### THERMODYNAMIC AND KINETIC MODELING OF STAINLESS STEELS PAST AND FUTURE TRENDS

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### Abstract

The development of stainless steels benefits particularly from thermodynamic and kinetic modeling. Despite their simple structure, in most cases the alloys are complex and their performance depends on a delicate balance between alloy composition, involving many alloy elements, processing and type of application. For example, already a long time ago pioneering work gave quantitative prediction of sensitization and self healing of austenitic stainless steels, the ferrite/austenite balance and sigma phase formation in duplex stainless steels, all by thermodynamic and kinetic calculations.

In this presentation some of the old work as well as more recent studies will be reviewed. The new trends in materials modeling and their consequences for research on stainless steels will be discussed. This involves ab-initio quantum mechanical calculations, CALPHAD, DICTRA and phase-field modeling.

### Introduction

Despite their relatively simple microstructure stainless steels have a rather complex alloy chemistry that may cause a number of difficulties during processing and usage. For example, the intergranular corrosion of austenitic stainless steels, sigma-phase formation in all kind of stainless steels and the 475-embrittlement in ferritic steels are all phenomena that will cause deteriation of the good properties. Nevertheless, the mentioned phenomena have in common that they are well understood in terms of basic thermodynamic and kinetic behaviour of the alloys. It is well known that the intergranular corrosion stems from Cr-depletion along austenite grain boundaries where Cr-rich carbides form and the 475-embrittlement stems from the miscibility gap at low temperatures in the binary Fe-Cr phase diagram. These phenomena are well suited for thermodynamic and kinetic modeling. The purpose of the present report is to review some of the old work as well as more recent studies. The new trends in materials modeling and their consequences for research on stainless steels will be discussed. This involves ab-initio quantum mechanical calculations, CALPHAD, DICTRA and phase-field modeling.

# Different types of modeling

One may distinguish between atomistic and continuum methods. In the atomistic modeling an assembly of discrete atoms is treated. In the continuum methods one represents the content of the various kind of atoms by continuous functions and apply equations for these functions. It goes without saying that the atomistic methods become very cumbersome or even impossible when a phenomenom involves too many atoms. The continuum methods are then the only alternative. By the same token the continuum methods cannot be very accurate if only a few atoms or

phenomena on a very fine scale are considered. Atomistic methods should then be used. The atomistic methods span from the ab-initio methods, that may involve up to 100 atoms and 0 K, to Monte-Carlo methods that may handle up to millions of atoms at finite temperatures.

The continuum methods may be divided into sharp interface and diffuse interface methods. The sharp interface methods have a long tradition and dates back to the old "Stefan problem". They have frequently been applied with great success in materials science. In the sharp interface methods the interface between two phases is treated as a mathematically sharp interface and the phases are assumed to have their normal properties up to that interface where the properties change discontinuously from one phase to the other. The popularity of method stems from the fact that it only involves bulk properties of the different phases and such properties may be obtained by independent experiments. The only non-bulk property that is sometimes added is an interfacial energy.

Also the diffuse interface methods have a long history, dating back to the work by Van der Waals, but not until the last 15 years they have become more widely used. The methods are based on the assumption that all properties vary continuously over the phase interface leading to simpler mathematical formulation. This allows the prediction of evolution of general 3D microstructures which is very difficult with sharp-interface methods. It is also straight forward to include various physical effects like anisotropic properties, solute drag, stresses etc. The drawbacks are that the computational time may be extensive and one has to assume some variation in properties over the interface. This variation may be difficult or impossible to determine experimentally.

# Examples of sharp-interface modeling

#### Sensitization

Already 1969 Stawström and Hillert [1] presented the first detailed analysis of grain boundary corrosion in austenitic stainless steels caused by grain boundary precipitation of  $M_{23}C_6$ . Their analysis was based on a mathematical treatment of the chromium-diffusion and the local thermodynamic equilibrium at the austenite/carbide phase interface. In order to simplify the treatment, they introduced several assumptions in their numerical calculations. However, despite these approximations they confirmed theoretically the chromium depleted zone close to the precipitates. Their model also predicted that the depleted zone would disappear after long annealing times and the steel would then become corrosion resistant again. Moreover, it was concluded that the calculated and experimental annealing time for self-healing were in satisfactory agreement. More recently [2], new simulations were carried out with the DICTRA code [4] using newly assessed thermodynamic and kinetic data. In that calculation most of the simplifying assumptions by Stawström and Hillert could be removed. Figure 1 taken from ref. [2] shows the calculated range of time and temperatures where an 18-8 steel with 0.06%C would be sensitive for grain-boundary corrosion. The symbols denote experimental data from Wiester et al. [3]. The time for loss of corrosion resistance was rather arbitrarily defined, as the timed needed to form a 20 nm thick chromium depleted zone. The calculated times for self-healing agree satisfactory with the experimental ones. The present result is thus quite encouraging and the capability of the DICTRA program is well demonstrated.



Figure 1. Calculated range of time and temperatures where an 18-8 steel with 0.06%C is sensitive for grainboundary corrosion. The symbols denote experimental data from Wiester et al. [3].

#### Sigma-phase formation

Erneman et al. [4] recently studied the  $\sigma$ -phase formation in a niobium-stabilized austenitic stainless steel (AISI 347). They compared metallographic observations with DICTRA simulations. The  $\sigma$ -phase that forms along grain boundaries, see Figure 2, generally is a severe problem when using standard austenitic stainless steels at elevated temperatures. The presence of  $\sigma$ -phase not only affects mechanical properties of the material detrimentally, but also reduces its corrosion resistance by removing chromium and molybdenum from the austenitic matrix. The problem was treated in DICTRA using a simplified geometry, see Figure 3.



Figure 2. σ-phase in austenite grain boundaries after isothermal treatment at 700°C for 69752 h (from ref. 5).



Figure 3.  $\sigma$ -phase is assumed to grow as a spherical shell around the austenite grains. In the calculation the grains were assumed to be spherical with the radius *R* set to 0.81 multiplied by the mean intercept length of the actual grain size (from ref. 5).

The simulated volume fraction of  $\sigma$ -phase as a function of time at 700°C is compared with the metallographic observations in Figure 4. The simulations are performed using different thermodynamic databases. The details are given in ref. [5]. This illustrates the importance of using accurate databases.



Figure 4.  $\sigma$ -phase fraction at 700°C compared to experimental results. The different symbols represent different etching techniques, see ref [5] for details.

# The evolution of secondary niobium carbonitrides during processing and long-term ageing

Niobium-stabilized steels like AISI 347 are suitable as material for superheater tubes in steam power plants. Such steels contain carbonitrides NbX that serve two purposes, one is to stabilize the material against intergranular corrosion by binding carbon, the other to provide good creep resistance in the material. Erneman et al. [6] recently studied the evolution of coarse primary as well as finer secondary carbonitrides during processing and long-term usage. The temperature cycle during processing is shown schematically in Figure 5 taken from their work.



Figure 5. A schematic diagram of the temperature cycle during the manufacturing process. From ref. 6.

In their modeling they considered each NbX particle the centre of a spherical austenite shell. The growth of NbX is controlled by Nb diffusion in the austenite and a local equilibrium condition at the phase interface. In the growth calculation each cell is treated as a closed system whereas during coarsening the cells are allowed to exchange material with each other but form a closed system together. The driving force for coarsening was achieved by adding an interfacial energy to the Gibbs energy of the particle. The geometrical model is shown in Figure 6 taken from their paper.



Figure 6. Spherical geometry of simplified growth mode, from ref. 6.

As an example of their work the simulated evolution of average size and volume fraction of the secondary NbX particles are shown in Figure 7. It should be mentioned that their simulation also covered the coarse primary NbX, the whole processing cycle and long-term aging as well.

### **Diffuse interface simulations**

The most widely used diffuse interface method is called the phase-field method because separate variables are introduced to denote what phase one has in a certain region of the material. The evolution of these field variables is goverened by separate differential equations. For example, if one would like to model the transformation between austenite and ferrite one may introduce a variable that is -1 for austenite and +1 for ferrite. In the phase interface there is a gradual variation of that variable. One may also introduce additional variables that denote crystallographic orientation etc.



Figure 7. Simulated particle radius and volume fraction of secondary NbX particles during processing and solution annealing. Simulations are performed for two different cell sizes; 90 nm and 134 nm, respectively. The experimental particle radius after the whole cycle is 14.5 nm. From ref. 6

Strandlund [7] recently considered the transformation between austenite and ferrite upon cooling in a duplex stainless steel using a commercial code MICRESS [8]. As an example we show his simulation of austenite growth into ferrite on cooling from 1100°C, 2K/s. After the calculation one may plot virtual "EDS-profiles", see Figure 8.



Figure 8. "Virtual "EDS-profiles for Cr and N after cooling from 1100°C at 2K/s. The Cr rich areas are ferrite, from ref. 7.

### Ab initio computations

Over the last few years the so called ab-initio computations, based on a quantum mechanical analysis of the system, have become more widespread. The only input to such computations can be found in the periodic table, i.e. no adjustable parameters are needed. The technique is thus very powerful in order to calculate quantities that are difficult to measure. Over the years, the computational techniques have been refined and calculations are now often made with

satisfactory accuracy. For example, ab initio calculations of the energies have been performed not only for pure elements in different crystalline structures [9], but also for compounds [10] and alloys [11] as well as energies of interfaces and surfaces [12–14]. While these calculations provide important information on the energies of compounds that are impossible or difficult to create in the laboratory, a drawback is that most of the calculations are performed at 0 K. More recently, it has become possible to compute entropy and thus determine the free energies at non-zero temperatures.



Figure 9. Calculated bulk (a) and shear (b) moduli of austenitic stainless steels as function of composition, from ref 15.

Vitos et al. [15] used the ab-initio approach to compute the elastic properties of austenitic stainless steels as function of composition, see Figure 9.

### Discussion

at.-> Cr

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One may conclude that the sharp-interface modelling and Calphad analysis still gives the most precise prediction of important properties. Such research thus needs further efforts. More sophisticated methods like the phase-field approach now are approaching some maturity and

hold great promises for the future. In particular they need to be combined with the Calphad analyses to be based on reasonable thermodynamic data.

The capability of ab-initio methods has improved much over the last few years and one may expect that their importance for engineering calculations will increase in the coming years.

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### COMPUTATIONAL THERMODYNAMICS AND COMPUTATIONAL KINETICS AS POWERFUL TOOLS FOR MODELLING FABRICATION ASPECTS OF STAINLESS STEELS

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### Abstract

Computational thermodynamics and kinetics are fundamental and powerful tools that can be applied to study a variety of scientific and technological areas of industrial importance. In this paper it is discussed how the computational tools may be applied to problems related to processing and operation of stainless steels.

### Introduction

During the last 30 years thermodynamic and kinetic calculation software have evolved to become important tools in the development of materials [1], and today accompanying databases exist for a large number of materials [2]. By using these software multicomponent phase diagrams, thermodynamic properties, temporal evolution of microstructure and material properties can be calculated. It is for example possible to study how small fluctuations in composition influence the stability of different phases or properties.

The purpose of this paper is to show how thermodynamic and kinetic calculation software may be applied to different problems related to stainless steels. First a short introduction to computational materials science and calculation software will be given, followed by some calculation examples.

### **Computational materials science**

During the last decades a large amount of work has been performed in the field of computational materials science. New physical models have been developed and new computational methods have been introduced and improved. This has resulted in improved predictive capabilities in the simulations and it has in many cases been possible to reduce the amount of experimental work needed to tailor material properties or improve processes.

It is common to divide the field of computational materials science into different branches such as computational thermodynamics, computational kinetics and computational mechanics. In this paper we will focus mainly on computational thermodynamics and computational kinetics but there is an overlap between the different branches and mechanical properties will to some extent be discussed.

#### **Computational thermodynamics**

To calculate phase diagrams and thermodynamic properties at equilibrium states (being full equilibrium, metastable equilibrium or para-equilibrium) the total energy of the system must be minimized. The common approach for this is to apply the CALPHAD method [3-4] and create a thermodynamic database consisting of parameters describing the total Gibbs energy for all phases in the system as a function of temperature, pressure and material composition. A numerical procedure for finding the lowest state of Gibbs energy for a defined multicomponent heterogeneous system is then applied.

The most frequently used software in the field of computational thermodynamics is Thermo-Calc [2]. Thermo-Calc has been developed for more than 30 years and has been applied to a large number of problems and materials, e.g. phase diagrams of multicomponent stainless steels, solidification of duplex stainless steels and corrosion in stainless steels. By using one of the Thermo-Calc programming interfaces, i.e. TQ or TCAPI [2], it is also possible to couple the Thermo-Calc calculation engine to external simulation software. One example where this has been done is in the phase-field software MICRESS [5], where the Thermo-Calc engine is used for calculating the thermodynamic driving force for phase transformations.

#### **Computational kinetics**

In computational kinetics the temporal and spatial evolution of a system is studied. Several different simulation methods are available, e.g. the phase-field method, atomistic methods and the sharp interface approach. In this paper the sharp interface approach for simulation of phase transformations is considered, and a general overview of different methods can be found in Ref. [6].

In the sharp interface approach the boundary between different phases is considered to be physically sharp, and local equilibrium (or para-equilibrium) is assumed at the phase boundary. The temporal evolution of the concentration fields are then solved for individually in each phase and a flux balance equation is applied to calculate the migration rate of the phase boundary.

