Grain Boundary Diffusion and Grain Boundary Segregation

Editors:

B. Bokstein and N. Balandina

SCITEC PUBLICATIONS

DiBoS-97

Grain Boundary Diffusion and Grain Boundary Segregation

Proceedings of the International Workshop
DiBoS-97
held in Moscow. Russia, May 1997

Editors:

B. Bokstein and N. Balandina

Scitec Publications Ltd
Member of the Trans Tech Group of Publishers

ISBN 3-908450-31-4

Volume 156 of
Defect and Diffusion Forum
ISSN 1012-0386
(Pt. A of Diffusion and Defect Data - Solid State Data (ISSN 0377-6883))

***Distributed** in the Americas by*

Trans Tech Publications Inc.
Post Box 699, May Street
Enfield, New Hampshire 03748
USA

Phone: (603) 632-7377
Fax: (603) 632-5611
e-mail: ttp@ttp.net
Web: http://www.ttp.net

and worldwide by

Scitec Publications Ltd
Brandrain 6
CH-8707 Uetikon- Zuerich
Switzerland

Fax: +41 (1) 922 10 33
e-mail: scitec@scitec.ch
Web: http://www.scitec.ch

Printed in the United Kingdom
by Hobbs the Printers Ltd,
Totton, Hampshire SO40 3WX

International Workshop on
Grain Boundary Diffusion and Grain Boundary Segregation
DiBoS-97

International Advisory Board

Organizing Committee

Co-Organizers and Sponors of DiBoS-97

Russian Ministry of General and Professional Education
Scientific Board on Metal Physics and Engineering, RAS
Russian Foundation of Basic Researches
Moscow Steel and Alloys Institute
Solid State Physics Institute, RAS

PREFACE

We are very happy to welcome our colleagues at DiBoS-97. They were very busy but they found the time to visit Moscow, to participate our workshop. In our opinion there were two great pleasures: a pleasure of our work, the work of our mind, our hands, our heart, our fantasy and - secondly - a pleasure of our relations with our families, friends and colleagues-friends.

When we began to think about this workshop, to consult with our colleagues (in August 1996, during DIMAT-96) we supposed that its content would have been very narrow: only one sufficiently unclear topic: interrelation between grain boundary diffusion (GBD) and grain boundary segregation (GBS). Everybody can see in these Proceedings that we have not succeeded. Both processes - GBD and GBS - were presented in combination as well as separately. Some other topics were presented: diffusion in triple junctions, diffusion, segregation and phase formation in thin films, electromigration, grain boundary wetting, diffusion under stresses, computer simulation, etc.

It is normal. It seems likely that it is impossible in principle to separate the single problem. It is growing with neighboring problems and they need to be discussed together. Everything is connected in our science as in our life.

Discussions, talking were an important part of the workshop. They were time consuming. All discussions - after talks and two round table discussions (Diffusion in Intermetallics and Grain Boundary Wetting and Liquid Grooving with Chr. Herzig and E. Glickman as a moderators) - were tape-recorded and decoded. It was a long and hard work. The readers can read it and estimate the result of this work. We had no possibility to show it to all participants of discussions (but only to the moderators) and to agree the text with them. So the responsibility for the possible inaccuracies will be on us.

The workshop was organized at Moscow State Steel and Alloys Institute - MS&AI (Technological University). Many people and organizations helped us. You can find their names in the front pages. We are grateful to all of them, especially to the Russian Foundation for Basic Researches and to the Rector of MS&AI, Professor Yu.S.Karabasov. MS&AI may be named University of Materials Science. It was established in 1918. Now it is one of the best centers of materials education and science in Russia. More than 6000 students are learning in MS&AI and more than 600 Professors train them not only in materials science but in metallurgy, engineering, economics, computer science, ecology, etc. Undergraduate and postgraduate students take the courses in metals and ceramics, ferrous and nonferrous materials, semiconductors and superconductors, superhard and superplastic, amorphous and nanocrystalline materials, etc.

More than 50 peoples from 14 countries have participated in our workshop. They did not only worked, but they had time to visit Kremlin, Tretyakov's Gallery, some Moscow sightseeings. A special lady program was organized.

