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Date: 23 Aug 1971

RESEARCH PROJECT INITIATION

Project Title: Chemisorption and Catalysis: Carbon Monoxide on Metals and Alloys

Project No.: E-19-609

Project Director: Dr. Helen E. Grenga

Sponsor: National Science Foundation

Agreement Period: From September 1, 1971 until February 28, 1974*

Type Agreement: Grant No. GK-26487

Amount: \$39,000 NSF (E-19-609)
9,039 GFT (E-19-316)
\$48,039 Total Budget

Reports Required: Annual Technical Report; Final Technical Report

Sponsor Contact Persons:

Technical Matters

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Washington, D. C. 20550

Administrative Matters

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Washington, D. C. 20550

*All commitments met by this date unless formal extension obtained. Basic work period (24 months) ends August 31, 1973.

Assigned to: School of Chemical Engineering

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SPONSORED PROJECT TERMINATION

Date: March 13, 1976

Project Title: Chemisorption and Catalysis: Carbon Monoxide on Metals and Alloys

Project No: E-19-609

Project Director: Dr. Helen E. Grenga

Sponsor: National Science Foundation

Effective Termination Date: 4/30/76

Clearance of Accounting Charges: 4/30/76

Grant/Contract Closeout Actions Remaining:

- ☐ Final Invoice and Closing Documents
- ☒ Final Fiscal Report
- ☐ Final Report of Inventions
- ☐ Govt. Property Inventory & Related Certificate
- ☐ Classified Material Certificate
- ☐ Other _____

NOTE: Continued by E-19-642.

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Annual Technical Report

Institution: Georgia Institute of Technology

Principal Investigator: Helen E. Grenga

NSF Grant No.: GK26487

Grant Title: Chemisorption and Catalysis:
Carbon Monoxide on Metals and Alloys

Starting date: Sept. 1, 1971

Expiration date: Feb. 28, 1974

The report for the first year of this grant can be divided conveniently into two areas: modification of the field-emission microscope to include the probe-hole technique, and field-ion microscope studies on Fe-C alloys.

1. Modification of Field-Emission System to Include Probe-Hole Technique.

Our initial studies on the chemisorption of carbon monoxide on ruthenium (Final Technical Report, NSF Grant GK4929) demonstrated the potential application of field emission and field desorption techniques to the illumination of mechanistic relations between chemisorption and catalysis. These initial investigations utilized a spot photometer, which was capable of resolving chemisorption states on different surface regions. Substitution of a probe-hole assembly would enable us to obtain more quantitative information on these chemisorption states and to relate them to single crystal planes and/or individual atomic sites.

Therefore, during this first year, we have designed and constructed a probe-hole assembly and are presently engaged in initial measurements using the probe-hole. The probe hole essentially consists of an image screen with a small (1 mm) hole in the center through which electrons can pass and a Faraday cup to collect and measure the current of these electrons. A specimen manipulator is presently being constructed and will allow the movement of the specimen so that any given plane of the specimen image can be centered over the hole, thereby enabling collection of electrons from that specific plane. These modifications should be completed and the microscope fully operational during the fall, at which time the proposed field emission experiments will be continued. One graduate student is presently working on this project for his Ph.D. thesis. Another graduate student has worked part-time on this project to help make the necessary equipment modifications.

2. Field-Ion Microscope Studies on Fe-C Alloys

While modifying our field-emission system as described above, it was both desirable and convenient to perform some of the proposed field-ion microscopy studies on two phase materials (Stage III in Outline of Proposed Research). A graduate student who used field-ion microscopy to study microstructures in steels for his Ph.D. thesis was supported for two quarters on this grant. The detailed results of these studies are included in his thesis, copies of which accompany this report. The results, which are most pertinent to field-ion microscopy studies on the catalytic reaction of CO on metals are those on contrast from Fe with varying amounts of C in solid solution and on carbide contrast. It was shown that a high degree of image irregularity results from the carbon in solid solution, a factor which must be carefully considered when interpreting field emission results from specimens which have been treated with CO for the decomposition reaction. It was also found that the iron carbides which formed both during early stages of precipitation as well as much later appeared dark in the hydrogen-ion images, thereby aiding identification of such precipitates. Due to the distinct carbide contrast, the size, shape, distribution and habit plane of the carbides were obtainable.

These FIM results on the Fe-C system demonstrated that carbon in solid solution and very small carbide particles can be distinguished so that FIM studies on the catalytic decomposition of CO on metals are capable of detecting and identifying reaction products.

