1990

The effect of temperature, humidity and silicon content on the oxidation of fine iron particles

Allan S. Hadad
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

Hadad, Allan S., "The effect of temperature, humidity and silicon content on the oxidation of fine iron particles" (1990). *Master's Theses*. 3260.
DOI: <https://doi.org/10.31979/etd.e7ey-6583>
https://scholarworks.sjsu.edu/etd_theses/3260

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313 761-4700 800 521-0600

Order Number 1340513

**The effect of temperature, humidity and silicon content on the
oxidation of fine iron particles**

Hadad, Allan S., M.S.

San Jose State University, 1990

U·M·I

**300 N. Zeeb Rd.
Ann Arbor, MI 48106**

**THE EFFECT OF TEMPERATURE, HUMIDITY AND SILICON CONTENT
ON THE OXIDATION OF FINE IRON PARTICLES**

A Thesis

Presented to

**The Faculty of the Department of Materials Engineering
San Jose State University**

In Partial Fulfillment

**of the Requirements for the Degree
Master of Science**

By

Allan S. Hadad

May, 1990

APPROVED FOR THE DEPARTMENT OF MATERIALS ENGINEERING

Dr. Patrick P. Pizzo, Thesis Advisor

Dr. Guna Selvadurai, Professor of Mat. Eng.

Dr. Irving Wolf, Ampex Recording Media Corp.

APPROVED FOR THE UNIVERSITY

Serena R. Stanford

ABSTRACT

THE EFFECT OF TEMPERATURE, HUMIDITY AND SILICON CONTENT ON THE OXIDATION OF FINE IRON PARTICLES

By Allan S. Hadad

In this study, the oxidation and electrochemical corrosion of Fe-Si particles used in magnetic recording are investigated under controlled thermal and relative humidity conditions. The relative humidity, above some threshold value, dominates the degradation behavior. Degradation kinetics increase greatly above this threshold; and a portion of the exposed particle population becomes completely oxidized. X-ray diffraction data confirm the appearance of α -Fe₂O₃ in addition to the usual γ -Fe₂O₃ following exposure to the high humidities. Increased silicon content increases the threshold humidity above which rapid degradation in magnetic properties occurs.

ACKNOWLEDGEMENTS

The author wishes to thank the following from San Jose State University: Dr. Patrick P. Pizzo, thesis advisor, for his guidance and perseverance in seeing this project to its completion, and Dr. Guna Selvaduray for his helpful advice. The author is also grateful for the support given at Ampex Recording Media Corporation by the following: Dr. Irving Wolf for his sponsoring the project and providing valuable advice, Dr. Ashok Jhingan for the TEM work, Dr. Carl Stahle and Doug Daeschner for the ESCA analysis, Jiri Petovsky for synthesizing the samples that were studied, and especially Joan Vassallo for typing this manuscript. Special consideration is given to Deborah Hadad for being so supportive during this ordeal.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iii
ACKNOWLEDGEMENTS	iv
LIST OF FIGURES	vi
LIST OF TABLES	ix
I. INTRODUCTION	1
A. Background	1
B. Passivity and Protective Film Considerations	6
C. Alpha Iron Particle Processing	12
II. EXPERIMENTAL	17
A. Materials	17
B. Experimental Procedure	18
C. Analytical Methods	20
D. Analysis of the Data	21
III. RESULTS AND DISCUSSION	26
A. Effect of Temperature	26
B. Effect of Humidity	47
C. Interaction of Temperature, Humidity and Silicon	62
IV. CONCLUSIONS	68
V. SUGGESTIONS FOR FUTURE STUDY	70
REFERENCES	71
APPENDIX	
A. Experimental Data	74
B. Statistical Data	80

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Magnetic Material Hysteresis Loop	2
2 Magnetic Hysteresis Curve Characteristics of γ -Fe ₂ O ₃ and α -Fe	5
3 Temperature-Composition Diagram for the Iron-Oxygen System	7
4 Standard Free Energy of Formation as a Function of Temperature	8
5 Oxidation Mechanism of Iron to Form a Three Layered Scale Above 570°C	10
6 Room Temperature Mössbauer Spectra of (a) Passivated Iron Powder, (b) α -Fe Foil, (c) α -Fe ₂ O ₃ , (d) γ -Fe ₂ O ₃ , and (e) Fe ₃ O ₄	13
7 Magnetic Moment Versus Time as a Function of Temperature at Low Humidity for 0.81% Silicon in Iron	27
8 Magnetic Moment Versus Time as a Function of Temperature at Low Humidity for 0.95% Silicon in Iron	28
9 Magnetic Moment Versus Time as a Function of Temperature at Low Humidity for 1.12% Silicon in Iron	29
10 Rate of Magnetic Moment Loss as a Function of Absolute Temperature at Low Humidity	31
11 XRD Pattern of As-Received Iron Particles Containing 0.81% Silicon	33
12 XRD Pattern of As-Received Iron Particles Containing 0.95% Silicon	34
13 XRD Pattern of As-Received Iron Particles Containing 1.12% Silicon	35
14 XRD Pattern of Iron Particles Containing 0.81% Silicon Exposed to 90°C/9% Relative Humidity/332 Hours	38
15 ESCA Fe(2p) Electron Profiles of α -Fe Particles; Oxidized and Annealed	30
16 ESCA Fe(2p) Electron Profile of As-Received Iron Particles Containing 0.81% Silicon	41

<u>Figure</u>	<u>Page</u>
17 ESCA Fe(2p) Electron Profile of Iron Particles Containing 0.81% Silicon Exposed to 90 ⁰ C/9% Relative Humidity/332 Hours	42
18 (a) Brightfield TEM and (b) Electron Diffraction Pattern of as-Received Iron Particles Containing 0.81% Silicon Before Transformation	43
19 (a) Brightfield TEM and (b) Electron Diffraction Pattern of As-Received Iron Particles Containing 0.81% Silicon After Transformation	44
20 Bright Field TEM of Iron Particles Containing 0.81% Silicon After Exposure to 120 ⁰ /3% Relative Humidity/ 120 Hours	46
21 Magnetic Moment Versus Time as a Function of Temperature at High Humidity for 0.81% Silicon in Iron	48
22 Magnetic Moment Versus Time as a Function of Temperature at High Humidity for 0.95% Silicon in Iron	49
23 Magnetic Moment Versus Time as a Function of Temperature at High Humidity for 1.12% Silicon in Iron	50
24 XRD Pattern of Iron Particles Containing 0.81% Silicon Exposed to 90 ⁰ C/74% Relative Humidity/332 Hours	52
25 ESCA Fe(2p) Electron Profile of Iron Particles Containing 0.81% Silicon Exposed to 90 ⁰ C/74% Relative Humidity/332 Hours	54
26 Bright Field TEM of Iron Particles Containing 0.81% Silicon After Exposure to 90 ⁰ C/74% Relative Humidity/ 5 hours	55
27 Rate of Magnetic Moment Loss as a Function of Absolute Temperature at High Humidity	57
28 Magnetic Moment Versus Time as a Function of Relative Humidity for 0.81% Silicon in Iron at 70 ⁰ C	59
29 Magnetic Moment Versus Time as a Function of Relative Humidity for 0.95% Silicon in Iron at 70 ⁰ C	60
30 Magnetic Moment Versus Time as a Function of Relative Humidity for 1.12% Silicon in Iron at 70 ⁰ C	61

