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Author
Morris, Jr., J.W.

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PHASE TRANSFORMATIONS, STABILITY AND MATERIALS INTERACTIONS

J. W. Morris, Jr., L. Brewer, J. R. Cost, and
P. Shewmon

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MATERIALS SCIENCES WORKSHOP ON

PHASE TRANSFORMATIONS, STABILITY AND MATERIALS INTERACTIONS

Held April 18 to 20, 1977 at Lawrence Berkeley Laboratory

Organizers

J. W. Morris, Jr., Lawrence Berkeley Laboratory
L. Brewer, Lawrence Berkeley Laboratory
J.R. Cost, ERDA, Division of Physical Research
P. Shewmon, The Ohio State University

Participants

H. Aaronson, Mich. Tech. Univ.
A. Ardell, UCLA
L. Brewer, LBL
J. Brophy, INCO
J. Cahn, NBS
I. Carmichael, U. C. Berkeley
R. Carpenter, ORNL
R. Coble, M.I.T.
J. Cost, ERDA
I. Cutler, Univ. of Utah
L. Darken, Penn. State Univ.
D. de Fontaine, UCLA
J. DeVan, ORNL
R. Dillon, Battelle NW
K. Drumheller, Battelle NW
J. Economy, IBM
J. Elliot, M.I.T.
A. Goldberg, LLL
L. Ianniello, ERDA
R. Jaffee, EPRI
B. Kear, Pratt and Whitney
D. Keefer, Idaho Nat'l Lab.
K. Kinsman, Ford Sci. Lab.
R. Landingham, LLL
R. McLean, ORNL
J.W. Morris, Jr. LBL
K. Natesan, ANL
F. Nolfi, ANL
W. Owen, M.I.T.
J. Phillips, Bell Labs.
R. Perkins, Lockheed Palo Alto
F. Pettit, Pratt and Whitney
R. Reed, NBS, Boulder
R. Richman, EPRI
A. Searcy, LBL
R. Sekerka, Carnegie-Mellon
R. Schwoebel, Sandia
D. Shannon, Battelle NW
P. Shewmon, Ohio State
D. Shirley, LBL
R. Staehle, Ohio State
R. Swendsen, BNL
D. Thomas, Westinghouse
G. Thomas, LBL
J. Verhoeven, Ames Lab.
D. Vermilyea, General Electric

I. WORKSHOP SCOPE AND PRIORITIES:

The materials sciences program workshop addressing basic research needs and priorities in the areas of Phase Transformations, Stability, and Materials Interactions was held at the Lawrence Berkeley Laboratory, April 18-20, 1977. The forty-two participants included representatives of ERDA laboratories, universities, and industrial research organizations. The participants spanned a range of research interests and competence from highly fundamental theory to applied materials development.

To consider the status of basic research and the choice of priorities for future research in the area of phase transformations, stability, and materials interactions the workshop was organized as follows. The first day was devoted to a survey of ERDA mission needs for research in the workshop area. For the remainder of the workshop the study groups were reorganized along technical lines. The reports and recommendations of both the ERDA mission and technical area study groups are included in the following. Highlights of the research recommendations may be summarized under three headings: Thermodynamics, Phase Transformations, and Corrosion and Environmental Interactions:

A. Thermodynamics: Virtually all participants in the workshop were deeply concerned by the current status of thermodynamic research and by the demise of the groups which had previously taken on the important task of providing critical compilations of thermodynamic data. The problem is made particularly acute by the increasing interest of ERDA mission groups in thermodynamically complex systems and non-equilibrium situations for which neither the theory nor the data are well developed. The workshop participants felt that the Division of Physical Research should move actively to revivify research in this important area. Four tasks were singled out for particular emphasis: (1) classical thermodynamics including high quality calorimetric measurements and equilibrium measurements of surface and interface properties; (2) thermodynamics of gaseous, liquid, and solid solutions emphasizing the interaction of theory and experiment and paying special attention to the complex solutions of interest to ERDA; (3) non-classical thermodynamics emphasizing new theoretical developments in irreversible processes and inhomogeneous materials; (4) critical evaluations and compilations of the relevant thermodynamic data.

B. Phase Transformations: The participants were on the whole enthusiastic about the status of research in this area. They felt that basic research in phase transformations has the momentum of a decade of significant accomplishment in problems ranging from fundamental theory and experiment to application in such exciting new areas as alloy design, glassy metals, and laser processing. Given the rapid current development of new theoretical tools, useful computer simulation techniques, and precise experimental devices for high resolution studies the participants felt that research in this area is entering a particularly productive period which, assuming the continuation of a reasonable level of support, should prove unusually fruitful in results of value both to fundamental science and to engineering practice. Specific areas for research emphasis include: (1) theoretical studies, particularly those at the interface between physics and materials science; (2) research on solidification and crystal growth with emphasis on fundamental interactions across interfaces, the control of structure and microstructure during solidification, and the technologically important problem of welding; (3) precipitation reactions in the solid state emphasizing the role of interfaces in defects in precipitation processes, the control of precipitation processes, and chemical stability during long time exposure to high temperature, to aggressive environments, or to radiation fields; (4) martensitic transformations in solids with particular emphasis on the nucleation of martensite and on the influence of mechanical deformation.

C. Corrosion and Environmental Attack: The current status of research on materials interactions is conditioned by the historical fact that this area has not received the basic research emphasis given other important scientific problems and by the trend for ERDA mission groups to establish a growing variety of relevant materials needs. As a result, while the participants were pleased at the recent rate of research progress, they emphasized that the current level of research in this area is not adequate to provide needed basic research support for the complex of ERDA needs. The Division of Physical Research should encourage a substantial growth in research on the related problems of corrosion and environmental attack including: (1) research on the environments of particular interest to ERDA considering species adsorption and scale formation of exposed materials surfaces and their influence in inhibiting chemical interactions; (2) the formation, integrity, and retention of natural protective films on engineering materials on exposure to aggressive environments including particularly the nature of flaws or imperfections which may act as short circuit diffusion paths allowing accelerated substrate attack; (3) modification of the substrate due to chemical interaction across the interface including the ingestion of deleterious species such as hydrogen, the leeching of useful alloying elements, and associated long term chemical and microstructural changes; (4) the development of protective coating schemes for engineering materials subjected to particularly severe environments including research on coating materials, deposition and adhesion, and interfacial integrity during long time exposure.