Publications, papers presented and theses resulting in part from this grant are as follows:

1. "Hydrogen-ion Image Contrast of As-quenched and Tempered Ferrous Martensite," with B. N. Ranganathan, to be submitted to J. Microscopy,

Sept., 1972.

2. "Hydrogen-ion Microscopy Studies of As-quenched and Tempered Ferrous Martensite," with B. N. Ranganathan, paper presented to 19th Field Emission Symposium, Urbana-Champaign, 1972.

3. "Field-Ion Microscope Investigation of Fine Structures in As-quenched and Tempered Ferrous Martensite," B. N. Ranganathan, Ph.D. thesis, Georgia Tech, 1972.

E-19609

FIELD-ION MICROSCOPE INVESTIGATIONS OF FINE STRUCTURES IN AS-QUENCHED
AND TEMPERED FERROUS MARTENSITE

A THESIS

Presented to

The Faculty of the Division of Graduate
Studies and Research

By

Brahmanpalli Narasimhamurthy Ranganathan

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy in the School
of Chemical Engineering

Georgia Institute of Technology

May, 1972

*Hedden
ganga*

SUMMARY

The microstructures of as-quenched and tempered martensites in an Fe-0.8%C-0.4%Mn steel were studied with hydrogen-ion microscopy at 78°K. Information on image characteristics and contrast features as well as crystallographic and morphological data on the fine structures of these materials were obtained, and a comparison was made between microstructure and hardness during tempering.

The hydrogen-ion images of ferrite, low-carbon martensite and high-carbon martensite differed in image contrast and regularity of net plane edges. This was attributed to the change in carbon content and strain in the matrix. The iron carbides were darker in the image than the ferrite matrix, probably due to the field-induced reaction of the hydrogen image gas with the carbide particles.

Hydrogen-ion images of as-quenched martensite revealed both twinned and untwinned martensite regions. Such an observation was consistent with the recent electron microscopy investigations on high-carbon martensites. In the field-ion images twins appeared as alternate bright and dark bands, the bright bands representing the twins and the dark bands the twin interfaces. In the twinned region {112} transformation twins were 25-100 Å wide, while in the untwinned region a high density of dislocations was observed.

In the first stage of tempering, fine ϵ -carbide particles, many as small as 20 Å, having a {100} habit precipitated on dislocations and along the sub-boundaries. The contrast around the carbide particles when

they intersected a $\{110\}$ region indicated the degree of coherency of these precipitates. Both coherent and partially-coherent ϵ -carbide particles were found throughout the first stage of tempering. At peak-hardness the average particle size and density were 60 \AA and 1.6×10^{17} particles/cm³, respectively, while later in the first stage of tempering the average particle size and density were 160 \AA and 8.3×10^5 particles/cm³, respectively. Therefore, it was concluded that dispersion hardening contributed more than coherency hardening to the peak-hardness in the first stage of tempering. These conclusions contradicted previous ones made from observations by other techniques and demonstrated the necessity of supplementary FIM results when studying microstructures with a high density of extremely fine particles.

In the third stage of tempering, cementite particles with both $\{110\}$ and $\{112\}$ habits were observed. The pronounced softening in this stage of tempering was associated with an increase in average particle size (600 \AA), a decrease in particle density (1.5×10^{15} particles/cm³) and the disappearance of twins.

Annual Technical Report

Institution: Georgia Institute of Technology
Principal Investigator: Helen E. Grenga
NSF Grant No.: GK-26487 (Amendment No. 1)
Grant Title: Chemisorption and Catalysis:
Carbon Monoxide on Metals and Alloys

Starting Date: September 1, 1971
Expiration Date: April 30, 1976

The report for the third year of this grant can be divided into four areas: (1) chemisorption studies, (2) surface rearrangement studies, (3) catalytic reaction studies and (4) publications, presentations and related activities.

It should be noted that during this year three new students have joined the program and are just beginning their research. A large amount of their time has been devoted to studying the problem and learning the specialized techniques for this research.

1. Chemisorption studies.

One Ph.D. thesis student is studying the chemisorption of CO on ruthenium at moderate temperatures. The probe-hole technique is being used in order to define chemisorption states on single crystal planes. This student entered the program in January 1974, after completing her B.S. in Chemical Engineering at Tech, and in the past seven months has acquired the necessary knowledge and skill to pursue the problem.