The sharp interface approach has been implemented into the software DICTRA [2], which is a general software for simulation of phase transformations in alloys in one dimension. Based on thermodynamic and kinetic databases assessed by the CALPHAD method DICTRA has been applied to a large number of problems and materials, e.g. sigma phase precipitation in austenitic stainless steels [7].

### **Examples and applications**

Thermo-Calc and DICTRA can be applied to study various aspects of production and operation of stainless steels. In this section some recent applications will be discussed. In all examples concerning stainless steels, the Thermo-Calc steel database TCFE5 [8] was used and in the DICTRA calculation the kinetic database MOB2 [9] was used in addition to TCFE5. The calculations in the salt corrosion example were performed using the SGTE molten salt and substances databases, SALT1 [10] and SSUB3 [11].

#### Phase diagrams and thermodynamic properties

With Thermo-Calc multicomponent phase diagrams may be calculated. In this example an isoplethal section for the duplex stainless steel SAF2507 (with the composition shown in Table 1) was calculated. By varying the amount of nitrogen and the temperature all stable

phase regions were mapped, and the result is shown at the left hand side in Figure 1. A large amount of information may be extracted from such a diagram, e.g. how the amount of nitrogen influences the temperatures for which different compounds, such as the sigma phase and the M23C6 carbide, becomes thermodynamically stable.

One important quantity that may be calculated with thermodynamic software is the Pitting Resistance Equivalent number (PRE). At the right hand side in Figure 1 the PRE number for austenite and ferrite is shown as a function of the amount of nitrogen. Here it was specified as a condition that the material should contain an equal amount of ferrite and austenite, i.e. the equilibrium calculations were performed at the temperature where we have 50% austenite and 50% ferrite.



Figure 1. At the left hand side an isoplethal section of the phase diagram for SAF 2507 is shown and at the right hand side the PRE numbers for ferrite and austenite are shown as a function of the nitrogen content.

Table 1. Composition fo	or SAF 2507.
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Element	Fe	Cr	Мо	Ni	Ν	С
Composition [wt%]	64.62	25	3.6	6.5	0.26	0.02

#### Salt corrosion

With the Thermo-Calc software used together with suitable databases, different kinds of corrosion phenomena of stainless steels and other alloyed materials (such as high-temperature gaseous corrosion, hot salt corrosion and aqueous corrosion) may be studied. In this example, we show how dissolution of a  $Cr_2O_3$  layer caused by the so-called hot salt corrosion can be predicted. A coated  $Cr_2O_3$  layer is the typical corrosion-protection layer on the surfaces of stainless steels, Ni-based superalloys or other alloys, under normal circumstances. However, such a layer, if exposed to molten salts at elevated temperature conditions under some specific salty environments (such as marine, salt lake, and salty rock bed environments), may be destroyed by aggressive molten salty agents, resulting in that the alloy materials may be exposed to further corrosion attacks by other oxidizing or reducing substances in their application life-cycles.

In Figure 2 the amount of stable phases (left hand plot) and Cr partitions in various stable phases (right hand graph) as a function of temperature are shown. The calculation was done for the heterogeneous equilibrium state in a multicomponent Cr-C-H-O-S-N-Na-Cl system which originally consists of 0.05 mole of  $Cr_2O_3$  solid, a salt mixture (0.01 mole of NaCl, 0.46247 mole of Na<sub>2</sub>SO<sub>4</sub> and 0.03253 mole of Na<sub>2</sub>CO<sub>3</sub>) and 431.16 grams of C-H-O-N gaseous mixture (that exists in a specific gas turbine). At an operation temperature of 750°C,

the  $Cr_2O_3$  layer dissolves (with a remaining amount of 0.031756 mole), forming a crystalline  $Na_2CrO_4$ - $Na_2SO_4$  solid solution (namely the Hexagonal phase) and a liquid mixture (namely Ionic\_Liquid) that are stable with an equilibrated gaseous mixture. As temperature increases, the hot salt corrosion becomes more serious; and when 1200°C is reached, the entire  $Cr_2O_3$  layer on the alloy surface may be completely destroyed if exposed for a long period under such a corrosive environment.



Figure 2. Stable phases remaining/formed and Cr-partition in various phases as a function of operation temperature condition, during the hot salt corrosion of the  $Cr_2O_3$  layer (on the surface of stainless steels, superalloys or other alloys) when it is attacked by a NaCl-Na<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>CO<sub>3</sub> salt mixture and C-H-O-N gas mixture.

#### Precipitation of sigma phase

Using Thermo-Calc it is straightforward to calculate the temperature for which the sigma phase becomes thermodynamically stable in a certain alloy, i.e. the sigma formation start temperature  $T^{\sigma}$ . In this example we study how fluctuations in composition influence  $T^{\sigma}$  in grade SAF2507. Using the TQ programming interface a small application program was written and coupled to Thermo-Calc, and the sigma start temperature was calculated for 248832 compositions uniformly distributed in the composition ranges shown in Table 2. In Figure 3 the result is plotted, showing that  $T^{\sigma}$  varies between 970°C and 1080°C with the mean value of 1025°C.



Figure 3. This figure shows how the sigma start temperature varies with fluctuations in composition.

Table 2. Variation of composition in the precipitation of sigma phase example.

Element	Fe	Cr	Ni	Мо	Ν	С	
Min [wt%]	32.25	23	6	3	0.25	0	
Max [wt%]	40.32	27	8	5	0.29	0.03	

#### Solidification of austenitic stainless steel

Different simplified models for simulating solidification of alloys are available. One of the most frequently used models is the Scheil-Gulliver model, where the diffusion in the liquid is assumed to be infinitely fast and the diffusion in the solid is neglected. The Scheil-Gulliver model is implemented into Thermo-Calc as an advanced module [12], namely SCHEIL, which may also take back diffusion of interstitially dissolved elements into account. An even more accurate approach would be to consider diffusion of all elements both in the liquid and the solid phases. This is possible in DICTRA and has been done frequently, see e.g. Ref. [13].

Using the three different methods described above solidification was simulated in AISI 304LN, with the composition shown in Table 3. At the left hand side in Figure 4 the calculated solidification paths is shown. In the same figure the segregation of Cr and Ni to the austenite calculated by the SCHEIL module is shown.



Table 3. Composition in the solidification example.

Figure 4. The left hand side figure shows the solidification range for grade 304LN during peritectic solidification. The solid curve corresponds to the Scheil-Gulliver model, the dashed line to Scheil-Gulliver with back diffusion of interstitials (nitrogen in this case) and the dotted line to a DICTRA simulation. The right hand side figure shows micro segregation of chromium and nickel in the FCC phase during solidification.

### **Discussion and conclusions**

Computational software, such as Thermo-Calc and DICTRA, are useful tools in the process of designing materials and tailor material properties. In this work the focus has been on stainless steels but a large number of databases are available enabling the user to perform calculations for a variety of materials, such as e.g. low alloyed steels, cast irons, nickel based super alloys, aluminium alloys, titanium alloys, magnesium alloys, zirconium alloys, solders, semiconductors and ceramic materials.

The programming interfaces of Thermo-Calc software makes it possible to use the Thermo-Calc engine together with external software, user made or commercial. In this way it is possible to use Thermo-Calc for calculating quantities needed for e.g. simulation of different metallurgical processes or calculation of mechanical properties.

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### USING GENETIC ALGORITHM TO DESIGN NEW ULTRA-HIGH STRENGTH STAINLESS STEELS REINFORCED BY SEPARATE PRECIPITATE FAMILIES

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### Abstract

A computational approach to design new stainless steels combining ultra-high strength, corrosion resistance and toughness is presented. The composition is optimized combining criteria based on thermodymamic, kinetic and mechanical principles through a genetic algorithm. Three composition scenarios utilizing different strengthing precipitates (Carbides, Cu and NiAl/Ni<sub>3</sub>Ti) are designed and optimized. The designed alloys are compared to a variety of existing commercial high-end engineering steels, showing that the design strategy presented here may potentially lead to significant improvements in strength.

### Introduction

Steels combining properties of ultra-high strength, corrosion resistance and high toughness are in great demand in aerospace, gear, bearing and other high tech industries. These applications are usually subjected to extreme mechanical loads and harsh environmental conditions in which corrosion is an important issue. However, the most commonly used steels for these applications (e.g. 300M) are non-stainless steel grades protected by a coating. Many efforts for developing ultra-high strength and high toughness stainless steels have been undertaken employing different methodologies, both by academy and industry. However, no alternative grades significantly better in strength than 300M have been designed yet.

Precipitation strengthening is one of the most effective ways of producing ultra-high strength alloys. Maraging steels are a very successful example of the use of precipitation strengthening by combining a fine lath martensitic matrix with finely dispersed precipitates. Therefore, maraging steels are an ideal candidate for the development of ultra-high strength stainless steels. Moreover, stainless steels also require the formation of a Cr-rich passive oxide film which protects the alloy surface from corrosion. Instead of the traditional semi-empirical 'trial-and-error' approach, alloy design is more oriented towards the goal/means direction (performance/property/microstructure/composition & processing) as suggested by Olson [1]. Once the desirable microstructures are determined for reaching the design goals, the alloy composition and heat treatment can be computationally designed and optimized by various criteria reflecting thermodynamic, kinetic and mechanical principles.

Precipitation strengthening steels are complex systems possessing typically more than 10 components aiming at purposes such as the promotion of desirable precipitates and the stabilisation of martensite. Each alloying element varies values over a wide range of concentration. Therefore, the computational alloy design represents not only a challenge in terms

of composition optimisation, but also in applying an efficient optimization technique so as to find the best grade in an extremely large solution space. Compared with combinatorial or iterative approaches, genetic algorithms are highly robust and efficient; they are especially suitable for complex multi-objective optimization problems.

In the present work, a computational approach to design a new ultra-high strength stainless steel grade is presented wherein advanced optimization schemes are combined with thermodynamic, kinetic and mechanical principles. Three alloy scenarios which utilising different families of strengthening precipitates are explored. The results are critically compared to existing grades, and show that the designed alloys have an important potential for increasing the alloy strength beyond current levels.

### Methods

#### Desirable microstructures and criteria development

#### Matrix

A lath martensite microstructure can be formed from the prior austenite grains by suitable solution treatment followed by water or oil quenching. Such steels contain parallel arrays or stacks of lath-shaped crystals which provide an essential microstructural element for obtaining both high strength and toughness. The substructure of lath martensite includes a very high density of dislocations, which provide a direct strengthening contribution, as well as potential nucleation sites for a fine-scale precipitate dispersion. Experimental observations on regular engineering steels have shown that an Ms temperature above 150 °C is required to obtain full lath martensite structures.

Ishida developed a model to estimate the Ms temperature accounting for both chemical and mechanical contributions of alloying elements [2]:

 $Ms(^{\circ}C) = 545.00 - 33000 \times C_{c} + 200 \times C_{Al} + 700 \times C_{Co} - 1400 \times C_{Cr} - 1300 \times C_{Cu}$ (1) -2300×C<sub>Mn</sub> - 500×C<sub>Mo</sub> - 400×C<sub>Nb</sub> - 1300×C<sub>Ni</sub> - 700×C<sub>Si</sub> + 300×C<sub>Ti</sub> + 400×C<sub>V</sub>, where all the concentrations are given in weight fraction.

Despite the simplicity of Eq. 1, it accounts for a wide range of components and has been successfully applied to various systems of up to 11 components. Therefore, a go/no-go criterion of Ms $\geq$ 200 °C was imposed in the optimisation procedure.

### Precipitation

The martensitically transformed alloy can be significantly further strengthened by forming networks of nanoprecipitates. MX carbonitrides have been reported and utilized as important strengthening precipitates in various of systems including PH 17-4 (17Cr-4Ni-1Mo [3], 16Cr-5Ni-1Mo [4]), 15Cr-1Mo alloys [5] and Ferrium S53 [6]. Alternatively, steel grades containing a small amount of C can be strengthened by intermetallic precipitates such as NiAl in PH13-8 [7], Cu precipitates in PH15-5 [8] and Ni<sub>3</sub>(Ti,Al) precipitates in a 12Cr-9Ni-4Mo-2Cu PH stainless steel [9].

The precipitation contribution to the alloy strength,  $\sigma_p$ , depends on the mean obstacle strength *F* [10]:

$$\sigma_p = \frac{MF}{bl},\tag{2}$$

where M is the Taylor factor, b is the magnitude of the Burgers vector and l is the mean effective particle spacing on the dislocation line. Considering Friedel's statistics for calculating the mean particle spacing, the precipitation strengthening contribution of sheared and by-passed particles can be expressed as:

$$\sigma_p^{sheared} = \sqrt{\frac{3}{4\pi\beta}} \frac{k^{3/2} M \mu}{\sqrt{b}} (f_v R)^{1/2} = c_1 f_v^{1/2} R^{1/2} \qquad (3a) \quad \text{and} \quad \sigma_p^{by-passed} = \sqrt{\frac{6}{\pi}} M \mu b \frac{f_v^{1/2}}{R} = c_2 f_v^{1/2} R^{-1}, \qquad (3b)$$

where  $\mu$  is the precipitate shear modulus, k and  $\beta$  are constants,  $f_{\nu}$  is the precipitate volume fraction and R is the average particle radius.

In general, the strengthening effect is promoted by the refinement of precipitate dispersions down to the nanometre level, which means that they are at the early precipitation stage (just after nucleation) and have a good coherency with the matrix. Assuming the precipitate particles are spherical, the critical nucleus size can be estimated as  $r^*=-2/\Delta G_{\nu}$ , where  $\sigma$  is the precipitate/matrix interfacial energy per unit area and  $\Delta G_{\nu}$  is the precipitation driving force per unit volume. A population of fine precipitates can be realized by increasing the driving force of precipitation. Moreover, in order to avoid significant growth and coarsening, a fast nucleation is required such that very fine precipitates become quickly stable by rapidly consuming most of the solute available from the matrix. The fast nucleation can be realized by increase of the precipitation driving force, which is consistent with refining the precipitate particle size.