New ventures in fossil, geothermal, solar and advanced nuclear energy production will require major materials improvements and sophisticated handling of new chemistries. In the area of high temperatures stability and corrosion ERDA faces increasing problems with an inadequate technical base. In thermodynamic research and data compilation, the effort is shrinking at a time when growth is badly needed. In phase transformations research recent advances offer the opportunity for significant new contributions to energy science and technology.

II. STUDY GROUP REPORTS - ERDA MISSION NEEDS

II-1 Energy Conservation

Chairman: K. Kinsman

Members: L. Brewer, W. Owen, J. Economy, G. Thomas, R. Landingham, D. Vermilyea

This sector represents a collection of activity that is related in a general way by the intended result of direct energy savings. As a group, we have chosen to address only selected activities, those of which we are aware and that have program content relating to the topic of the workshop: phase transformation, stability and material interactions. Even so, the breadth of scientific issues encountered is large, reflecting the variety of engineering systems challenges.

Materials problems and basic research opportunities include metals, ceramics, and polymers. Research activity in the broad sense ought to be multidisciplinary. The consensus of the group was to emphasize the value (and expediency) of interaction among disciplines particularly with regard to technique development and application (and interpretation).

Pervasive problem areas were corrosion and environmental interaction (hostile), and phase transformations and phase stability. The first includes a range extending from "familiar" stress corrosion cracking phenomena on "conventional" materials to interactions of new corrosive media ("relevance pull") with a host of new and old materials and material systems. The challenges of hydrogen containment as currently recognized will become more severe in new power systems, requiring evaluation of new materials, (i.e. ceramics) against phenomena that are currently not understood. Phase stability and phase transformations in the broad sense provides a base upon which other "design" phenomena rely, i.e. mechanical behavior and durability, electrical properties, etc. With the trend to high temperatures in energy systems microstructural stability is paramount. Concommitantly, the emerging advantages of ceramics and polymers requires a reassessment of the fundamental understanding of phase relations in these "unfamiliar" systems. The status of useful sophistication among ceramics, metals, and polymers varies greatly. Thus, for example, in steels and aluminum alloys, basic research problems could involve the subtleties of (both chemical and physical) microstructure management to optimize physical properties. By contrast, in ceramics the challenges in many cases revolve around first-cut processing issues in the sense that material preparation is often a pacing item. Nevertheless, to meet the requirements for engineering application, fundamental knowledge of these same materials (i.e. structural ceramics and fiber composite matrices) must have virtually the same base as the more familiar systems. In many cases this base simply is not yet being developed.

The following list contains a summary of research opportunities based upon some of the principal engineering challenges in energy conservation. Some basic research areas are more clearly defined than others; this is not meant to imply priority but rather reflects the personality of the group.

Group Consensus of Systems Challenges and Research Opportunities

System	Issues

Energy Storage

-Battery Systems (e.g. Na_xS_y, Li_xS_y) — Corrosion, Electrolyte Performance

Research Opportunities:

·Material interaction with polysulfides (corrosion), sulfide corrosion chemistry as influenced by temperature, composition, purity, etc.

·Solid electrolyte - (β"-alumina)

-Fundamentals of ion transport mechanisms as influenced by material microstructure, electric field, etc.

-Structural stability (fracture mechanisms) as influenced by metal ion transport, impurities, electric field variables, etc.

-Develop analytical techniques to permit spatial differentiation (identification) of phases - paramount to accurate studies of microstructure development.

-Fundamentals of sintering doped materials; microstructure control.

-Stored Energy of Phase Transformations — Innovation

Research Opportunities:

·The system Na_2SO_4

·Structurally reversible materials - martensitic "memory" alloys - fundamental understanding of microstructural mechanisms.

-Hydrogen Storage — Environmental Interactions, Containment

Research Opportunities:

·Hydrogen-materials interactions, hydride formation (influence on structurally significant properties), hydrogen attack, hydrogen transport - in both metals and ceramics.

-Other Stored Chemical Energy (heat pipes, etc) — High Temperature Interactions

Research Opportunities:

·Thermodynamics and Kinetics of chemical energy storage

Advanced Power Systems

-Turbines — Corrosion, Microstructural Stability

Research Opportunities:

·Thermodynamics and kinetics of material-environment interactions

·Microstructural stability (phase transformations of two phase composites (directionally solidified eutectics, eutectoids, etc.)

·Structural ceramics (special effort to achieve scientific/technological currency)

-Phase relations and phase transformations
-Diffusion (mass transport in sintering, etc.)
-Structural characterization and influence of structure upon properties
-Environment - material interactions

-New Engines (e.g. Stirling, Na heat engine) — Environmental Interactions, Ceramic Membrane Development

Research Opportunities:

·Fundamentals of hydrogen-material interactions (as above)
·Ceramic material understanding (as above)

-Fuel Cells — Microstructural Stability, Environmental Interactions

Research Opportunities:

·Stability of ceramics (as above)

Transportation

-Light weight materials — Conservation of Alloying Elements, Optimal Structure-Property Relationships, Environmental Interactions, Phase Stability and Transformation

Research Opportunities:

·Continual improvement in understanding of structure-property relationships in physical metallurgy with the tacit goal of optimizing properties (for applications which will have energy savings potential). For example, it is not enough to develop materials with high strength/weight ratios without giving consideration to attaining it along with properties (e.g. "formability") which make possible application in significant quantities and competitive cost.

·Role of alloying elements with consideration to replacing expensive or availability-limited elements with others. Influence of these changes upon time-temperature schedules (i.e. processing) to produce equivalent (or improved) properties. Systems analysis of whether the trade-offs really net an energy save.

·Fiber reinforced polymers

-Stability of polymer matrix (co-polymer) materials and fiber-matrix interfaces

-Fuel Efficiency (catalysis) — Particle Morphological and Stability

Research Opportunities:

·Morphological stability of fine particle arrays. (Coarsening)

·Role of trace impurities (innate and those occuring in the use environment) upon particle stability

-Tribology — Materials Interaction

Research Opportunities

·Fundamentals of friction and wear - influence of structure and environment upon the phenomenon. A basic systematic understanding is needed

·Stability of lubricants under high pressure and temperature Chemistry of lubricant (degradation) stability

<u>Insulation</u> Microstructural Stability, Environmental Interaction

Research Opportunities:

·Stability of high temperature insulators, typically glasses and ceramics subjected to a range of environments.