<u>Figure</u>	<u>Page</u>
31 Contour Plots of Magnetic Moment Degradation Rate as a Function of Temperature, Humidity and 0.81% Silicon in Iron Particles	64
32 Contour Plots of Magnetic Moment Degradation Rate as a Function of Temperature, Humidity and 0.95% Silicon in Iron Particles	65
33 Contour Plots of Magnetic Moment Degradation Rate as a Function of Temperature, Humidity and 1.12% Silicon in Iron Particles	66

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Fe and Si Self Diffusion and Diffusion Coefficients in Corresponding Oxides at Various Temperatures	16
2	As-Received Silicon Content of Specially Prepared Iron Particles	18
3	Environmental Exposure Conditions for Silicon-Containing Iron Particles	19
4	Qualitative Rating of the "Goodness of Fit" from ANOVA Data	25
5	Magnetic Measurements Following Exposure to Low Humidity	30
6	Reflections of Possible Species Present in Silicon Containing Iron Particles	36
7	Magnetic Measurements Following Exposure to High Humidity	51

CHAPTER I

INTRODUCTION

A. Background

Gamma iron oxide ($\gamma\text{-Fe}_2\text{O}_3$) is the backbone of the magnetic recording industry. Although the concept of magnetic recording was established by Vladimar Poulsen in the late 1880's, it wasn't until the 1930's to 1940's that the method was perfected by scientists in Germany. They used an iron oxide coating on a paper backing as a recording medium and, with improvements in electronics, very accurate reproductions of voice and music were produced. The German military was able to use this new technology to their advantage during World War II to fool the Allies. After Allied bombers would attack a German city, a mobile transmitting station would be set up and a pre-recorded radio program normally scheduled for that time would be broadcast, thus leading the Allies to believe they had missed their targets.

The sound quality of those recordings by today's standards is considered poor. Improvements in electronics have resulted in tape transports capable of recording high frequency signals for both video and audio information. Improvements in materials have led to better record/reproduce heads and improved magnetic particles with which the recording tapes are made. This project is concerned with these magnetic particles.

The parameters that describe the hysteretic properties of magnetic materials can be seen in Figure 1⁽¹⁾. Saturation magnetization, M_s ,

Figure 1. Magnetic Material Hysteresis Loop

expressed in Gauss is the total magnetization of the magnetic material in an applied external magnetic field when the sample is fully magnetized. M_S can also be expressed as:

$$M_S = 4 \pi I_S \quad (1)$$

where I_S is the magnetic moment per unit volume. The units of I_S are EMU/cm³. The specific magnetic moment, σ_S , is the more conventional value used to describe a magnetic material in powder form. σ_S , which is I_S divided by the material's bulk density, has the units of EMU/gram. From a practical standpoint, σ_S is easier to use, especially since accurate bulk density measurements of the powders are rather difficult to measure.

Remanent magnetization, M_r , is the induction remaining due to the sample after the applied magnetic field is reduced to zero. The units are also in Gauss. It is this value that relates to recorded information on magnetic tapes, disks, etc.

The magnetic squareness, $\square$, is the ratio of the remanent magnetization to the saturation magnetization.

The coercivity, H_C , measured in Oersteds, is the field required to reduce the magnetization or induction from a saturated magnetized sample to zero. It is in effect a material's resistance to being magnetized. This is important in determining the strength of field that is necessary to record or fully erase a recorded tape.

The most significant trend observed in the magnetic tape industry over the last 40 years has been the storage of more recorded information in less space through greater track densities (primarily mechanical improvements) and in more flux transitions per inch due to improvements in magnetic particle and magnetic head technology. Originally, magnetic recording was done using plain γ -Fe₂O₃ particles that averaged 0.75 μ m in length by 0.09 μ m in diameter with a coercivity of 270 Oersteds. The magnetic moment (σ_s) for these particles is 73.5 EMU/gram⁽²⁾. In order to achieve greater flux changes per inch, the particles have been made smaller (less than 0.25 μ m in length and 0.04 μ m in diameter). In order to improve the volumetric efficiency of the particles, a change was made from γ -Fe₂O₃ to pure iron (α -Fe phase), thus eliminating the oxygen that had occupied much of the crystal volume. The coercivity of these fine iron particles is as high as 1500 Oersteds and their magnetic moments are as high as 130 EMU/gram. The iron particles could be made much smaller than those of γ -Fe₂O₃ without the onset of paramagnetism. Figure 2 compares the magnetic hysteresis curves of γ -Fe₂O₃ and α -Fe particles.

Figure 2. Magnetic Hysteresis Curve Characteristics of $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}$

B. Passivity and Protective Film Considerations

The iron-oxygen system phase diagram shown in Figure 3⁽³⁾ shows that above 570°C a three layered scale consisting of (in order of formation from the iron surface) FeO, Fe₃O₄ and Fe₂O₃ forms. At temperatures below 570°C, iron oxidizes to form a two layered scale consisting of a magnetite (Fe₃O₄) inner layer and Fe₂O₃ outer layer.

The conditions under which the various oxides of iron will form are dictated by thermodynamics. A comparison of the standard free energy of formation (ΔG^0) versus temperature of various oxides using an Ellingham diagram is very useful in showing if the oxide state of a particular element is preferred. Figure 4⁽⁴⁾ shows the relative stability of the various oxides of iron. It can be seen that all of the iron oxides readily form even at low temperatures in the presence of as little as 10⁻¹⁰⁰ atm of oxygen.