Based on precipitation strengthening theories, small and hard precipitate particles are more prone to shearing; soft and big ones tend to be by-passed and the transition critical size of the two mechanisms is usually at the nanometre scale. In maraging steels, the strengthening carbide and intermetallic particles are harder than the matrix but whether their sizes are above the critical size and become by-passed is not clear and it depends on the precipitation kinetics. Given the particle size is refined by maximizing the precipitation driving force, the precipitates become more likely to undergo shearing. Therefore, the shearing mechanism (Eq. 3a) may become dominant in the newly designed alloy, making the strengthening contribution proportional to  $f_v^{1/2} R^{1/2}$ . However, this criterion is not consistent with particle refinement as bigger particle sizes will lead to larger strengthening effects (Eq. 3a). If the particle size goes beyond the transition size, a different strengthening mechanism takes place and Eq. 3b should be used. In order to reach a compromise between the conflicting objectives, an optimization factor of  $\sigma_p^{sheared}/R$  is applied so as to balance the requirement of strength maximisation and particle size minimisation. Such index  $(\sigma_p^{sheared}/R \propto f_v^{1/2} R^{1/2})$  can be considered as a mixed shearing  $(f_v^{1/2} R^{1/2})$  and by-passing mechanism  $(f_v^{1/2}R^{-1})$ . Due to the fast nucleation process, the *R* is taken as the critical nuclei size. The thermodynamic calculations for the alloy composition considered and imposing a fixed precipitation temperature of 500 °C were performed with ThermoCalc<sup>®</sup> software.

While fostering the formation of desirable precipitates (carbides or intermetallics) as described above, the formation of phases limiting strength or toughness (e.g.  $M_{23}C_6$ ,  $M_6C$  and  $M_7C_3$ , cementite,  $\mu$  phases,  $\chi$  phases) should be prevented. For undesirable phases which could not be completely avoided, a total maximum volume fraction of 1% was accepted.

#### Cr concentration in the matrix

The formation of a Cr-rich passive oxide film at the surface requires a reservoir of at least 12 wt% Cr in the matrix. This was enforced imposing such a minimum Cr level to the matrix upon completion of the precipitation reactions.

#### Desired alloy system and compositional constraints

The alloy system considered in the calculations is based on 13 alloying elements: C, Cr, Ni, Ti, Mo, Al, Cu, Co, Nb, N, V, Mn and Si. The concentration ranges employed for each element in the optimization procedure are summarised in Table 1; they account for the industrial and technological constrains related to the ability to fabricate the alloys. It is also important to notice that several alloying elements may have conflicting interactions as to the desired microstructures. Therefore, the alloy composition optimization has to systematically balance the amount of different alloying elements, find a compromise between the positive and negative effects of each component, and evaluate their influences on forming the desirable microstructures while suppressing those undesirable.

	С	Cr	Ni	Ti	Mo	Al	Cu	Со	Nb	Ν	V	Mn	Si
Min	0.0005	0.12	0.01	0.0001	0.005	0.0001	0.005	0.0001	0.0001	0.0001	0.0001	0.005	0.003
Max	0.0020	0.20	0.15	0.0150	0.100	0.010	0.100	0.0200	0.0010	0.0001	0.0020	0.005	0.010

Table 1. Concentration ranges of all components employed in the optimization. [in wt. %]

# **Calculation and Algorithms**

#### **General algorithm**

Except for N and Mn, the concentrations of all other alloying components are varied within the range shown in Table 1. For each candidate solution, the following algorithm (Figure 1) is applied for evaluating the criteria described in previous section: 1) The system is defined in ThermoCalc and the calculation conditions (composition and temperature) are input. 2) The Ms temperature is calculated from Eq. 1. 3) A thermodynamic equilibrium calculation is performed; the volume fraction and composition of the equilibrium phases are recorded. The total volume fraction of undesirable phases is summed up and the Cr concentration in the matrix is recorded. The candidate alloy is discarded if the total volume fraction of the undesired phases exceeds 0.01 or if the Cr matrix concentration is lower than 12 wt%. 4) The Fe-rich BCC phase is set as matrix and the precipitate driving forces are calculated. 5) The strengthening factor  $f_v^{1/2}R^{-1/2}$  is calculated.

#### **Optimization scheme: Genetic Algorithm**

To scan the enormous solution space of candidate alloys, a suitable optimization algorithm is essential. Genetic Algorithms (GAs) are recognized as a powerful strategy for multi-parameter multi-objective optimization, especially for those having very complex expression or implicit criteria. To this aim, a master-slave FORTRAN program was developed where the master role is taken by the genetic algorithm, and the slave routine performs the thermodynamic calculation and assesses the evolution criteria (Figure 1). Each candidate solution is coded as a binary string (chromosome) by concatenating the concentration of each element expressed in base-2 (genes). Five binary bits are linked to each component and thus, each potential composition set is represented by a binary string of  $11 \times 5 = 55$  bits.



Figure 1. General algorithm of the thermodynamic calculation and Figure 2. Flowchart of Genetic Algorithm. criteria evaluation.

### **Results and discussions**

The computations were performed on a Dell precision<sup>®</sup> 380 dual-core workstation. Three alloy scenarios of different strengthening systems were considered. In all cases, the criteria of Ms≥200 °C, a maximum of 1% in the overall volume fraction of undesirable phases and 12 wt% of Cr in the matrix after precipitation completion were imposed. The strengthening factor  $(f_v^{1/2}R^{-1/2})$  was maximized for alloys containing: 1) MC carbide, 2) Cu particles and 3) Ni-rich particles (NiAl and Ni<sub>3</sub>Ti). The compositions are summarized in Figure 3. The driving forces and volume fractions for each alloy are plotted in Figure 4a and 4b. The precipitation strengthening factor according to sheared (Eq. 3a) and by-passed (Eq. 3b) mechanisms are shown in Figure 4c and 4d, respectively.



Figure 3. Optimum compositions of Alloy 1-3 (normalized to maximal concentration in Table 1).



Figure 4. Comparison of designed Alloys: a) driving force for precipitation, b) volume fraction and precipitation strengthening factor calculated by sheared mechanism (c) and by-passed mechanism (d). Symbols indicate values for commercial steels.

The convergence of the genetic algorithm was also assessed by applying different initial alloy candidate pools generated from different random numbers. The same optimum results were obtained although they were achieved after a different number of generations, and also a totally different optimizing history. Moreover, the effects of each alloying element on precipitation are studied for Alloy 1 by varying its optimized composition over a wide range; the results show that the concentrations optimized through the genetic algorithm are the best values in the searching domain for each component. This strongly suggests that the optimization via the genetic algorithm has encountered and evaluated a sufficient number of generations and therefore the global optimum is likely to have been reached.

For validation purposes, the model was also applied to 11 commercial precipitate hardened steels and the results are shown in Figure 4. The comparison of designed and existing commercial alloys clearly indicates that the strengthening factors of designed alloys are higher than any existing one when considering either the shearing by-passing mechanisms. Moreover, the precipitation strengthening contributions of the existing alloys versus the strengthening factor calculated by the shearing (Eq. 3a) and by-passing models (Eq. 3b) are plotted in Figure 5 and the potential strength of designed alloy 1-3 are also demonstrated. The figures clearly show the designed alloys possess higher precipitation strengthening contribution.



Figure 5. Validation of the strengthening contribution model and the potential strength of design alloy 1-3.

### Conclusions

A FORTRAN master-slave program employing genetic optimization framework for maximazing the precipitation strengthening contribution has been developed to design a 13 alloying element stainless steel. Three alloy scenarios are designed wherein different strengthening systems are utilized. The results are compared to existing commercial precipitation strengthened steels and show a significant potential for strength increase.

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### MODELLING OF MICROSTRUCTURAL EVOLUTION AT JOINTS OF DISSIMILAR STEELS

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### Abstract

A model that allows 1D simulations to be made without limitations regarding phase constitution is presented and applied to an  $\alpha$ + $\gamma$  Fe-Cr-Ni diffusion couple. The model is based on the assumption of local equilibrium, long-range diffusion and locally averaged kinetic properties. Good agreement with experimental data is obtained.

### Introduction

In this report we shall present results of a new simulation model for multiphase long-range diffusion processes. These simulations are important in order to understand the properties of, e.g., welded joints, steel composites or coatings. Diffusion across such joints may give rise to changes in the phase constitution, i.e. precipitation and/or dissolution. The present model is an extension of the model suggested by Engström et al. [1] which is available in the DICTRA software package [2]. Engström's model is limited to situations where a single continuous matrix phase exists across the domain. The present model does not have this limitation and has now been implemented into DICTRA. More details of the present model can be found in Ref. [3].

# The Model

#### **Basic assumptions**

Composition may only vary along one spatial coordinate although the geometry may be either planar, cylindrical or spherical. It is assumed that only substutional elements contribute to the volume and that the molar volume  $V_S$  of all substitutional elements is constant and equal. With these assumptions it is convenient to use the u-fraction which in terms of the mole fraction  $x_k$  is defined as

$$u_k = \frac{x_k}{\sum_{j \in S} x_j} \tag{1}$$

where  $j \in S$  means that the summation is to be taken over the substitutional elements only. The flux  $J_k$  of component k in the z-direction in the lattice-fixed frame of reference is given by

$$J_{k} = \frac{-1}{V_{S}} y_{Va} M_{k} u_{k} \frac{\partial \mu_{k}}{\partial z}$$
<sup>(2)</sup>

where  $M_k$  and  $\mu_k$  are the mobility and chemical potential of component k, respectively and  $y_{Va}$  is the fraction of vacancies.

These fluxes are transformed into a more practical volume-fixed frame of reference by

$$J'_{k} = J_{k} - u_{k} \sum_{j \in S} J_{j}$$
<sup>(3)</sup>

#### **Multiphase simulations**

In order to perform multiphase simulations it is assumed that equilibrium holds locally, i.e. in a small volume element the phase fractions, phase compositions and chemical potentials are given by the equilibrium corresponding to the local overall composition (and the global pressure and temperature). The local kinetic properties are found by choosing a suitable "averaging function" and a number of such functions suitable for different conditions have been implemented, see below. All the averaging functions have in common that it is the product  $y_{Va}^{\varphi}M_k^{\varphi}u_k^{\varphi}$  of each phase and the volume fraction  $f^{\varphi}$  of phases that is considered. We therefore define

$$\Gamma_{k}^{\varphi} = y_{Va}^{\varphi} M_{k}^{\varphi} u_{k}^{\varphi}$$
(4)  
and rewrite Eq. 2 as  

$$J_{k} = \frac{-1}{V_{S}} \Gamma_{k}^{*} \frac{\partial \mu_{k}^{l.eq.}}{\partial z}$$
(5)

The asterisk indicates that a locally averaged kinetic coefficient is used and "*l.eq*." stands for local equilibrium.

#### Averaging kinetic properties

Three basic groups of averaging functions have been implemented.

#### Wiener bounds

The Wiener bounds [4] are given by

$$\Gamma_k^* = \sum_{\varphi} f^{\varphi} \Gamma_k^{\varphi} \tag{6}$$

for the upper bound (or rule of mixtures) and

$$\Gamma_k^* = \left[\sum_{\varphi} \frac{f^{\varphi}}{\Gamma_k^{\varphi}}\right]^{-1} \tag{7}$$

for the lower bound (or inverse rule of mixtures). Summations are to be taken over all phases  $\varphi$ . These bounds correspond geometrically to continuous layers either parallell with (upper bound) or orthogonal to (lower bound) the direction of diffusion.

#### Hashin-Shtrikman bounds

The Hashin-Shtrikman [5] bounds are given by

$$\Gamma_{k}^{*} = \Gamma_{k}^{\alpha} + \frac{A_{k}^{\alpha}}{1 - \frac{A_{k}^{\alpha}}{3\Gamma_{k}^{\alpha}}}$$
(8a)

$$A_{k}^{\alpha} = \sum_{\varphi \neq \alpha} \frac{f^{\varphi}}{\frac{1}{\Gamma_{k}^{\varphi} - \Gamma_{k}^{\alpha}} + \frac{1}{3\Gamma_{k}^{\alpha}}}$$
(8b)

where

$$\Gamma_{k}^{\alpha} = \min[\Gamma_{k}^{\beta}, \Gamma_{k}^{\delta}, \Gamma_{k}^{\varepsilon}, \dots]$$

$$\Gamma_{k}^{\alpha} = \max[\Gamma_{k}^{\beta}, \Gamma_{k}^{\delta}, \Gamma_{k}^{\varepsilon}, \dots]$$
(9a)
(9b)

for the general lower and upper Hashin-Shtrikman bound, respectively. The geometrical interpretation of the Hashin-Shtrikman bounds are concentric spherical shells of the phases; for the case of two phases the Hashin-Shtrikman bounds are identical to the approximate formula given by Rayleigh [6] for the effective conductivity of a medium consisting of spheres of one material set on a simple cubic lattice in a matrix of a second material.

