THERMODYNAMICS AND PHASE TRANSFORMATIONS

THE SELECTED WORKS OF MATS HILLERT

Scientific Editors : John Ågren, Yves Bréchet, Christopher Hutchinson, Jean Philibert, Gary Purdy

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Scientific Editors:

John Ågren, KTH, Stockholm
Yves Bréchet, INPG, Grenoble
Christopher Hutchinson, Monash University, Melbourne
Jean Philibert, Université Paris Sud
Gary Purdy, Mc Master University, Hamilton

EDP SCIENCES

17, avenue du Hoggar
Parc d'activités de Courtabœuf, BP 112
91944 Les Ulis Cedex A, France

Illustration de couverture : Divergent pearlite in Fe-C-Mn.
Photo Chris Hutchinson.

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A short biography of Mats Hillert

Mats Hillert was born in Gothenburg, Sweden on 28th of November 1924. He was the youngest of the three sons of Anna and Hildding Hillert. As they were very lively the young Hillert brothers were well known in the local neighbourhood.

Mats grow up in Gothenburg and went to high school at Realläroverket, later named Vasa Läroverk. He earned his B.S. in chemical engineering at Chalmers Technical University in Gothenburg in 1947 with a bachelor's thesis on diffusion of radioactive Ag in Ag_2HgJ_4 under the supervision of Karl Erik Zimen, a former student of Carl Wagner whose oxidation theory connected electrical conductivity with diffusion.

After his military service Mats started his research career as a scientist at the Swedish Institute for Metals Research in 1948. Mats was assigned to look into the use of internal friction but was left with a high degree of freedom. On the side he could thus start to work on the use of radioactive isotopes to study the distribution of various elements in metals. He also contacted Gudmund Borelius, who was professor of physics at Royal Institute of Technology, KTH, wanting to register for graduate studies. He was told that he first had to take the undergraduate courses for physicists that were not included in the chemistry curriculum. For a few years he spent most of his spare time on those studies, which was possible because his girl friend still went to school in Gothenburg. At work Mats came in contact with Sten and Helfrid Modin, two Swedish metallographers and early pioneers in the use of electron microscopy to study the microstructure of steels. Sten Modin inspired Mats to add yet another undergraduate course at KTH and thus participated in the lectures of Axel Hultgren who was professor in physical metallurgy at the nearby KTH. Mats says that his life-long deep interest in phase transformations and thermodynamics started with a scientific argument after one of these lectures. Mats felt that Hultgren's reasoning on the effect of Ni on carburization of steel was thermodynamically incorrect and told Hultgren his opinion. Hultgren, the grand old man of Swedish physical metallurgy, became impressed of this young scientist who showed such a remarkable intuition in thermodynamics and suggested that one should resolve the issue by an experiment. Of course the experiment showed that Mats was correct and it eventually led to a joint publication of Hultgren and Hillert in 1953. At that time Hultgren had developed the concept of paraequilibrium, which also concerned the effect of alloying elements on transformations in steel. This contact with Hultgren resulted in a number of manuscripts centred around the concept of paraequilibrium and isoactivity lines in phase diagrams and their applications to transformations in steels. Mats assignment on internal friction was simply forgotten by that time.

Eric Rudberg, who was the director of the Swedish Institute for Metals Research, encouraged Mats to apply for a grant from the Sweden-America Foundation. With his wife since 1951, Gerd, he thus moved to Boston and MIT in 1953 and started his studies under the supervision of the legendary teacher Morris Cohen. At MIT he also met Carl Wagner who taught thermodynamics and gave Mats valuable advice on some of his manuscript, which had all been rejected. He was then able to publish some, some were published later but one was not published until the present volume. His topic for the Master's thesis was an experimental study of the thermodynamics of the Ag-Al system. Inspired by one of his fellow students, Larry Kaufman, who was modelling the thermodynamic properties of the Fe-Ni system, Mats applied a similar model to the Ag-Al system and that work was the starting point for his life-long interest in the thermodynamics of alloys. Mainly by the efforts of Kaufman, that procedure has since developed into what is now called CALPHAD. From another fellow student, Eric Kula, he learned about the effect of fine inclusions on grain growth, which inspired him to start developing a mathematical theory for grain growth. After a Master's degree Mats was invited to stay for the Doctorate and while spending a semester to prepare for the qualifying exam he could not help worrying about the strange behaviour of Au-Ni alloys that one of his room mates, Ervin Underwood, was studying. He connected it with the phenomenon later called spinodal decomposition, which was the main research interest of Borelius at KTH. It lead him to developing a theory for that phenomenon. Fortunately, this topic fitted into one of Cohen's research programs and Mats could finish his degree after adding an experimental study of spinodal decomposition. He left MIT with a Doctor of Science in 1956 and returned to the Swedish Institute of Metal Research in Stockholm. A coincidence deserves mention. Another of Mats' room mates was John Hilliard who brought a copy of his thesis with him when he left for GE in Schenectady in 1956. There he met John Cahn and together they completed the theory of spinodal decomposition and thus opened up a new field.

