FRONTIERS IN MATERIALS SCIENCE

Contributors | **Y. Ustinovshikov et al.**

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List of Abbreviations

CDF	Cumulative distribution function
AFM	Atomic force microscopy
BCC	Body-centered cubic
EISC	Electrolyte with internal source of the current
FCC	Face-centered cubic
FFT	Fast Fourier transformation
FEA	Finite element analysis
ISE	Indentation size effect
MS	Mosaic structure
NPL	National Physical Laboratory
PC	Polycarbonate
PDF	Probability density function
RVE	Representative volume element
SEM	Scanning electron microscopy
SPM	Scanning probe microscopy
SMAT	Surface mechanical attrition treatment
TEM	Transmission electron microscope
VTMS	Vinyltrimethoxysilane
XRD	X-ray diffraction

List of Contributors

Y. Ustinovshikov
Ural Division of Russian Academy of Sciences, Physical-Technical Institute, Izhevsk, Russia

Kurbangali B. Tynyshtykbaev
Institute of Physics and Technology, Almaty, Kazakhstan

Talant Aitmukan
Institute of Physics and Technology, Almaty, Kazakhstan

Ainur T. Issova
Institute of Physics and Technology, Almaty, Kazakhstan

Bagdat A. Rakhymetov
Institute of Physics and Technology, Almaty, Kazakhstan

Mukhtar A. Yeleuov
Institute of Physics and Technology, Almaty, Kazakhstan

Serekbol Zh
Institute of Physics and Technology, Almaty, Kazakhstan

Tokmoldin
Institute of Physics and Technology, Almaty, Kazakhstan

Li Ma
National Institute of Standards and Technology, USA

Lyle Levine
National Institute of Standards and Technology, USA

Ron Dixson
National Institute of Standards and Technology, USA

Douglas Smith
National Institute of Standards and Technology, USA

David Bahr
Washington State University, USA

Jaroslav Menčík

University of Pardubice,, Czech Republic
Jiří Němeček
Czech Technical University in Prague, Faculty of Civil Engineering, Department of Mechanics, Czech Republic

Hongwei Zhao
Jilin University, China

Hu Huang
Jilin University, China

Zunqiang Fan
Jilin University, China

Zhaojun Yang
Jilin University, China

Zhichao Ma
Jilin University, China

L. Zhang
National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki,, Japan

T. Ohmura
National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki,, Japan

K. Tsuzaki
National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki,, Japan
Graduate School of Pure and Applied Sciences, University of Tsukuba, Ibaraki, Japan

Bruno A. Latella
Commonwealth Science and Industrial Research Organisation, WA,, Australia

Michael V. Swain
Biomaterials Science, Faculty of Dentistry, University of Sydney, NSW,, Australia

Michel Ignat
Physics Department, School of Engineering, University of Chile, Beauchef, Santiago, Chile

Bruno B. Lopes
São Paulo State University, Brazil

Rita C.C. Rangel
São Paulo State University, Brazil

César A. Antonio
São Paulo State University, Brazil

Steven F. Durrant
São Paulo State University, Brazil

Nilson C. Cruz
São Paulo State University, Brazil

Elidiane C. Rangel
São Paulo State University, Brazil

Preface

Materials science is the branch of science dedicated to the study of materials. The text *Frontiers in Materials Science* provides up-to-date knowledge and the latest scientific concepts and technological developments in the processing, characterization, testing, mechanics, modeling and applications of a broad range of advanced materials. A new paradigm for metallic alloys in materials science has been focused in first chapter. Self-organizing processes in semiconductor materials science on the example of nanostructuring of por-Si have been presented in second chapter. The aim of third chapter is to state the challenges and limitations for extracting the initial plastic yield stress from nanoindentation with the spherical indenter tip assumption. Fourth chapter provides an overview of sources of uncertainties and errors in instrumented testing. Nanoindentation based analysis of heterogeneous structural materials has been proposed in fifth chapter. In sixth chapter, a novel and miniaturization *in situ* indentation device has been presented. In seventh chapter, the application of nanoindentation technique in the martensitic structures (lath martensite and lenticular martensite) has been introduced. In eighth chapter, nanoindentation and tensile testing are surveyed as tools to characterize film properties, fracture behavior, and adhesion to the underlying substrate of a variety of model hybrid films. Last chapter describes an investigation of the mechanical and tribological properties of silicon containing organic coatings deposited by plasma enhanced chemical vapor deposition from hexamethyldisiloxane, HMDSO, and oxygen mixtures.