Fe₂O₃ exists in two forms; non-magnetic α -Fe₂O₃ (hematite) which is rhombohedral, and ferromagnetic γ -Fe₂O₃ (maghemite) which is cubic. The γ form has an internal energy which is 6 kcal/mole higher than the α form making it less stable.⁽⁵⁾ The conversion of γ to α starts at 427°C and is complete by 510°C.⁽⁶⁾ Hematite is slightly oxygen deficient, Fe₂O_{3-x} (x<0.01).⁽⁷⁾

The ferrimagnetic Fe₃O₄ phase (magnetite, also expressed as FeO·Fe₂O₃) is an inverse spinel which is a fcc arrangement of oxygen

Figure 3. Temperature-Composition Diagram for the Iron-Oxygen System from Ref. (3)

Figure 4. Standard Free Energy of Formation as a Function of Temperature from Ref. (4)

ions with half of the Fe^{3+} ions in the tetrahedral sites; and the remaining half of the Fe^{3+} and all the Fe^{2+} ions are located in the octahedral sites. The magnetic moments are associated with each iron ion. The tetrahedral structure has moments oriented opposite to those in the octahedral structure resulting in complete cancellation of the contribution due to Fe^{3+} ions. The net magnetic moment arises entirely from the Fe^{2+} ions.

Defects occur in both octahedral and tetrahedral sites as magnetite can have a deficiency of cations, $\text{Fe}_{3-x}\text{O}_4$, which increases as $p(\text{O}_2)$ increases. Consequently, iron ions diffuse through the structure. The $\gamma\text{-Fe}_2\text{O}_3$ structure is essentially a defect spinel where again Fe^{3+} ions are relatively free to move through the structure. It is accepted that growth of the scale proceeds outward.⁽⁸⁾ Figure 5⁽⁹⁾ illustrates a three layer scale formed on iron with the diffusion steps and the interfacial reactions indicated.

The initial oxidation of iron proceeds at a constant rate (linear rate law) independent of the scale thickness⁽¹⁰⁾. Eventually there is a transition to the parabolic rate law as proposed by Wagner⁽¹¹⁾ where the oxidation rate is inversely proportional to the scale thickness. Transport of iron ions to the surface is the rate controlling step. The rate is controlled by the random jumping of the ions in three dimensions with a frequency dependent on their concentration. The thicker the oxide, the longer it takes for iron ions to reach the surface. Once on the surface, the chemical reaction between oxygen and iron proceeds very rapidly. It is the slowing down of the ions through the thickening

Figure 5. Oxidation Mechanism of Iron to Form a Three Layered Scale Above 570°C from Ref. (9)

oxide scale that leads to the condition of passivity. The oxide layer in effect protects the pure iron beneath it from further oxidation.

The continued stability of iron particles is controlled by the integrity of the oxide layer and the kinetics of diffusion of iron ions through it. A pure iron particle with a surface oxide layer, if left long enough or exposed to elevated temperature, will continue to oxidize as iron ions migrate to the surface and react with ambient oxygen. As the process continues, vacancies accumulate at the interface between the oxide and the elemental iron, forming voids⁽¹²⁾. Cracks in the oxide due to the specific volume difference between the iron and the oxide formed allow oxygen to penetrate to the surface of the voids and begin the rapid oxidation process again. Presumably, the process continues until the iron has completely oxidized.

In a study done by Lee et al.⁽¹³⁾, iron particles stored at 50°C under nitrogen for one month began to burn almost instantly when exposed to air. Auger spectroscopy showed an increase in the surface iron concentration with time when particles were heated in a vacuum to 300°C.

The presence of water vapor has been shown to disrupt the passive layer subsequently increasing the oxidation of the iron so that it again follows the linear rate law. The primary cause is through the establishment of electrochemical corrosion. The oxide shell is no longer protective but is penetrated by moisture and electrolytic cells are formed. The oxygen rich oxide layer will act as the cathode and the

iron will be the anode. This effect of electrochemical corrosion is much more devastating to the iron than chemical corrosion. Chemical corrosion results in the formation of an adhered scale leading to the condition of passivity.

C. Alpha Iron Particle Processing

Alpha iron particles (α -Fe) used for magnetic recording are prepared through a series of dehydration and reduction steps of γ -Fe₂O₃ resulting in acicular, polycrystalline body centered cubic (bcc) α -Fe particles that are single magnetic domains. A key step to producing stable (passivated) iron particles is in controlled oxidation of the surface as a final step in their processing. The usual technique of producing the protective oxide layer is through re-oxidation of the iron particle's surface starting with a mixture of 0.1% O₂ and 99.9% N₂. The oxygen content is slowly increased to 20% (the composition of air). This normally results in a particle that is stable in air provided it is not subjected to any form of 1) mechanical abuse that could disturb the outer layer, or 2) source of heat that would initiate combustion.

The nature of the passive layer that forms on the outside of iron particles following controlled exposure to oxygen has been found to consist of either Fe₃O₄, γ -Fe₂O₃ or a mixture of the two. Mössbauer spectra (Figure 6)⁽¹⁴⁾ of passivated iron particles does not show the characteristic lines of any of the possible oxide species present. The broad background of the passivated iron sample indicates the presence of the oxide in a magnetically or crystallographically ill-defined state.

Figure 6. Room Temperature Mössbauer Spectra of (a) Passivated Iron powder, (b) α -Fe Foil, (c) α -Fe₂O₃, (d) γ -Fe₂O₃, and (e) Fe₃O₄ from Ref. (12)

Identification of which iron oxide is present by X-ray diffraction is difficult because the patterns of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ are very similar. The two oxides are actually the final products of a series of continuous solid solutions having the spinel structure with an increasing deficiency of iron ($\text{Fe}_3\text{O}_4 \rightarrow \gamma\text{-Fe}_2\text{O}_3$)⁽¹⁵⁾. The thickness of the passivation (or total) oxide layer is typically about 3.0 nm⁽¹⁶⁾. As stated earlier, the condition of passivity slows down the oxidation of iron. But, the formation of the iron-oxide layer around metallic iron particles does not preclude further oxidation. Since iron particles used for magnetic recording are small, additional oxidation has a direct impact on performance especially where archival storage of recorded information for long periods of time (i.e., 25+ years) is important. Further stabilization chemistry/processes had to be developed to guarantee that iron particles could be considered as a viable long term recording medium.

In an effort to retard the diffusion of iron ions through the oxide layer, other elements have been added to the base iron to promote more dense scale formation or to alleviate some of the non-stoichiometric behavior of the oxide or both. Silicon, aluminum and chromium have been used as additives to form protective scales on iron based alloys used for high temperature service⁽¹⁷⁾.

The effect of adding silicon to iron to decrease its high temperature oxidation rate has been well documented^(18, 19). It has been shown that silicon-rich scale forms, limiting subsequent diffusion of iron ions to the surface due to the fact that the diffusion

coefficient of iron in SiO_2 is much lower than it is for iron through any of the iron oxides. Table 1⁽²⁰⁾ gives relevant diffusion coefficients at various (high) temperatures.

