Summary Notes of the Workshop on the Effects of Alloying Elements on Gamma to Alpha Transformation in Steels, October 8th, 2000:

The workshop began at 8:00 a.m. in the Laclede Room of the Regal Riverfront Hotel, St. Louis, Missouri. The participants are listed in Appendix I, and the workshop agenda in Appendix II.

Mats Hillert welcomed those present, reviewing the background and objectives of the workshop as outlined in the invitation (Appendix III). The intention was to provide extensive opportunities for discussion, for the open exchange of ideas and for the eventual development of collaborative studies of these important and challenging problems. He underlined the need for joint activity, i.e. that we have to bundle our individual competences and work together to achieve real progress. In such collaborations a fast exchange of ideas and results is mandatory. (Mats noted that this might seem in conflict with the prevailing natural and healthy attitude, which places emphasis on competition rather than collaboration; in publications, each participant should make an effort to give due credit to group members for suggestions and ideas. After each workshop, there will be an open publication summarizing the meeting and mentioning the essential contributions from each of the participants.)

Hub Aaronson presented a detailed and comprehensive review of the experimental information available on kinetics and morphology of the products of diffusional transformation of austenite in alloy steels. He then focused on the system Fe-Mo-C, and on the various microstructures that occur within the region known as the "bay" in the TTT curves. Ferrite nucleation and growth were reviewed, with emphasis on the effects of ledge growth and solute drag on growth kinetics and morphology. He identified as key questions for study the spacing and heights of growth ledges, and the correlation between interfacial structure and chemistry. It was noted also that the precipitation of carbides will interfere with studies of ferrite growth, and that alloy compositions can be chosen so as to minimize this possibility as well as to stabilize the austenite phase to room temperature.

Mats Hillert offered a number of suggestions for the study of the kinetics of ferrite-austenite interfaces. He advocated beginning with an examination or re-examination of the kinetics of the massive transformation in pure iron and in binary substitutional alloys Fe-X. (This could be done indirectly by measuring thermal arrest temperatures at different cooling rates.) Next, by adding carbon, and thereby slowing the growth processes, a range of kinetic states could be accessed. He also suggested the use of carefully designed specimens containing composition gradients, either of carbon or of the alloying element. He further emphasized the value of using some microanalytical technique to measure the local carbon content at or close to the advancing alpha/gamma interface.

John Xgren then reviewed several existing theories of solute drag as they might apply to the growth of ferrite from austenite. Many similarities were pointed out, as well as several important distinctions. Many of the treatments reviewed were seen to be based implicitly on continuum diffusion models applied to the interface region. After correcting some minor details, these treatments are essentially identical and no conflict seems to exist. The SDLE (solute drag-like effect) proposed by Aaronson is also closely related. Finally Xgren drew attention to a modified sharp interface model presented by himself and Liu, in which the interface composition is described by a "representative" value which may be more physically plausible and which makes the computational handling much quicker. This model may be particularly useful in the future for considerations of interfacial properties which vary with position along the interface. Masato Enomoto then presented the results of recent modeling of the growth of ferrite in alloy steels. His kinetic equations include a first-order interaction of the two solutes C and X within the moving interphase boundary. A further approach to the modeling of the ternary transformation was briefly discussed by Ernst Kozeschnik.

The experimental measurement of solute concentrations at static and (interrupted) moving interfaces was reviewed by Gary Purdy, who spoke of current unpublished FEG-STEM measurements of Mo in Fe-C-Mo alloys (Fletcher, Garratt-Reed, Aaronson, Purdy, Reynolds and Smith) and of 3-D atom probe results on Nb accumulation at moving grain boundaries in Fe-Nb alloys (current work by Maruyama and Smith). Bill Reynolds then reviewed the basic principles of the atom probe and noted the difficulties in obtaining samples containing interfaces of interest. Suresh Babu then presented his atom-probe results on ferrite-cementite interfaces at different stages of tempering of alloy steels, which demonstrated a complete lack of partitioning of Si and Mn at early stages.

Gerhard Inden discussed the prediction of overall transformation kinetics for different alloy steels, pointing out the areas of disagreement between current models and experiment. Sybrand van der Zwaag then reviewed the extensive program of research at Delft, in which interfacial mobilities were inferred from the kinetics of transformation of binary Fe-X alloys, and then applied to the modeling of transformation kinetics in alloy steels. Mattias Militzer spoke of possible new directions for research in this area, noting the need for bringing fundamental approaches to the prediction of microstructure development.

In subsequent general discussion, it was clear that there is a widespread willingness to take part in collaborative research, and to share information. The question of availability of existing high-purity alloys was considered. Bill Reynolds and Suresh Babu offered to report on the amounts and compositions of alloys available. In terms of directions for research, there was a division of opinion concerning the advisability of focusing first on the kinetics of binary Fe-X systems. It appears that there is room for both approaches, one dealing with an extension of binary data to the ternary systems Fe-C-X, and a second aimed at the determination of interfacial chemistry and structure in ternary and higher order systems. A second meeting of those interested in pursuing experimental studies in this area was scheduled for the afternoon of Wednesday, October 11th. Several of the interested researchers were unable to stay for the second meeting, but communicated their interest and advice to the organizers separately. Their comments are taken into account in the following recommendations.

