



Akademie věd České republiky

Teze disertace  
k získání vědeckého titulu "doktor věd"  
ve skupině věd .....**Technické vědy**...

**Microstructure of Selected Structural Materials**  
(Mikrostruktura vybraných konstrukčních materiálů)

.....  
název disertace

Komise pro obhajoby doktorských disertací v oboru **Materiálové vědy a inženýrství**

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Pracoviště uchazeče ... **Ústav fyziky materiálů AV ČR, v.v.i.** .....

Místo a datum ..... Brno, 2008 .....



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## Résumé

Předkládaná disertační práce je pojednána jako komentovaný soubor prací [A1–A23] uveřejněných v mezinárodních časopisech v letech 1998 až 2007. Zabývá se tematikou vybraných konstrukčních materiálů pro vysokoteplotní aplikace, kde klíčovou roli pro praktické použití z hlediska funkčnosti hraje mikrostrukturní stabilita.

První okruh prací [A1–A11] se zabývá mikrostrukturou a výpočty rovnovážných fázových diagramů řady modelových niklových slitin, které obsahují tři nebo čtyři složky typické pro niklové superslitiny: Ni–Al–Cr, Ni–Al–Cr–Mo, Ni–Al–Cr–Co, Ni–Al–Cr–Ti, Ni–Al–Cr–W a Ni–Al–W. Pro mikrostrukturní studium i termodynamické výpočty byly voleny rozsahy chemického složení a žíhacích teplot, které jsou zajímavé z hlediska využití superslitin a zároveň umožňují získat experimentální údaje s vysokou výpovědní hodnotou pro následné termodynamické modelování.

Výsledkem studia mikrostruktury metodami analytické transmisní a řádkovací elektronové mikroskopie (TEM a SEM) jsou cenné experimentální údaje o fázovém složení slitin, morfologii a chemickém složení jednotlivých fází. V práci [A10] je navržena metodika vyhodnocení spekter energiově dispersní rentgenové analýzy vícesložkových slitin, použitá pak v ostatních pracích. Výsledkem termodynamického modelování jsou vypočtené fázové diagramy uvedených systémů při teplotách v rozmezí 1173 až 1373 K. Experimentální údaje ve většině případů korelují dobře s termodynamickými výpočty. U systémů Ni–Al–Cr–Co a Ni–Al–Cr–W byla na základě zjištěných experimentálních dat navržena úprava některých termodynamických parametrů vedoucí k lepší shodě modelových výpočtů s experimenty. V práci [A11] je sledován vývoj mikrostruktury nerovnovážných systémů laboratorních svarových spojů (difúzních párů) niklových slitin při 1273 a 1473 K. Výsledkem je rozbor koncentračních profilů v okolí spojů a profilů fázového složení. Experimentálně zjištěné hodnoty jsou velmi dobře reprodukovány také pokročilým modelováním kinetiky difúzních procesů.

Druhý okruh prací [A12–A18] se zabývá detaily uspořádávacích procesů v niklových slitinách a jejich souvislostí s elastickými parametry. K tomu jsou použity atomistické simulace Monte Carlo, provázané v některých případech s metodou molekulární dynamiky. Výsledky ukazují postupný vývoj systému z neuspořádaného stavu směrem k rovnovážné, zpravidla vícefázové struktuře, která obsahuje uspořádané domény. Změny jsou registrovány jak pomocí integrálních charakteristik (energie systému, mřížkový parametr,

parametry uspořádání na krátkou vzdálenost) tak prostřednictvím lokálních atomových konfigurací v různých stupních vývoje. Z nich jsou vyvozeny závěry o substitučním chování jednotlivých příměsí. Také je zřejmé, že největší změny integrálních charakteristik jsou způsobeny změnami lokální atomové konfigurace v počátečním stádiu uspořádání, tj. tvorbou uspořádaných klastrů; zatímco další růst domén je doprovázen poměrně menšími změnami integrálních charakteristik. Podobný závěr platí i pro elastické parametry modelovaných materiálů.

V práci [A16] se spojují výsledky experimentálního studia, termodynamického modelování a atomistických simulací při studiu slitin Ni–Al–Cr–Co–Re–W. Použití komerční termodynamické databáze po námi navržené úpravě parametrů vede při modelování k velmi dobré shodě s realitou zjištěnou experimentálně. Atomistické simulace kvalitativně správně předpovídají přednostní zastoupení složek v jednotlivých fázích, nicméně při použití jednoduchého modelu s párovými potenciály nemohou soupeřit s fenomenologickým modelováním ve stanovení správného složení fází. Přesto atomistické simulace mají rozhodující roli při studiu řady jevů: např. práce [A18] demonstruje, že i při použití jednoduchých potenciálů lze reprodukovat poměrně složitý proces směrového hrubnutí (tzv. rafting) pozorovaný v mechanicky namáhaných niklových superslitinách.