The only citations found in the literature regarding the subsequent stability of passivated iron and iron alloys containing the stabilizing additives were conducted at relatively high temperatures (150°C - 1000°C). Since these temperatures are beyond those that would be experienced by iron particles used in the production of magnetic recording media, this study was undertaken to examine the degradation in magnetic properties as a function of both temperature and humidity on silicon-containing iron particles between 50 - 120°C and 3-89% relative humidity. Silicon-containing iron particles were chosen for the following reasons:

- a. The silicon content could be systematically varied in iron made from a single batch of precursor.
- b. The effect of silicon on decreasing the oxidation rate of iron (albeit at high temperatures) is well documented.

Table 1 - Fe and Si Self Diffusion and Diffusion Coefficients in Corresponding Oxides at Various Temperatures

Solute	Solvent	D at 900°C (cm ² /sec)	D at 1000°C (cm ² /sec)	D at 1100°C (cm ² /sec)	Activation Energy (eV/mole)
Fe	FeO	3.6x10 ⁻⁸	2.3x10 ⁻⁷	1.6x10 ⁻⁷	
Fe	Fe ₃ O ₄	1.0x10 ⁻⁶	5.0x10 ⁻⁶	1.0x10 ⁻⁵	1.63
Fe	Fe ₂ O ₃	1.0x10 ⁻¹³	1.0x10 ⁻¹³	1.0x10 ⁻¹²	3.46
Fe	SiO ₂	7.0x10 ⁻¹⁶	1.7x10 ⁻¹⁴	4.1x10 ⁻¹³	
O	FeO	2.3x10 ⁻⁹	4.8x10 ⁻⁸	6.3x10 ⁻⁷	
O	SiO ₂ (glass)	1.0x10 ⁻¹⁴	2.2x10 ⁻¹⁴	5.0x10 ⁻¹⁴	
Si	Fe(lattice)	7.7x10 ⁻¹¹	5.6x10 ⁻¹⁰	3.1x10 ⁻⁹	2.54
Fe	Fe	-	2.5x10 ⁻¹⁰	1.4x10 ⁻⁹	2.55
Si	SiO ₂	2.0x10 ⁻¹⁰	-	-	
O	Fe ₂ O ₃	1.0x10 ⁻¹⁴	1.0x10 ⁻¹³	1.0x10 ⁻¹³	

CHAPTER II

EXPERIMENTAL

A. Materials

To study the effect of temperature and humidity on the stability of passivated iron particles as a function of silicon content, three batches of particles were produced by the acidic preparation procedure. Yellow iron (III) hydroxide (2FeOOH or $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$) was precipitated from an aqueous solution of ferrous sulfate upon the addition of NaOH solution. The desired amount of sodium silicate was stirred into the solution containing the precipitate and the pH adjusted to 8-9. This insures minimum solubility of the sodium silicate in the solution and maximum affinity for the yellow iron oxide particle's surface. The Si coated particles were filtered, dried and heated to $600\text{-}700^\circ\text{C}$ for 3 hours to produce the red, rhombohedral $\alpha\text{-Fe}_2\text{O}_3$. Heating in a rotary kiln in the presence of hydrogen at 450°C reduces the $\alpha\text{-Fe}_2\text{O}_3$ to the spinel magnetite (Fe_3O_4) within 15 minutes and to the bcc $\alpha\text{-Fe}$ in 4-5 hours. The particles were then stabilized by passing a mixture of 0.2% oxygen and 99.8% nitrogen over them at room temperature. The oxygen content was slowly increased to 20%, never allowing the exothermic reaction to increase the powder batch above room temperature. At that point, the particles were deemed stable under ambient conditions and provided the starting material for this study. Table 2 gives the composition (determined by atomic emission spectroscopy) and the as-received magnetic properties of the three pre-passivated particles used for this study.

TABLE 2 - As-Received Silicon Content of Specially Prepared Iron Particles

Silicon (Weight %)	σ_s (EMU/gr)	Hc (Oersteds)	Br/Bs -
0.81	127.70	975	.402
0.95	125.01	1123	.448
1.12	95.43	1263	.493

The as-received powder samples were passed through a number 35 sieve (500 μ m) to ensure uniform agglomerate size. The particles were then exposed to various environmental conditions as described in the next section.

B. Experimental Procedure

The various temperature and humidity environments were created inside closed glass dessicators that had been placed in a Blue M^R air circulation oven that could maintain temperature within $\pm 1^\circ\text{C}$. The treatment environments were allowed to come to equilibrium overnight prior to introducing the samples. Approximately 1 gram of iron powder was placed in separate glass vials corresponding to the number of exposure times investigated per temperature/humidity condition. In this way each exposure time specimen could be removed with minimum influence on the other specimens and each was small enough so that exposure within the specimen was uniform. The exposure conditions investigated are shown in Table 3.

TABLE 3 - Environmental Exposure Conditions for Silicon-Containing Iron Particles

Silicon Content (weight %)	Temperature (°C)	Humidity	
		(% Relative)	(% Absolute)
0.81	50	18	1.38
"	50	52	4.10
"	50	66	5.25
"	50	89	7.17
"	70	7	1.36
"	70	47	9.54
"	70	59	12.21
"	70	74	15.83
"	90	9	3.94
"	90	74	39.93
"	105	4	3.04
"	120	3	3.13
0.95	50	18	1.38
"	50	52	4.10
"	50	66	5.25
"	50	89	7.17
"	70	7	1.36
"	70	47	9.54
"	70	59	12.21
"	70	74	15.83
"	80	7	2.06
"	80	77	26.24
"	90	9	3.94
"	90	74	39.93
1.12	50	18	1.38
"	50	52	4.10
"	50	66	5.25
"	50	89	7.17
"	70	7	1.36
"	70	47	9.54
"	70	59	12.21
"	70	74	15.83
"	90	9	3.94
"	90	74	39.93
"	105	4	3.04
"	120	3	3.13

The lowest relative humidity for each temperature (i.e., 50°C/18% RH, 70°C/7% RH, etc.) was obtained by placing a layer of CaCl_2 desiccant in the bottom of the desiccator that the samples were contained in during exposure. For the intermediate relative humidities at 50°C (52% and 66%), a beaker of saturated NaBr and KI, respectively, was placed in the closed desiccator. The same solutions were used to prepare the 70°C/47% RH and 70°C/59% RH conditions. The highest relative humidities studied at each temperature were obtained by placing a beaker of de-ionized water in the desiccator. Humidities were measured using an Abbeon hydrometer. After the specimens were removed from the treatment environment, they were placed in a closed desiccator with CaCl_2 for 24 hours at 20°C before the magnetic measurements were made.