-Devitrification of glasses

-Stability of high temperature fire brick. Development of ceramics for higher temperature applications. Hot metal/slag erosion and corrosion of materials

·Influence of environment in degradation of spectral reflectivity of low temperature thermal insulations

·Stability of interfaces in multicomponent insulation material

<u>Recycling</u> Environmental Interactions

Research Opportunities:

·Systematics of complex chemistry and physics of retained extraction

II-2 Fossil Energy

Chairman: R. Jaffee

Members: J. Brophy, R. Perkins, I. Cutler, R. Staehle, B. Kear

The panel recommends that programming in fossil energy research supported by the Basic Energy Sciences Division of ERDA be confined to coal as the energy source. The nature of the research supported should be aimed at a better understanding of critical issues in the performance of metallic and refractory materials in coal conversion to clean fuels, coal combustion, and conversion from heat to power.

A. Coal Conversion and Combustion: The pressure vessel used for coal conversion to liquids and gases are currently designed by ASME codes and correlation with past experience without benefit of how a flaw in the vessels might grow to critical size in an aggressive environment containing H_2 and H_2S at elevated temperature and pressure. What is needed is a fracture mechanics analysis and supporting data on pressure vessel steels tested in metallurgical conditions of significance to the application and in coal conversion environments. Subcritical crack growth measurements under cyclic and steady loads, with particular attention to the threshold are particularly needed. The temperature range should embrace regimes where plane strain crack growth and creep-fatigue crack growth occur.

Coal liquifaction let-down valves and slurry pumps are subject to severe erosion-corrosion conditions. A predictive theory supported by data are needed on erosion of hard materials as a function of composition and microstructure to provide a rational basis for materials design. This effort should be coupled with parallel efforts in fluid dynamics and correlated with component design.

Low oxygen activity in the presence of multiple oxidants in coal gasification and fluidized bed combustion environments poses a very severe challenge to metallic materials such that operational regimes will be drastically curtailed and that recourse will have to be made to use ceramic materials. Information is needed on corrosion chemistry and short circuit diffusion paths in reaction products on metallic materials. Refractories also are subject to corrosion by slags and gaseous corrosive species, and an analogous body of corrosion chemistry information is needed. Erosion by particulate matter is less of a problem at low velocity and for small particle size, but should be studied over the ranges of interest, particularly those found in cyclone separators, similar to those suggested for let-down valves.

Fireside and steamside corrosion of conventional boiler superheater and reheater tubes will become a more severe problem as lower rank coals are utilized and when higher steam temperatures than 1000F (540°C) are generated. The corrosion reactions in both regimes need much better understanding if better boiler tube materials are to be developed. Also important will be the improvement of creep rupture properties of superheater tube materials to couple with improved corrosion behavior.

B. Heat/Power Conversion: The coal-fired steam plant consists of a boiler, steam turbine, condenser, and various auxiliary pumps and heaters. Improved materials technology for the steam power plant will pay great dividends in terms of improved reliability and efficiency in the near term. ERDA is urged to direct substantial resources to research in steam plant materials. Some of the problems needing attention are: (1) stress corrosion and crack propagation in steels used for rotors and discs; (2) the effect of impurities condensed from contaminated steam on turbine blade fatigue and stress corrosion water droplet erosion of last stage blade materials; (3) thermal stresses and creep-fatigue interaction in high-pressure rotors, etc.

The corrosion of heat exchanges tubes in coal fired fluidized bed boilers is similar to corrosion of coal gasification internals, but is aggravated by corrosive deposits. Basic attention is needed for both. If the fluidized bed combustion is pressurized , the expander turbine will be subject to high temperature corrosion-erosion and fouling by high velocity particulate matter and alkali sulfates, even after hot gas cleanup. Combustion gas turbines fired with coal derived fuels also will be subject to combined erosion-corrosion. What is needed is an understanding of degradation mechanisms of turbine materials in this environment, which will provide a basis for designing improved materials.

Gas turbines of the closed cycle type with air, helium, or metal vapor as the working fluid, heated by combusted coal in a heat exchanger, are an alternative power conversion cycle. Corrosion is expected in the fireside of the heat exchanger. Corrosion by the metal vapor or by impurities in the helium working fluid needs fundamental attention, as this is another example of corrosion in low-oxygen environments where protective oxide scales are not formed.

Charge transport by electron emission or by arcing is important in coal-fired MHD ducts, and is a subject particularly needful of fundamental attention. Fuel cells utilize fossil fuels, which ultimately must be derived from coal. A current problem is instability of platinum catalysts. A future problem will be development of base metal catalysts.

II-3 Nuclear Fission

Chairman: D. Thomas

Members: R. Carpenter, P. Shewmon, J. DeVan, J. Verhoeven, D. Keefer

The study group derived suggested research areas from a consideration of materials problems which exist in the several reactor systems currently utilized or being developed.

I. LMFBR

Research Areas	Technological Concern
•Diffusion in a temperature gradient	Fuel Stability (Mixed oxide or Mixed Carbide)
•Phase Stability	
•Radiation damage, swelling and radiation induced phase stability	Fuel/Clad Interaction " " "
•Diffusion	" " "
•Grain boundary penetration effects	" " "
•Short circuit diffusion	Primary circuit, alloy stability
•Fe-Ni-Cr Phase Diagram	" " " "
•Phase relations in heat affected zone of welds	Phase stability in welding in primary circuit
•Phase relations in stainless steel castings	Pump and valve stability
•Interstitial diffusion in austenitic steels	Primary circuit carbon transport
•High temperature oxidation in steam atmosphere with and without a heat flux	Steam generator tube integrity
•Phase relations in ferritic steels	" " " "

II. HTGR

•Thermal gradient induced mass transport	"Amoeba" effect in fuel particles
•Internal oxidation of high temperature materials at low oxygen activities	Oxidation of critical metallic components in primary circuit
•Internal carburization of high temperature materials at low carbon activities	Internal carburization of critical metallic components in the primary circuit
•Stability of ordered structural alloys of the A_3B type under creep conditions	Advanced alloys for primary circuit applications