Okruh prací [A19–A22] se zabývá dynamickým vývojem mikrostruktury při creepu pokročilých chromových ocelí pro aplikace v energetice. Důraz je kladen na detailní kvantifikaci mikrostrukturních parametrů získaných pomocí analytické elektronové mikroskopie a obrazové analýzy. Je vyhodnocena napěťová akcelerace kinetiky růstu subzrn a precipitátů sekundárních fází. Analýza vývoje distribučních křivek velikosti precipitátů ukázala, že paralelně s hrubnutím precipitátů dochází v průběhu creepu k nukleaci a růstu karbonitridů. Jako první jsme popsali v tomto typu ocelí výskyt tzv. Z-fáze, jejíž precipitace může ovlivnit zastoupení ostatních sekundárních fází a tedy i mechanické vlastnosti materiálu. V práci [A23] je sledován vývoj mikrostruktury laboratorního svarového spoje nízkolegované oceli s chromovou ocelí jako častého případu v praktických aplikacích. Výsledkem je rozbor redistribuce intersticiálních příměsí v okolí spoje a identifikace sekundárních fází v různých lokalitách. Přesto, že se jedná o případ s větším počtem sekundárních fází, souhlasí experimentální výsledky velmi dobře s koncentračními a fázovými profily získanými modelováním kinetiky difúzních procesů a ukazují tak možnosti reálného použití kinetického modelování pro řešení praktických úloh.

## **Preface**

The dissertation is drawn up as a commented collection of original papers. The focus is on the microstructure of selected model Ni-based alloys and advanced steels. Further text is subdivided into following parts: *Aims* of the work, introduction to *Experimental materials* studied in the dissertation, introduction to *Methods* applied, *Summary of the most important results* with *Bibliography* and the *List of papers* published by the author between the year 1998 and 2007, which are the part of the dissertation. Most of the work has been carried out in The Institute of Physics of Materials, Academy of Science of the Czech Republic, Brno, Czech Republic; smaller part has been done during stays at École Polytechnique Fédérale de Lausanne, Switzerland and at McMaster University in Hamilton, Canada.

## **Acknowledgements**

The author would like to express his cordial thanks to his co-authors, to his diploma and PhD. students, and to all colleagues at IPM AS CR Brno, who had helped him to accomplish the work, which became the subject of this thesis.

Regarding the financial support, the research was supported by grant projects of the Czech Science Foundation (106/95/1528, 106/95/1530, 106/99/1176, 202/01/0383, 106/02/0876 and 106/02/0608) and by the Institute Research Plans (AV0Z2041904 and AV0Z20410507).

## **Aims of the work**

Ni-based alloys and advanced chromium steels are two important classes of structural materials for high temperature applications. Depending on chemical composition and thermal treatment, the characteristic microstructure develops, which predetermines mechanical and other material properties. For high temperature applications, especially the microstructure stability at service conditions is crucial. Thermodynamic calculations of equilibrium phase diagrams and kinetic modelling provide valuable insight into the character of possible structural changes and mark compositional ranges suitable for practical use.

The aims of this work are *(i)* to evaluate the microstructure of a range of model Ni-based alloys and to calculate the relevant phase diagrams for typical service temperatures, *(ii)* to model microstructure evolution of selected Ni-based systems on atomic level and *(iii)* to provide a detailed quantitative description of microstructure evolution during creep of advanced chromium steels.



## **Experimental materials**

Two classes of materials were studied, namely model Ni-based alloys and advanced chromium steels. The connecting link is the application of both classes as structural materials for various high temperature applications. Hence, the microstructural stability is crucial in both material classes. In the case of Ni-based alloys, the multicomponent model systems similar to commercial Ni-base superalloys were prepared and assessed both experimentally and by modelling. In the case of advanced chromium steels, commercial materials were studied mostly experimentally.

### *Ni-based alloys*

Ni-based superalloys are leading modern materials for high temperature applications [1]. The onset of superalloys (even if not called so that time) dates back to 1930s or 1940s. Since then a number of commercial alloys appeared on the market: e.g. Hastelloy, Incoloy, Nimonic, Inconel, Waspaloy, Astroloy, Rene, MAR-M-, PWA- and CMSX- series. Frequent application of these materials can be found in turbine disks, blades and vanes, both in aircraft gas turbines and in land-based ones. Both wrought and cast Ni-based superalloys have become the predominant alloys of choice for the most strength-critical applications. Since the 1960s and 1970s, the optimization of technology for the best performance has resulted in columnar grain directionally solidified materials and single-crystal directionally solidified components, namely turbine blades. Gas turbine component surfaces need to be protected from degradation owing to gaseous and deposit-modified corrosion. Substantial increases in life at engine operating temperatures and the minimization of hot corrosion attack in many applications was attained by using aluminide diffusion coatings and MCrAlY-type (where M = Fe, Ni, Co or their combinations) overlay coatings.

The structure of superalloys consists of cuboidal particles of ordered intermetallic phase  $\gamma'$  ( $\text{Ni}_3\text{Al}$ ,  $L1_2$ -type structure) in disordered face centred cubic (fcc) matrix  $\gamma$  (Ni-rich terminal solid solution) [2]. Other alloying elements (Cr, Mo, Co, Ti, Ta, W, Re etc.) are added to obtain higher corrosion and creep resistance. Some of them also substantially improve the strength of  $\gamma$  matrix by solution hardening effect. Small amounts of carbides and borides are often present mainly at grain boundaries. Various modelling approaches are useful for understanding the properties and structure of advanced superalloys and for

their further development. Modelling generally comprises technology processes (casting, solidification, remelting) as well as kinetic and thermodynamic modelling for the prediction of interphase spacing, structural transitions, microstructure evolution under various loading conditions, microsegregation defects and existence of various secondary phases. Here we focus on thermodynamic modelling. Owing to the rather complex alloying of common superalloys with over 10 alloying elements, it is unavoidable to study the equilibrium states on model systems. The Ni–Al–Cr–X systems (X is any other typical alloying element) investigated in this dissertation represent relatively simple, yet sufficiently representative subsystems for commercial superalloys. In recent years, several assessments including various model descriptions of ordered phases have been made with the aim to describe phase diagrams of relevant binary, ternary and some quaternary Ni-based systems. Nevertheless, there is still a lack of reliable experimental data and a need for optimization of thermodynamic parameters describing important composition and temperature regions.