Recommendations:

1) *That an inventory of existing high purity iron-based alloys be established.* In this respect, several members of the workshop offered to provide lists of existing alloys, along with compositions and amounts where possible. Bill Reynolds will let us know details of the stock of alloys given in his care by Hub Aaronson, and Suresh Babu will contact Harry Bhadeshia with a request for information on the

availability of alloys of Fe, C, Mn and Si which allow the retention of some austenite, and in which carbide precipitation is suppressed.

2) *That a series of high-purity binary alloys be commissioned, based on the systems Fe-Mn, Fe-Ni, Fe-Cr and Fe-Si*. These alloys would then serve as the basis for studies of the fast transformations on cooling from austenite. They would also form the basis for ternary alloys with carbon, which would be prepared by gas carburizing the binaries to levels appropriate for specific experiments. The suggested alloys are (in mass %):

Fe-2, 4, and 7 % Ni,

Fe- 2, 4, and 7.8 % Cr (the last composition to be refined to represent the minimum in the gamma loop.)

Fe-1.5, 3 and 5 % Mn,

Fe- 1% Si and Fe-2 % Si,

Fe-2% Si + 3%Mn + .43%C. (the last to approximate the composition used by Bhadeshia and his associates, and to form part of a suite of alloys based on Fe-Mn, and Fe-Si.)

3) *That the following series of experiments be undertaken* (in addition to any others suggested by members of the community):

- *Measurements of equilibrium segregation of alloying elements to austenite/ferrite interfaces in binary Fe-X and ternary Fe-C-X alloys*. In light of discussions at the workshop, it seems that the most practical method for these measurements at this time relies on scanning areas containing the interfaces with an FEG-STEM. Atom probe instruments offer superb resolution but suffer from sampling problems; as the technique evolves, these instruments will undoubtedly become more applicable to these studies in the near future.

- *Measurements of dynamic segregation of alloying elements to moving (quenched) interfaces in the same systems.* Again, the FEG-STEM offers high promise for these measurements, as does the atom probe. Regarding the latter technique, a group at Rouen (supported by IRSID) is currently undertaking a series of atom probe experiments to evaluate Mn and C profiles near advancing ferrite-austenite interfaces; they should be invited to join the collaboration.

- *Measurements of the kinetics of ferrite-austenite interface migration in the above alloys.* Initially, these measurements would involve thermal analysis of fast-quenched binary alloys (Delft?) and the growth of Widmanstatten plates and grain boundary allotriomorphs in selected ternary and quaternary alloys. In certain cases the controlled decarburization of alloy steels would be used to establish overall rates of diffusional interface migration (McMaster). (Note: it may be possible to perform some of these studies “in situ”, provided that an appropriate hot-stage optical, thermionic emission, or scanning electron microscope can be found. Members of the workshop are asked to look into the availability of such an instrument.)

- *Studies of the correlation of local interfacial chemistry (at the highest possible resolution), with local interfacial structure*, with emphasis on compositions that retain austenite in the vicinity of the transformation interfaces.

4) *That a second meeting of the workshop be held in about one year's time, preferably just before the beginning of the academic year.* Gerhard Inden suggests that the next meeting might be held in Germany; he will look into this possibility.

Appendix I: List of Participants:

Christopher Hutchinson	U Virginia
Mats Hillert	KTH Stockholm
John Agren	KTH
Gerhard Inden	M.P.Dusseldorf
Hub Aaronson	CMU
Gary Purdy	McMaster
Hatem Zurob	McMaster
Bill Reynolds	Virginia
Yves Brechet	Grenoble
Suresh Babu	ORNL
John Vitek	ORNL
Masato Enomoto	Ibaraki
Tadashi Furuhara	Kyoto
Sam Allen	MIT
Sybrand van der Zwaag	Delft
Jian-Feng Nie	Monash
Matthias Militzer	UBC
Ernst Kozeschnik	Graz
Joakim Odquist	KTH
Malcolm Hall	Birmingham
Zi-Kui Liu	Penn State
Bob Hackenberg	U Virginia

Appendix II: Agenda, October 7th, 2000, St. Louis MO

8:00 Welcome and Introduction: Mats Hillert

8:15 Hub Aaronson: *The current state of knowledge about alloying element effects*
9:10 Discussion

9:30 Mats Hillert: *What information do we need on the formation of ferrite (bainite)?*
10:20 Discussion and coffee

11:00 John Ågren: *Current approaches to solute drag theory*
Masato Enomoto: *Modelling of solute drag in steels*

11:45 Discussion

12:00 Lunch

13:00 Gary Purdy: *Review of experimental methods*
Bill Reynolds: *Comments on atom probe methods*
Suresh Babu: *Atom probe results*