C. Analytical Methods

The magnetic properties of the specimens were determined using a vibrating sample magnetometer (Model 155) built by Princeton Applied Research. An applied field of 7500 gauss was used to fully saturate the samples and determine coercivity (H_c), squareness ratio (B_r/B_s) and specific magnetic moment (σ_s). This enabled data plots of changing magnetic properties to be produced. The magnetics data measured herein represent average values. The maximum variation in the measurements (absolute precision of the data) was $\pm 2\%$.

Several specimens were examined using X-ray diffraction (XRD) to relate any changes observed in the magnetics of the powders after exposure to various environmental conditions to the nature of the oxide

formed. The XRD apparatus used was a Philips Diffractometer with monochromator and $\text{Cu K}\alpha$ radiation. Samples were prepared by pressing the powder into a 5/8" diameter x 1/16" deep recess machined into a sample holder made of a piece of 1-1/2"x 3/4"x 1/8" polyethylene.

Some samples were also examined using a Zeiss EM10C/CR transmission electron microscope operated at 100 kV in an attempt to resolve internal structure and determine if any morphology changes could be observed.

Evaluation by X-Ray Photoelectron Spectroscopy (XPS) using the VG ESCALAB apparatus was performed to determine, if possible, any changes in chemical bonding of the oxides.

D. Analysis of the Data

As stated earlier, the oxidation process of iron particles is diffusion controlled. The rate at which the oxide layer builds up is determined by how fast the iron ions can move to the surface. A number of methods to measure the rate of oxidation could thus be employed including weight gain, oxide thickness or magnetic properties change. Measuring the oxide thickness could have been done using direct TEM imaging. But, a large number of high magnification photographs would have been necessary to obtain statistically valid data. Weight gain provides better information on average behavior as does measuring the decrease in magnetic moment. If it is assumed that reduction in σ_s is proportional to the growth in oxide thickness as the iron core is

oxidized, then Fick's second law of diffusion for concentration dependent systems can be applied:

$$X \cong \sqrt{D t} \quad (2)$$

where:

X = diffusion distance in cm

D = diffusivity in cm^2/sec

t = diffusion time in sec.

For this analysis, the data are plotted as specific magnetic moment versus the square root of time. The resultant slope (rate of degradation expressed as $\text{EMU}/\text{gram}\cdot\text{sec}^{0.5}$) for a given temperature and humidity condition is then plotted against the inverse of absolute temperature in typical Arrhenius fashion to show the effect of temperature, humidity and percent silicon on the oxidation rate of the iron particles. The energy of activation for the process is directly calculated from the Arrhenius plot.

Analysis of the interactive effects of temperature, humidity and percent silicon on the degradation of magnetic properties of iron particles were determined using XSTAT, a statistical experimental design package run on an IBM AT compatible computer. The factor settings that were input into the computer were those found in Table 3 with the exception of the 105°C and 120°C runs. This represents a modified three variable, three level factorial experiment. The characteristic measured was the $\log_{10}$ of σ_s loss per second $^{0.5}$ (rate of degradation).

PLEASE NOTE:

Page(s) not included with original material
and unavailable from author or university.
Filmed as received.

U·M·I

The procedure of analysis consists of selecting an initial mathematical model (usually a quadratic equation to analyze interaction and curvature effects of the form $Y = C_0 + C_1X_1 + C_2X_2 + \dots + C_{12}X_1X_2 + C_{13}X_1X_3 + \dots + C_{11}X_1^2 + C_{22}X_2^2 + \dots$). The model is then used to "fit" the data.

A table of residuals is generated to observe how well the tentative model predicts the given characteristic. The table shows the actual data as well as the predicted data and the variation between the actual and predicted data. Discrepancies of many kinds can be detected by examining the differences between the actual and predicted values (residuals) versus experimental conditions, factor levels, time, temperature, etc. The residuals are what remains after the contributions from the model are removed. The residuals should be distributed randomly. If the residuals show a trend, the model should be suspect. A scatter plot of the residuals, therefore, should have the appearance of a normal distribution.

An analysis of variance (ANOVA) is performed to determine how well the regression equation predicts the data (what percent of the variance is explained) and how much lack of fit is attributed to pure error: Qualitative ratings of the strength of the percent variance explained are shown in Table 4.

TABLE 4 - Qualitative Rating of the "Goodness of Fit" From ANOVA Data

<u>% Variance Explained</u>	<u>Rating</u>
95-100	Excellent
85-94	Good
75-84	Fair
< 74	Poor

The regression coefficients are then generated to see what the equation looks like. The confidence level of each of the coefficients is also calculated and displayed. The model is then modified if necessary; coefficients are dropped one at a time starting with the least significant until the best model is obtained which will accurately predict the data and have the least amount of error. This model is used to generate a response surface map. The response surface map is a two dimensional contour plot which shows how a characteristic varies as a function of two variables while holding all other variables constant.

CHAPTER III

RESULTS AND DISCUSSION

The oxidation data for the Si-containing Fe particles of this study are reported in Appendix A and summarized in this chapter. The chapter will be divided into three sections: Effect of Temperature; Effect of Humidity; and the Interaction of Temperature, Humidity and Silicon.

A. Effect of Temperature

Oxidation rate studies are generally done as a function of temperature without reference to humidity. It is assumed that the ambient humidity present is 1) either too low to have any effect, especially at the high temperatures studies are usually performed, or 2) constant at all test conditions so that any change in oxidation rate is assumed to be only a function of the exposure temperature. As stated earlier, low humidity control was obtained in this study by using CaCl_2 to absorb as much ambient moisture as possible.

The first series of oxidation rate experiments were run at as low relative humidity as possible for the selected temperatures. Oxidation at various temperatures allowed generation of σ_s vs. time curves for iron particles containing 0.81, 0.95 and 1.21% silicon. The data are shown in Figures 7, 8 and 9. The rates of magnetic moment loss for the respective curves are reported in Table 5.