### ***Advanced chromium steels***

The high-chromium (9–12 wt%) tempered martensite ferritic steels (TMFS) were developed during the last century and have a long history of use in the power-generation industry as boiler and turbine materials. TMFS present considerable high temperature creep strength, high corrosion cracking resistance, low oxidation rate and excellent weldability [3]. An increasing demand for power plants with higher efficiency finds the most economical solution in the use of steam plants operating at higher temperatures and higher pressures. This is the reason why TMFS, namely the P91 type, have been a subject of extensive investigations within projects of European co-operation (COST) as well as national projects of the member countries and a lot of new results on their heat resistance and mechanical behaviour at elevated and high temperatures have been gathered [4,5]. For service at elevated temperatures, TMFS are strengthened by precipitation hardening upon tempering. The martensitic laths are transformed during tempering onto elongated subgrains decorated by massive precipitation of secondary phase particles acting as a subgrain boundary stabiliser. It is assumed that numerous fine and stable Nb or V carbonitrides in P91 stabilise the dislocation networks most effectively.

About 10 years ago, when papers [A19–A21] were published, the modified 9% Cr P91 steel was one of the actually employed materials at about 580°C and only the lack of complete microstructural data on long term stability and on long term structure-property relationship hindered its use at and above 600°C. Advanced high chromium steels are now being developed with a target operating temperature of 650°C and a 10<sup>5</sup> h creep rupture strength of 180 MPa. Similar steels resistant to radiation damage are being developed for nuclear power plants [6].

Finally, it should be noted that various kinds of CrMoV steels are universally employed in the fabrication of components for fossil fired power plants. Thus joining dissimilar steels by welding cannot be avoided there, namely the dissimilar welds of low-alloy ferritic steels and modified 9–12% Cr steels. Investigating and understanding structural stability of welds is crucial for reliable life expectancy assessment.

## **Methods**

### ***Analytical electron microscopy***

Since the construction of first transmission electron microscope (TEM) by M. Knoll and E. Ruska in 1931, electron microscopy has gradually become a standard direct method of microstructure investigation [7,8]. First scanning electron microscope (SEM) was constructed about ten years later. The wavelength of accelerated electrons used for imaging in TEM enabled to overcome resolution limitation imposed by the wavelength of visible light. Advances in sample preparation and many construction improvements including field emission gun sources have led through the years to the resolution of recent TEMs around 0.1 nm and the one of SEMs around 0.5 nm. Grain and subgrain boundaries, interfaces, dislocations and other types of crystal defects can be studied on the submicron and (in the TEM) even on the atomic level.

TEM requires preparation of very thin foils (typically 10–100 nm thick) transparent to electron beam; it enables investigation of a bulk (even if thin) material. Electropolishing and ion milling were until recently two main methods of TEM sample preparation; lately the focussed ion beam has appeared as a convenient way of preparation of uniformly thick and site specific samples [9]. SEM is based on secondary electron or backscatter electron imaging of surfaces and it has advantages of relatively simple specimen preparation and use of larger specimens. There have also emerged some new types of SEM, such as the

environmental SEM (ESEM) working at low vacuum condition, and the low voltage SEM which uses accelerated voltage below 5 kV.

Interaction of incident electron beam with the sample results (among others) in generation of characteristic X-rays, which can be processed and used for analysis of chemical composition [10]. Energy- and wave dispersive X-ray analysis (EDX and WDX) have become a frequent complement of both TEMs and SEMs. From the two methods, EDX is faster and less demanding for hardware; WDX is more accurate and more suitable for quantification of the amount of light elements. Electron microscopy equipped with EDX and/or WDX is often referred to as analytical electron microscopy (AEM). The possibility of combination of imaging, diffraction and chemical analysis from microvolumes makes AEM quite powerful and truly irreplaceable. For purpose of the work reported here, transmission and scanning electron microscopy (TEM and SEM) with energy dispersive X-ray chemical analysis was used to accomplish various frequently solved tasks, namely the identification of crystal structure of various phases using selected area diffraction (SAD), measuring their composition, evaluation of various topological and geometrical parameters of individual secondary phase particles, dislocations and subgrains and measuring composition profiles across planar interfaces.

### ***Thermodynamic modelling***

Phase diagrams describe in a compact form the equilibrium phase constitution of an alloy depending on its chemical composition and temperature (more precisely also on other state variables, which we here take as constants). Calculation of phase diagrams is a step towards better understanding material properties and it is almost indispensable for sophisticated design of new complex materials, which is not entirely based on trial-and-error approach. Together with kinetic modelling, it also essentially helps with understanding some processes of material degradation, which are often very lengthy and can be hardly investigated in real time.

In this work, we use semiempirical approach for phase diagrams modelling, the so-called CALPHAD (CALculation of PHase Diagrams) method [11,12]. This approach is based on the fact that thermodynamic properties of the system are the sum of properties of individual phases. It is thus possible to calculate a phase diagram by first assessing the thermodynamic properties of all the phases in the system. Thermodynamic properties of

each phase are described with a mathematical model containing adjustable parameters. The parameters are evaluated by optimizing the fit of the model to all the information available so far. The philosophy of the CALPHAD method is to obtain a consistent description of the phase diagram and the thermodynamic properties so to reliably predict the set of stable phases and their thermodynamic properties even in regions, where experimental information is not yet available. The adjustable parameters of model can be further optimized to adapt to new experimental data. The strength of the CALPHAD method is that the descriptions of the constituent subsystems (unary, binary etc.) can be combined to calculate a phase diagram of a multicomponent system by comparing the thermodynamic stabilities of the phases involved in each subsystem.