14:00 Gerhard Inden: *Materials inventory, recent studies with IRSID*
Zybrand van der Zwaag: *Current work at Delft*
Mattias Militzer: *Suggestions for future work*

15:00 Open Session: *Where do we go from here? Present plans and willingness to take part in collaborative efforts. Key areas for future study.*

16:00 Adjournment

Appendix III; The Original Proposal:

A Workshop on effect of alloying elements on the γ to α tranformation in steels

Background: The theoretical understanding of the effect of alloying elements on the γ>α transformation took a big step forward with Hultgren's introduction of the concepts of para and ortho 1947. The basis for a more refined understanding was laid by the treatments of solute drag in 1961 by Lücke et al. and by John Cahn. However, in spite of this firm basis and in spite of the impressive efforts over the years by a considerable number of researchers, we are still in doubt about important features. To some part this is understandable because the experimental technique of studying exactly where the solute atoms are, relative to the migrating phase interface, has been lacking. At last, this technique now seems to be available and Hub Aaronson is attempting to make several groups join forces in order finally to reach a real understanding.

Is there a need for further collaboration? We are enthusiastic about Hub's initiative and would like to take the opportunity to start a wider collaboration by emphasizing the kinetic aspects. We strongly feel that progress should have been much more rapid, had we been able to work closer together in the past. The literature is full of reports on various aspects of the effect of alloying elements and efforts to explain the results from some theoretical basis but it is striking how each piece of information or understanding is separated from the rest

1) by differences in technique, the kind of measurement, the choice of alloying additions, the purity of the alloys etc etc.

2) by difference in (scientific) language, largely depending on differences in the theoretical understanding

3) by a strong separation in time.

Our hope: It is possible that efficiency could be greatly improved:

1) by using a common stock of well defined alloys

2) by thoroughly discussing the planning of new experiments with the group of collaborators

3) by speedy transfer of new results, preferably well before publication, in the hope of evening out differences in opinion regarding how to interpret the results before going to the "general public"

4) by frequent discussions (workshops) in order to develop a common language, a common understanding and to stimulate the definition of new, hopefully "critical" experiments.

Definition of topic: The topic of the collaboration should be strictly defined. It should be limited to the γ->α transformation in Fe-C-X alloys, possibly including precipitation reactions that may occur in the "bay" and help explain the "bay" effect. It should concern interstitial free alloys as well as alloys with carbon or nitrogen. It would involve grain boundary allotriomorphs and Widmanstätten plates and it would involve the reactions behind plateaus I and II (defined in continuous cooling experiments) in the interstitial free alloys, i.e., it would involve massive and acicular growth. It would not involve martensitic transformations. It should not primarily be concerned with the complications that may arise when carbides form in bainite, except maybe in the case of the bay effect.

Organization: We propose that a workshop be organized in order to gather representatives from various groups that are known to have strong interest and expertise in the field. The workshop could be organized in the following parts.

1) Reviews of the theoretical understanding.

2) Reviews of the significant experimental information available, including old and new information.

3) Discussions in order to reach an agreement on what new information might be needed in order to put the understanding on a firmer basis.

4) Presentation of theoretical approaches and discussions on what could be improved.

5) Each group should inform about their present plans and their willingness to expand their activities if collaboration can be established.

6) Brain storming in the whole group and discussions in smaller groups in order to plan for future work and collaborations.

7) Presentations of results from discussions.

Future interactions: If the first workshop turns out well, then there should be frequent meetings in the future, at least once a year. Those meetings could gradually become more and more open but in the beginning it is essential to be a well defined group. From the start one may plan for a restricted length of time, say 5 years, because the hope is really to solve problems within a limited time.

Competition vs. Collaboration: It must be recognized that all participants are normal scientists who normally get their satisfaction from the credit earned by publicizing their work. Normally, there would thus be a hesitation to reveal to the collaborators (competitors) a bright idea about how to proceed. It is essential to eliminate that tendency as far as possible and to encourage an open exchange of ideas. In a smaller group this is usually accomplished by an agreement to co-author a future publication. In the larger group we now have in mind, that may not be practical. A possibility would be to publish a summary of the discussions at the workshop in such a way that a future publication by some of the participants can give credit to the group as a whole or some individual who is not a co-author. In order to be effective, this necessitates that the workshop publication is of the archival type. We can imagine that J Phase Equilibria could be interested. If not, maybe Canadian Metallurgical Quarterly or Scandinavian J. of Metallurgy would do.

Alloys: It is our hope that one of the participants in this project will be a strong organization that is able and willing to provide the whole project with the alloys needed. Furthermore, it would be a great advantage if that organization would be willing to keep the alloys in stock for some time after the project and to provide samples of the alloys to anybody who in the future would like to check, amend or continue the work of the project.

Quick exchange of results: In order to speed up the future work, it would be advantageous to distribute results as soon as possible, i.e., before a paper has been published and even before a manuscript has reached its final form. That could be done electronically but we don't propose an open web-site. Exchange by e-mail should be sufficient.

Mats Hillert
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