Science and education become more and more international. The boundaries are no more barriers, they transform themselves to the paths of the fast diffusion of ideas and their accumulation. We hope that proceedings of DiBoS-97 will assist the new step in solution of this universal problem.

B. Bokstein

N. Balandina

Rector of Moscow Steel and Alloys Institute Prof. Yu.S. Karabasov

and Chairman of DiBoS-97 Prof. B.S.Bokstein

LIST OF PARTICIPANTS

1. A.N.Aleshin — Solid State Physics Institute, Chernogolovka, Moscow District, 142432, Russia
e-mail:aleshin@issp.ac.ru

2. N.M.Amirkhanov — Ufa State Avia-Technical University,
K.Marks str., 12, 450001, Ufa, Russia
Tel:7(3472) 235244
Fax:7(3472) 233422
e-mail:tantal@ippm.rb.ru

3. I.V.Apykhtina — Physical Chemistry Department, Steel and Alloys Institute,
Leninsky Pr. 4, 117936 Moscow, Russia
Tel:7(095) 2304664

4. N.B.Balandina — Physical Chemistry Department, Steel and Alloys Institute,
Leninsky Pr. 4, 117936 Moscow, Russia
Tel:7 (095) 2304667
Fax:7 (095) 2308007
e-mail: ilb@phch.misa.ac.ru

5. D.L.Beke — Department of Solid State Physics
L.Kossuth University, 4010 Debrecen, P.O. Box 2, Hungary
Tel: 36(52) 316073
Fax:36(52) 316073
e-mail:dlbeke@tigris.kltc.hu

6. V.V.Belousov — Physical Chemistry Department, Steel and Alloys Institute,
Leninsky Pr. 4, 117936 Moscow, Russia
Fax:7(095) 2308007

7. J.Bernardini — Laboratoire de Métallurgie, unité mixte CNRS,
Université Aix-Marseille III (UMR 6518),
Faculté des Sciences et Techniques de St. Jérôme, F-13397
Marseille Cedex 20, France
Tel: 33(4) 91288566
Fax:33(4) 91288556

8. B.S.Bokstein — Physical Chemistry Department, Steel and Alloys Institute,
Leninsky Pr. 4, 117936 Moscow, Russia
Tel: 7(095) 230 44 66
Fax:7(095) 2308007
e-mail:bokst@phch.misa.ac.ru

9. F.Cabane — Laboratoire de Métallurgie, unité mixte CNRS,
Université Aix-Marseille III (UMR 6518),
Faculté des Sciences et Techniques de St. Jérôme, F-13397
Marseille Cedex 20, France
Tel:33(4) 91288555
Fax:33(4) 91288556
e-mail:francoise.cabane@edifis.u-3mrs.fr

10. J.Cabane | Laboratoire de Métallurgie, unité mixte CNRS,
Université Aix-Marseille III (UMR 6518),
Faculté des Sciences et Techniques de St. Jérôme, F-13397
Marseille Cedex 20, France
Tel:33(4) 91288555
Fax:33(4) 91288556

11. S.V.Divinski | Institute for Metal Physics, NAS of Ukraine
36 Vernadsky str., Kiev-142, 252680, Ukraine
Tel:38(044) 4449584
Fax:38(044) 4442561
e-mail:divin@d24.imp.kiev.ua

12. V.V.Dyakin | Institute of Metal Physics
Ural Branch, RAS, 620219, Yekaterinburg, Russia

13. P.Gas | Laboratoire de Métallurgie, unité mixte CNRS,
Université Aix-Marseille III (UMR 6518),
Faculté des Sciences et Techniques de St. Jérôme, F-13397
Marseille Cedex 20, France
Tel:33(4) 91288556
Fax:33(4) 91288756
e-mail:patrick.gas@EDIFIS.U-3mrs.fr

14. E.E.Glickman | Faculty of Engineering,
Electrical Engineering-Physical Electronics Department,
Tel Aviv University, Ramat Aviv, P.O. Box 39040,
Tel Aviv 69978, Israel
Tel:972(3) 6409985
Fax:972(3) 6423508
e-mail:evgeny@eng.tau.ac.il