The sub-lattice model developed by Hillert and Staffansson [13] and extended later by Sundman and Ågren [14] is frequently used for crystalline materials, as it allows using the existing experimental information about structure, crystallographic parameters and distribution of elements on sub-lattices. This approach combines thermodynamic and experimental phase diagram data to calculate a relevant phase diagram. The non-ideality is described by thermodynamic interaction parameters. Ordering processes (encountered frequently in our calculations of Ni-based systems) can be described in sub-lattice model according to Ansara et al [15,16] by analogous description of ordered and disordered phases imposing additional constraints on the interaction parameters. An alternative thermodynamic description was proposed by Huang and Chang [17], where the disordered phase and the ordered phase are described with two different models.

The above mentioned ideas are implemented in the widely recognized software package Thermo-Calc [18], which was used for all thermodynamic calculations in this dissertation. The program facilitates numerous types of thermodynamic calculations including optimization of thermodynamic parameters based on the supplied experimental data. Basic thermodynamic databases are included in the package; specialized databases for particular material classes can be added optionally (such as the database TCNI [19], which covers important subset of Ni-based alloy systems).

The DICTRA software package [20] is coupled with Thermo-Calc for necessary thermodynamic calculations. Based on a local phase equilibrium condition, DICTRA enables modeling of diffusion-controlled processes. Numerical simulation of a non-equilibrium two-phase system proceeds by solving diffusion equations on both sides of the

interface in every time step plus the movement of the phase interface [21]. An important prerequisite for kinetic calculations is hence the database of atomic mobilities based on diffusion measurements. DICTRA simulations offer the time- and distance dependences (profiles) for frequently requested quantities (molar phase fraction, bulk concentration, phase element concentrations, phase volume fractions, activity, chemical potential, etc.). A number of practical tasks can be solved, e.g. movement of phase interface, solidification and cooling, calculation of TTT diagrams, homogenization, carbonizing, nitriding, kinetics of diffusion couples and particle coarsening. However, it should be noted that many of these calculations are carried on under severe geometrical simplifications and that complex multicomponent and multiphase systems still cannot be worked out due either to computing power limitation or insufficient theoretical description.

### ***Monte Carlo atomistic simulation of ordering***

Monte Carlo (MC) method is a computation algorithm that relies on repeated random sampling to compute its results. It has a broad range of applications, e.g. in finance, biology, environmental science, mathematics, computational physics and physical chemistry. Here we use its power in studying systems with a large number of degrees of freedom, namely for studying ordering processes in multicomponent alloys [22,23]. Ordering phenomena in solid solutions have been a subject of continued interest for many years. They take place in many substitutional and interstitial systems and often have important practical implications as they can substantially change material properties. Besides long range ordering, short range ordering often takes place during or after quenching from a temperature above the long range order–disorder transition temperature  $T_C$ . Even above  $T_C$  some tendency for ordering or clustering is observed.

In a system consisting of over  $10^5$  atoms, we randomly change the atomic configuration and let the system lower its energy till it eventually gets close to its equilibrium state. Various structural parameters can be evaluated and collected in course of the simulation, including detailed atomic arrangement. The state of ordering can be conveniently described by a set of Warren–Cowley short range order (SRO) parameters [24], which describe the deviation from a random distribution of atoms in particular coordination spheres. Direct visualisation of the simulated lattice in various stages of ordering is possible. In simple cases, regions of various crystal structures can be identified

and their chemical composition evaluated, hence we may finally obtain outputs comparable with thermodynamic modelling and with experimental data.

Interatomic potentials are the most important input parameters of any type of atomistic simulation. Many types of atomic potentials are available in the literature [25,26]. They are often constructed for particular systems to reproduce properties like correct equilibrium crystal structure and its lattice parameters, enthalpy of vacancy formation, bulk modulus and other elastic constants. Lennard–Jones potentials used in this work serve as an example of simple central force pair potentials, which depend only on the distance and quality of two atomic species [27]. More complex potentials may be noncentral and/or many body (e.g. angular-dependent Tersoff–Brenner potential [28] or embedded atom potential [26]).

MC simulation of ordering on rigid lattice with pair potentials is computationally efficient, as the time consuming calculation of pair energies has to be performed only once. It is demonstrated further, that even this simplified approach yields valuable results. However, for simulation of e.g. uniaxial straining and for calculation of elastic parameters it is advisable to couple MC simulation with molecular dynamics code (using the same interatomic potentials) to take into account local relaxations of atomic positions.

## Summary of the most important results

### *Microstructure and phase diagrams of model Ni-based alloys [A1–A11]*

Microstructure of series of alloys of ternary and quaternary Ni-based systems was studied and obtained quantitative data were used for optimization of thermodynamic parameters [A1–A9]. Studied systems include Ni–Al–Cr, Ni–Al–Cr–Mo, Ni–Al–Cr–Co, Ni–Al–Cr–Ti, Ni–Al–Cr–W and Ni–Al–W alloys. Paper [A10] deals with the methodology of EDX spectra evaluation used in AEM measurements. Paper [A11] goes beyond equilibrium thermodynamic calculations: AEM measurements on diffusion couples are accompanied by kinetic modelling.