During the Mats' stay in the US professor Hultgren had retired and Curt Amberg, a well known industrial researcher and an expert in heat treating, had been appointed as the new professor in physical metallurgy. However, he became seriously ill and passed away 1959. Mats was then appointed as a temporary replacement and started teaching in physical metallurgy. The coming years he published a large number of papers, some of them ground breaking, and when the position as professor in physical metallurgy was announced, Mats applied and was appointed full professor 1961. He remained at that position until his retirement 30 years later.

As a professor Mats taught several generations of Swedish metallurgists the most up to date knowledge in the fundamentals of physical metallurgy. He launched the graduate teaching on the subject and acted as the main supervisor of more than 30 doctors which are now active in Swedish industry or academia worldwide.

Mats Hillert is a fellow of the Royal Swedish Academy of Engineering Sciences and the Royal Swedish Academy of Sciences. He is also a fellow of ASM International and a Fellow of Met. Soc. AIME (TMS). His list of awards is impressive and includes, to mention only a few, R.F. Mehl medalist (Met. Soc. AIME), Bakhuis Roozeboom Gold Medal (Royal Acad. Netherland), Acta Metallurgica Gold Medal, Murakami Gold Medal (Japan Inst. Metals, Japan), Björkén award (Uppsala University, Sweden), Hume-Rothery Award (TMS, USA).

Mats Hillert at the TMS fall meeting in 1991.

Foreword

For over half a century, Mats Hillert has contributed greatly to the science of materials. He is widely known and respected as an innovator and an educator, a scientist with an enormous breadth of interest and depth of insight. In acknowledgment of his many contributions, a conference was held in Stockholm in December 2004 to mark his eightieth birthday.

This volume was conceived prior to, and publicly announced during the conference. The difficult choice of twenty-four papers from a publication list of more than three hundred was carried out in consultation with Mats. He also suggested or approved the scientists who would be invited to write a brief introduction to each paper.

A brief reading of the topics of the selected papers and their introductions reveals something of their range and depth. Several early selections (for example, those on "The Role of Interfacial Energy during Solid State Phase Transformations", and "A Solid-Solution Model for Inhomogeneous Systems") contained seminal material that established Mats as a leading figure in the study of phase transformations in solids. Others established his presence in the areas of solidification and computational thermodynamics. A review of his full publication list shows that he has consistently built upon those early foundational papers, and maintained a dominant position in those fields. Although many of his contributions have been of a theoretical nature, he has always maintained a close contact with experiment, and indeed, he has designed numerous critical experiments.

This volume represents a judicious sampling of Mats Hillert's extensive body of work; it is necessarily incomplete, but it is hoped and expected that it will prove useful to students of materials science and engineering at all levels, and that it will inspire the further study and appreciation of his many contributions.

The editors are very grateful to Arcelor Research for their financial support and to EDPSciences who have lavished much care in the production of this volume.

John ÅGREN
Yves BRECHET
Christopher HUTCHINSON
Jean PHILIBERT
Gary PURDY

List of contributors

Hubert I. Aaronson[1],
Department of Materials Science and Engineering
Carnegie Mellon University, USA

John Ågren
Department of Materials Science
KTH (Royal Institute of Technology), Sweden

Michael J. Aziz
Division of Engineering and Applied Sciences,
Harvard University, USA

Yves Bréchet
Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques,
Institut National Polytechnique de Grenoble, France

John W. Cahn
Materials Science and Engineering Laboratory
NIST, USA

Masato Enomoto
Department of Materials Science,
Ibaraki University, Japan

Paul C. Fife
Department of Mathematics,
University of Utah, USA

Hasse Fredriksson
Professor in Casting of Metals
KTH (Royal Institute of Technology), Sweden

Ola Hunderi
NTNU
Trondheim, Norway

Christopher R. Hutchinson
Department of Materials Engineering,
Monash University, Australia

Gerhard Inden
Max-Planck-Institut für Eisenforschung
Düsseldorf, Germany

Larry Kaufman
Chair, CALPHAD Advisory Board

Jack S. Kirkaldy
Brockhouse Institute for Materials Research,
McMaster University, Canada

[1] Hubert Aaronson passed away on December 13, 2005.