15. V.Gostomelski | Siemens AG, 81377 München, Fürstenriederstrasse 303, Germany
Tel:49(89) 7195144

16. D.Gupta | IBM Research Division, T.J. Watson Research Center
Yorktown Heights, NY 10598, USA
Tel:1(914) 9451665
Fax:1(914) 9452141
e-mail:GUPTA@WATSON.IBM.COM

17. Chr.Herzig | Institut für Metallforschung, Universitat Münster,
Wilhelm-Klemm str. 10, D-48149 Münster, Germany
Tel:49(251) 8333573
Fax:49(251) 8338346
e-mail:herzig @NWZ.UNI-MUENSTER.DE

18. F.Inoko | Department of Mechanical Engineering,
The University of Tokushima, 2-1 Minamijosanjima-cho,
Tokushima 770, Japan
Tel:81(8) 6567361
Fax:81(8) 6556589
e-mail:inoko@me.tokushima-u.2c.jp

19. V.A Ivanov — Physical Chemistry Department, Steel and Alloys Institute, Leninsky Pr. 4, 117936 Moscow, Russia

20. V.N.Kaigorodov — Institute of Metal Physics
Ural Branch, RAS, 620219, Yekaterinburg, Russia
Tel:7(3432) 499074
e-mail:diffus@ifm.e-burg.su

21. L.M.Klinger — Department of Materials Engineering
Technion, Haifa 32000, Israel
Tel:972(4) 8294595
Fax:972(4) 321978
e-mail:mtrkli@vmsa.techion.ac.il

22. P.A.Korzhavy — Moscow Steel and Alloys Institute,
Leninsky Pr. 4, 117936 Moscow, Russia

23. M.I.Kurkin — Institute of Metal Physics
Ural Branch, RAS, 620219, Yekaterinburg, Russia
Tel:7(3432) 444312
e-mail:diffus@ifm.e-burg.su

24. P.V.Kurkin — Moscow Steel and Alloys Institute,
Leninsky Pr. 4, 117936 Moscow, Russia
Tel:7(095) 2304667
e-mail:kurkin@phch.misa.ac.ru

25. R.Le Gall — Laboratoire de Génie des Matériaux, ISITEM, BP 90604, 44306 Nantes, France
Tel:33(2) 40683129
Fax:33(2)40683199
e-mail:legall@isitem.unir.nantes.fr

26. W. Lojkowski — High Pressure Research Centre, Polish Academy of Sciences
Sokolowska 29, 01-142 Warsaw, Poland
Tel:48(22) 6324302
Fax:48(22) 6324218
e-mail:wl@iris.unipress.waw.pl

27. A.Yu.Lozovoi — Moscow Steel and Alloys Institute,
Leninsky Pr. 4, 117936 Moscow, Russia
Tel:7(095) 9550062
e-mail:lozovoi@trf.misa.ac.ru

28. Maksimovich L.P. — Kiev Politechnical Institute
Department of Metal Physics
Prospect Peremogy 37, 252056, Kiev-56, Ukraine
Tel:38(044) 2161038

29. D.E.Mekki — Université de Annaba, Institut de Physique
BP12, 23000 Annaba, Algerie
Tel:213(8) 863693
Fax:213(8) 872436

30. Yu.A.Minaev — Physical Chemistry Department, Steel and Alloys Institute, Leninsky Pr. 4, 117936 Moscow, Russia
Tel:7(095) 2304664
Fax:7(095) 2902320

31. Yu.S.Nechaev — Institute of Metallurgy RAS, Leninsky Pr., 49, 117333 Moscow, Russia
Tel:7(095) 1358691

32. A.S.Ostrovsky — Physical Chemistry Department, Steel and Alloys Institute, Leninsky Pr. 4, 117936 Moscow, Russia
Tel:7(095) 2304667
e-mail:ostr@ phch.misa.ac.ru

33. S.J.Pennycook — Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6030, USA
Tel:1(423) 5745504
Fax:1(423) 5744143
e-mail: pyk@ornl.gov

34. A.L.Peteline — Physical Chemistry Department, Steel and Alloys Institute, Leninsky Pr. 4, 117936 Moscow, Russia
Tel:7(095) 2304667
e-mail:sasha@ phch.misa.ac.ru