III. LWR

•Precipitation and segregation in stainless steels and Inconel in the sensitizing regions	Stress corrosion cracking in BWR primary loop environments and PWR secondary environments
•Relationship of microscale structural changes during deformation & fracture to the fracture mechanics of pressure vessel steels-irradiated and unirradiated	Pressure vessel integrity

II-4 Magnetic Fusion

Chairman: R. Reed

Members: A. Ardell, F. Nolfi, J.W. Morris, R. Swendsen, K. Natesan

The panel recommends that the currently projected materials requirements of magnetic fusion energy would be considerably assisted by the following fundamental research projects:

A. Irradiation of Alloys: The complex metallurgical problems associated with the construction of fusion reactor first walls and blankets requires a detailed understanding of the effects of irradiation on alloy stability. Phenomena such as irradiation induced non-equilibrium segregation, phase boundary shifts, defect-impurity interactions, and accelerated precipitation kinetics are presently not well understood, especially in the presence of the transmutation products helium and hydrogen.

B. Stability of Coatings During Irradiation: Reactor first walls may be constructed using protective, low-Z coatings. For these coatings, radiation induced sputtering requires adequate characterization. Research considering ion size, energy and incident angle, as well as alloy chemistry, would supply much-needed background information. Also, assessment is needed of the effects of radiation-induced phenomena such as cavity formation and enhanced diffusion of coating-wall bond integrity.

C. Irradiation Studies of Organic Materials: Reactor electrical insulation and superconducting magnet electrical and thermal insulation requirements will require the use of organic films and composites. Studies of irradiation effects inorganic insulator materials are generally sparse, and at 4K (superconducting magnets) studies of these effects have apparently never been carried out. Fundamental studies, considering polymer types and temperature effects and directed toward radiation-insensitive material development, should be initiated.

D. Welding: The large magnetic forces generated from high-field magnets require very thick sections of structural alloys for containment. Weldability may well be a limiting parameter of the use of refractory metals for first walls. Basic research on welding has not been prominent. It is recommended that research be initiated to consider phase stability and grain boundary segregation of austenitic stainless steels and the role of impurities/solutes in refractory metal welding.

E. Martensitic Transformations: Superconducting magnets will probably require the use of structural alloys, such as austenitic stainless steels, that have possible martensitic transformations at cryogenic temperatures. Proper characterization of the role of deformation, welding-induced precipitation and chemical segregation, magnetic fields, and temperature on martensitic transformations in austenitic stainless steels would assist in alloy selection and welding procedure selection.

F. Liquid Lithium Characterization: Currently, liquid lithium is the leading candidate for the coolent and breeding materials in fusion reactors. Basic information on the thermodynamics and kinetics of interstitial migration in high magnetic fields is needed. Studies are needed on interactions between lithium interstitial elements and structural alloys and on corrosion rates of structural materials in lithium environments as a function of temperature, alloy chemistry, and lithium purity.

G. Metallurgy of Superconductors: In the quest to obtain useable NbTi and Nb_3Sn superconducting wires and cables, most research and development has concentrated on the maximazation of the critical current as a function of magnetic field. Surprisingly, there has not been characterization of the phase stability and deformation modes of these alloys at low temperatures.

These recommended projects are not necessarily listed in a priority order and are not all inclusive.

II-5 Solar Energy

Chairman: R. Richman

Members: J. Cahn, K. Drumheller, J. Phillips, A. Searcy, R. Sekerka

The field of solar energy is so new that the problems have not yet been defined or even identified, in contrast to a more mature technology such as nuclear fission. However, the study group agreed that the direct conversion of light (or heat) to electricity probably offers the best opportunities for supporting basic research. Following is a list, largely by program, of solar-related research topics pertinent to this workshop.

I. <u>Solar Heating and Cooling</u>

A. Phase Separation and Devitrification

·Most soda-lime glasses are two-phase on a microscale... Structures might be tailored by heat-treatment, selective leaching, etc.

·Stability at temperatures higher than the present 300°-400°F for cover glass

·Glass solders for device fabrication

·Polymers

B. UV-Induced Degradation of Glasses and Polymers

·Reflectivity and transmittance

·Electrical properties

·Mechanical properties

C. Surface Preparation

·Thermally processed layers, as by laser glazing. Rapid solidification on surfaces of non-metallics; structure of surface transformations

·Diffusion produced coatings; the moving-boundary problem

·Chemically produced coatings, such as dark conversion coatings on solar absorbers. Also, techniques will be needed for property predictions and lifetime projections.

II. <u>Direct Conversion</u>

Research on this topic will be necessary to achieve inexpensive photovoltaics and thermovoltaics.

A. Liquid-Solid-Gas Interfaces

·Dihedral angles in non-equilibrium situations is a basic underlying topic about which almost nothing is known.

·Refers mostly to silicon now, but will apply to whole field of inexpensive strip semiconductors.

B. Growth Morphologies in Anisotropic Circumstances

·Inexpensive wafer materials from the melt

·Structure of thin layers grown by reaction between solid substances; e.e., Si/transiton-metal reactions.

C. Epitaxial Growth

·Is thin-film science likely to be the foundation for cheap, extended converters?

·Can bring defective bulk material into specification only where it is needed, i.e., at the surface.

·Liquid-phase epitaxy

D. General Interactions

·Purity; definitive information about limits in silicon and other semiconductors.

- Dopant effects
- Metallurgical structure

III. <u>Solar Thermal</u>

A. Diffusion in Thermal Gradients

- Carriers
- Impurities
- Interface stability
- Thermal cycling; two phases may be in equilibrium at T_1, but excursions to T_2 may cause microstructural instability.

B. Thermal Storage

- Cyclic degradation of media that rely upon phase-change latent heat.
- Peritectics offer advantages but they have not been studied much, certainly in metallurgical systems.
- Cyclic growth of crystals from the storage-medium melt.

IV. <u>General Topics</u>

A. Accelerated Testing

- A crucial issue; since we cannot afford 20-year tests, we must be able to predict all aspects of stability in order to make lifetime projections.
- Time/temperature parameters for extrapolation

B. Corrosion

- Interaction of materials with low-temperature ocean water, intermediate-temperature organic working fluids, and high-temperature gases.