The geometrical interpretation suggests more varieties and several such modifications have been implemented:

- Predefined matrix phase: In some cases it may be known that the system under consideration involves a certain continuous matrix phase and it is then natural to set this matrix phase as the " $\alpha$  phase".
- Majority phase as matrix phase: With this setting the phase with the highest local volume fraction is the local " $\alpha$  phase".
- Upper and lower bound with excluded phases: A system may consist of a few phases that make up most of the volume and in addition contain some dispersed phases occupying a small volume fraction. The dispersed phases may then be excluded from Eq. 9a/b. This is particularly useful if  $\Gamma$  of the dispersed phases is very small which make the general lower bound useless.

#### Labyrinth factor

A "labyrinth factor" was used successfully by Engström et al. [1] to take the generally impeding effect of precipitates on the long-range diffusion into account. This has also been implemented for the present model. To use this function a single continuous matrix phase  $\alpha$  must exist and

(10)

$$\Gamma_k^* = \left(f^{\alpha}\right)^n \Gamma_k^{\alpha}$$

where *n* is set to either 1 or 2.

#### Fluctuations in composition profiles in multiphase regions

A fluctuation in composition in a single phase region will die out over time as this fluctuation always will be accompanied by a corresponding fluctuation in chemical potential. In a multiphase region, however, a fluctuation in composition may occur such that the chemical potentials do not change. This can result in oscillations in the composition profile. To amend this, a small ideal contribution can be added to the flux, viz.

$$J_{k}^{ideal} = \frac{-1}{V_{s}} \varepsilon y_{Va} M_{k} u_{k} \frac{\partial \mu_{k}^{ideal}}{\partial z} = \frac{-1}{V_{s}} \varepsilon y_{Va} M_{k} RT \frac{\partial u_{k}}{\partial z} \cong \frac{-1}{V_{s}} \varepsilon \frac{\Gamma_{k}^{*}}{u_{k}} RT \frac{\partial u_{k}}{\partial z}$$
(11)

where the value of the parameter  $\varepsilon$  could be in the range 0.01 - 0.05.

#### Implementation

The model was implemented using a conservative, implicit, finite volume method; the system is divided into "slices" and the fluxes between slices are evaluated using finite differences.

### **Example Simulations**

The Fe-Cr-Ni diffusion couple given in Table 1 was considered and a heat treatment of 100 h at 1100°C was simulated corresponding to an experimental investigation by Engström [7]. Independently assessed thermodynamic and kinetic data from the TCFE3 and MOB2 databases (available from Thermo-Calc software AB) were used in simulations.

Table 1. Composition (mole-%) of simulated diffusion couple.

Alloy	Cr	Ni	Fe
#1	25.7	6.5	bal.
#2	42.3	27.6	bal.

Both alloys of the diffuion couple are duplex  $\alpha + \gamma$ , but the majority phase in Alloy #1 is  $\alpha$  and in Alloy #2 it is  $\gamma$ . Experimentally it was found that a  $\gamma$  single phase region approximately 50  $\mu$ m wide had formed at the interface after heat treatment.

Chromium mole fraction profiles at the end of the heat treatment using several different averaging functions are shown in Figure 1 together with the experimental data from Engström. It can be seen that the best fit with experimental data is in this case given by the general lower Hashin-Shtrikman bound. The nickel mole fraction profile and the  $\alpha$ -fraction profile as obtained from a simulation using the general lower Hashin-Shtrikman bound together with experimental data are shown in Figures 2 – 3. In Figure 4 are shown chromium mole fraction profiles obtained using the Hashin-Shtrikman function with the majority phase as matrix phase. Without an ideal flux contribution oscillations occur in the simulated composition profile, but these vanish gradually with an increasing value of the parameter  $\varepsilon$  as can be seen in the figure. The profile for  $\varepsilon = 0.01$  is virtually identical to the profile obtained using the general lower Hashin-Shtrikman bound.

### Discussion

In the present report we have applied a conceptually very simple model to represent the very complex process of multicomponent and multiphase diffusional interactions. In reality the process involves both long range as well as short range diffusional transport combined with the evolution of an intricate microstructure. More detailed analysis of these type of problems could be performed by means of the phase-field method but leads to much longer computation times on a too restricted geometrical size to be statistically significant. It is encouraging that the simple concept of local equilibrium and long range diffusion gives such a good representation of the experimental data without the need of any input data except the CALPHAD thermodynamics and the diffusional mobilities in the two phases, i.e. there are no adjustable parameters. In particular the observed extension of the single-phase  $\gamma$  zone, see Figure 3, agrees very well with the calculated extension. It is thus concluded that the present approach should be suitable as an engineering tool to study diffusional interactions in various types of joints.



Figure 1. Chromium mole fraction profiles obtained from simulations using different averaging functions and experimental data from Engström [7]. Distance is in [m].



Figure 2. Nickel mole fraction profile obtained from simulation using the general lower Hashin-Shtrikman bound and experimental data from Engström [7]. Distance is in [m].







Figure 4. Chromium mole fraction profiles obtained from simulations using the Hashin-Shtrikman function with the majority phase as matrix phase. Ideal flux contributions as indicated. Distance is in [m].

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### MODELING OF DIFFUSION IN WUSTITE AND SIMULATION OF OXIDATION OF IRON AT 600°C

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### Abstract

A long missing feature in the diffusion simulation software DICTRA has been the diffusion in oxides. Recently, this capability was implemented and in this report we present some results of the current achievements.

DICTRA can now treat diffusion in basically any oxide, provided that there is diffusion data available and that the necessary mobilities have been assessed. The first system to be addressed was the important Fe-O system. It contains three different oxides, from the simple wustite to the complex magnetite, which has the spinel structure. The current approach was successful and the work was continued with the Cr-O system and the technically important Fe-Cr-O.

We will present the diffusion models and the results of the assessment, as well as successful simulations of oxidation where layers of oxides grow on top of an Fe or Fe-Cr substrate.

### Introduction

In many practical applications it would be very valuable to be able to predict the rate of oxidation of a given alloy. Oxidation occurs by diffusion of cations and anions through one or more oxide scales growing on top of the alloy. To the knowledge of the authors, no software is capable of performing such simulations in a general manner until now, at least not on a more fundamental level. The new version of the diffusion simulation software DICTRA [1] is capable of doing such simulations. Hallström et. al. [2] have introduced a model for diffusion in the two most complex oxides in the Fe-O system, the hematite and magnetite phases. In the present work the diffusion model for the third oxide, wustite, is shown and compared with experimental data. The parameters obtained from the assessment were added to the kinetic database and allowed simulation of oxidation above the wustite forming temperature, i.e. 557°C.

### **Defects and diffusion**

Sundman [3] evaluated the thermodynamic properties for the Fe-O system using the CALPHAD technique and all thermodynamic parameters in this work come from his assessment.

Wustite is the most iron rich of the three iron oxides and it has a considerable solubility range. It is iron deficient, with oxygen anions on an fcc lattice and iron cations dissolved interstitially on octahedral interstices. The wustite is modelled with two sublattices as  $(Fe^{+2}, Fe^{+3}, Va)_1(O^{-2})_1$ . The off stoichiometry is obtained by introducing vacancies on the first sublattice. In order to obtain electroneutrality two Fe<sup>+3</sup> ions form for every vacancy created. The stable temperature range for wustite is between about 830K and 1700K.

In this paper we use the same approach as in [2], which is summarized here. In the stable temperature range wustite is a half metal, the electrons move much faster than the ions. It is thus reasonable to neglect the different valence states when considering diffusion. Instead only some average type of ion is considered, and the model of the phase can then be simplified to  $(Fe,Va)_1(O)_1$ .

Assuming that the cation diffusion occurs by a vacancy mechanism, the iron flux can be expressed as follows in the lattice fixed frame of reference:

$$J_{Fe} = -\left(y_{Fe^{+3}} + y_{Fe^{+2}}\right)y_{Va}M_{FeVa}\frac{1}{V_m}\frac{\partial\mu_{Fe}}{\partial z} = -y_{Fe}y_{Va}M_{FeVa}\frac{1}{V_m}\frac{\partial\mu_{Fe}}{\partial z}$$
(1)

where  $y_{Fe^{+3}}$ ,  $y_{Fe^{+2}}$  and  $y_{Va}$  are the site fractions of the ions and vacancies on the interstitial sublattice,  $M_{FeVa}$  is the Fe mobility, a kinetic parameter describing the thermally activated jumps.  $\mu_{Fe}$  is the chemical potential of iron and V<sub>m</sub> is the molar volume per mole of oxygen. According to absolute reaction rate theory the mobility has the form of an Arrhenius expression.

From Eq. 1 the expressions for the tracer diffusion coefficient and the chemical diffusion coefficient in the lattice-fixed frame of reference can be derived. They are given in Eqs. 2 and 3, respectively.

$$D_{F_e}^* = RTy_{F_e} y_{V_a} M_{F_e V_a} \frac{1}{n_{F_e}}$$

$$\simeq D_{F_e}^* = \partial \mu_{F_e}$$
(2)

$$\widetilde{D}_{Fe} = \frac{D_{Fe}}{RT} n_{Fe} \frac{\partial \mu_{Fe}}{\partial n_{Fe}}$$
(3)

The defect structure mentioned above has been questioned. In fact, it seems clear that some clustering on interstitial sublattices can occur. Chen and Peterson [5] discuss these defect structures and diffusion mechanisms, and conclude that even if they do exist they are much less mobile than what they refer to as the "free mobile vacancies". If the main contribution to cationic diffusion comes from cations exchanging places with these free mobile vacancies, the above model should sill be valid. Contributions from other effects, such as clustering or site-blocking, can be taken into account by some interaction parameter which can be concentration and/or temperature dependent.

#### Comparison with experimental data

Chen and Peterson [5] used the serial-sectioning technique to evaluate the tracer diffusion coefficient in the temperature range 973-1613K and composition range 0.445-0.486 mole fraction Fe. The tracer diffusion coefficient does not depend strongly on composition. If the mobility is modeled as independent of composition, the composition dependence of the tracer diffusivity is overestimated compared to the experimental results. If the mobility is constant the whole composition dependence comes directly from the off-stoichiometry. It is convenient to express the composition dependence using Redlich-Kister expansion. The "excess activation energy" is then written in the CALPHAD way as:

$${}^{E}Q_{Fe} = u_{Fe} u_{Va} {}^{0}Q_{Fe,Va}$$
(4)

where  ${}^{0}Q_{Fe,Va}$  is an interaction parameter. Figure 1 shows the result of the optimization of the tracer diffusion coefficient and how it compares with the experiments from ref. [5]. The fit is very good, and the parameters seem to be in the order of magnitude expected if the diffusion occurs interstitially by a vacancy mechanism. The obtained parameters are:

$$M_{Fe} = 3.15 \cdot 10^{-5} \exp\left(\frac{-89280 + u_{Fe}u_{Va}(-585900 + 188.7 \cdot T)}{RT}\right) m^2 s^{-1}$$

Once the tracer diffusion coefficient is known, it is possible to calculate the chemical diffusion coefficient from eq. 3. The thermodynamic factor and  $n_{Fe}$  are taken from the assessment by Sundman [3]. Figure 2 shows the resulting chemical diffusion coefficient as function of the reciprocal temperature, and the predicted coefficient is only a factor of two off compared with experiments by Millot and Berthon [4]. Their values were not used in the optimization of the mobility. As for the case of chemical diffusion in magnetite [2], the absolute values also for wustite are noticably high.



Figure 1. Concentration and temperature dependence of tracer diffusion coefficient in wustite. Symbols denote experiments from [5], thin solid lines are calculated from the optimized parameters, and the bold lines show the stable composition range for wustite at the different temperatures.

In their paper, Millot and Berthon discuss disagreements in the literature regarding various reported chemical diffusion experiments. They argue convincingly that the errors are large in some of the published data, e.g. due to inappropriate boundary conditions in the post-experimental numerical analysis.



Figure 2. Temperature dependence of the predicted chemical diffusion coefficient in wustite. Symbols denote experiments from [4], solid lines are calculated from the optimized parameters and the thermodynamic assessment by Sundman [3].

### **Example oxidation simulations**

The mobility database for iron oxides now contains properly assessed kinetic data for cation diffusion in all three oxides. However, oxidation of iron does not only involve diffusion of cations. Looking at cross sections of oxidized iron one realizes that also diffusion of oxygen must play an important role, since the oxides also grow inward. That can only be accomplished by oxygen diffusion through the oxides. In the present paper however, the oxygen diffusion is not considered. At the temperatures of interest for these materials, grain boundaries and other fast diffusion paths may play important roles in the oxidation process and they have to be taken into account. At the time of writing this paper, such a model is under development and has not yet been implemented into the DICTRA code. However, meanwhile it is possible to account for those effects in a simplified manner by multiplying the diffusivities in the different phases by arbitrary user-defined functions. One way to take grain boundary diffusion into account is by assigning the grain boundaries a certain width and a fraction of the total volume (e.g. from the approximation  $f^{gb} \approx \delta/D$ ), where  $\delta$  is the grain boundary width and D the avarage grain size. From that the effective diffusion coefficient can be calculated as a weighted sum of the different contributions, provided that the grain boundary mobility is known.

The grain boundary width can be approximated to 5Å. Experimental results from [6] are used to estimate the necessary parameters. The avarage grain size of magnetite is approximately 3  $\mu$ m, and that of hematite can be as small as 0.1  $\mu$ m. The grain boundary fractions become  $1.7 \times 10^{-4}$  and  $5 \times 10^{-3}$ , respectively. As a rule of thumb, the activation energy of grain boundary diffusion can be set to half the activation energy for bulk diffusion. These assumptions makes it possible to relate some effective mobility to the evaluated bulk mobility and use that effective value in the simulations. The simulation conditions are set to be comparable to the experiments in [6]. For an oxygen partial pressure of 0.05 atm at 600°C for 24 hours, this approach results in thicknesses of hematite, magnetite and wüstite that are approximately 0.2, 2.7 and 46  $\mu$ m, respectively. The experimental thicknesses of the oxide scales are not in exact agreement, though it

should be noted that this simple method gives results more or less in the right order of magnitude.