2. Surface rearrangement studies.

Partial support from this grant was given to one of my students, R. Kumar, who studied the faceting behavior of several metals in vacuum and in hydrogen for his Ph.D. thesis. Detailed results of these studies are given in his Ph.D. thesis ("FIM Studies on Surface Energy Anisotropy and Faceting Behavior of Metals," R. Kumar, Ga. Tech., 1974) and copies of the thesis summary accompany this report. The significance of Kumar's work to this grant include the design and construction of a reliable temperature controller for FIM and FEM specimens, the development of a model to explain the diffusion process on highly curved

surfaces of such specimens, the development of analytical procedures to interpret images of FIM specimens annealed in gaseous environments, and pertinent information concerning the interaction of hydrogen with metal surfaces at moderate temperatures.

One Ph.D. thesis student is extending these studies to investigate the surface rearrangements and faceting behavior of ruthenium in the presence of carbon monoxide at moderate temperatures. These results will compliment those of chemisorption studies with field emission so that the effects of rearrangements and changes in area can be determined. This student entered the program in June, 1974, after completing his M.S. in Engineering Science at Tennessee Tech. His M.S. thesis was "Determination of Geometrical End Forms of Field Ion Specimens." His theoretical background was therefore very good, and in the past three months he has gained the necessary experimental skills to pursue this problem.

3. Catalytic reaction studies.

One M.S. Thesis student, who joined the program in September, 1973, is studying the crystallographic specificity for carbon monoxide reactions on ruthenium. Thus far he has prepared the ruthenium single crystal specimens and has designed, acquired and partially assembled the high vacuum system. Results of these studies are expected within the next few months.

4. Publications and related activities.

Publications resulting in part from this grant for this year are:

"Field-ion Microscopy of Tempered Martensite," with B. N. Ranganathan
Phil. Mag. 30, 161 (1974).

"Surface Energy Anisotropy of Iridium," submitted for publication to Surface Science, with R. Kumar 1974.

"Field-ion Microscopy Studies on Surface Energy Anisotropy and Faceting Behavior of Metals," R. Kumar, Ph.D.Thesis, Ga. Tech, 1974.

Other publications include:

"Auger Analysis of Surface Films on Ag_3Sn ", with J. Carden, T. Okabe, and R. Hochman, paper presented to 52nd General Session of IADR, Atlanta, March, 1974; submitted for publication to J. Biomed. Materials, May, 1974.

Related activities include:

Development of Special Topics course in Catalysis (Met. 8100); taught in Spring Quarter, 1974 to 9 students.

Development of experiments in catalysis and field-ion microscopy for Surface Science and Technology summer laboratory (part of interdisciplinary program leading to M.S. in chemistry, chemical engineering and physics); supervised 2 students in this laboratory, Summer, 1974.

Attended Engineering Foundation Conference, Henniker, N.H., August, 1974.

To serve as chairman of 22nd International Field Emission Symposium to be held in Atlanta, August, 1975.

R. Kumar, Ph.D. Thesis
Georgia Tech., August, 1974

SUMMARY

The purpose of this work was to study the faceting behavior of iridium, tungsten, iron and platinum in vacuum and in hydrogen and to determine their surface energy anisotropies. High purity metals were annealed in the selected environment and observed with field-ion microscopy. From the size of the resulting facets, the surface energy anisotropy was calculated.

The observed anisotropies in vacuum were compared with those predicated by Morse and Mie potentials, and pairwise bonding theory. For iridium and platinum the best fit was found with the pairwise bonding theory with $\sigma_2=0.4$, $\sigma_3=0.2$ and $\sigma_2=0.3$, $\sigma_3=0$, respectively. For tungsten and iron the results were in close agreement with those predicted by Mie potential calculations with $m=5$, $n=7$, and $m=6$, $n=12$, respectively. The maximum anisotropy values were found to be 8.8, 4.3, 6.6, 16.8% for iridium, tungsten, iron and platinum, respectively.

The facets formed in hydrogen were generally larger than those formed in vacuum under the same annealing conditions. The higher growth rate was attributed to a weakening of the metal-metal bond energy, and therefore a lowering of the surface energy. For iridium and tungsten, hydrogen lowered the surface energy of the closest packed planes by more than 1%, which is a significant value for these calculations. For iron, the surface energy of (110) planes was lowered by approximately 14%.

The growth rates of iridium (111) and tungsten (110) facets were measured in vacuum, and it was found that the changes in facet sizes

were proportional to $t^{0.36}$ and $t^{0.315}$, respectively, and the facet sizes were proportional to $t^{0.20}$ in both cases.

The activation energies for growth of iridium (111) and tungsten (110) facets were also found to be 45.7 and 54.5 k cal/mole, respectively. These activation energies can be explained as the result of a surface diffusion mechanism in which detachment of atoms from kink sites is the rate controlling step.