Contents

Chapter 1

A NEW PARADIGM FOR METALLIC ALLOYS IN MATERIALS SCIENCE

Y. Ustinovshikov

Ural Division of Russian Academy of Sciences, Physical-Technical Institute, Izhevsk, Russia

ABSTRACT

In the article, taking into account the phase transition "ordering-phase separation" discovered in alloys, new concepts about the diffusion phase transformations in alloys are formulated: chemical interaction between dissimilar atoms exists always in all alloys and at any temperature of heating; alloys offer a surprising and not previously known property of changing the sign of the chemical interaction between dissimilar atoms at a change of the temperature or composition of alloys; diffusion processes occurring in alloys at different temperatures depend on the sign and the absolute magnitude of the energy of the chemical interaction between dissimilar atoms. All these three concepts are analyzed in detail, by the example of Ni-based and Co-based binary alloys using experimental results obtained by transmission electron microscopy. It is shown, on these ideas, how to carry out heat treatment of alloys more rationally, what principles should underpinned in the base of the construction of phase diagrams, how the microstructures of ordering and phase separation affect some properties of alloys.

INTRODUCTION

The existing ideas about the microstructure of metallic alloys were formed as far back as the first half of the twentieth century. They were based on experiments being carried out on liquid molecular solutions, which showed that the solubility of salt in water increased with increasing temperature. Although the nature of the intermolecular interactions in aqueous solutions was very different from the nature of the atomic interactions in metallic solid

solutions, they believed that if the kinetics of precipitation of crystals of excess phase from the aqueous solution and the kinetics of precipitation of particles of a new phase from the metallic solid solution were similar, then the mechanism of these processes should be one and the same. This was how such concepts as the solubility of atoms of one component in the lattice of the other, direct dependence of solubility on temperature, the supersaturated solid solution, etc., were taken from the theory of aqueous solutions appeared in the theory of alloys. They believed that the solubility at some temperature depended mainly on the ratio of the sizes of the solvent and the solute atoms. At the same time, they believed that chemical interactions between dissimilar atoms in solid solutions began to appear only when the atoms of the solute were involved in formation of particles of a new phase. Up to this moment, as they were believed, the chemical interactions between dissimilar atoms did not manifest themselves. They considered the disordered solid solution to be the initial phase, supposing that at high temperatures it was the equilibrium phase, in which the component atoms were chaotically distributed over the lattice sites (substitutional alloys) and interstices (interstitial alloys) [1] . At a decrease of the temperature, when the atomic interaction potential became substantially larger than the thermal energy, the mutual arrangement of component atoms in the solid solution was determined from the condition of the minimum free energy of the alloy [1] and an order-disorder phase transition began in it. It was considered that the physical reason for ordering was an elastic interaction between the component atoms constituting the solid solution [1] .

This very principle was used in the construction of equilibrium phase diagrams: in them, in overwhelming majority of cases, regions of solid solutions were shown at high temperatures, and two-phase regions at low temperatures. In heat treatment practice, a two-stage scheme "high-temperature quenching + tempering (aging)" was mainly used, which presupposed that before getting a desired microstructure of the alloy, it was necessary to form the microstructure of a disordered solid solution, i.e., to quench the alloy in water from a high temperature. All these ideas, formed about 100 years ago, when modern methods of investigation of the crystal structure of alloys did not yet exist, flourish in Materials Science until now, still virtually intact.

Experimental studies of the crystal structure of alloys conducted later with the help of X-ray diffraction (XRD), seemed to have fully confirmed these views. Indeed, when this method was applied to alloys quenched from high temperatures, no other phases besides the solid solution were found. On the basis of these data, they came to the conclusion that at high temperatures, the microstructure of alloys was a disordered solid solution, which fully coincided with the thesis that the solubility of one component in the lattice of the other rose with temperature.