In a review paper, Chen and Yuen [7] conclude that from the eutectoid temperature up to about 700°C, the resulting oxide thicknesses depend a lot on the thermal history and surface condition of the substrate. At 580-600°C the scales have been reported to contain phase fractions ranging from almost only hematite, to be dominated by wustite with an extremely thin outermost hematite layer. At temperatures closest to the eutectoid temperature (570-580°C), wustite sometimes does not form at all for up to 24h, or does not form a uniform layer. The example simulations shown here do not take such effects into account. It is rather assumed that very thin layers of all oxides are present at time t = 0 s.

The calculated wustite thickness should thus be regarded as an upper limit, but if it is assumed that magnetite and hematite quickly form uniform layers, their calculated thicknesses should not be so different from the experimental ones. The activation energy for grain boundary diffusion was initially only estimated from a rule of thumb, and one can ask what it should be to get more correct thicknesses. It turns out that they do not have to be changed very much. For hematite, the thickness becomes 1.9  $\mu$ m if the activation energy for grain boundary diffusion is set to 0.36 times the bulk activation energy, and for magnetite the thickness becomes 9.5  $\mu$ m using 0.4 times the bulk activation energy.



Figure 3. Thicknesses of wustite (a), magnetite (b), and hematite (c) as functions of time after simulation at 600°C for 24 hours in an atmosphere with 0.05 atm oxygen.

Atkinson and Taylor [8] measured bulk and grain boundary tracer diffusion coefficients in hematite. They report a frequency factor for bulk diffusion as high as  $1.6 \times 10^5 \text{ m}^2/\text{s}$ , compensated by a very large activation energy (about 600 kJ/mol). Although these values are quite unrealistic it is worth noting that their fitted activation energy for grain boundary diffusion is approximately 180 kJ/mol. That is around 1/3 of the bulk activation energy, in accordance with our simple method. Figure 3 shows how the simulated thicknesses vary with time under these conditions.

### Conclusions

It is demonstrated that the new facilities in DICTRA combined with our recent assessment of diffusion in iron oxides and reasonable assumptions on grain-boundary diffusion yield predictions in satisfactory agreement with recent experimental observations on the rate of oxidation of iron.

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### FIRST-PRINCIPLES CALCULATIONS AS A NEW TOOL IN STEEL RESEARCH

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#### Abstract

Great scepticism over the earliest applications of the first-principles theory to the calculation of the ground state properties of real systems in the 70's and 80's has gradually turned into a widespread belief in its quantitative accuracy and predictive power, due to a great number of successful applications to very different systems and problems, so that several leading materials manufacturing companies have initiated first-principles based research programs aimed at design of new materials. However, the role of first-principles calculations in the design process, and, most importantly, their potential, remain quite obscure. We therefore try to give a "balanced" view on the possibilities of first-principles calculations, not only telling success stories, but also discussing their problems and limitations. Then, we demonstrate uniqueness of the information that can be obtained using first-principles methods. Thus we determine their place among the traditional research methods and tools in materials science. In order to show the capabilities of first-principles calculations, we present some recent applications of first-principles methods to investigation of the thermodynamic and kinetic properties of austenitic (including high-nitrogen) and ferritic steels, at the atomic level. Finally, we indicate problems, related to steel research and development, where first-principles methods (together with other experimental or theoretical techniques) can lead to substantial progress or even breakthroughs.

### Introduction

All physical and chemical properties of ordinary matter can, in principle, be derived "from first principles", i.e. by solving basic quantum-mechanical equations that describe the motion of the electrons and nuclei. In practice, these equations must be simplified before they can be applied to many-particle systems such as solids. Density functional theory (DFT) makes first-principles calculations applicable to systems of any elements of the Periodic Table, to obtain the total energy of the ground-state electronic configuration [1]. The energy can be obtained using a wealth of computer codes; a number of useful properties can then be calculated from the total energy as derivatives with respect to concentration, nuclear positions, etc. [2]. The accuracy of DFT calculations for the simplest properties of crystalline solids (e.g., heats of formation, lattice parameters, or elastic moduli) is still less than that of corresponding experimental data [3]. Importantly, DFT calculations also provide access to many other properties that are not so easily measured experimentally. The energies of various defects, atomic configurations, and processes in solids are now amenable to first-principles calculations. Such energy parameters play an important role in many microscopic theories of physical metallurgy [4]], [[5]. DFT calculations allow us to see (in a broad sense) how Nature works at atomic scale [6]-[9]. Only if properly combined with other experimental and theoretical techniques, will they be able to bring alloy research to a new qualitative level [10]-[12]. Recent developments make it possible to have a

theoretical "look" into steel. Some applications of first-principles calculations to problems of steel research will be reviewed here.

# Methodology

The compositional, structural, and magnetic complexity of steel continues to challenge scientists. Let us just briefly mention the theoretical techniques that have been developed in order to handle different aspects of this complexity in efficient ways.

### Substitutional disorder

The coherent potential approximation (CPA), a technique to calculate the electronic structure and other ensemble-averaged quantities for a random substitutional alloy of an arbitrary composition, was proposed in 1967 [13] and became mature in the 1980's [14]. A practical realization of this technique can be applied to study the physical and chemical properties of *multicomponent* solid solutions, solution phases, and alloy surfaces [15]. Extensions of this technique allow one to consider short-range order effects [16] and to compute interatomic interactions [17] in alloys.

### Magnetism and magnetic disorder

The importance of magnetism for understanding the properties of iron and steel has been recognized more than a century ago [18]-[19]. Many features of the Fe-based alloy phase diagrams (for instance, the shape of the  $\gamma$ -loop in the Fe-Cr system) are determined by the magnetic free energy contribution [20]-[22]. In order to be useful for phase diagram calculations, first-principles calculations should be able to treat not only the ferromagnetic  $\alpha$ -Fe (ferrite) but also other phases of iron having complex disordered magnetic structures, such as paramagnetic  $\gamma$ -Fe (austenite) or paramagnetic  $\alpha$ -Fe [23]. Paramagnetic disorder of the iron phases may be included in the first-principles scheme using the CPA, within the disordered local moment (DLM) model [24]. The technique mentioned above [17] can also be used to compute the effective magnetic interactions, to be then used in statistical-mechanical modelling [25].

### Interstitial atoms and lattice distortions

The presence of interstitial impurities, such as C and N, is essential for the properties of steel, but represents a serious obstacle for first-principles calculations due to the long-range lattice distortions due to these impurities. A technique that can simultaneously treat lattice distortions, substitutional disorder, and magnetic disorder in alloys has been proposed [26]. This technique, which is a combination of the exact muffin-tin orbital method with the full-charge density and the coherent potential approximations (EMTO-FCD-CPA), was shown to reproduce correctly the elastic properties of steel [27], including the high elastic anisotropy of Fe-Ni-Cr austenite [28].

# Applications to phases in steel: Examples

### Ferrite or martensite

### Fe-Cu

Precipitation of copper has a strengthening effect on iron and steel [29]. The solubility and diffusivity of Cu in Fe undergo dramatic changes [30] at the Curie temperature  $T_{\rm C}$ , making it difficult to predict the rate of Cu precipitation in  $\alpha$ -Fe upon low-temperature annealing or under irradiation. Here first-principles calculations are providing us with very valuable and detailed information about the interactions and dynamics of point defects in  $\alpha$ -Fe [31]-[34].

#### Fe-Cr

A potential application of ferritic stainless steel as a construction material for nuclear fusion reactors [12] has recently revived scientific interest to the Fe-Cr alloys. Advanced first-principles methods open new possibilities to establish a microscopic picture of the ordering and decomposition phenomena in Fe-Cr alloys [35]-[38]. Unfortunately, in some studies the very important effects of magnetic disorder have been neglected [37]. It is clear that a quantitative theory of ordering and decomposition in steels must fully account for their magnetism [38].

#### Multicomponent solutions

First-principles techniques based on the coherent potential approximation (EMTO-CPA, for example) have one important advantage over the techniques that rely on cluster expansion [39] or utilize supercells [40] in order to generate random configurations. While the latter techniques are mostly restricted to binary alloys [33], the CPA-based methods allow one to calculate ensemble-averaged properties for a *multicomponent* alloy phase, as a function of composition, thereby enabling accurate calculations of *concentration derivatives* [35] of these properties, e.g., partial molar quantities. Thus, EMTO-CPA was recently used in order to calculate the chemical potentials for the eight components of a bcc alloy Fe<sub>723</sub>Cr<sub>.130</sub>Ni<sub>.085</sub>Mo<sub>.023</sub>Cu<sub>.017</sub>Ti<sub>.011</sub>Al<sub>.007</sub>Si<sub>.004</sub> [41], as well as to evaluate the thermodynamic driving forces for precipitation of various intermetallic phases from the solid solution (martenisite) upon aging at 475°C. These data were useful for the interpretation of 3D Atom Probe results obtained in the same study [41].

#### Austenite

#### Stacking fault energy of Fe-Cr-Ni austenite

The leading role of the magnetic disorder contribution into the stacking fault energy of austenite was recognized long ago [42]. First-principles studies of austenite are only in their initial stage. The disordered local moment (DLM) model of the paramagnetic state was used in the framework of the EMTO-CPA method to calculate the elastic properties of the Fe-Ni-Cr-based austenite as a function of composition[27]-[28]. Even more refined model of the paramagnetic state, which takes into account longitudinal spin fluctuations, was necessary in order to explain, from first principles, both the compositional and temperature dependence of the stacking fault energy in austenitic steels [43]. This achievement opens up a unique opportunity for multiscale modeling of dislocations in steels.

#### Austenite in high-nitrogen steel

First-principles methods open totally new possibilities for studying steels. The first question, which should be answered before starting any modelling of steels, is what their structure and atomic configuration at the atomic scale are. Let us note that the common techniques of structural analysis, such as X-ray and neutron diffraction, can only supply information about average distribution of atoms on the lattice. Besides, their use is restricted almost exclusively by two-component systems. There is only few experimental data for atomic distribution in 3-compenents systems, including one set for austenitic stainless steel [44] and none for 4-component systems. On the other hand, finding such configurations from first-principles calculations is a problem that *can* in principle be solved, although for steels this can be practically done only by employing special techniques that can treat complex magnetic states. Such methods have been developed by Ruban *et al.* [17], together with the corresponding simulation techniques that allow one to determine the atomic configurations in alloys at a given temperature.

These methods have been applied to study the solubility of N in austenitic steels. Since nitrogen is usually introduced at relatively low temperatures, where the bulk diffusion of substitutional

atoms is very slow, the problem of N distribution has been solved assuming *fixed* atomic configurations of Ni and Cr in austenite. The latter had been derived using the interatomic interactions obtained in the first-principles calculations [17], via the statistical-thermodynamic simulations at temperatures of the usual heat treatment of austenitic steels. The nitrogen-nitrogen and the nitrogen-metal interactions were then determined using first-principles calculations. Finally, these interactions were used as an input to statistical-thermodynamic simulations of N solubility in austenitic steel. The simulations showed:

 the existence of an ordering transition at about 800 K (depends on the alloy composition) in austenitic steels, driven by strong interactions between Ni and Cr solute atoms;
 quasiordering transitions of N in the interstitial sites of austenitic steels, due to the specific distribution of Cr and Ni.

#### Sigma phase

A combined first-principles and Calphad modelling study was performed of the electronic and atomic structure of some Fe-based and Co-based binary sigma phases [45]. The experimentally observed site occupancy in the FeCr sigma-phase was reproduced. More importantly, the nearly equiatomic composition of the  $\sigma$ -FeCr phase was shown to be a result of magnetic entropy contribution (due to the magnetic moment disorder of the Fe atoms occupying the high-coordination number sites in the structure). Indeed, non-magnetic  $\sigma$ -phases in the isoelectronic binary systems tend to occur near the concentration ratio 1:2, e.g.,  $\sigma$ -RuMo<sub>2</sub> [46].

# Conclusions

The reviewed results of selected first-principles studies applied to iron alloys clearly show that steel research has got a new scientific instrument to try. As any other instrument, it must be properly used in order to address the right kind of questions (e.g., the questions of atomistic mechanisms of various processes such as ordering or decomposition phenomena) that are not so easily addressed by other experimental or theoretical techniques. And, similarly to other modern instruments, first principles calculations require highly qualified personnel. There are steel companies that consider this theoretical activity a strategic direction of research and development. One may expect a synergistic interaction between the first-principles based theoretical modelling and new experimental microscopic techniques.

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### RECRYSTALLISATION OF STAINLESS STEELS AND ITS EFFECTS ON MECHANICAL PROPERTIES

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### Abstract

Stainless steels possess an excellent combination of high corrosion resistance, tensile strength and ductility and also workability is good. Despite decades of investigations the evolution of these steels is not finished yet. In particular, the advantages of modern processing by thermomechanical rolling with integrated heat treatment are not so far exhausted but offer new chances. Basis for the optimisation of utilization of existing and new technologies is precise knowledge on the deformation behaviour and on the process-dependent microstructure evolution during and after hot working. Mostly they can be derived both from the results of mechanical tests and metallographic investigations or predicted by mathematical models. In this paper the relationships between deformation conditions, deformation behaviour and microstructure evolution are presented exemplarily for some steel grades. This also includes examples of dynamic and static softening processes for selected microstructure conditions as well as for the mechanical properties of fully austenitic and austenitic steels with a higher content of  $\delta$ -ferrite. Separately, the effect of the initial microstructure on flow stress is shown.