Figure 7. Magnetic Moment versus Time as a Function of Temperature at Low Humidity for 0.81% Silicon in Iron

Figure 8. Magnetic Moment Versus Time as a Function of Temperature at Low Humidity for 0.95% Silicon in Iron

Figure 9. Magnetic Moment Versus Time as a Function of Temperature at Low Humidity for 1.12% Silicon in Iron

TABLE 5 - Magnetic Measurements Following Exposure to Low Humidity

Temperature (°C)	% Relative Humidity	Degradation Rate, EMU/gram-sec ^{0.5}		
		0.81	0.95	1.12% Si
50	18	0.0043*	-0.0110	-0.0071
70	7	-0.0094	-0.0128	-0.0133
80	7		-0.0203	
90	9	-0.0184	-0.0313	-0.0240
105	4	-0.0320		-0.0387
120	3	-0.0503		-0.0635

* Spurious measurement as only one data point was taken

As temperature increased, the rate of degradation of σ_s also increased. Differences in the rate of degradation at a given temperature between specimens of different silicon content are slight. What is obvious is the difference in the initial magnetic moments for the samples. As silicon is increased from 0.81 to 0.95% by weight there is little change in the initial σ_s . However, when the silicon content has been increased to 1.12% the decrease in the starting value of σ_s is much more pronounced. The effect of silicon on the magnetics appears to be greater than can be explained by simple dilution alone. An explanation for this phenomenon drawn from the X-ray data will be presented later.

Figure 10 is a plot of the rate of σ_s loss versus the inverse of the absolute temperature. Apparently the particles all behave the same independent of Si content or initial σ_s value. Conceivably, the amount of silicon present at the scale-Fe interface is insufficient to form a continuous protective barrier; or the diffusion rate at the low temperatures studied is too slow for a barrier of predominantly silicon to form.

Figure 10. Rate of Magnetic Moment Loss as a Function of Absolute Temperature at Low Humidity

Calculating the slopes of each of the lines in Figure 10 results in activation energies of 0.383, 0.263, 0.333 eV for the 0.81, 0.95 and 1.12% silicon-in-iron powder samples, respectively. The energy requirement to initiate the oxidation reaction for the various Si-contents is essentially the same and all degrade at essentially the same rate as a function of temperature. These activation energy values are only 10% of the values shown in Table 1. The implication is that the primary mechanism for the loss in magnetic properties is not due to lattice diffusion but rather diffusion along some short circuit path such as defects present in the oxide shell. The activation energy for grain boundary diffusion in fcc metals is generally 1/2 the activation energy required for lattice diffusion. The large difference between the apparent activation energy through the oxide matrix observed in this study versus the values shown in Table 1 indicates the presence of considerable energy in the form of strain (i.e., atomic mismatch at the metal/oxide interface and grain boundaries, high surface area to volume ratio, twinning, etc.). Grain boundary diffusion apparently is not the only explanation for the loss in magnetic properties at temperatures between 50°C and 120°C at low humidity.

In an effort to study the nature of the passive layer, x-ray diffraction patterns were obtained for selected specimens. The diffraction patterns for the as-received powder samples containing 0.81, 0.95, and 1.12% silicon (shown in Figures 11, 12 and 13, respectively) are interpreted as a mixture of α -Fe and an oxide of iron (either γ -Fe₂O₃ or Fe₃O₄ or both). Comparing the peak positions in the figures with predicted values (Table 6) does not reveal the true nature of the

Figure 11. XRD Pattern of As-Received Iron Particles Containing 0.81% Silicon

Figure 12. XRD Pattern of As-Received Iron Particles Containing 0.95% Silicon

Figure 13. XRD Pattern of As-Received Iron Particles Containing 1.12% Silicon

TABLE 6 - Reflections of Possible Species Present in Silicon Containing Iron Particles
(Cu Radiation)

hkl	Alpha iron (6-0696)			Gamma iron oxide (4-0755)			Gamma iron oxide (13-458)			Fe3O4 (11-614)			Alpha Iron Oxide (13-534)			FeSi (1-1271)			FeSi2 (1-1285)		
	d (A)	I/Io	2θ	d (A)	I/Io	2θ	d (A)	I/Io	2θ	d (A)	I/Io	2θ	d (A)	I/Io	2θ	d (A)	I/Io	2θ	d (A)	I/Io	2θ
001																					
012																					
003																					
101																					
102																					
103																					
104																					
110			44.72																		
111	2.027	100																			
113																					
116																					
200			65.09																		
210	1.433	20																			
211																					
212	1.170	30	82.42																		
213																					
214																					
220	1.013	10	99.06																		
221																					
222	0.828	6	137.39																		
300																					
310	0.906	12	116.55																		
311																					
313																					
321	0.766																				
333																					
400																					
422																					
440																					
620																					
1010																					

oxide. However, there is enough similarity between the 2θ angles of the diffraction patterns and the values from the card file to suggest a mixed oxide. The relative intensity ratios imply a mixture of $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 . Comparing the ratios between the oxide peaks and the $\alpha\text{-Fe}$ peaks seems to indicate essentially the same degree of oxidation for the 0.81 and 0.95% silicon as-received samples. However, the 1.12% silicon as-received sample appears to be oxidized (pre-passivated) to a greater extent. This would explain the lower initial σ_s value for the high Si-content particles.

Following exposure to $90^\circ\text{C}/9\%$ relative humidity for 332 hours, the intensity of the iron peaks ((110),(220)) decreased and the intensity of the oxide peaks had increased (Figure 14). The identity of the mixed oxide remains the same as the as-received sample. The same behavior was observed for the 0.95% and 1.12% silicon-containing particles.

Electron Spectroscopy for Chemical Analysis (ESCA) can distinguish between the various oxidation states of iron that are present in a mixed oxide system. Application of this technique was attempted to provide more information than that obtained with X-ray diffraction into revealing the true nature of the oxide present on the silicon-containing particles used for this investigation. In a study by Tagawa et al.⁽²¹⁾ ESCA Fe(2p) electron profiles were produced of two iron particles samples; one being oxidized at 50°C and the other annealed at 300°C for an unspecified amount of time. It can be clearly seen in Figure 15 that only one peak corresponding to Fe^{3+} (Fe_2O_3) is present in the oxidized sample while the annealed sample exhibits a weak shoulder due to the

Figure 14. XRD Pattern of Iron Particles Containing 0.81% Silicon Exposed to 90°C/9% Relative Humidity/332 Hours

Figure 15. ESCA Fe(2p) Electron Profiles of γ -Fe Particles; Oxidized and Annealed from Ref. (21)

presence of Fe^{2+} (Fe_3O_4) in addition to Fe^{3+} . The presence of a mixed oxide is readily identified by this technique.

In an effort to determine the composition of the oxide present on the iron powders used in this study, ESCA profiles were produced for the as-received specimen containing 0.81% silicon and the same specimen after exposure to 90°C at 9% relative humidity for 332 hours. The profiles are shown in Figures 16 and 17. The profiles indicate that the surface composition is primarily Fe_2O_3 . No significant differences are seen even after the temperature exposure: formation of Fe_3O_4 is unlikely due to the lack of an Fe^{2+} shoulder.