C. Fatigue

- Mechanical, as in wind devices
- Thermal, as in central-cavity receivers.

II-6 Geothermal

Chairman: A. Goldberg

Members: I. Carmichael, F. Pettit, L. Darken, D. Shannon, R. Dillon

The geothermal energy conversion systems considered for identification of areas of needed research are based on hydrothermal reservoirs, vapor reservoirs, hot rocks and lava beds. The problem areas identified are listed as follows:

A. Scale Formation: Scale deposition buildup, caused by a temperature drop or by flashing, can rapidly decrease flow capacity to unacceptable values. Entrapped particles downstream from flashing can cause serious erosion problems. Scale has been shown to both decrease and increase corrosion. Information on the thermodynamics of scaling from aqueous geothermal systems and the kinetics of scale formation must be obtained over a range of pressures, temperatures and pH values. One must also obtain basic information on the influence of hydrodynamic conditions on the morphology of scale deposition. Synergism between scale deposition and corrosion must be studied.

B. Materials Behavior: The geothermal resources will present aggressive environments to various degrees depending upon both the particular reservoir and the location within any given energy conversion system, e.g., well casing, surface piping, heat exchangers, turbine system, valves, pumps and the effluent treatment and discharge system. Behavior of materials in these various environments is virtually unknown and this must be examined with respect to stress corrosion cracking, corrosion fatigue, erosion/corrosion and other forms of failure and wastage.

C. Improved Performance: Basic research must be performed which could lead to better materials systems and cost effectiveness. The effect of alloy additions in simple Fe-base systems on corrosion resistance for low cost piping and plant materials should be studied. The potential use of coatings, liners, or claddings with low cost structural steels must be considered by studying the interaction of candidate coating, liner or cladding materials with the geothermal environments. Research should be performed which isolates the effects of erosion from corrosion and thereby identifies which materials are most suited to resist wastage by either one of both of these mechanisms.

D. Lava Beds: Lava beds are now mainly of geological interest, but their potential must not be overlooked. Temperatures are of the order of 1200 to 1300°C. Materials which are now being developed for MHD and coal gasifier internals should be studied for their interactions with lava compositions in this temperature range.

II-7 Environment and Safety

Chairman: R. L. Schwoebel

Members: H. Aaronson, D. deFontaine, R. Coble, J. Elliot, J. Cost, R. McLean

Environmental and safety concerns represent important driving forces for the selection and development of various alternatives in energy generation. A perceptive ranking of such alternatives in terms of environmental and safety efforts is a complex task requiring the interdisciplinary efforts of experts in several fields.

The two principal areas discussed by this subcommittee were the environmental and safety problems associated with the large scale utilization of fossil fuels, particularly coal, and the disposition of fission products and transuranic nuclide wastes associated with nuclear reactors. Our recommendations for research in support of these two areas are as follows:

A. Coal Utilization: Concepts for the beneficiation of coals prior to combustion or conversion should be pursued to reduce sulfur, trace impurities such as arsenic, cadmium, mercury, and other elements detrimental to eco-systems. There is also a need for definitive characterization of the chemical evolution of sulfur and nitrogen bearing compounds, and identification of the most important species in terms of health effects. This is particularly true in the case of coal gasification and liquification processes which are thought to produce organic fragments that evolve into carcinogenic and mutagenic species.

There is a critical need to accumulate selected thermodynamic data to establish predictive performance and failure models for pressure vessels, etc. This would include phase diagram determinations, interdiffusion data, surface and interfacial energies, and boundary diffusion parameters.

B. Nuclear Reaction Operations: Biofouling of reactor cooling equipment continues to be a problem which significantly impacts the ecology surrounding water cooled power reactors. This phenomena apparently depends on several parameters including the surface morphology and composition of cooling systems and further study is required.

A principal problem in the development of nuclear power is the safe disposition of radioactive wastes associated with the fuel cycle. Several long lived nuclides are extremely toxic and effective isolation is required for extended intervals. Although vitreous waste forms have been under development for many years, there is still a need for definitive characterization of these waste forms with regard to physical and chemical stability. This would include microscopic studies of nuclide chemistry, homogeneity, effects of transmutation and radiation damage, and identification of significant processes associated with devitrification and interactions with the disposal environment. We also recommend the pursuit of alternative crystalline waste forms selected on the basis of known or predicted stability. This would require the study and modeling of the chemical and physical stability of particularly transuranic compounds of high radiation fields.

II. STUDY GROUP REPORTS - TECHNICAL AREA RESEARCH PRIORITIES

III-1 Thermodynamics

Chairmen: L. F. Darken
J. F. Elliot

Members: L. Brewer, R. Schwoebel, J. Economy, J. Verhoeven, F. Nolfi

We noted first the current dismal level of support for thermodynamic investigations, in fact the termination of many. We deplore the general lack of interest even in presumable informed quarters - even in the University communities. In strong contrast to this attitude we note the essentially universal permeation of thermodynamics into the physical sciences and technologies. In particular all the "tutorial speakers" for the other areas of this Workshop made explicit or implicit reference to the use of thermodynamics in their presentations - reminscent of the famous quotation from G. N. Lewis on "the broad highway of thermodynamics".

Our study group stressed the need for support agencies to seek out and support: (1) the relatively few scientists capable of advanced thermodynamic thinking (including those outstanding in modern physics); (2) outstanding, well-equipped experimentalists in the field. Otherwise, these scientists drift to other fields with almost irretrievable loss.

General areas where we feel strong support is needed are:

A. "Classical Thermodynamics": There is a critical need for high quality (a) calorimetric measurements and, (b) equilbrium measurements including surface and interface properties (related to catalysis wetting combustion and corrosion phenomena).

B. Thermodynamics of Solutions: Gaseous (including ions), liquid and solid. Models should be built to facilitate the interaction of theory and experiment (methodology). Special attention should be paid to elements, oxides, halides, sulfides, polysulfides, suphates and aqueous solutions at high temperature and pressure.

C. Now-Classical Thermodynamics: Efforts should continue to be made to push thermodynamics to its limits. Areas here include irreversible thermodynamics, quasi-equilibria (as for systems subject to high radiation flux), systems in high magnetic fields, stressed solids, high gradients of various sorts, defect structures, glasses, polymers, and multiple adsorption phenomena.