35. S.A.Peteline — Physical Chemistry Department, Steel and Alloys Institute, Leninsky Pr. 4, 117936 Moscow, Russia

36. J.Philibert — Laboratoire de Métallurgie structurale
Université de Paris-Sud, 91405 Orsay Cedex, France
Tel:33(1) 39732937
Fax:33(1) 39732937
e-mail:jean.philibert@metal.u-psud.fr

37. Z.N.Portnaya — Institute of Metallurgy RAS, Leninsky Pr., 49, 117333 Moskow, Russia
Tel:7(095) 1358691

38. S.I.Prokofjev — Solid State Physics Institute, Chernogolovka, Moscow District, 142432, Russia
Fax: 7(8257) 64111
e-mail: prokof@issp.ac.ru

39. S.L.Sass — Department of Materials Science and Engineering
Cornell University, Ithaca, NY 14853, USA
Tel:1(607) 2555239
Fax:1(607)2552365
e-mail:sls7@cornell.edu

40. J.-C. Shin — Pohang Research Institute of Industrial Science and Technology
790-330 POSTECH APT#5-1504 JIKOK-DONG 756 PPOHANG, KOREA
Tel:82(562) 2796004
Fax82(562) 2796199
e-mail:jcshin@RISTNet.rist.re.Kr:

41. L.S.Shvindlerman — Laboratory of Grain Boundaries
Solid State Physics Institute, Chernogolovka, Moscow District,
142432, Russia
Tel:7(095) 9132324

42. B.B.Straumal — Max-Planck-Institut für Metallforschung and Institut für
Metallkunde, Seestr. 75, D-70174 Stuttgart, Germany
e-mail:straumal@vaxww1.mpi-stuttgart.mpg.de

43. A.N.Timofeev — Institute of Metal Physics
Ural Branch, RAS, 620219, Yekaterinburg, Russia
Tel:7(3432) 499040
e-mail:diffus@ifm.e-burg.su

44. Zs.Tokei — Laboratoire de Métallurgie, unité mixte CNRS,
Université Aix-Marseille III (UMR 6518),
Faculté des Sciences et Techniques de St. Jérôme, F-13397
Marseille Cedex 20, France
Fax:33(4) 91288756

45. I.Vavra — Institute of Elektrical Engineering, Slovak Akademy of Sciences,
Dubravska cesta 9, SK-842 39 Bratislava, Slovak Republic
Tel:42(7) 375806
Fax:42(7) 375816
e-mail:elekvavr@savba.sk

46. Yu.Kh.Vekilov — Moscow Steel and Alloys Institute,
Leninsky Pr. 4, 117936 Moscow, Russia
Tel:7(095) 2304506

Table of Contents

Defect and Diffusion Forum Vol. 156 (1998) pp. 1-8

Grain Boundary Diffusion and Oxidation Processes

J. Philibert

Métallurgie Structurale, Université de Paris-Sud, F-91405 Orsay Cedex, France

Keywords: Oxidation, Parabolic Rate Constant, Nernst Equation, Wagner Equation, Grain Boundary Diffusion, Oxides, Non-Stoichiometry, Alumina, Chromia

Abstract
Oxidation of metals and alloys is controlled by diffusion and interface reaction processes. The role of grain boundary diffusion and segregation is discussed. The microstructure of the scales is complex and as it plays a critical role in diffusion and oxidation kinetics, several diffusion paths are involved, so that the relative importance of grain boundaries in the overall process remains questionnable.

Introduction

Oxidation processes play an important role in metallurgy, as a corrosion mechanism, or as a protection method. Modelling of this reaction is required for industrial needs. Oxidation belongs to the general category of Reactive Diffusion. Such processes are controlled by :

— atomic transport of chemical species, including point defects, by diffusion through the reaction product(s) : intermetallic compound, oxide, sulphide... Diffusion (sometimes gas permeation) proceeds through the lattice as well as along grain boundaries and short circuits (pores, cracks, fissures or crevices,...). Diffusion on surfaces and at metal/oxide interface are other paths of transport.

-— interface reactions, since the reaction product is growing either at the inner (metal/oxide) or the outer (oxide/atmosphere) interface.