### Introduction

Cr-Ni steels are the most important group of stainless steels. From 61 steels listed in DIN EN 10088 thirty are austenitic, six austenitic-ferritic and nineteen martensitic. Enormous growth rates of consumption of stainless steels reflect soaring applications of classical Cr-Ni-steels such as 1.4301 (X5CrNi18-10) and 1.4541 (X6CrNiTi18-10) in many branches. Furthermore, steels with higher contents of chromium, nickel and molybdenum show excellent corrosion resistance even in aggressive media.

The useful properties of these steels can be tuned by conventional deformation processes plus final heat treatment. For hot rolled products, the solution annealing before cold rolling stage can be omitted in many cases, if the hot deformation process is controlled concerning recrystallisation and precipitation in such a way that after the deformation a nearly precipitation free and soft recrystallised structure exists. The requirement "recrystallised and precipitation-free" can be realised only by appropriate knowledge about the processes of microstructure evolution and deformation processes. This includes kinetics of dynamic and static recovery incl. grain size as well as the strain induced precipitation.

The focus of the present paper consists of the deformation behaviour, kinetics of precipitation and mechanical properties of stainless Cr-Ni-Ti and Cr-Ni-Mo steels. Both the results of single stage tests and multipass deformation tests will be discussed. The appearance of nonhomogeneous microstructure will be shown and analysed. Finally, the effect of finish deformation temperature on the mechanical properties will be discussed.

# Steels and experimental conditions

The chemical composition of some of the investigated steels is summarised in Table 1. Five steels with different chemical compositions were used. The basis is the 18/10 Cr-Ni steel, followed by the groups of Ti-stabilised, Mo-Ti and a higher alloyed Ni-Cr-Mo-Cu steels. The base steel and the following three ones were used for investigations on the deformation behaviour (flow stress, plasticity) and for the determination of mechanical properties. The last steel was used mostly in connection with studies on the restoration processes and microstructure formation.

Steel	С	Si	Mn	Р	S	Cr	Ni	Мо	Ti
X5CrNi18-10	0,025-	0,26-	1,61-	0,025-	0,003-	17,0-	8,0-	0,1-	0,003-
	0,056	0,51	1,91	0,033	0,028	18,22	10,5	0,45	0,005
X6CrNiTi18-10	≤0,08	≤1,00	≤2,00	0,045	0,030	17-19	9-12	-	1,0
X8CrNiTi18-10	≤0,10	≤0,80	≤2,00	0,045	0,030	17-19	9-12	-	1,0
X8CrNiMoTi18-10	≤0,10	≤0,80	≤2,00	0,045	0,030	16,5-18,5	8-10	2-2,5	1,0
X1NiCrMoCu31-27	0,22	0,09	1,56	0,14	0,03	26,74	30,70	3,65	-

Table 1. Chemical composition of investigated steels.

The trials, test conditions and objectives of the investigations are summarised below. For investigations with a light microscope the specimens were quenched into water immediately after the deformation or after the certain holding time.

### **Experimental series**

- ngle-stage compression tests and wedge rolling trials to determine flow curves and investigate dynamic softening processes, plasticity and microstructure (strain  $\varphi = 0.05 1.2$ , strain rate  $\dot{\varphi} = 0.1 15 \text{ s}^{-1}$ , deformation temperature  $950 1250^{\circ}\text{C}$ )
- Multi-pass compression tests and wedge rolling trials to determine plasticity, microstructure and the correlations between dynamic and static recrystallisation ( $\phi = 0.05 1.2$ ,  $\dot{\phi} = 0.1 2.0$  s<sup>-1</sup>, deformation temperature 950 1250°C, pause time 0.5 15 s)
- Rod rolling trials in an industrial pilot rolling mill ( $\phi = 0.07 0.9$ ,  $\dot{\phi} = 6.2 37.5 \text{ s}^{-1}$ , deformation temperature 775 1250°C, pause time 2 10 s).

### Results

#### **Flow stress**

The studies on hot flow stress of X5CrNi18-10 and X8CrNiTi18-10 with different contents of Mn and Ti revealed no significant differences between these steel grades in a temperature range 950 to 1250°C. For steel X6CrNiTi18-10 the chemical composition (Cr, Mo, Ni and Cu) was varied in quite a wide range. Figure 1 shows the flow stress of this steel for different contents of Cr and Mn in relation to the deformation temperature. It can be seen that the effect of deformation temperature is significant. Maximum flow stresses at 950°C are 180–230 MPa while 60-75 MPa at 1200°C. In contrast, the effect of alloying is faint. Exceptions are alloying versions with higher contents of Mo, especially at deformation temperatures below 1100°C. Microstructure has also an effect on flow stress. It is known that the flow stress of cast grain structures is lower than those of annealed structures [1], whereby also a directional dependence exists. If one considers the flow stress of highly alloyed Cr and Cr-Ni steels, whose phase composition can be characterized by the Cr-Ni-equivalent in the Schaeffler diagram(Figure 2), then at a given Cr-Ni-equivalent, austenitic steels have a higher flow stress than that of steels

whose austenitic matrix still contains (Fe, Cr) – carbides. The difference increases with increasing carbide fraction. For the two-phase (austenite-ferrite) Cr-Ni steels and ferrite-pearlitic Cr steels, the flow stresses are closer to each other. This figure again confirms the conclusion drawn earlier that the mixed crystal structure with dissolved elements increases the hot flow stress more than precipitates in the solid solution do.



Figure 1. Flow stress (peak stress) of steel X8CrNiTi18-10 dependent on alloying elements (Cr or Mo) and deformation temperature at the strain rate of  $0.16 \text{ s}^{-1}$ 



Figure 2. Influence of phase structure on the base value of the flow stress  $\sigma_{fl}$  of high alloy Cr-Ni steels and Cr steels [1]

#### Plasticity

The influence of the elements Cr, Ni and Mn on plasticity can be described by a complex power function of strain and the effect of S, Mo, Cu and  $\delta$ -ferrite by a simple power function in a linear multiple regression. Increasing contents of  $\delta$ -ferrite, S, Cu and Mo decrease the plasticity; on the other hand, plasticity can be improved by elements such as Ni and Mn. The optimum Cr-content is near  $\approx 16.5\%$ , the fact, which is also connected with the  $\delta$ -ferrite content.

Plasticity can by described by the following mathematical equations [1], whose constants are summarised in Table 2.

 $\varphi_{\text{fracture}} = \varphi_{\text{fracture}-0} * K(Cr) * K(Ni) * K(Mn) * K(S) * K(Cu) * K(Mo) * K(Ti) * K(\delta-ferrite)$ 

 $\phi_{\text{ fracture - 0}}$  = 2.7155 (at 1150°C and  $\dot{\phi}$  = 0.16 s<sup>-1</sup>)

	Validity	alidity Equation for $K_{(Element)} =$		Constants				
	Range [%]	K (element)	1.00 at x [%]	A <sub>i</sub>	Bi	Ci		
Mn	0.201.60	$A_i \cdot exp(B_i \cdot ([\%Mn]) \cdot [\%Mn]^{Ci}$	0.70	1.0289	-0.0136	0.0533		
S	0.010.10	$A_i exp(B_i ([\%S]))$	0.02	1.0322	-1.5851	-		
Cr	14.019.0	$A_i exp(B_i ([\%Cr]) [\%Cr]^{Ci}$	17.5	6.4205*10 <sup>-16</sup>	-1.1735	19.3974		
Ni	8.013.0	$A_i exp(B_i ([\%Ni]) [\%Ni]^{Ci}$	10.0	5.9948*10 <sup>-7</sup>	-1.0377	10.7289		
Мо	0.100.30	$A_i exp(B_i ([\%Mo]))$	0.30	1.0883	-0.1572	-		
Cu	0.100.30	$A_i exp(B_i ([\%Cu]))$	0.20	1.0107	-0.0534	-		
δ-ferrite	1.0023.0	$A_{i} exp(B_{i}([\% \delta-ferrite]))$	5.00	1.0677	-0.0131	-		

Table 2. Constants for the plasticity calculation of austenitic Cr-Ni steels [1].

#### **Restoration Processes**

#### Dynamic Recrystallisation

The flow stress curves have shown that the critical degree of deformation for the beginning of dynamic recrystallisation depends on the deformation temperature [1]. At a given temperature and initial grain size the kinetics of the microstructure evolution is a function of strain and deformation rate. A significant influence of the chemical composition exists below 1050°C only. For steel X1NiCrMoCu31-27 Figure 3 shows examples of the effect of the true strain on the kinetics of dynamic recrystallisation. As described in the literature, the dynamic recrystallisation initiates near the grain boundaries and especially at the triple-points, and later it covers all grain boundaries and consumes the interior of the grains [4]. At practical deformation rates, however, dynamic recrystallisation requires very high deformation temperatures and deformation degrees. In rolling experiments carried out, the highest fraction of dynamic recrystallisation was found at the highest deformation temperature and a maximum reduction (true strain) of  $\varphi = 0.7$  used [4], but even then, completely dynamically recrystallised microstructure was not created.



Figure 3. Effect of rolling reduction (true strain) on dynamically recrystallised structure in X1NiCrMoCu31-27; wedge rolling trials.

#### Static Recrystallisation

In multistage deformation the coarse grain structure is refined by dynamic and mainly by static recrystallisation. The recrystallised fraction depends on the deformation conditions and pause times between the deformation steps. The kinetics of static recrystallisation can be characterised by a S-shaped curve showing the fraction vs time. The investigations have revealed that Mo-free steels recrystallise faster than steels containing Mo. For instance, after a strain of  $\varphi = 0.3$  at 1050°C, Mo-free steels can become completely recrystallised even within 50 s, whereas Mobearing steels need pause times 10 times longer. Figure 4 displays three static recrystallisation curves for steel X1NiCrMoCu31-27, showing the effect of deformation temperature and time after the deformation on the recrystallised fraction. The recrystallisation behaviour follows the well-known Avrami-type kinetics.



Figure 4. Effect of holding time after the first deformation step on recrystallisation kinetics (compression tests,  $\phi_1=0.3$ ;  $\dot{\phi}=0.1s^{-1}$  steel X1NiCrMoCu31-27

Figure 5 gives examples for the microstructure evolution for steel X1NiCrMoCu31-27 in the course of a three-step deformation. Recrystallisation remains partial only, so that while fine recrystallised grains are created, the non-recrystallised initial grains become hardened. In the recrystallised grains some coarsening occurs while nucleation of new grains in the coarse grains continues. After the last pass and holding the structure is still not completely recrystallised, but a mixed grain structure exists consisting of the relicts of initial coarse grains and the fine



recrystallised grains. At lower deformation temperatures the formation of mixed partially recrystallised grain structure is even more pronounced.

Figure 5: Microstructure evolution in multipass compression, each pause time about 5 s, (X1NiCrMoCu31-27, compression tests on a deformation dilatometer  $\dot{\phi}$  =0.1s<sup>-1</sup>

# **Mechanical properties**

Concerning the tensile mechanical properties of 18/10-steels from the three investigated groups with varying contents of Cr, Mo, Ni and Cu, rolled in a pilot mill, the yield strength showed a significant dependence on Mo content. At the Mo content between 0.1 and 3% the yield strength  $Rp_{0,1}$  increased by about 30% (from 280 to 360 MPa). An effect of Cr was also found (ca. 13% at Cr contents from 15 to 20%). The effect of Mo and Cr was completed by the indirect positive influence of  $\delta$ -ferrite. On the contrary, the tensile strength  $R_m$  was found nearly independent of Cr and Mo contents. The same is valid for the total elongation  $A_5$  and the reduction of area Z. Alloying elements such as Ni and Cu improve the elongation marginally.

The rolling temperature affects the mechanical properties of hot rolled band significantly. This interrelation is shown in Figure 6 for steel X6CrNi18-10 and X8CrNiTi18-10. Typical values for the solution annealed condition of X6CrNi18-10 are marked in the figure by dotted lines. Both  $Rp_{0,2}$  and  $Rp_{0,1}$  rise strongly at low finish rolling temperatures below 980°C. Above 980°C the values correspond to the solution annealed conditions. The elongation has an opposite tendency. The scatter band of X8CrNiTi18-10 shows the same tendency The obvious reason for the

influence of deformation temperature is the difference in the degree of recrystallisation, partially recrystallised contra to non-recrystallised structure or rather  $\sigma$ -phase precipitations in the ferrite bands.



# Summary

The properties of hot rolled austenitic and austenitic-ferritic 18-10 Cr-Ni steels are influenced by their chemical composition. On the other hand, by using thermo-mechanical treatment it is also possible to tune the mechanical properties economically in large spectrum. An accurate control can be realised by precise knowledge on the kinetics of dynamic and static recrystallisation. By higher degree of strain hardening at low rolling temperatures both tensile and yield strength can be further improved, with comparatively small losses in elongation.

The plasticity can be damaged by the formation of mixed grain structure. This can be avoided by a selective control of the dynamic and static recrystallisation.

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### AN EXPERIMENTAL STUDY OF RECRYSTALLIZATION ANNEALING IN MARTENSITIC STAINLESS STEEL STRIP BY MEANS OF EBSD AND EMPIRICAL MODELLING

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#### Abstract

Unlike conventional microscopy with LOM and SEM, EBSD can successfully characterize recrystallized structures in annealed martensitic chromium steel strip and with high accuracy measure grain size, particle size and recrystallized fraction. This information can be used to understand, evaluate, control and even predict the recrystallization annealing process by building relatively simple empirical models for determination of recrystallization degree, as a function of the annealing parameters and the deformation history.