D. Critical Evaluations and Compilations: Our group felt it a matter of the utmost urgency to re-institute the critical evaluations and compilations of thermodynamic data so that thermodynamic information may be readily available to those who need it.

We feel that Alvin Weinberg's criteria of technological, scientific and social merit are more than fulfilled by these areas of thermodynamic research.

The appended table summarizes present and contemplated needs for new thermodynamic data on materials species and phases which are critical to the successful development of energy systems.

Summary Chart: Areas Where Thermodynamic Information is Needed and Kind of Information Desired

System	Thermo. Prop.	Solutions	Surface Phenomena	Phase Stability
*(N) Fossil Energy	Complex Spec. Complex Comp. Polycyclic Comp. (V,VI)**	Coal Slags Liquid Coal Polycyclic Comp. (V,VI)	Conversion (V,VI)	Structural Materials (Phase Trans. and Stability) (II, III)
(N) Energy Conservation	Compounds, e.g., (V,VI) Si_3N_4, SiC, Na_xS_y	Alkali Poly. Sulfides (V,VI)	Friction and wear (V,VI)	Waste processing structural materials; polymers
(M) Energy Storage	Electrolytes (V) Fluids	------------	Catalytic effects	------------
(M) Fission Energy	Actinide Comp. V.P. of Fission Prod. Cmpds.	H.T. Aqueous soln. (V,VI)	--------------	Struct. Materials (IV); Fuel stability
(L) Geothermal	Complex Sulfides (V)	High Temp. Aq. Soln. (V)	--------------	------------
(L) Magnetic Fusion	Ion Properties at high T. and Mag. fields	Alkali Metals (V,VI)	Sputtering (VI) surface phenomena	Metals, Ceramics; Org. Materials
(N) Environment and Safety	Gaseous species in atm. and combust. gases	Aqueous ionic species	Atmospheric part. matter (combustion gases)	Actinide cmpds (storage)
(L) Solar	Prop. of high temperature liquids	-----------	Absorbtivities and photocatalysis	Struct. Materials in sunlight

* Term interest, N=near, M=medium, L=long

** Areas of study-group Discussion: II-Solid.+ H.R., III-Ppt. and Coarsening, IV-Mart. Trans and Crit. Phenomenon, V-Corrosion, VI-Environmental Attack.

III-2 Solidification and Homogeneous Transformations

Chairmen: R. Coble
B. Kear

Members: J. Cahn, K. Drumheller, R. Jaffee, R. Reed, R. Sekerka

The prospects for significant advances in understanding in these areas are related to new or advanced tools or techniques for the conduct of experimental programs. Rapid solidifications by atomizing liquids into gases, and laser or electron-beam melting of surfaces on crystals which then self-quench, provide the possibilities of sample purification, and of model testing, and generation of data on epitaxial relations on re-growth, the growth vectors in high temperature gradients, and non-equilbrium segregation of components. With the theories now available these studies will permit determination of the anisotropy of the atom attachment kinetics during solidification. The theory applies to simple systems; studies of the influences of 3rd (or more) components on these phenomena are needed for the next step in understanding more complex systems. The cellular: dendritic transition can also be addressed using high cooling rate experiments. Metastable phases, easily produced, can also be studied more intensively because of different composition ranges that can be converted to: glasses or metastable crystalline phases. The glass transition itself is not fully understood for metals, ceramics, or polymers and deserves intensified effort. Decomposition of glassy or metastable crystalline phases have been observed to evolve through sequences of metastable phases prior to formation of equilibrium phases. Studies of these evolutions are needed to deduce why the sequence appears. Thermodynamic data and chemical diffusivities in these multicomponent systems will be required for basic testing of the applicability of nucleation/spinodal, etc. models.

Texture generation in unidirectional solidification is appreciated for all classes of materials. Polymers may be further "textured" to produce chain alignment by controlled shear in fabrication. Metals, ceramics, and polymers should be studied for texture development due to re-crystallization, and/or growth, under variable temperature and stress gradients imposed during annealing (in the solid state).

Tri-junctions in float-zone growth of Si (e.g) show non-equilibrium wetting angles (at the solid liquid gas junctions). These as well as moving solid I, solid II, liquid junction morphologies should be studied because of their importance in shape control of solidified materials, and potential insight to be gained from this phenomenon that is not understood.

Basic studies of reactions across interfaces are needed particularly for slag, melt interactions, and the process of grain growth. Polymer to metal/ceramic attachments presents further complexity because of the variable chain orientations which can be controlled (parallel/perpendicular to the surfaces) with important consequences for lubrication versus bonding characteristics, respectively.

Finite element analysis techniques now available should be applied to the moving boundary problem, to thick-plate welding, to determine how the heat affected zone might be altered as a function of the variables, number of passes, power and feed rate. Hot tearing should similarly be attacked with elastic and plastic modeling of the stress fields generated.

High resolution instrumentaion must be applied to the structure determinations of interfaces and grain boundaries, and to the chemistry of each for proper characterization of these features in order to understand their mobilities and the reactions which may take place across them. Fundamental work is needed on plasma-materials interactions, but may now be used empirically for refining purposes. Boundary growing experiments and solid faceting at liquid interfaces can now be used to deduce interface energies and their anisotropics; liquid crystals add anisotropy from the liquid components in polymeric systems as well.

Basic data needed to support these efforts are on thermodynamics and transport in non-metallic crystals and liquids, the structure of interfaces, liquids and glasses, chemical diffusivities in multicomponent liquids and solids, interface energies and their anisotropy, and interface diffusivities.

III-3 Precipitation and Coarsening Phenomena

Chairmen: A. Ardell, G. Thomas

Members: H. Aaronson, R. Carpenter, J. Brophy, K. Kinsman, I. Carmichael, D. Thomas

The study group concentrated its efforts on two broad areas of research: A. Precipitation in general, including homogeneous and heterogeneous nucleation, growth, discontinuous or cellular precipitation, and coarsening; B. Irradiation effects, including the effects of neutron and charged-particle irradiation on several of the phenomena cited in (A) and phenomena that appear to be unique to the irradiation environment, such as irradiation-induced segregation and associated precipitation phenomena. In discussing these topics the group attempted to highlight those areas in which basic research was needed, and to provide a loose assessment of the extent of the effort required. These are summarized below.