However in the sixties-seventies of the XX century, when the method of transmission electron microscopy (TEM) became widely used in the study of the microstructure of alloys, many authors were surprised to find that the microstructure of many alloys, quenched from the region of solid solutions, was two-phase and contained either particles of a new phase in the solid solution or modulations of the composition. Examples that have become classic are alloys of the systems Ni-Mo [2] , Fe-Be [3] , Al-Zn [4] , Cu-Be [5] , Nb-Zr [6] and many others, which, according to phase diagrams, at high temperatures, had regions of the solid solution. Detection of such two-phase microstructures was sometimes attributed to the fact that the regions of the solid solution in the phase diagrams had not been determined accurately enough [6] . In most cases, however, they agreed in the opinion, that the decomposition of alloys proceeding via the spinodal mechanism, occurred during the very process of quenching, i.e., a very short period of time, comparable with the time of cooling the alloy in water. The last point was explained by the fact that during spinodal decomposition, the stage of critical nuclei formation was absent [2] -[5] . This explanation contradicts both Cahn's theory of spinodal decomposition (Cahn considered spinodal decomposition as a diffusion process) and experimentally determined magnitudes of diffusion coefficients, which are by four orders of magnitude lower than it is necessary for the formation of new phase particles to occur during cooling of the alloy in water.

Not to become a prisoner of these "singularities" of quenching, we must recollect how existing now phase diagrams were constructed. The times when the X-ray diffraction analysis was considered to be almost the only direct method allowing determining the phase composition of alloys in this or that point of the phase diagram passed long ago but phase diagrams constructed with the help of the method at that time, continue to be a general aid for researchers. However, as far back as his time, Guinier pointed out that XRD was unable to identify second-phase particles with sizes smaller than the regions of coherent X-ray scattering [7]. This meant that all highly dispersed phases, which precipitate in alloys of these or those systems could not be registered by the XRD method and, therefore, were absent in existing equilibrium phase diagrams of these systems. In its turn, the latter circumstance could be interpreted as the fact that the solid-solution regions in the phase diagrams are not solid-solution regions as such, but two-phase regions. In this connection, the main role of a tool to be used for determining the phase composition of alloys in this or that point of the phase diagram should be given to a local method of research— transmission electron microscopy. As it was noted, in studies conducted with this method, it had been found that phase composition of many alloys in fact did not correspond to the composition of the regions shown in existing phase diagrams.

The conclusion that the solid-solution regions in equilibrium phase diagrams are in fact two-phase regions agrees with the well-known axiom of thermodynamics that in nature all solutions are non-ideal and have either positive or negative deviations from Raoult's law. This can lead to decomposition of such solutions at the higher temperatures of heating also. If the regions in the phase diagram, which are now referred to as regions of solid solutions are in fact two-phase regions, then quenching in water from such a region will also lead to fixation of a two-phase structure, not a solid solution at all.

As is well known, ideal solutions are not normally found in nature and, therefore, one should expect that any solid solution, in any alloy, at temperatures sufficient for diffusion of species over long distances, is bound to decompose (Solutions close to ideal may be observed only at very high dilution). However, in all known equilibrium phase diagrams, the areas of the solid solution are considered as an equilibrium phase. The sign of the ordering energy was usually determined by the method of measuring the partial pressure of the vapors of components at temperatures close to the melting point. Since at a decrease of the temperature this pressure abruptly drops, and, beginning with certain temperatures, it is impossible to measure it, then it was tacitly assumed that the sign of the ordering energy determined at very high temperatures remains the same at lower temperatures as well. This gave birth to the idea that each binary system is characterized by its own sign of the ordering energy, which is constant for this system at any temperature.

Thus, the existing conceptual views about these or those processes occurring in alloys constantly come into conflict with experiment. The situation in this area of knowledge began to change only when it had been proved that the chemical interactions between component atoms exist always, in all alloys and at any temperature (even in the liquid state), that alloys have a surprising and not previously known property of changing the sign of the chemical interaction between the dissimilar atoms at a change in the temperature of heating (sometimes at a change in the concentration of the alloy). In other words, our understanding of the nature of alloys began to change only when the phase transition "ordering-phase separation" was experimentally discovered [8] . This transition occurs at a temperature specific for each system, at which the sign of the chemical interaction between atoms of A and B is reversed. Earlier it was considered that each binary system had its own sign (plus or minus) of the chemical interaction energy, which was constant for this system at any temperature. Now, when the transition "ordering-phase separation" in alloys has been discovered, this idea is being revised. Today, it is clear that in every system, the sign of the chemical interaction energy can change at a change in the temperature, sometimes more than once. At first, the transition occurs