Transport by diffusion and reaction occur in series, so that the kinetics of the whole process (the thickness x or the mass of the reaction product) follow a parabolic law

$$x^2/k_p + x/k_l = t - t_o \quad \text{eq.1}$$

If only one species is diffusing, the parabolic rate constant k_p is proportional to some coefficient of diffusion of this species and the linear constant k_l measures the interface reaction rate. When two species (e.g. metal and oxygen) contribute to the process, the parabolic rate constant is a function of the respective diffusion coefficients *and* the interface reaction rate constants.

Moreover internal stresses can play an important role on the overall kinetics. These stresses arise from epitaxial coherency, volume differences (the so-called Pilling & Bedworth ratio), the concentration dependence of the lattice parameter.

Grain boundary diffusion

The microstructure of the reaction product(s) cannot be neglected, mainly at relatively low temperatures. In the simplest case the microstructure consists of columnar grains. Diffusion occurs through the lattice and along the grain boundaries, i.e. it follows two parallel paths. The overall flux - the effective flux— is just the weighted sum of the lattice flux J and the GB flux J', according to the relation:

$$J_{eff} = (1 - f)\, J + f\, J' \quad \text{eq.2}$$

where f is the volume fraction of GB sites, or with the conventional GB thickness δ :

$f = 3\ \delta/d$ eq.3

with the average grain size d. The formula remains valid for equiaxed grains as demonstrated on a simplified model by Yarmolenko [1]. However, in many cases the microstructure is duplex, with an outer columnar zone and an inner equiaxed one, so that two different grain sizes are to be considered. Some migration of GBs is also possible , which makes the application of the above formula dubious.

Parabolic rate constant

Let us consider the formation of a compound controlled by the diffusion of one species M. According to Nernst formula, the parabolic rate constant is given by :

$k_p = \langle c \rangle\ \Omega\ D^*\ (\Delta G/kT)$ eq.4

$\langle c \rangle$ is the average M concentration of the inter metallic, Ω the molar volume per atom M, D^* the M self diffusion coefficient and ΔG the Gibbs free energy of the compound per M atom. For a stoichiometric compound, $\langle c \rangle\ \Omega = 1$. This formula generalises easily when both species contribute to the process. For instance in the case of $CoSi_2$ growth in a Co/Si couple :

$k_p = [\ D^*_{Co} + (1/2)\ D^*_{Si}\ ]\ (\Delta G/RT\ )$ eq.5

The self diffusion coefficients are effective D's in order to take in account lattice and GB diffusion. In order to calculate k_p , there is only one free parameter : the grain size d. This system was studied by Barge and Gas [2] : they measured the lattice and GB self diffusion of both species in $CoSi_2$ (actually they used Ge as a tracer for Si). The calculated results agree well with two series of measurements , on thin films (around 400-500°C) and bulk specimens (900-1000°C) with respective grain sizes of 10 nm and 20 mm.

For extended solutions — oxides namely — eq.4 remains a fair approximation, but it is recommended to use Wagner's equation, that, thanks to an integral from the inner to the outer interface, takes in account the concentration dependence of the coefficients of self-diffusion.

GRAIN BOUNDARY DIFFUSION IN NON-STOICHIOMETRIC OXIDES

The situation is not that clear in oxides, because of the particular microstructure of scales and the lack of reliable data on GB diffusion. As compared to metals, many questions remain open concerning D'/D and Q'/Q ratios, GB width, GB segregation , GB diffusion mechanism...

To the author's knowledge, the diffusion mechanism in oxides has been identified in a very few cases. In Cu_2O, the same $p(O_2)$ dependence was found for lattice and GB oxygen self-diffusion, a result which favours a neutral oxygen interstitial (power approximately 1/2 of $p(O_2)$)[3].