A. Precipitation:

1. Nucleation: Homogeneous nucleation theory has never been tested in solid systems by direct measurement. Since the formalism serves as a basis for heterogeneous nucleation theory as well, an effort to test the theory should be made. Although the measurements are difficult, a relatively small effort would suffice to provide the necessary data on nucleation rates and incubation times as a function of undercooling.

Heterogeneous nucleation is in particularly bad shape with regard to the theory of nucleation on dislocations. A moderate effort should be made to develop an appropriate theory incorporating elasticity theory and precipitate morphology in an attempt to rationalize existing observations.

2. Growth: What is needed here is knowledge of the detailed structure of interphase interfaces so that growth kinetics could be compared to the predictions of various models as a test of theory. A moderate effort, involving the application of high resolution electron microscopy and analytical techniques, should be supported.

3. Discontinuous Precipitation: The major problem in this area is to provide a definitive explanation for the known effects that third elements have on the suppression of this reaction. This has important consequences on mechanical behavior. A small but continuing effort should be supported.

4. Coarsening: An explanation of the resistance to coarsening in certain alloys (e.g. θ' in Al-Cu alloys) is worth pursuing because of its implications in high-temperature microstructural stability of alloys. Other problems, such as the role of strain energy, also remain unsolved and a small to moderate effort is definitely worthwhile in this area.

B. Irradiation Effects:

1. Parallel Studies: The need was expressed for studies on the effect of irradiation on phenomena, such as particle coarsening, to be conducted in parallel with studies on identical alloys in the absence of an irradiation environment. In view of the large number of variables and potential alloys involved, a large effort would be required to get the job done.

2. Unique Effects: Recently discovered phenomena, such as irradiation-induced segregation to free surfaces and precipitation in otherwise stable solid solutions, are as yet poorly understood. A large effort, both theoretical (e.g. the thermodynamics of systems containing large excess amounts of point defects) and experimental, is clearly necessary to elevate our present level of understanding.

C. General Concerns:

In addition to the research areas cited above, the study group was particularly cognizant of the lack of ancillary data available to properly interpret experimental results. Conventional data on solution thermodynamics, diffusion rates, interfacial energies, single crystal elastic constants of solid solutions and binding energies between solute (and solvent) atoms and point defects are sorely needed.

New methods of materials characterization have been, and are being, developed which should be brought to bear on the problems cited. Indeed, recent advances in high resolution electron microscopy, electron energy loss spectroscopy and X-ray analysis, will eventually become indispensible in solving the current and future problems.

Finally, the study group emphasized that the problems cited should not be viewed only in their own light, but that they have important implications and applications in alloy design and behavior.

III-4 Martensitic Transformations and Critical Phenomena

Chairmen: J.W. Morris, Jr.
W. Owen

Members: D. de Fontaine
J. Phillips
R. Swendsen

The subjects of martensitic transformations and critical phenomena fall in a vital area of current research activity which is alive with many important new ideas. Recent progress in this area has been stimulated by the development of a variety of new theoretical approaches. These include techniques in statistical mechanics, such as renormalization group theory, cluster variation methods, and Green's function techniques, tools in solid state physics, such as pseudo-potential theory which permits the estimation of thermodynamic functions, and powerful new numerical techniques, particularly computer simulation techniques which permit detailed studies of the behavior of simple systems through pseudo experiments carried out in the computer. Recent theoretical progress has been paralleled by major advances in experimental devices & methods. These include ultra high resolution microscopy, the application of dynamical diffraction theory to the interpretation of electron microscope images, the study of dynamical effects on neutron diffraction, synchotron radiation, the study of defects by diffuse intensity measurements (x-rays and neutrons), and a variety of other tools and techniques.

The research topics of major current interest include: soft mode transformations, ordering-clustering phenomena, amorphous materials, micro-domains, defect stabilization of unstable structures, phase instabilities (compositional lattice, electronic and magnetic) and precursor phenomena (including pre-martensitic precursors) and fluctuations. In each of these subjects exciting advances are being made in physics, in metallurgy, and in materials engineering. Progress in fundamental physics is indicated by the rapidity with which new and probative ideas are being introduced in each of these research topics. Progress in metallurgy is indicated not only by the rapid growth in understanding of these phenomena and the increasing recognition of their importance but also in the manner of which these various phenomena are being integrated into a more unified theory of phase transformations. Progress in materials engineering is indicated by the quickness with which these new research ideas have been adapted to interpret important aspects of the behavior of engineering materials and to create new engineering materials of unusual and important properties.

Given its perception of the current state of research in the areas of martensitic transformations and critical phenomena the highest priority recommendation of this study group is that ERDA maintain levels of support and encouragement to sustain scientific momentum in this important research. Specific research topics which should receive emphasis in theory, experiment, and applications areas include the following:

A. Theoretical Research: While a wide variety of theoretical investigations could have a significant impact, those which should receive greatest emphasis were, the study group felt, those which focus on problems at the interface between fundamental physics and materials science. These include, in particular, (a) dynamical studies which theoretically model systems in real time yielding new information on the kinetics of phase transformations; (b) theoretical studies which include the effects of elastic interactions on phase transformations permitting better understanding of transformations in real solids; (c) theoretical work on the role of defects in solids including, in particular, the role of dislocations and other defects on the occurence and kinetics of martensitic transformations. It is felt that in many cases the best theoretical route to follow in these investigations blends sound fundamental theory with computer simulation studies to monitor the details of phase transformations in model systems. It is important in this context that the Division of Physical Research insure the availability of the facilities and funds needed for large computer simulation studies.

B. Experimental Studies: The experimental studies of highest scientific priority are those which utilize the high resolution available in powerful new research tools to conduct detailed studies of phase transformation phenomena, particularly where these may be examined in situ in real time. Specific investigations having particularly high priority include the following: (a) high resolution transmission electron microscopy studies of the initial stages of phase transformations and of the structure of critical defects, including surfaces, which participate in the nucleation phase of the transformation; (b) in situ experiments using TEM and other high resolution techniques which follow the progress of transformations in real time with particular emphasis on critical fluctuations, precursor phenomena, and the features controlling transformation kinetics; (c) high resolution studies using well defined model systems, particularly those in which experimental results and theoretical studies can be directly matched for critical evaluation of the theories.