at the level of changes in the electronic structure of the alloy, as evidenced by a change in the shape of the valence bands of the X-ray photoelectron spectra, determined by the method of XPS [9] [10] . The change of the sign of the chemical interaction between dissimilar atoms changes the direction of diffusion between them to the opposite one, which affects a change in the type of microstructures [11] [12] . It has been shown experimentally that atoms of any one component can participate in the formation of a chemical compound with atoms of another component only if the sign of their chemical interaction is negative [9] [10] . If the sign of the chemical interaction energy between the dissimilar atoms is positive, then there takes place a process of phase separation of an alloy into clusters (grains) consisting of atoms of any one sort, which in conventional phase diagrams is commonly presented as formation of eutectics (eutectoids). Such a transition from one type of the chemical interaction (attraction between dissimilar atoms) to another type (repulsion between them) naturally passes through the point, where the energy of the chemical interaction is zero, i.e. where the microstructure of a disordered solid solution is to be formed [13] . Therefore, the discovery in 1996, of the phase transition "ordering-phase separation" [8] , occurring (as it turned out later) in alloys of a large number of systems, allowed to overcome many of these contradictions, allowed to reach a consensus with thermodynamics, and also allowed to correct our concepts in accordance with experimental results. It is these issues that the present article addresses to.

THE HISTORY OF THE DISCOVERY OF THE PHASE TRANSITION "ORDERING-PHASE SEPARATION"

Alloys of the Fe-Cr System

In thermodynamics, it is assumed that if the sign of the deviations from Raoult's law has been determined at any single range of the temperatures, this sign is preserved at all other heat treatment temperatures of the alloy. In alloys of the Fe-Cr system, positive deviations from Raoult's law were found at high (1040°C - 1400°C) temperatures by the vapor-pressure method [14] . However, at temperatures of 440°C - 830°C, a chemical compound (σ-phase) was detected in alloys of Fe-Cr system, though, as is generally known, its formation is possible only at negative deviations from ideality. At the same time, according to reference book on phase diagrams [15] , phase separation structures were found not only at high temperatures (1040°C - 1400°C) but at temperatures below 550°C as well. Such contradictions existing in the phase diagram of Fe-Cr, made the authors [8] set themselves the following questions: Why does the chemical compound-σ-phase form in Fe-Cr alloys at positive

deviations from ideality? Why do positive deviations from Raoult's law occur at high temperatures, whereas phase separation structures are found only at low (550°C and below) temperatures? What is the sign of the chemical interactions in the temperature range of 440°C - 550°C, which is marked in the phase diagram as belonging to both the regions: phase separation and ordering? To answer these questions and resolve the contradictions, the authors [16] [17] conducted a detailed structural study of five binary alloys containing 10% to 50% chromium (the rest is iron) over a wide temperature range (up to 1400°C).

Electron microscopy studies of Fe-Cr alloys, quenched in water from temperatures of 1200°C - 1400°C, led to unexpected results. The microstructure of the studied alloys after such quenching was not a solid solution at all. Figure 1 shows microstructures (a) and the electron diffraction pattern (b) of the $Fe_{50}Cr_{50}$ alloy after quenching in water from 1200°C. Two types of particles are detected in Figure 1(a): 1) coarse particles along the crystallographic directions of the matrix and 2) small disperse particles, which are randomly located in the rest of the matrix. The bright fields surrounding the coarse particles (Figure 1(a)) testify that the latter are formed at the expense of the dissolution of disperse particles. The electron diffraction pattern taken from a coarse particle inFigure 1(a) shows satellites near the fundamental reflections (Figure 1(b)). Such an electron diffraction pattern may be interpreted as obtained from two solid solutions with different lattice parameters—depleted (bright fields) and enriched in chrome (dark precipitates).

The first attempt to verify experimental results indicating the existence of high-temperature phase separation in Fe-Cr alloys was made using TEM [18] . After water quenching from 1200°C, the Fe-45% Cr alloy had the same microstructure that is shown in Figure 1(a). However, the authors [18] believed that such a microstructure could be the result of any processes other than high-temperature phase separation. They classified the precipitates presented in Figure 1(a) as "foreign" phases, namely, as chromium nitrides CrN. They thought that when heat treated in low vacuum (heating in quartz ampoules) as in Refs. [8] [16] [17] , iron-chromium alloys were saturated with air nitrogen to concentrations of the order of 1 at% [18] . Even if we agree with the authors [18] that Fe-Cr specimens sealed in evacuated quartz ampoules can be saturated with nitrogen to a concentration of 1 at% at 1200°C, then we should admit that this saturation will lead to formation of nitrides (CrN), in the amount of no more than 1 vol.%. It undoubtedly contradictsFigure 1(a), in which the volume fraction of dark precipitates is about 50%.