Bright field transmission electron microscopy was performed before and after exposure of selected iron powders to various environmental conditions. The as-received specimen containing 0.81% silicon was not stable under the electron beam. As soon as an image was formed at a minimum of 10,000X magnification, the particles would undergo an in-situ transformation from fine needles to large spheres. Figures 18 and 19 show the particles before and after transformation and their respective electron diffraction patterns. The pattern before transformation shows the characteristic ring pattern for the bcc phase iron and one ring that could either be $\gamma\text{-Fe}_2\text{O}_3(313)$ or $\alpha\text{-Fe}_2\text{O}_3(110)$. The two superimposed ring patterns are somewhat diffuse indicating very small grain structure. There are no resolvable spots on the ring attributable to the oxide structure. After transformation the ring patterns became more refined and include many resolvable spots. The bcc phase iron pattern is still quite prevalent. The first four rings with diameters

Figure 16. ESCA Fe(2p) Electron Profile of As-Received Iron Particles Containing 0.81% Silicon

Figure 17. ESCA Fe(2p) Electron Profile of Iron Particles Containing 0.81% Silicon Exposed to 90°C/9% Relative Humidity/332 Hours

(a)

(b)

Figure 18. (a) Brightfield TEM and (b) Electron Diffraction Pattern of As-Received Iron Particles Containing 0.81% Silicon Before Transformation

(a)

(b)

Figure 19. (a) Brightfield TEM and (b) Electron Diffraction Pattern of As-Received Iron Particles Containing 0.81% Silicon After Transformation

inside the α -Fe(110) ring indicate the presence of an oxide; but the calculated d-spacings are not exact. It appears that the transformation was to a more thermodynamically stable shape as opposed to the formation of an oxide from residual oxygen remaining in the microscope. The formation of the large spheres indicates that there is metal-to-metal contact which allows rapid Fe-transport to occur in response to the rather large capillary forces involved. The thin as-received oxide structure is apparently not robust enough to withstand the particle dispersion process used in preparing the TEM samples.

After the 0.81% silicon material was exposed to 120°C at 3% relative humidity for 120 hours, it was stable enough to be examined in the TEM. No in-situ transformation was observed. Figure 20 reveals a central dark region of α -Fe surrounded by a lighter contrast oxide layer. The oxide appears to be loosely attached to the core. This is consistent with an observation made by Kaito⁽²²⁾, where a particle of iron that had been heated to 500°C for 10 seconds consisted of a central and surrounding dark region separated by a light region. The light area appears to be either a cavity or an area filled with amorphous material. The light region was observed to grow when the particle was subsequently heated for extended times. Electron diffraction of the particles indicates that the outer shell consists of γ -Fe₂O₃ and a small amount of α -Fe₂O₃ and Fe.

The decrease in degradation rate of the magnetic properties of the iron particles with time for this study was attributed to the expanding oxide scale. With increasing time, it takes longer for the iron ions to

Figure 20. Bright Field TEM of Iron Particles Containing 0.81% Silicon After Exposure to 120⁰/3% Relative Humidity/120 Hours

migrate to the surface. An additional hypothesis would postulate that if contact is lost between the scale and the Fe-particle core due to rapid iron depletion and if the core remains intact, then iron could no longer migrate as easily to the surface, leading to a decreased rate of degradation.

B. Effect of Humidity

The second set of oxidation experiments were run at as high a relative humidity as possible for the given temperatures without observable condensation occurring during the exposures. The magnetic moment vs. time curves for the 0.81, 0.95 and 1.21% silicon-in-iron are shown in Figures 21, 22 and 23. It is immediately obvious that the initial rate of degradation for all three samples is much higher than was observed when humidity was very low. The initial rate of change for the 0.81 and 0.95% silicon samples is now exhibiting a steep drop while the 1.12% silicon sample shows a less steep drop due to the lower initial σ_s value. Following the initial rapid decrease, it is seen that the magnetic moment appears to reach some saturation limit.

The initial slopes of the degradation curves for the high humidity conditions are reported in Table 7. The degradation appears to stop after the σ_s value reaches 50-60 EMU/gr for the 0.81% silicon sample (Figure 21). As stated earlier, the σ_s value for $\gamma\text{-Fe}_2\text{O}_3$ is 73.5 EMU/gr. A calculation done by Kishimoto⁽²³⁾ using the occupation value of iron particles with the surrounding iron oxide layer based on TEM micrographs established the σ_s of the oxide to be about 40 EMU/gr.

Figure 21. Magnetic Moment Versus Time as a Function of Temperature at High Humidity for 0.81% Silicon in Iron

Figure 22. Magnetic Moment Versus Time as a Function of Temperature at High Humidity for 0.95% Silicon in Iron

Figure 23. Magnetic Moment Versus Time as a Function of Temperature at High Humidity for 1.12% Silicon in Iron

TABLE 7 - Magnetic Measurements Following Exposure to High Humidity

Temperature (°C)	% Relative Humidity	Degradation Rate, EMU/gram-sec ^{0.5}		
		0.81%	0.95%	1.12% Si
50	89	-0.2640	-0.2111	-0.0103
70	74	-0.2432	-0.1952	-0.0286
80	77		-0.4111	
90	74	-0.5694	-0.4715	-0.0492

This calculation assumed the particles to be cylinders, ignored end effects and assumed that the oxide phase was continuous. Based on the saturation limit of <50 EMU/gr for the high humidity exposures of this study, a significant volume fraction of the iron particles must have been oxidized to a non-magnetic form. TEM and XRD data will be presented which supports this.

The X-ray diffraction pattern (Figure 24) of the 0.81% silicon exposed to 90°C/74% relative humidity for 332 hours shows the presence of the same oxide phase found in the as-received sample (Figure 11) and in the sample exposed to 90°C/9% relative humidity for 332 hours (Figure 14), only in much greater quantity. In addition, there is evidence of α -Fe₂O₃ and FeSi₂. The presence of these two non-magnetic species offers an explanation as to why the specific magnetic moment value drops below the values for either γ -Fe₂O₃ or Fe₃O₄ magnetic oxides.

Reactions that occur with iron in the presence of both moisture and air (oxygen) are:

Figure 24. XRD Pattern of Iron Particles Containing 0.81% Silicon Exposed to 90% Relative Humidity/332 Hours

where $2\text{Fe}(\text{OH})_3$ is also expressed as $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (hydrated, non-magnetic alpha-hematite). The reason that the kinetics of degradation of the iron in the presence of moisture is so much faster than in air alone may be related to the fact that the additional partial pressure of water vapor is altering the defect concentration in the oxide layer making it easier to transport iron ions to the surface. Additionally, the electric field present due to the formation of an electrical double layer at the surface as oxygen and water ionize may provide an additional driving force for the iron ions to migrate.