In [A1] the phase equilibria in Ni–Al–Cr system were studied experimentally and modelled in the  $\gamma+\gamma'$  phase region at 1173 K, where the lack of experimental data was found in the literature. Microstructure was studied and chemical composition of phases quantified by means of AEM. The phase boundaries and chemical composition of  $\gamma$  and  $\gamma'$  phases were calculated by means of the software Thermo-Calc applying both the Ansara's compound energy model [16] and the alternative model by Huang and Chang [17]. Two different sets of thermodynamic parameters of Ni–Al–Cr system [29,30] developed for the two types of thermodynamic models [16,17] respectively, give rise to similar plots of phase diagrams. Comparison of experimental and theoretical results shows that the results based on thermodynamic description according to Dupin [29] fit our experimental data in 1173 K phase diagram better than those based on the data from Huang and Chang [30].

In [A2] the influence of chemical composition and the temperature of long term annealing on the microstructure of four quaternary Ni–Al–Cr–Mo alloys was studied using TEM in the composition range of coexistence of several long range order crystal structures. Long term annealing at 873K leads to complex microstructure formed by  $\gamma/\gamma'$  and  $\text{Ni}_2(\text{Cr},\text{Mo})$  superstructure. Particles of other intermetallic phases were found and identified by SAD as Mo-rich P phase [31]. This phase was discovered in the Ni–Cr–Mo system [32] and it does not appear in any of the binary subsystems. To our knowledge, the presence of this phase in Ni-based superalloys has not yet been reported in the literature. The occurrence of P phase exclusively at grain boundaries is correlated with the formation of adjacent coarse  $\gamma'$  precipitates. In course of  $\gamma'$  coarsening Mo goes preferentially to  $\gamma$  channels and its concentration in Mo-rich alloys is sufficient for P phase precipitation. It is



important to take into account the possible occurrence of this phase as it can significantly change the phase relations and the alloy chemistry. Its presence at grain boundaries can adversely influence the mechanical properties of polycrystalline superalloys. It was also found, that annealing alloys with lower Mo/Cr ratio at 873K caused additional precipitation of very fine  $\gamma'$  dispersion in original  $\gamma$  channels. Measurements in the grain interiors indicated a substantial increase of microhardness caused by precipitation of both  $\text{Ni}_2(\text{Cr},\text{Mo})$  superstructure and fine  $\gamma'$  particles.

Another 5 alloys of the Ni–Al–Cr–Mo system were studied experimentally and theoretically at 1173 K in [A3]. The CALPHAD formalism based on the Hillert–Staffansson sublattice model with Ansara’s model of ordering in the  $\gamma$  phase [16] was used for theoretical calculations. The thermodynamic parameters for the calculations were taken from several literature assessments of binary and ternary systems. Phase diagram calculations based on prediction from the lower order systems yielded reasonably good agreement between theoretical and experimental data even without further optimization of thermodynamic parameters.

The Ni–Al–Cr–Co system was studied theoretically and experimentally at 1173 K [A4] and later on also at 1273 and 1373 K [A5,A6] in the  $\gamma+\gamma'$  phase region interesting for high temperature applications. Some nominal compositions hit also the phase  $\beta$ , which is known from the Ni–Al system as the NiAl ordered phase and during fast cooling it transforms to the martensitic phase  $\beta'$ . Extensive new experimental information has been obtained. The phase compositions and the amount of phases were measured and used for further thermodynamic modelling. The necessary thermodynamic database was constructed on the base of information available for lower order systems. The Calphad formalism based on the Hillert–Staffansson sub-lattice model with modification for ordering in the  $\gamma$  phase according to the model of Ansara et al. [16] was used. Based on the results measured on alloys with about 70 at. % Ni annealed at 1173 K, several thermodynamic parameters were modified to reach better agreement between calculated data (composition of phases and their volume fractions) and measured ones. In most cases the results of calculation show good agreement with experiment also for alloys with about 60 at.% Ni annealed at 1273 and 1373 K and they confirm the applicability of developed database of thermodynamic parameters for the modelling of the  $\gamma+\gamma'$  equilibria in Ni–Al–Cr–Co system.

Ni–Al–Cr–Ti [A7] is another important model subsystem for Ni-based superalloys. Eight alloys were prepared and their microstructure was studied after long term annealing at 1273 and 1373 K by means of SEM and TEM. Some of the alloys show rather complex phase structure: together with  $\gamma+\gamma'$  structure also the Cr-rich body centred cubic phase  $\alpha$  and plate-like phase  $\eta$  ( $D0_{24}$  structure derived from  $Ni_3Ti$  [31]) were found. Phase diagrams were calculated using Thermo-Calc software and the commercial database [19]. Most of predictions are correct regarding the phase composition, however explanation of several discrepancies remains open for future research.

In [A8] microstructure of several alloys of the Ni–Al–Cr–W quaternary system was studied quantitatively after long-term annealing at 1173 and 1273 K using AEM. Thermodynamic modelling of the system was done by means of the Thermo-Calc software package. The thermodynamic parameters for the calculations were taken from commercial database for Ni-base superalloys. Two sections of quaternary phase diagrams at 1173 and 1273 K with constant Ni level of 71 and 76 at.% were discussed. Based on the comparison of our new experimental data with the results of thermodynamic modelling, two of the interaction parameters describing the Ni–Al–W ternary subsystem were adjusted and better agreement of calculations with experiments was attained. Further on, the adjustment of the thermodynamic parameters was verified experimentally on several ternary Ni–Al–W alloys annealed at 1173 K [A9]. An important finding was made regarding the binary Al–W subsystem: contrary to the description used in the commercial database, there is an undisputable solubility of Al in W-rich phase  $\alpha$ . Ongoing work recently accepted for publication [33] resulted in further modification of thermodynamic parameters.