Dmitri V. Malakhov
Department of Materials Science and Engineering
McMaster University, Canada

Thaddeus B. Massalski
Department of Materials Science and Engineering
Carnegie Mellon University, USA

John E. Morral
Department of Materials Science and Engineering
Ohio State University, USA

Jean Philibert
Université Paris-Sud
Orsay, France

Gary Purdy
Department of Materials Science and Engineering
McMaster University, Canada

Nils Ryum
NTNU
Trondheim, Norway

Peter W. Voorhees
Department of Materials Science and Engineering
Northwestern University, USA

Pavel Zieba
Institute of Metallurgy and Materials Science
Polish Academy of Sciences, Poland

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1 Introduction to “Nuclear Reaction Radiography”

published in *Nature* (1951)

Originality is a hallmark of Mats Hillert’s work. He was often the first to recognize a problem or formulate a solution to an existing problem. There is no better example of his being first than his short paper in Nature on Nuclear Reaction Radiography, in which he proposed a variation of autoradiography to determine the distribution of boron in steels. Instead of using the decay products of radioisotopes to mark a film, he demonstrated that alpha particles resulting from the transmutation of boron into lithium could be used to mark film and indicate the location of boron atoms.

The article was published in 1951, just four years after he graduated from Chalmers University with a B.S. in Chemical Engineering. Five years later he obtained a Ph.D. from M.I.T. His approach was referenced in the 1950’s in the biological [1] and chemical [2] literature from the 1950’s, but wasn’t referenced in metallurgical literature until Barbara Thompson’s article [3] appeared in 1960. Unfortunately the reference to his paper was omitted from much later work which focused on analyzing nuclear reaction autoradiography data and identifying both the location of boron in steel [4–6] and the mechanism of boron hardenability [7]. Instead the articles referred to Thompson’s paper as the earliest important reference. However, this oversight doesn’t change the fact that his article planted the seed from which the later work grew and flourished.

John E. Morral

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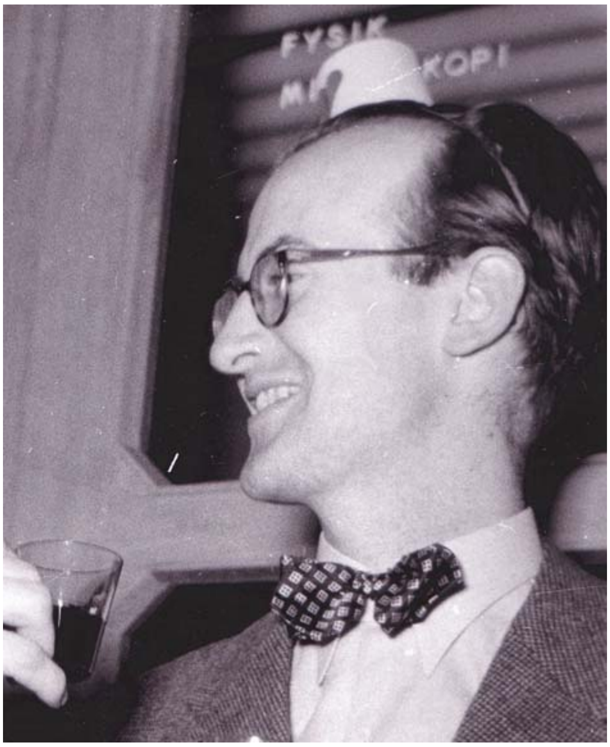


Mats Hillert in 1951.

Transcribed from Nature, vol. 168, (1951), pp 39,40

Nuclear Reaction Radiography

AUTORADIOGRAPHY has been employed for many years for the purpose of determining the distribution of an element in a given material. The essential requirement for the use of this method is that the element in question itself should emit a radiation which can be registered on a photographic film pressed against the surface of the sample. To make an element betray its presence in thins way, one provides a certain fraction of marked atoms by adding a small amount of radioactive isotopes of the same element.

