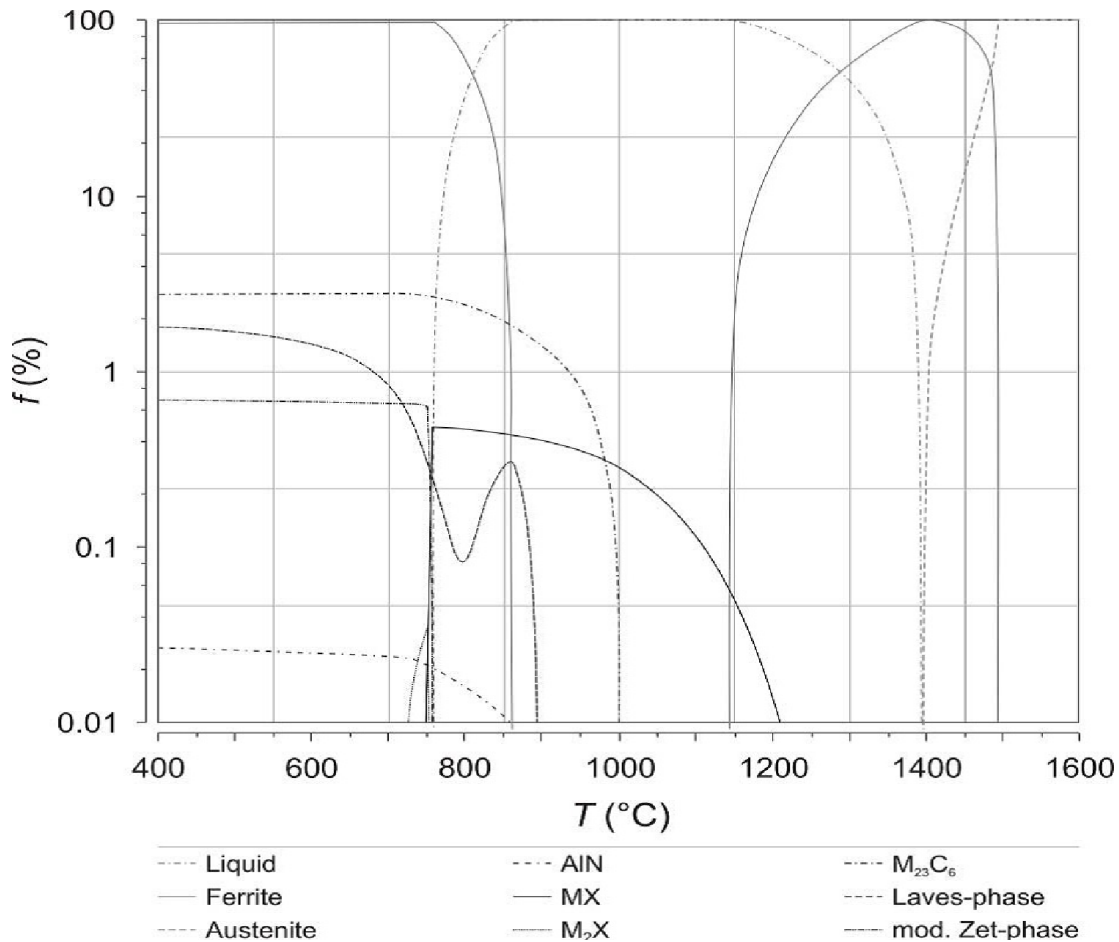
**Computer simulation of 12%Cr Steel**

In the following, the MatCalc model is applied to the simulation of the precipitate evolution during the entire heat treatment and service of the 12%Cr steel.

First, a thermodynamic equilibrium analysis of this steel is performed, which provides an overview of the type and amount of different phases that can be expected to occur at given chemical composition and temperature. Then, the results of the kinetic simulation are discussed [11].

**Thermodynamic equilibrium analysis**

The thermodynamic equilibrium analysis is an important step in a comprehensive material Characterization. By this method, information can be obtained about, Figure 1 contained phase fraction diagram of 9-12%Cr Steel.