The second attempt was made when the $Fe_{51}Cr_{49}$ alloy quenched from the temperatures of 900°C - 1185°C was investigated [19] One should bear in mind that this range of temperatures is somewhat below the interval of phase

separation (1200°C - 1400°C). Using the Mossbauer spectroscopy method, the authors [19] expected to observe that the partial gamma-resonance peak corresponding to pure iron would grow with an increase of alloy decomposition. However, their expectations did not come true. Based on the above fact, they concluded that high-temperature phase separation did not occur in Fe-Cr alloys. Indeed, using TEM, phase separation microstructures are not found after heat treatment at 900°C - 1185°C, but they are always found after heat treatment in the temperature range of 1200°C - 1400°C [16] [17] .
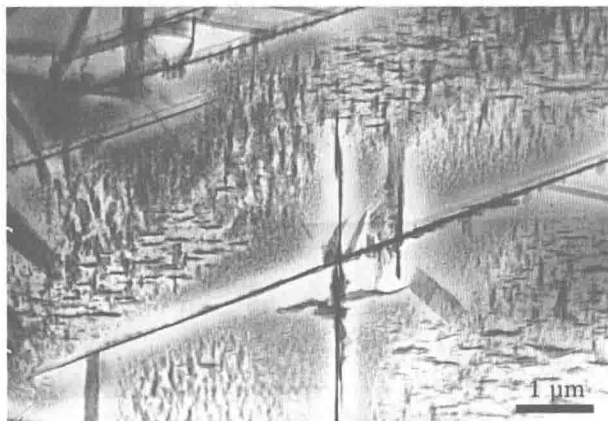
(a)

(b)

Figure 1: $Fe_{50}Cr_{50}$ alloy .Water-quenching from 1200°C: (a) Bright-field micrographs; (b) Electron diffraction pattern taken from the coarse particle in (a).

According to the accepted phase diagram of Fe-Cr [15] , in the temperature range of 440°C - 830°C, there is a region of the FeCr chemical compound

(σ-phase). The formation of such a phase is possible only when the deviations from ideality have a negative sign. Based on this, we can conclude that in this temperature range the sign of the chemical interaction between the atoms of Fe and Cr is negative. Such a conclusion automatically implies the existence of a phase transition, which, at a temperature decrease from the range of 1200°C - 1400°C to 440°C - 830°C, should result in the change of the sign of the chemical interaction between the atoms of the components.

However, as far as σ-phase precipitation is concerned, the conclusion that the sign of the deviations from ideality at such a precipitation will necessarily be negative, does not find understanding with some authors. This is due to the fact that in Fe-Cr alloys, the σ-phase is formed only in a thin surface layer of the specimen [20] [21] . Based on these data, Turchi, Reinhard and Stocks [22] , referring to the positive deviations from Raoult's law revealed at high temperatures [14] , believed that these deviations should exist in this system at all other temperatures. They concluded that the sign of the deviations from ideality in the Fe-Cr system depends on who wins in the competition between the "macroscopic" tendency to phase separation and the "local chemical" tendency to ordering. They reasoned that each of the tendencies is characteristic of a certain coordination sphere; phase separation, for example, is characteristic of the first coordination sphere, whereas ordering is characteristic of all other coordination spheres. Moreover, they considered the formation of the σ-phase at 440°C - 830°C not as the result of the tendency to ordering, but as one of "the phenomena pertaining to surfaces (reconstruction, segregation, etc.)" [22] . The σ-phase is really formed on free surfaces [20] [21] ; however, it does not mean that it is not a chemical compound [23] , and, therefore, its formation is not pre-determined by the tendency to ordering. Ohnuma et al. [24] thought that the presence of the σ-phase in the Fe-Cr system, in which positive deviations from Raoult's law were observed at high temperatures, was due to the magnetic contribution to the Gibbs energy. They supposed that the interaction between chemical and magnetic ordering influenced both the magnetic properties of alloys and the thermodynamics and kinetics of atomic ordering. However, they did not find any convincing experimental evidences of such influence in the literature.

The X-ray diffraction patterns obtained from the surface of the $Fe_{50}Cr_{50}$ alloy specimen after heat treatment at different temperatures and exposures indicate the formation of a dense continues layer of the σ-phase on the surface. The maximum depth of the surface layer of the σ-phase reaches 0.4 mm [16] . The σ-phase was not found in the internal volume of the specimen even after prolonged heat treatment [16] [22] . It was considered [22] that the reasons for this were high elastic stresses that arise when the bcc lattice of the solid