Papers [A1–A9] use extensive EDX analyses for quantification of chemical composition. The high accuracy of both the nominal alloy composition and the chemical composition of individual phases obtained by EDX is crucial to provide reliable input parameters for thermodynamic modelling. Making EDX analyses both in SEM (to obtain the nominal alloy compositions from large volumes) and in TEM (to obtain local compositions of constituent phases), we often face some discrepancies between the two sets of experimental data that have to be assessed prior to their usage as an input for thermodynamic modelling. EDX spectra measured in SEM are evaluated by built-in software using well developed standard ZAF corrections (i.e. corrections on absorption, atomic number and fluorescence) for quantification. EDX spectra measured in TEM on

thin foil (and generated in much smaller interaction volume) are quantified using so called Cliff–Lorimer  $k$ -factors [34,35], which directly express the proportionality between intensities of characteristic X-ray emission and the weight fractions of particular atomic species.  $k$ -factors depend on the geometry and other parameters of particular device. In [A10] the method of adjustment of  $k$ -factors for standardless spectra processing was developed and successfully demonstrated on two- and three-phase Ni–Al–Cr and Ni–Al–Cr–W alloys.

Calculation of equilibrium state for particular alloy composition and temperature is definitely important for estimation of the structure stability. However, welds of dissimilar materials appear in many technical applications and they represent even more critical point than the welded materials themselves. Hence in [A11] we attempted besides equilibrium calculations also advanced theoretical modelling of diffusion processes. Three laboratory diffusion couples were prepared from dissimilar binary or ternary Ni-based alloys and annealed at 1073 K and/or 1273 K. The experimental investigation of diffusion couples by means of AEM was complemented by modelling of kinetics of changes taking place during long term annealing at elevated temperatures. Thermodynamic parameters for equilibria calculations were taken from the commercial TCNI database [19]. Mobilities for calculation of diffusion matrix were taken from user database DIF, based on literature data [36]. The software package DICTRA was used under assumption of local equilibrium in each part of diffusion couple [21]. Comparing our experimentally measured profiles and calculated ones, it can be generally concluded that the method used provides results of good accuracy, which reflect phase structures and the redistributions of the elements in studied diffusion couples.

### ***Ordering processes in Ni-based alloys [A12–A18]***

The focus on ordering processes in this work is evoked by the fact, that the existence of ordered domains in fcc lattice is the main structural feature of Ni-based superalloys and it is also found in most of our model alloys dealt with in the previous section. As mentioned above, the degree of ordering is conveniently described by SRO parameters [24]. Papers [A12,A13] analyse evolution paths of SRO parameters and describe constraints imposed on them by the geometry of atomic arrangement. Papers [A14–A16] deal with simulation of ordering in series of model Ni-based alloys. Papers [A17,A18] are directed at relation

between ordering and elastic properties of model alloys. All the results shown below were obtained using the in-house software written by the author.

In [A12] the nature of the relationships between the low-index SRO parameters in an fcc stoichiometric  $A_{0.5}B_{0.5}$  binary alloy is discussed. A region of allowed combinations of SRO parameters describing the ordering in two nearest coordination spheres is demonstrated and it is explored in relation to so called Clapp–Moss diagram [37], which binds interaction parameters with equilibrium crystal structure of a stoichiometric fcc  $A_{0.5}B_{0.5}$  system. Evolution paths of ordering in the SRO space obtained by Monte Carlo simulation using an Ising model [22] with first- and second-nearest-neighbour pairwise interaction parameters are presented and discussed. A method is proposed for the estimation of the interaction parameters from the initial trend of the evolution path of a disordered system.

This work is further continued and substantially extended in [A13], where the more general case is discussed for both AB and  $A_3B$  systems, taking into account three SRO parameters. From the results it is obvious that although all SRO parameters  $\alpha_i$  may theoretically be in the range from  $-1$  to  $+1$ , a large portion (namely 94% in stoichiometric system AB) of  $[\alpha_1, \alpha_2, \alpha_3]$  combinations is forbidden due to geometric and compositional constraints. Therefore, the knowledge of allowed  $[\alpha_1, \alpha_2, \alpha_3]$  combinations can be generally useful for an independent check of correctness of measured data. Allowed combinations fill a polyhedron in space of SRO parameters. The ordered structures represented by polyhedron vertices are possible candidates for low-energy ordered states. Evolution paths of ordering in SRO space obtained by Monte Carlo simulation using an Ising model with first and second nearest neighbour pairwise interaction parameters are an informative way to describe the ordering processes. The initial direction of the evolution paths in  $\alpha_1$ – $\alpha_2$  plots is shown to be sensitive to the interaction parameters, but not to the composition. This makes experimental studies of initial states of ordering suitable for the evaluation of interaction parameters.

In [A14] ordering processes in the Ni–Al–Cr–X quaternary systems ( $X=Co, Mo, W$ ) were simulated using a Monte Carlo technique. The Ising Hamiltonian was used to express the configurational energy of the system. Pair interactions were introduced by means of phenomenological Lennard–Jones potentials [27]. The interactions up to the third coordination sphere were taken into account. The ordering process itself was realized by

direct atomic pair exchanges (Kawasaki dynamics) [38]. The value of an average lattice parameter was readjusted periodically during the calculation to minimize the total energy. The atomic structure of a model crystal after 10,000 Monte Carlo steps was shown to contain ordered domains of several phases depending on the nominal composition. Evolution paths of individual SRO parameters were correlated with formation of various ordered phases.