#### Introduction

Recrystallization annealing, a repeated heat treatment between different stages of cold rolling of martensitic chromium steel strip, is successful when neither high rolling forces nor wear of the working rolls occur during the subsequent cold rolling. Easily measurable mechanical properties such as yield strength, tensile strength, elongation and hardness have described, by tradition, the quality of the annealing process. The recent development of instruments and methods for material characterization has accentuated the important role played by the microstructural properties, e.g. recrystallization degree in the evaluation of the heat treatment. The first part of this work shows how microstructure investigations by scanning electron microscopy, with field emission gun (FEG-SEM) and electron back scatter diffraction (EBSD), can successfully characterize fully or partially recrystallized structures in annealed martensitic chromium steels, in contrast to the traditional methods as light optical (LOM) and scanning electron microscopy (SEM) with back scattered electrons (BSE). The second part presents two simple empirical models, describing the recrystallization degree, measured by EBSD, as function of annealing temperature, soaking time and cold reduction in strip made from two cold rolled and annealed martensitic chromium steel grades from Sandvik: Sandvik 13C26, a traditional martensitic chromium steel grade with ca 13% chromium, and Sandvik 7C27Mo2, a similar steel grade, alloved with molybdenum but with lower carbon content. The annealed microstructure of these grades consists usually of secondary phases as M<sub>23</sub>C<sub>6</sub> and M<sub>7</sub>C<sub>3</sub>, sometimes even Cr<sub>2</sub>N, uniformly spread in a ferrite matrix. The microstructure is often a combination of fully recrystallized, sub-structured or deformed grains, where extreme grain growth usually does not occur. The sample manufacturing, heat treatment, modelling and microstructure investigations by LOM and SEM-BSE described in this article, were carried out at Sandvik's R&D Centre in Sandviken, while microstructure investigations by FEG-SEM and EBSD were done at KIMAB in Stockholm. Observe that the possibility to interpret the microstructures presented is diminished because of the black and white printing of the figures in this article.

### Image analysis with conventional microscopy

LOM was found capable only to describe the distribution of secondary carbides, and could not reveal the grain structure. None of the samples investigated in LOM were suitable for automatic image analysis, and therefore the necessity to use SEM instead was obvious. SEM-BSE microscopy with a magnification of 8000x could be employed successfully for describing the secondary carbide distribution in samples etched with Nital 1% and Murakami. Characterization of the grain geometry, in the samples prepared by electrolytic etching in hydrochloric acid, was possible with SEM-BSE, but the accuracy was not satisfactory.

## Image analysis with EBSD

The EBSD investigations were carried out with a LEO Gemini Field Emission Scanning Electron Microscope. The samples were cut with water jet, and then at KIMAB the specimens were placed in holders made of similar material and polished mechanically with grinding paper and diamond suspension. The polished surface was the long section of the plate (rolling direction vs. normal direction), where the final polishing step was done with 0.25  $\mu$ m diamond suspension. After this stage the specimens were polished at least 10 minutes with an oxide polishing suspension (a combined mechanical - chemical polishing with 0.06  $\mu$ m silica oxide and an etching suspension, PH 9.8). All polishing was performed in a (semi-) automatic Struers Abramin polishing device.

During the automated EBSD analysis, a predefined grid is scanned and provides a microstructure map with information on crystal orientations, phases, etc. The step length of the scanning determines the resolution of this map, and for texture analysis a step length somewhat longer than the average grain size (in this case  $1 - 2 \mu m$ ) is used. For analysing ferrite grain size, grain boundaries and recrystallization degree a smaller step size must be used, for a step size not longer than one fifth of the mean grain diameter is recommended to get reliable results (in this case  $0.25 \mu m$ ). For the size distribution of secondary phases (carbides) the same rule gives a step of about 0.05  $\mu m$  in this investigation. The choice of step length is very important to get high quality results, for a too small step length gives, due to the limited scanned area, poor statistics and a too large step length results in poor resolution. The consequence is that at least two, perhaps three parallel investigations are needed in order to describe correctly both the texture and grain/particle sizes.

#### **Recrystallization degree**

The software used for EBSD analysis was "Channel 5" from HKL Technology, containing several tools that process the scanned data and present it graphically or tabulated. In this case the tool was "Tango" and the components used to describe the microstructure by presenting it in "EBSD Orientation Maps" were as follows:

a- IPF, "Inverse pole figure component" – gives an interpretation of the crystallographic orientations (directions) in a co-ordinates system related to the sample e.g. parallel or perpendicular to the rolling direction.

b- GB, "Grain boundaries" – gives the possibility to plot the grain boundaries depending on the crystals' misorientations. Different types of grain boundaries, e.g. HAGB or LAGB can be plotted with different types of lines.

c- BC, "Band Contrast" – is a quality measure of EBSD, the higher quality the better patterns. Deformed zones and grain or phase boundaries, for example, have low BC values.

d- RF, "Recrystallized fractions" – detects recrystallized grains. The algorithm works as follows: first the grain size is decided by a given definition of the misorientation, for grain boundaries, e.g. 10°, then the average misorientation is calculated between the scanned points within every grain. If the average misorientation exceeds the lower limit for a sub grain, e.g. 1.5°, the grain

will be classified as "deformed". If some grains consist of sub grains and each of them are below the limit, but among the sub grains the misorientation is higher than the limit angle, the grain will be classified as "sub structured". All other grains will be classified as "recrystallized". See an example in Figure 1.





Figure 1. Sandvik 7C27Mo2 scanned with a step length of 0.05 µm. Magnification bar is 20 µm.

a) - Crystal orientation according to the inverse pole figure in Figure 1c. Thick (black) lines are grain boundaries with misorientations higher than 10°, thin lines are sub grain boundaries with misorientations between 1.5° and 10°. b) - Graphical description of recrystallized grains shown with dark (blue) colour. c) - Inverse pole-figure index (Euler space), key to colours in Figure 1a. d) - Recrystallized fraction with key to colours in Figure 1b. Information limited in black and white version of the article.

#### Grain and secondary phase size distribution



Figure 2. Sample Sandvik 13C26 analysed with 0.05 µm step size. a) - Crystallographic orientation (Euler space). b) - Band contrast, M23 carbide (blue), Chromium nitride (yellow) and M7 carbide (red) and phase boundaries (red), grain boundaries in M23 phase (black) plus twin boundaries in M23 phase (green). Information is limited in black and white version of the article.

New EBSD scans with a finer step size  $(0.05 \ \mu\text{m})$  were performed on Sandvik 13C26 in order to detect grains (BCC phase) and secondary phases as M23-carbides (M<sub>23</sub>C<sub>6</sub>), M7-carbides (M<sub>7</sub>C<sub>3</sub>) and Cr-nitrides (Cr<sub>2</sub>N). Figure 2 presents the OM (orientation map) of an annealed sample with a

magnification bar of 10 um. In Figure 2b the microstructure is presented by the band contrast component, which gives a detailed map of the microstructure where secondary phases and grain boundaries can be studied much better than in the Euler space from Figure 2a. In Figure 2.b the identified secondary phases were coloured dark grey  $(M_{23}C_6 - blue if in colour and M_7C_3 - red if$ in colour) and light grey (Cr<sub>2</sub>N – yellow if in colour). Once again, the advantage of the band contrast cannot be accentuated as the pictures in the article are black and white. The fraction M23-carbides was between 8 % and 10 %, the fraction Cr-nitrides between 0.1 % and 0.2 % and the fraction M7-carbides was detected on a very low level (below 0.01 %) in all samples, which is normal for annealed Sandvik 13C26. The characterization of secondary particles can also be executed by semi-automatic or automatic image analysis methods based on micrographs from the FSD ("Forward Scattered Detector") in a SEM. Imaging with the forward scatter detector is usually carried out with the specimen tilted 70° from the horizontal plane in the same way as for EBSD. The electrons incoming angle is 20° and the high-energy "back scattered" electrons therefore becomes "forward scattered" electrons. The detector for these electrons is mounted on the EBSD screen. Due to the low incoming angle, small deviations in topography are enlarged and this is sometimes a problem due to the shadowing effect from particles. The surface preparation is therefore very important. By choosing relatively high magnification (about  $25\ 000x$ ) these micrographs become very detailed and particles smaller than 0.1  $\mu$ m can be characterized with high precision. See Figure 3.



Figure 3. a) - FSD micrograph used for evaluation of particle sizes and distributions in Sandvik 13C26. Magnification bar 1  $\mu$ m. b) - same micrograph including circles that define the particles.

The characterization of secondary phase from FSD micrographs was performed using the Metreo software from Kappa opto-electronics GmbH. This software provides tools for measuring particles semi-automatically and stores the information in text files. The particles were measured manually (computer assisted) by defining circles of equivalent area around each particle. See Figure 3b.

#### Further work with EBSD

a- Further development and refinement of the surface preparation methods will increase the detection accuracy of carbides and nitrides, and permit accurate study also of steel strip in the as-cold rolled condition.

b- Transmission Electron Microscopy (TEM) could be used for finer particles. If it is important to characterize particle behaviour during annealing, then probably most action takes place at a very fine scale. Particles smaller than 0.1  $\mu$ m (5 nm - 100 nm) must probably be characterized. A growth of large particles (on behalf of small) is very hard to detect by characterizing large particles, a volume increase of a sphere of 50% is equivalent of a radii increase of less than 15%. c- Use of Thermo-Calc software could help to calculate which and what amount of secondary phases are to be found after hot rolling and after different heat treatments. Thermo-Calc and Dictra software can also be used to predict the behaviour of the secondary phases during

annealing. A new database was developed recently at KIMAB (TOOL05) that can be used for this kind of steels with high accuracy.

d- Further data processing from EBSD scanning can be useful for a better description of the microstructure. For example, the average grain size is not relevant when the material is partially recrystallized, a separate analysis of the recrystallized, sub structured and deformed microstructure should be recommended instead.

e- There are good possibilities to calculate other material properties with EBSD, such as the driving forces for grain growth by analysing LAGB in a non deformed structure. Even the Zener pinning effect can be computed from detailed EBSD scans or from analysis of particle sizes from FSD images. Further on, EBSD gives large opportunities for studying the recrystallization mechanisms and their relation to texture changes, as well as for defining what if continuous or discontinuous recrystallization was the dominant mechanism during annealing.

# Empirical modelling of recrystallization degree in annealed strip

### Sandvik 7C27Mo2

A first empirical model for recrystallization degree of Sandvik 7C27Mo2, as a function of annealing temperature, soaking time, previous cold reduction and heating time, was created with Umetrics' software for experimental design, MODDE 8.0. An experimental matrix based on 21 samples of Sandvik 7C27Mo2 cold rolled strip, with different reductions and afterwards exposed to different heat treatment parameters, was set up. Recrystallization degree or fraction recrystallized was measured with EBSD, according to the procedure described above (limits for LAGB and HAGB were set to 2.5° and 10° respectively). The input parameters (annealing temperature, heating rate, soaking time, cold reduction and heating time) and the response (fraction recrystallized, grain size, carbide size, mechanical properties as  $R_m$ ,  $R_{n0.2}$  and elongation) were modelled, and the different mathematical expressions proposed by MODDE 8.0, were evaluated with regard to the variation and reproducibility of the calculated response, the significance of the model coefficients and Analysis of Variance (ANOVA), among others. A D-Optimal design with 21 runs for a quadratic model with Response Surface Modeling (RSM) as an objective was chosen. Models containing other responses than the recrystallization degree were unsatisfactory, and the factor heating time had to be removed as non-significant. The model was fit with MLR and it had one component, 15 degrees of freedom and a condition number of 3.595. The optimal model described the recrystallized fraction as a function of annealing temperature, soaking time and cold reduction, through the function RecrDegree =  $C_0$  +  $C_1$ ·Tanneal +  $C_2$ ·ColdRed +  $C_3$ · $t_{soak}$  +  $C_{12}$ · $T_{anneal}$ ·ColdRed +  $C_{33}$ · $t_{soak}^2$ . The model showed a high measure of fit (R2 just below 0.9) and a good predictability (Q2 just above 0.7). The first observation was that the model did not depend on the heating time or rate. With regard to the narrow range of heating rates, specific for recrystallization annealing of martensitic chromium steel strip, this was expected. It is consistent with studies on aluminium alloys showing, that in order to obtain a visible variation of the recrystallization temperature, the heating rate must be increased by a factor 50, according to [5]. The model makes it possible to choose optimal values of the annealing temperature, the cold reduction and the soaking time, in order to achieve a maximal recrystallization degree.



Figure 4. MODDE 8.0: 4-D Contour of recrystallization degree for Sandvik 13C26, by (a) short, (b) average and (c) long soaking time.

#### Sandvik 13C26

Using the same strategy and experimental design as for Sandvik 7C27Mo2 a new better empirical model could be set up for Sandvik 13C26. MODDE 8.0 proposed 27 different experiments where annealing temperature, soaking time and cold reduction were varied. Based on the experience gained with the model for 7C27Mo2, the factor heating rate was removed already from the beginning.