**Figure 1: Calculated phase fraction diagram of 12% Cr Steel**

### 3 DISCUSSION OF RESULTS

Precipitation strengthening is a key mechanism for improving mechanical properties of creep resistant materials. A corresponding methodology is introduced in this chapter. With the simulation software MatCalc and ThermoCalc, which is based on independent thermodynamic and kinetic databases and on a novel theoretical approach to model multi-component multi-phase precipitation kinetics, the strengthening contribution from precipitates is predicted for the entire life time of a sample on the example of the 9-12% Cr steels.

The initial microstructure of the simulated samples showed  $M_{23}C_6$  carbides and MX particles and which calculations at the tempering temperature are in agreement with the thermodynamic equilibrium as shown in figure 2.

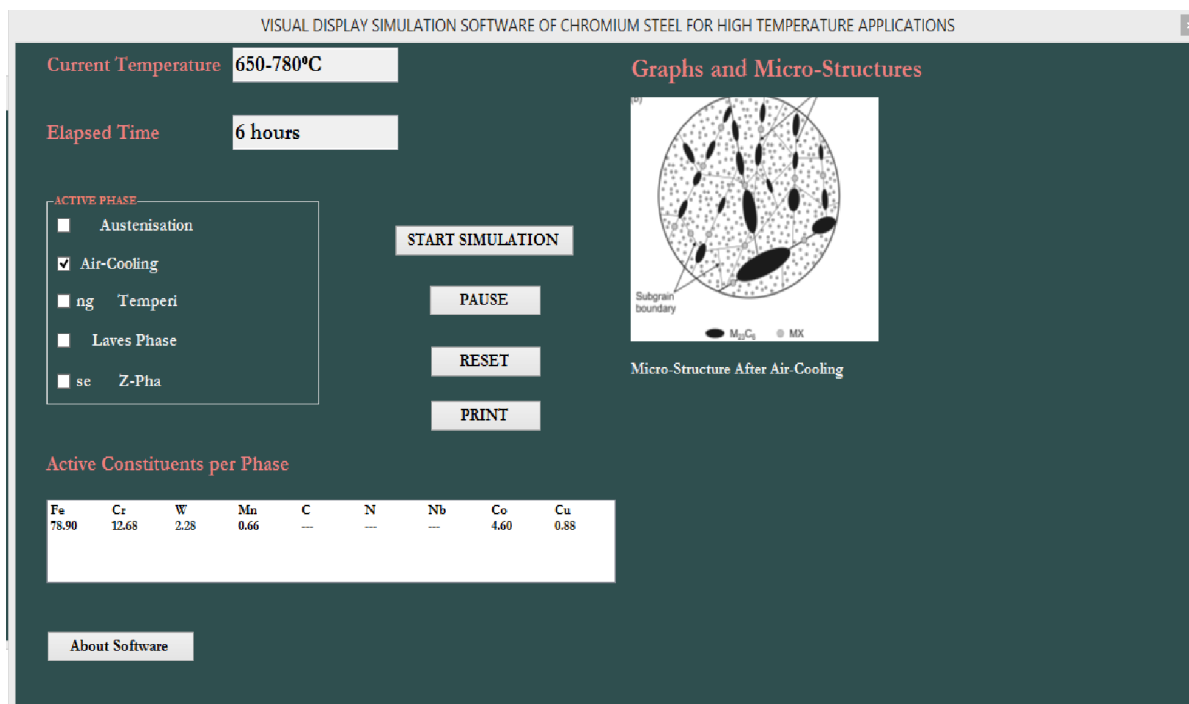


Figure 2 Visual Display Simulation Software showing microstructure of Cr Steel during tempering at 650-780°C

The observed phases after creep ( $M_{23}C_6$  carbides, V-MX and Nb-MX particles and Laves phase) are in good agreement with the MatCalc and ThermoCalc calculations except for the Z-phase phase. The Z-phase was not detected in the microstructure after creep probably due to the slow precipitation kinetics of the Z-phase in the 9% Cr steels.

### 4 CONCLUSION

In the present work, a new methodology to model strengthening in steel was outlined on the basis of a physical microstructure-property relationship and heat treatment in combination with numerical simulations carried out with the software MatCalc and ThermoCalc.

Correlations between the microstructure evolution and the mechanical properties were studied. The conclusions of this part of the study are summarized as follows:

Processing parameters (austenisation and tempering temperatures) were defined based on the phase diagram information. Investigations of the microstructures showed good agreement with the predicted phases of the thermodynamic modeling.

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