In [A15] an improved method of quantitative analysis of simulated structures of multicomponent Ni-base alloys with fcc lattice is proposed. It makes use of the substitutional behaviour of alloying elements deduced from the evolution of SRO parameters, it accounts for phase boundaries between ordered and disordered phase and checks for the elemental mass balance. By this way a multicomponent atomic configuration can be pre-processed and transformed to the binary data structure suitable for further cluster analysis [39]. Computer code was written and successfully tested on multicomponent Ni–Al–Cr–Co–Re–W alloys with  $\gamma+\gamma'$  structure.

Ni–Al–Cr–Co–Re–W alloys were studied in detail in [A16], where several approaches mentioned above were integrated: quantitative evaluation of microstructure by means of AEM, thermodynamic modelling using Thermo-Calc software with modified commercial database TCNI and Monte Carlo simulations of ordering processes. Five annealing temperatures in the broad range from 1173 K to 1573 K were used; alloy compositions were close to the application range of advanced Ni-based superalloys. Six-component system was quite demanding for thermodynamic calculations, nevertheless the results of modelling correlated very well with experimental data. Besides pair Lennard–Jones potentials used for Monte Carlo simulations so far, also cohesive energies of tetrahedral atomic clusters were calculated *ab initio* using software Wien2K [40]. The course of ordering starting from random distribution was traced by evolution of SRO parameters. By comparison of selected curves it was possible in some cases to make a conclusion about the substitutional behaviour of the alloying elements: e. g. Re resides preferentially in Al sublattice of ordered  $\gamma'$  phase. Regarding the energy changes it is apparent that the most dramatic changes occur at the very beginning of the ordering (during the first 10 Monte Carlo steps). This is the effect of atoms rearrangement and forming the ordered clusters. The slow energy decrease in the later stages is caused by domain coarsening. It eventually stops only after forming a single ordered domain in the

whole modelled block. Comparing volume fraction of phases and their chemical composition, Monte Carlo simulation gives correct preference of atomic species for either  $\gamma$  or  $\gamma'$  phase. However, while the results of thermodynamic modelling agree quite well with experimental data, Monte Carlo simulations generally exaggerate the composition differences between the two phases. Namely, the content of Cr, Co, Al and W is lower in  $\gamma'$  and higher in  $\gamma$  compared to the other two methods. It indicates that the quality of potentials used in Monte Carlo simulations still might be worked on to reach the better agreement with reality. Another point is the limitation of the model used for atomistic simulation. Calculation of broader dataset of cohesion energies for larger clusters (octahedrons) would probably further improve the applicability of atomistic simulations for phase diagram calculations.

[A17] focuses on the relation between the degree of ordering in a multicomponent Ni-based alloy and its response to straining in elastic range. Monte Carlo simulation with Lennard–Jones pair potentials was used, with account for relaxation of local atomic positions by molecular dynamics calculations. Redistribution of alloying elements in course of phase separation leads to the formation of elastically soft ordered phase coexisting with comparatively tougher disordered one. Straining computer experiments and calculations show, that the bulk modulus undergoes comparatively large changes at the beginning of ordering process, i.e. due to local atomic rearrangement without forming well defined ordered domains. Orientation dependent Poisson ratios reveal high degree of anisotropy: only small changes ( $\leq 2\%$ ) caused by ordering are detected for straining along cube edge [001] and along cube diagonal [111], lateral relaxation in close packed (111) planes being smaller than that in (100) planes. However, ordering substantially influences the Poisson ratio while straining the materials along [110] direction. With only two-fold symmetry of (110) planes with close packed atomic lines along  $[-110]$ , the relaxation of lateral dimensions takes place predominantly along [001], where atoms are at spacing of second nearest neighbours.

The importance of taking into account the relaxation of local atomic positions in ordering and straining atomistic simulations is discussed and demonstrated in [A18]. The changes of configuration energy and lattice parameter caused by ordering are obviously dominant in the early stage of ordering starting from the random configuration. However, the changes due to local relaxations of atomic positions are also not negligible. The mean

shift of an atom from its node in the rigid lattice is about 1% of the lattice parameter in later stages of ordering. This value is higher for disordered structures and it also slightly increases in the deformed state. Taking into account the local relaxations in course of MC simulation is straightforward and makes the model more realistic. On the other hand it goes along with the dramatic slowing down of the program run, despite writing the most critical procedures in assembler. The crucial test for the new program was the simulation of structure changes under applied stress. The rigid lattice model certainly could not reproduce the directional coarsening (rafting) observed often experimentally in stressed single crystal Ni-base superalloys [41]. We started the simulation from the characteristic structure of aligned  $\gamma'$  cubes separated by narrow channels of phase  $\gamma$ . Tensile deformation was applied to the model crystal along [100] direction and 200 MCS were done with account for local relaxations at each exchange. Compositional profiles along low-index directions show convincingly that channels perpendicular to the applied load remain stable whereas the other channels start to dissolve. This is (given the crystallographic orientation, the mismatch of the lattice parameters of both phases and the sign of deformation) exactly what is observed experimentally during high temperature creep of superalloys. It means that the atomistic model, even if using quite simple pair potentials, can successfully reproduce the rafting effects.