In the case of NiO , there were some suggestions of identical mechanisms for Ni self-diffusion [4-5], but the disagreement between different sets of data must keep us away from a definite conclusion [9]. The GB Ni diffusion was found to be several order of magnitude lower in bicrystals than in sintered specimens or in NiO scales [6-7]. The last material does not well lend itself to reliable measurements, not only because of the surface roughness, but also because of many crevices and/or connected pores : nice diffusion profiles were obtained without any thermal treatment just after deposition of an aqueous solution of the tracer (fig.1) [7]. Autoradiographs evidenced the continuity of tracer penetration along some channels up to depths of more than 50 mm [7]. Such channels have been recently observed by transmission electron microscopy on NiO scales grown on a Ni-1% Cr alloys oxidised at 1000 °C [8]. A critical review was published by M. Déchamps and F. Barbier [9]. In these conditions the agreement claimed by Atkinson between diffusion data and oxidation rate constant between 300 and 900 °C is questionable. A more recent and detailed study discards GB diffusion as an important factor in the kinetics of nickel oxidation [10] : absence of a correlation between k_p and the grain size, absence of GB segregation of the added elements (Ca or Sr) that slow down the kinetics. Surface diffusion (outer and pore surfaces) should play an important role at temperatures lower than 900 °C where the scales present some roughness and porosity.

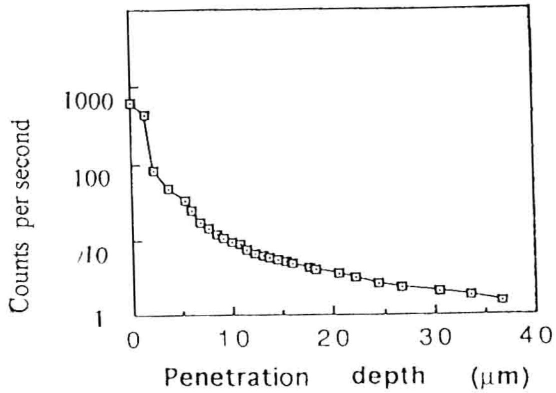

Fig. 1 - ^{63}Ni penetration profile measured on NiO scales just after tracer deposition, without annealing treatment [7]

Our former questions about GB diffusion has now to be completed as follows :

• Do the grain boundaries in oxide scales and bulk specimens (e.g. bicrystals) have identical atomic structure and chemistry and therefore equal coefficients of diffusion ?

• Is there a segregation of some elements (impurities or alloying elements) in scale grain boundaries and how does it modify the diffusivities ?

• What is the meaning of penetration profiles obtained on scales, and what kind of diffusion coefficient can be determined from such experimental curves ?

IONIC OXIDES : AL_2O_3 AND CR_2O_3

These oxides raise specific difficulties for several reasons :

— the very low coefficients of diffusion to be measured (departure from stoichiometry is negligible in Al_2O_3) and the very large range of oxygen activities in which measurements are required (in scales oxygen activity varies from about 10^5 or 10^4 Pa down to 10^{-25} Pa at the inner interface).

—because of the low or negligible departure from stoichiometric composition, impurities dominate the nature of defects, so that the studied regime is the extrinsic one, certainly in GB's (because of the segregation) and probably also in the lattice.

—finally experiments on scales are difficult due to the rough geometry of the surface and the microstructure defects that vary largely depending on the temperature, the atmosphere and the metal composition : in such conditions the meaning of the penetration curves is still a matter of debate.

Grain Boundary Diffusion

Some progress has been made in this respect in the course of recent studies on Al_2O_3 and Cr_2O_3 oxidation of alumina and chromia former alloys. A thorough investigation of diffusion was undertaken a few years ago, with a double aim :

• compare diffusion data of both cation and anion obtained on "good" specimens and on scales,

• introduce these data in Wagner's formula and compare with the parabolic rate constants measured on alloys forming chromia and alumina scales.

There are a lot of disagreement on the published data in these materials and different interpretations are given [9]. Open questions concern :1) the relative values of the metal and oxygen diffusivities, in the lattice and along GB's , 2) the role of the segregation of added elements on these diffusivities, with a possible inversion of their relative values.

In the course of these new measurements the value of the GB activation energy came as a surprise : in Al_2O_3 single crystals, a trail on oxygen penetration profiles — measured with a SIMS — was interpreted as due to diffusion along dislocation networks [11]. From the corresponding D's an activation energy Q' *larger* than the Q for lattice diffusion was determined. A similar trend was observed on Cr_2O_3 for both elements [12]. A possible explanation could be found in the segregation of some impurity. The sapphire crystals were contaminated by silicon (about 100 ppm).