I have investigated another method, which may be termed nuclear reaction radiography, since it makes use of the property of the non-radioactive element in question of reacting with an external particle radiation in such a way that a new radiation is born in the process, which is then registered on the photographic film. To use this method, the photographic film must be insensitive to the primary particle radiation used for exciting the reaction. This requirement would seem to restrict the species of available primary radiations at present to one kind, namely, neutrons. Another requirement is that the element to be detected should have a much higher probability of reacting with the primary radiation than other elements present in the material under investigation. This can be achieved in some cases by the choice of neutrons with suitable energy, making use of the fact that different reactions have different resonance energies. Finally, the radiation produced in the reaction must be of such a nature that it can be properly registered on the film.

Boron is one of those elements where the ordinary autoradiographic method fails, since no suitable radioisotope is available. Instead, conditions would seem to be favourable for the use of nuclear reaction radiography in this case. The reaction which suggests itself is:

$$ {}_5^{10}\mathrm{B} + {}_0^{1}n \rightarrow {}_3^{7}\mathrm{Li} + {}_2^{4}\alpha $$

For thermal energy neutrons, the cross-section has the very high value of 3,000 barns. The α-particle is emitted with an energy of 1.5 MeV., which is a very favourable value for photographic trace production. The range of these particles is about 5 μ in the emulsion, and in iron it is considerably less than this. Hence, the method should be capable of yielding very high resolution. I have investigated this method, using Kodak Autoradiographic plates. These photographic plates give very good resolution because (i), the emulsion is very fine grained, (ii) the emulsion can be stripped directly from the glass plate and mounted directly on the sample under investigation. A further advantage with this material is that the sensitivity to γ-radiation is very small, whereas the sensitivity to α-radiation is high.

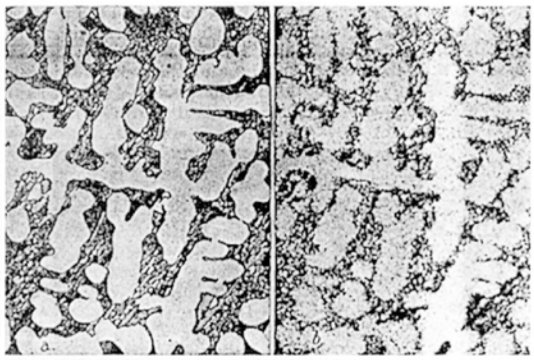
The method has been tested on an experimental alloy made up of 98 per cent iron and 1 per cent boron. A small sample of this was ground, polished and etched, and given a thin protective coating of collodion in order to keep the surface free from tarnish in the subsequent work (otherwise it will rust very readily). The collodion film was less than 1μ thick. The freshly stripped, wet emulsion was placed on top of this and was allowed to dry in position, which made it adhere firmly to the sample. The sample was then placed in a light-tight container, where it was irradiated for 16 min. with neutrons from a cyclotron. A block of lead, inserted between the sample and the cyclotron, served to reduce as much as possible the amount of γ-radiation reaching the emulsion. The sample was surrounded by paraffin wax in order to obtain a favourable proportion of thermal neutrons. After irradiation, the emulsion was developed and compared with the metal surface in an ordinary microscope. The results are illustrated by the accompanying reproductions. It is evident that the emulsion stripped form the sample reproduces the distribution of boron quite accurately, and that it is possible to work at quite considerable magnification.

I am grateful to the Nobel Institute for Physics in Stockholm, where Mr. S. Thulin kindly carried out the cyclotron irradiation, and to Mr. L. Erwall of the Division of Physical Chemistry at the Royal Institute of Technology, Stockholm, who placed the Kodak Autoradiographic plate material at my disposal; this emulsion undoubtedly played an important part in the success of the experiment.

MATS HILLERT

Swedish Institute for Metal Research,
Stockholm.

April 12.



(a) Photomicrograph of the metal surface. Light areas: iron; darker parts: eutectic of iron and Fe_2B. x 100

(b) Reaction radiograph of the same surface as that shown in (*a*). Dark spots are produced by α-particles, showing position of reacting atoms of boron. x 100

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