### ***Microstructure and creep properties of advanced chromium steels [A19–A23]***

The microstructure–creep property relationship of 9–12%Cr steels based on a detailed quantification of observed microstructural features is the main topic of papers [A19–A22]. The study of complex systems of laboratory welds of dissimilar steels by means of AEM [A23] is successfully complemented by advanced kinetic modelling.

In [A19] we report the results of microstructural assessment of modified P91 steel after long term creep at 873 and at 923 K. Two main microstructural features characteristic of TMFS, namely subgrains and secondary phase particles are investigated separately by means of TEM techniques and computer image analysis. Four secondary phases are fully identified.  $M_{23}C_6$ , Laves phase and fine precipitates of Nb-rich and V-rich carbonitrides are present at both creep temperatures. Large nitride plates of so called Z-phase (Cr(Nb,V)N with tetragonal structure [31]) were only detected at 923 K. Although, Z-phase has been observed in austenitic steels [15], to our knowledge, the formation of Z-phase at 923 K

within the ferritic matrix of P91 is reported in [A19] for the first time. The particle coarsening upon ageing is accelerated under creep condition. The separate contribution of stress free ageing and stress under creep condition on particle coarsening is quantitatively determined: linear stress dependence of the effective activation energy of particle coarsening was deduced. The subgrain size is the microstructural parameter most directly connected with material creep properties. The smooth increase of subgrain size resulting from stress free ageing is strongly accelerated by applied stress. The mean subgrain area increases more than twice during creep under 165 MPa. Comparing the effect of applied stress on individual structure features, it has much stronger influence on subgrain structure than on particles. The stress results in larger mean particle diameter in crept specimens compared to head parts, but in the series of three samples crept under stress  $\sigma_1 < \sigma_2 < \sigma_3$  for time  $t_1 > t_2 > t_3$  (all three combinations resulting in a similar level of the total strain), the importance of time is still prevalent. On the other hand even at shortest time of creep exposition the highest stress results in the highest increase of the subgrain area.

A similar study was conducted in [A20] on P91 steel produced by Vítkovice Steel. The investigation of a microstructural evolution of P91 TMFS during creep at 873 K has shown that the high creep strength of the material is due the coexistence of subgrains and precipitates, the latter acting as subgrain boundary stabiliser. The microstructure evolution consists in a growth of subgrain size and a change of subgrain shape towards more equiaxed one. This process, connected with a removal of substructure hardening of the material, is retarded by the influence of dispersed phases that originate from the process of tempering and are subject to further evolution in the course of the creep and of the annealing process. The smooth increase of subgrain size resulting from stress free ageing is strongly accelerated by the applied stress. The particle coarsening upon ageing is accelerated under creep conditions. Contrary to the subgrain size, the evolution of particle mean size is not monotonic: the initial increase is followed by final decrease. This fact suggests the idea of new particles generation at the beginning of creep life, which may be attributed to the precipitation of new MX and M<sub>2</sub>X fine particles in the subgrain interiors.

A co-operation with another research group with long term background in TMFS investigation resulted in deeper analysis of microstructural data [A21]. It was found that the variation of the subgrain size with strain conforms to an exponential change from the initial to the stress dependent steady-state value. Analysis of the size distributions of



precipitated particles confirmed the previous result that in P91 there is a superposition of growth of particles with the dynamic precipitation of new particles. Under some simplifying assumptions we succeeded in separation of integral particle size distributions into two main ‘families’. From the distributions the numerical fractions of two types of particles, i.e. a predominating population of  $M_{23}C_6$  carbides and a population of fine particles representing mostly carbonitrides of MX type, and their sizes could be deduced. The variation of the creep rate with strain is in qualitative agreement with these microstructural changes.

Physical models used in the prediction of microstructure–creep property relationship in creep-resistant steels are discussed in [A22]. Detailed microstructural investigation of new chromium martensitic TAF 650 steel of the 9–12%CrMoV steel class was done to explain the marked decrease of its creep strength after long-term creep exposure. It is shown that dramatic deterioration of creep properties occurs by the formation of Cr-, Nb- and V-rich modified Z-phase after long-term creep exposure at the expense of the fine (Nb,V)X particles responsible for the stabilization of lath martensitic microstructure and the retardation of mobile dislocations. The synergetic effect of Z-phase precipitation and tungsten depletion of solid solution due to  $Fe_2W$  Laves phase formation could be the reason for the sigmoidal shape of the creep strength curves of TAF 650 steel during long term creep exposure.

Various kinds of CrMoV steels are universally employed in the fabrication of components for fossil fired power plants. Thus welds of dissimilar steels (typically welds of low-alloy ferritic steels and modified 9–12% Cr steels) cannot be avoided and their microstructural stability could be decisive for power plant life expectancy. Complex systems of dissimilar laboratory ‘welds’ of bainitic T25 and modified martensitic P91 steels were studied in [A23]. Both steels were nitrided prior to welding and then annealed under protective atmosphere. Fast diffusion of interstitials (C, N) during annealing resulted in formation of depleted/enriched zones and forming various phases in the vicinity of T25+N | P91+N interface. Carbon and nitrogen redistribution measurement was complemented with microhardness measurement and with detailed microstructural analysis aimed at the phase profiles and chemical composition of coexisting carbides and carbonitrides in particular regions of the weld joint. Results of experimental work were compared with the thermodynamic and kinetic modeling using the DICTRA software. The

simulation and experimental results correlated very well and they enabled understanding the processes taking place in the diffusion-affected zone of the studied weld joint under different temperature conditions. It was shown that the simulation method can offer reliable outputs applicable for the evaluation of long-term microstructural stability of weldments at high temperatures.

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