The optimal quadratic model, fit by PLS, describes the recrystallization degree, defined by the limits for LAGB and HAGB which were set to 1.5° and 7.5°, as a function of annealing temperature, soaking time and cold reduction. The model's summary of fit, shows values of measure of fit (R2), predictability (Q2), validity and reproducibility above 0.8. The model, also quadratic, has 3 components, 19 degrees of freedom and a condition number of 5.592. The quadratic model of the type: RecrDegree =  $C_0 + C_1 \cdot \text{Tanneal} + C_2 \cdot \text{ColdRed} + C_3 \cdot t_{\text{soak}} + C_3 \cdot t_{\text{soak}}$  $C_{12}$ · $T_{anneal}$ ·ColdRed +  $C_{13}$ · $T_{anneal}$ · $t_{soak}$  +  $C_{11}$ · $T_{anneal}^2$  +  $C_{22}$ ·ColdRed<sup>2</sup>, was refined by removing the quadratic term of the soaking time, among others. Figure 4 shows graphically how the model can be used by choosing, in the diagram, the optimal annealing temperature, soaking time and cold reduction, for a maximal recrystallization degree. Measurements of the material properties of all 27 samples were carried out in order to control the proposed model. Figure 5 shows that at a temperature between 675 and 700°C, the strength of the material decreases and its deformability respectively increases abruptly, which can be explained by the fact that the material starts to recrystallize. The curves flatten out above 700°C, which proves that the model is correct. Both models, based on lab scale annealing tests, are valid within certain soaking times, because recovery and grain growth are predominant at shorter and longer soaking times, respectively.



Figure 5. Mechanical properties of Sandvik 13C26 as a function of annealing temperature for different cold rolling reductions (CR).

### Conclusions

EBSD has proven to be capable to characterize the microstructure in annealed martensitic chromium steel strip in a very detailed way that was not possible by traditional metallography. Unlike conventional microscopy with LOM and SEM, EBSD is able to reveal the grain shapes as well as separate grains and identify the different phases in this kind of steel (ferrite, M23-, M7- carbides and Cr-nitrides). Important parameters such as grain size, particle size and recrystallized

fraction can be measured with high accuracy. This information can be used to understand, evaluate, control and even predict the recrystallization annealing of martensitic chromium steel, by building relatively simple empirical models for determination of recrystallization degree related to the annealing parameters of the strip and its cold deformation history.

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### SYNCHROTRON X-RAYS FOR STRUCTURAL CHARACTERIZATION OF STAINLESS STEELS

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#### Abstract

High-energy x-rays as produced from one of the three large scale synchrotron sources world wide have the capacity to penetrate millimeters of stainless steel and thus it provides a suitable probe for bulk characterization. Further, the high brilliance of the x-rays enable kinetic studies and the possibility to probe the meso-scale structure such as single grains and dislocation structures embedded in the steels. The current paper provides an overview of the work conducted using synchrotron x-rays for structural characterization of stainless steels. Synchrotron x-ray characterization is also discussed in the light of other experimental techniques. We provide scientific examples of synchrotron x-ray diffraction studies on metastable austenitic and duplex stainless steel taken from our own work, and additional examples from the literature are given. When looking at the recently published literature many new insights in metal behavior have been gained by the utilization of synchrotron x-ray characterization. However, this type of research has only started and we predict more frequent usage and that these techniques will contribute significantly to the advance of our current understanding of polycrystalline metals, e.g. stainless steels.

#### Introduction

The relationship between microstructure and material properties is fundamental in material science, and the progress in material science is often related to improvements or discoveries of new experimental techniques. For instance, the advent of x-ray diffraction in the early 1900s has markedly changed our conception of materials crystallography. Moreover, the transmissionelectron microscopes frequently becoming used in the mid 1900s have given us a much better understanding of e.g. defect structures. Most common experimental techniques for structural characterization are however surface techniques, where conventional x-ray diffractometry and scanning electron microscopy are both restricted to the near surface, and in stainless steel the penetration depth is limited to a few um. Transmission-electron microscopy has even higher limitations concerning the penetration depth and is solely restricted to the investigation of thin foils (~100 nm) [1]. Even though the surface structure of materials is clearly relevant and it can be a good approximation to the interior structure, there are exceptions. For instance, in the case of deformation-induced martensitic phase transformation in stainless steels it is difficult to quantify the phase fractions using a pure surface method [2]. Another example comes from material modeling and concerns the building of the next generation polycrystalline plasticity models. The over simplified traditional models do not take the local neighborhood of single grains into consideration, but this is appreciated in the more recent models which are finite element based [3]. Neighboring grains needs to have compatibility across the grain boundaries and this imposes deformation constraints between the grains. The result is a different deformation behavior between single crystals, bicrystals and polycrystals [4]. The deformation

constraint has mainly been investigated using transmission-electron microscopy and these investigations have contributed to the understanding of compatibility constraint. However, to fully comprehend this behavior in polycrystalline materials it is necessary to investigate the behavior of single grains embedded in an aggregate of grains, i.e. polycrystalline aggregate. Therefore, researchers have for some time searched for experimental techniques capable of probing the meso-scale structure (e.g. single grains and dislocation structures) within the bulk of polycrystals, since this would help in the understanding of polycrystalline materials (e.g. stainless steels). Attention has therefore been given to three-dimensional characterization, where novel techniques have emerged. One of these techniques is the combination of scanning electron microscopy (SEM) and focused ion beam (FIB), where serial sectioning using the FIB enables the collection of images through the depth of a sample by SEM. These images can then be put together to form a three-dimensional micrograph [5]. The high resolution of a Field-emissiongun (FEG)-SEM means that high resolution ( $\sim 1$  nm) three-dimensional micrographs can be recorded. The major drawback is however the destructive nature of the FIB-SEM and it is therefore not possible to conduct kinetic studies. Additional drawbacks for 3D characterization by FIB-SEM are the introduction of radiation damage and limited erosion rate. Another technique which has been around for some time is neutron diffraction. The neutrons have the penetration depth of centimeters in stainless steels and it is thus suitable for three-dimensional characterization, as demonstrated in [6-9]. Moreover, neutron diffraction is non-destructive enabling investigations of microstructure evolution. However, the data acquisition time is rather slow and the spatial resolution of neutron diffraction is not sufficient to probe the meso-scale structure. High-energy x-ray diffraction is an excellent complementary technique to neutron diffraction [10]. These x-rays are capable of penetrating millimeters of stainless steels and for modern steels with  $\mu$ m grain sizes this is a suitable bulk probe. Further, high-energy x-ray diffraction provides considerably better time resolution compared to neutron diffraction and in addition it enables meso-scale structural characterization within the bulk of stainless steels.

The subsequent part of this paper provides an overview of synchrotron x-ray characterization and the work conducted to date on stainless steels. Scientific examples are divided in three categories: phase transformations, residual stresses and single bulk grain behavior. The examples are mainly collected from our own work, but it also comprises an overview of research conducted by other researchers in the field.

### Synchrotron x-ray characterization of stainless steels

As mentioned above, high-energy x-ray diffraction has the capacity to fill the gap between some of the more established experimental techniques for structural characterization. The high-energy x-ray diffraction technique cannot compete with the Scanning Probe Microscopy (SPM) concerning spatial resolution, since the SPM has a true atomic spatial resolution in best case. However, SPM is a pure surface probe, while diffracted high-energy x-rays will penetrate millimeters of steel. On the other hand neutrons have better penetration power than high-energy x-rays, but the temporal and spatial resolution is worse.

The characteristics of the high-energy x-rays with a penetration power of about 5 mm at an x-ray energy of 50 keV and a µm spatial resolution has opened up a new field of research. It is the first technique truly capable of probing the meso-scale structure embedded in the bulk of materials. This was first realized by researchers at Risø National Laboratory who developed a technique called three-dimensional x-ray diffraction (3DXRD) in collaboration with researchers at the European Synchrotron Radiation Facility (ESRF). The 3DXRD technique enables characterization of single grains and dislocation structures embedded in the bulk of polycrystals [11-12]. In addition to the high-energy synchrotron facility ESRF in Grenoble, France, there are two more high-energy synchrotron facilities: the Advanced Photon Source (APS) in Argonne, II,

USA and the Super Photon Ring 8 (SPRing8) in West Harima, Japan. These sources can produce highly energetic x-rays, preferred for bulk studies. The synchrotron x-ray characterization is becoming more accessible to the research community, since many new facilities are being established today. The experiments conducted by Hedström et al. and presented here are all conducted at the 1-ID beamline at the Advanced Photon Source [13]. This undulator beamline is dedicated to high-energy x-ray scattering techniques and it is a versatile beamline where different environments for the sample can be used [14-16]. The measurements presented here are all in situ x-ray diffraction measurements during tensile loading of stainless steels and the typical setup is demonstrated in Figure 1. The white x-rays generated from the synchrotron source are made monochromatic and then allowed to pass through the stainless steel sample. The x-rays are scattered in the sample and the diffracted x-rays are collected with an area detector located behind the specimen. Two different types of measurements have been conducted, where the first is average grain measurements as exemplified in the diffraction pattern on the left hand side. The other type of measurement is the single grain measurement, where the x-ray probe is made small to only allow diffraction signal from a few grains as seen in the spotty diffraction pattern on the right hand side.



Figure 1. Typical setup for transmission x-ray diffraction

We will in the coming paragraphs present a review of the work conducted to date on stainless steels using synchrotron x-ray diffraction in three areas, namely phase transformations, residual stresses and single bulk grain behavior.

#### Kinetics of phase transformations

There are quite a few examples of *in situ* characterization of phase transformations in stainless steels. Several of these investigations deal with phase transformations during welding. Elmer et al. used time resolved x-ray diffraction to investigate the solidification in the weld pool of a 304 stainless steel. Their good time resolution of 50 ms provided the first direct proof that  $\delta$ -ferrite is the first phase to solidify [17]. Elmer and coworkers have further investigated the ferrite, austenite and sigma formation during heating and cooling of duplex stainless steels using synchrotron radiation [18-19]. Feaugas et al. investigated the nitriding of stainless steels surfaces using small-angle x-ray scattering at a synchrotron source. The high brilliance of the x-ray source allowed *in situ* observations of the nitridation process [20]. The formation of a thin passive layer of chromium-oxide on the surface of stainless steels was investigated by photoelectron spectroscopy with a tailored synchrotron x-ray beam to see chromium and iron [21]. The strain-induced martensitic phase transformation in metastable austenitic stainless steels has been investigated in [22]. The effect of cold rolling reduction and different strain rates on the strain-induced martensitic transformation and the mechanical properties of a 301 stainless steel were investigated. Autocatalytic martensitic transformation triggered by strains from the transformation itself could be observed at high applied strains, and this autocatalytic

transformation contributes significantly to the ductility of the steel [13]. Further, the load sharing between austenite and  $\alpha$ '-martensite could be determined *in situ* during loading and this provided sound data for evaluation of material modeling of the load response of 301 stainless steel [23].

#### **Residual stress evolution**

The residual stresses in the bulk of stainless steels have been examined by a number of authors using neutron diffraction [e.g. 24-25]. Synchrotron x-ray residual stress characterization is more scarce in the literature, but Hedström et al. have investigated the residual stress evolution during tensile loading for cold rolled stainless steel 301 using synchrotron x-ray diffraction [26]. In addition, the lattice strain evolution during *in situ* continuous tensile loading was followed. The results showed that the harder  $\alpha$ '-martensite phase is put in a tensile residual stress state along the rolling direction after cold rolling. Balancing compressive residual stress in the austenite phase was found. The opposite residual stress state was found in  $\alpha$ '-martensite and austenite transverse to the rolling direction. The hkl-dependent lattice strain evolution was also determined and the significant differences between crystallographic planes were noticed, which is an important aspect to consider in the residual stress determination from x-ray diffraction data.

#### Single bulk grain behavior

The three-dimensional x-ray diffraction technique has been used for some recent scientific highlights [27-29]. For instance, the transformation of single bulk grains from austenite to ferrite was followed during cooling of a carbon steel [28] and recrystallization of single bulk grains during heating of an aluminum specimen was investigated [29]. However, the only investigations on single bulk grains in stainless steels are gathered in [22]. Hedström et al. investigated the elastic strain tensor evolution of 15 single bulk grains during tensile loading of a duplex stainless steel [30]. Hedström et al. also investigated the elastic strain tensor evolution of 15 single bulk grains. The elastic strain evolution of 7 austenite grains in 301 stainless steel during tensile loading. The elastic strain evolution of 7 austenite [31]. Further, another sample was loaded to 20% applied strain and it was possible to follow the rotation of 7 austenite grains and the formation of  $\alpha$ '-martensite in two of the austenite grains [32].

# Outlook

The continuous development to improve state-of-the-art synchrotron facilities and equipment will continue to push the boundaries for materials characterization. As reviewed in this paper it is possible to conduct true three-dimensional characterization with a time resolution on the order of milliseconds and a spatial resolution on the order of µm. The near future holds further advance and a nano-scope is currently being developed at the ESRF in Grenoble [33]. Thus it is likely to enable advanced experiments where the fundamentals of nano-materials (e.g. precipitation hardened stainless steels with nano-precipitates) can be tested. The even higher brilliance of the x-ray sources and foremost the better detectors will improve time resolution and provide even better time resolved kinetic studies. Currently the free-electron laser x-ray sources are being commissioned and already totally novel experiments with time resolutions down to femtoseconds has been conducted. Moreover, at this point in time steps are taken to build a new synchrotron source in Sweden (MAX IV) that would cater primarily to Scandinavian users with one dedicated beamline for the type of work outlined in this paper [34]. To summarize, the x-ray diffraction results presented here from work conducted at synchrotron facilities is just the beginning of the development where traditional materials such as stainless steels will be reinvestigated in the light of better experimental methods and this will improve our current understanding of these materials.

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