C. Applications Oriented Research: The importance of critical phenomena to materials science lies mainly in the domain of electronic and magnetic materials which are discussed in a separate workshop. The understanding of martensitic transformations, however, is directly relevant to the design of structural materials, in particular alloy steels, and properly falls in the domain of this workshop. Recent research has led to the identification of several new facets of the martensite transformation which may be of considerable significance to the performance of energy systems. These should be the subject of high priority research. They include: (a) the nucleation of martensite in steel with particular emphasis on nucleation at low temperatures under conditions of stress or electromagnetic fields of the sort which may be encountered in cryogenic devices; (b) the retention of austenite in the interstices of martensite plates or in the boundaries of martensite lathes which may not only have a significant effect on the mechanical properties of steel but may also contribute to embrittlement phenomena in ways that are only now coming to be understood; (c) the reversibility of the martensite transformation on thermal cycling, a problem which is important in the advanced processing of a variety of steels including both austenitic steels and high strength martensitic steels for advanced applications; (d) other in depth studies of the relation between the martensite transformation, the structure of the resulting martensite, and the mechanical properties of the martensitic steel.

III-5 Corrosion

Chairmen: R. Staehle, R. Dillon

Members: J. DeVan, A. Goldberg, D. Keefer, D. Shannon, D. Vermilyea

The primary objective of work in corrosion studies is to inhibit or retard degradation of substrates by chemical-mechanical influence of environments. This inhibition is accomplished primarily by modifying the environment, the substrate, the stress-time wave, and the geometry. seven component areas can be identified where fundamental work should be undertaken. Underlying these component areas are the areas of thermodynamics and equipment application. Finally, there are five important logistical considerations; equipment, talent, interaction with designer, interdisciplinary interaction and financial resources.

The mechanical part of the environment includes both the initiation and propagation of cracking, but within a framework of the mechanical parameters of cyclic frequency, wear stress, stress ratio, wave shape and non-conformity or randomness of load cycle. In general, SCC and CF should be at either end of the mechanical continuum with phenomena of creep, fracture, and fatigue as affected by environments key parts of this set. This mechanical part also includes the thermal fatigue phenomenon of fracture mechanics analyses.

The thermodynamic underpinning should include aqueous solutions especially concentrated ones and at temperatures above room temperature. Other important environments with dissolved species are steam, molten salts, and liquid metals. Properties of complex protective oxides and solutes (C in Fe) in metals are also important.

The seven component areas with priorities are:

A. Protective Films: Structure, composition, reactivity, nucleation and growth, alloy influence, Soret effect, transport of electronic and ionic defects, epitaxy electropolishing films.

B. Substrate: Grain boundary composition including segregation and precipitation, slip including grain boundary deformation, coplanarity, surface interaction, mass transport, surface energies, matrix structure.

C. Hydrogen-Metal: Entry (poison effects), defect interaction hydrides, void stabilization, dislocation motion, M-M vs M-H bonds, thermal and stress gradient diffusion.

D. Film Free Dissolution: Alloy effects, enrichment, ionized or non-ionized dissolution.

E. Adsorption Effects: Inhibition, fracture.

F. Cathodic Reduction Processes: H^+, O_2, Anion, Location of reaction, mass transport.

G. Fluid-Surface Boundary: Mass transport, double layer.

III-6 Environmental Attack

Chairmen: A. Searcy
I. Cutler

Members: J. Cost, R. Landingham, R. McLean, K. Nateson, R. Perkins, F. Pettit, P. Shewmon

We have distilled from our discussion two short lists of areas in which we judge that an increase in basic research effort could be particularly helpful to efforts to improve resistance of materials to attack in the high temperature environments of the energy utilization programs. Most high temperature environmental problems overlap those addressed by the corrosion panel, but we decided that we need not consider attack by aqueous solutions or the influence of mechanical stress. Each of our two lists is arranged in decending order of priority on the basis of our collective judgement of the interaction of two factors: (a) the benefit that a successful basic research program could provide to energy programs; (b) the probability of significant success for a basic research study in each given area.

A. Thermodynamic Studies:

1. Phase equilibria and activities should be studied for oxide-sulfide, oxide-carbide, oxide-halide, and oxide-oxide (including sulfate) systems. Mixtures of such phases are encountered in the processing of hydrocarbons at high temperatures, but little thermodynamic information is available. Particular emphasis should be given to determination of liquidus temperatues and the variation of solid and liquid phase boundary compositions with temperature.

2. Theoretical models for extrapolation of measured thermodynamic data for inorganic systems should be developed so that realistic predictions and interpretations of behavior in multicomponent systems can be made from data for systems of fewer components.

3. Devices for quickly and inexpensively monitoring the thermodynamic activites of sulfur and of carbon in high temperature systems should be developed if possible.

B. Kinetic Studies:

1. Chemical attacks through coatings and scales appear usually to proceed much more rapidly than can be accounted for by bulk diffusion. Diffusion along grain boundaries and along interfaces in complex scales and the mechanisms of reaction in complex systems (especially O + S + metals or binary alloys; O + C + metals or binary alloys) are important subjects for increased basic research. Because the systems are complex it is essential that these studies emphasize as complete characterization of the reaction parameters as possible. Thus, while the experimental thermodynamic investigations that we recommend require mainly that well-known experimental techniques be applied to little known systems, effective kinetic studies for complex reactions systems require that a broader range of experimental techniques be applied than have been applied in most past solid state reaction studies.

2. Corrosion of refractory oxides, and selected nitrides, carbides, oxy-nitrides and oxycarbides by the gases and liquids characteristic of

high temperature energy systems should be investigated. Little information is yet available, but serious environmental attack problems are almost certain to be encountered.

3. Studies of mechanisms of erosion of oxides and metals by solid particles should be augmented.

4. If programs that give real promise of increasing our fundamental understanding of mechanisms of adhesion of scales on structural metals and alloys are identified, they should be supported. The prediction and control of adhesion is one of the most important problems, not just in reducing environmental attack, but in all of Materials Science, but really useful basic research in this general area is hard to devise.

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