The ESCA Fe(2p) profile for the 0.81% silicon-containing sample exposed at $90^\circ\text{C}/74\%$ relative humidity for 332 hours (Figure 25) was identical to the as-received and $90^\circ\text{C}/9\%$ relative humidity/322 hour samples (Figures 16 and 17, respectively). No evidence of Fe^{2+} (Fe_3O_4) was observed.

Figure 26 is a 50,000X brightfield TEM micrograph of the specimen containing 0.81% silicon and exposed to $90^\circ\text{C}/74\%$ relative humidity for 5 hours. This corresponds to the point in Figure 21 where the magnetic degradation has reached the saturation limit. Examination of the micrograph reveals a number of particles with constant, light contrast throughout. Particles with a visible oxide shell and an iron core apparently are not affected by the exposure and account for higher coercivity values than would be observed if the conversion to $\gamma\text{-Fe}_2\text{O}_3$ was complete.

Figure 25. ESCA Fe(2p) Electron Profile of Iron Particles Containing 0.81% Silicon Exposed to 90°C/74% Relative Humidity/332 Hours

Figure 26. Brightfield TEM of Iron Particles Containing 0.81% Silicon After Exposure to 90°C/74% Relative Humidity/ 5 hours

Figure 27 shows degradation rate versus $1/T$ for the high humidity samples. It is apparent that silicon is playing a role in reducing the oxidation rate of the iron in the presence of high humidity. The 1.12% silicon sample shows an order of magnitude less loss rate versus the 0.81% and 0.95% silicon samples. This is consistent with the X-ray data which indicates that the 1.12% silicon sample is already in a state of higher passivity when received. This could be possible if the high silicon content were to make the particle more reactive during the pre-passivation step resulting in more oxide and lower initial σ_s .

The lowest temperature data (50°C) indicate that there is no decrease in rate for the 0.81% and 0.95% samples from the 70°C data point, an apparent anomalous trend. Absolute humidity was not controlled in the study. Therefore, the high relative humidity at 50°C obtained by the method employed was considerably higher than for the 70 and 90°C high humidity exposures. This can be seen in the data of Table 7. The presentation of the data in the form of an Arrhenius plot to determine activation energy is no longer possible because of the contribution from relative humidity to the degradation rate. The parallel mechanisms of thermally activated diffusion and electrochemical processes can lead to apparently anomalous behavior when the data is presented in the form of Figure 27. The next section which addresses the interactive effects of temperature and humidity will explain the anomalous results of Figure 27.

Figure 27. Rate of Magnetic Moment Loss as a Function of Absolute Temperature at High Humidity

The evidence that silicon protects the particles in the presence of humidity is further substantiated by Figures 28, 29 and 30. Magnetic moment loss is shown as a function of humidity at constant temperature for the 0.81, 0.95 and 1.12% silicon samples, respectively. As the humidity increases, the rate at which the magnetic moment degrades increases markedly for the sample containing 0.81% silicon. The sample containing 0.95% silicon is more resistant to degradation until the relative humidity is above 59% at 70°C. Finally, the sample containing 1.12% silicon is the most resistant to degradation exhibiting almost the same rate of loss at 7% relative humidity as it does at 74% relative humidity.

The apparent threshold value of humidity that is observed at the 0.95% silicon level and possibly the 1.12% level, above which the degradation rate increases very rapidly, is consistent with results reported by Uhlig⁽²⁴⁾. He reports that a critical humidity exists below which corrosion is negligible. For steel, copper, nickel and zinc the critical value is between 50 and 70% relative humidity. The time of exposure must also be considered in defining the threshold.

There is evidence in this study that as silicon content increases, the critical humidity (at a given temperature where rapid degradation occurs) also increases.

Figure 28. Magnetic Moment Versus Time as a Function of Relative Humidity for 0.81% Silicon in Iron at 70°C

Figure 29. Magnetic Moment Versus Time as a Function of Relative Humidity for 0.95% Silicon in Iron at 70°C

Figure 30. Magnetic Moment Versus Time as a Function of Relative Humidity for 1.12% Silicon in Iron at 70°C

C. Interaction of Temperature, Humidity and Silicon

From the previous two sections it has become obvious that the three variables studied (temperature, percent relative humidity and percent silicon content) interactively influence the degradation of the iron particles. Statistical analysis was performed to quantify the contribution of each variable and present it in a manner that could be easily visualized.

The analysis maintained the variables as temperature, percent relative humidity and weight percent silicon in iron. The measured characteristic was the $\log_{10}$ of the degradation rate in specific magnetic moment (EMU/gram-second^{0.5}) as previously determined.

The design predictor equation determined for the $\log_{10}$ (degradation rate) using XSTAT is as follows:

$$\begin{aligned}\log_{10}(\text{Rate}) = & -14.76 + 25.26(X_{Si}) + 0.04176(X_{RH}) + 0.00015(X_T * X_{RH}) \\ & -0.05963(X_{Si} * X_{RH}) + 0.000068(X_T)^2 - 12.49(X_{Si})^2 \\ & +0.000219(X_{RH})^2\end{aligned}\quad (5)$$

where:

X_{Si} = concentration of silicon in weight percent

X_T = temperature in degrees Celsius

X_{RH} = percent relative humidity.

The % variance explained is 96.03% so an "excellent" rating is assigned to the model as per Table 4. Full statistical information is shown in Appendix B.

Solving the predictor equation via the computer produces two dimensional contour plots of percent relative humidity versus temperature at constant silicon content. The values of constant degradation rate were transferred to a psychrometric chart (Figures 31, 32 and 33) so the relationships between absolute humidity (as pounds of water per pound of dry air), percent relative humidity and temperature as a function of silicon content could be observed. The non-linear degradation behavior becomes very obvious when presented in this manner. A rate value can be taken from the contour plots for a given temperature, humidity and percent silicon content and be used to determine how long it would take for the magnetic moment to degrade to some predetermined value.

It is interesting to note that, for a fixed moisture content, if the temperature is raised the degradation rate can actually decrease. It appears that relative humidity is the controlling factor. The reverse of this was actually observed in Figure 27 when the 50°C/89% relative humidity exposure condition exhibited the same degradation rate as the 70°C/74% relative humidity exposure condition for the 0.81 and 0.95% silicon samples. This serves to point out the value of the XSTAT analysis.

Figure 31. Contour Plots of Magnetic Moment Degradation Rate as a Function of Temperature, Humidity and 0.81% Silicon in Iron Particles

Figure 32. Contour Plots of Magnetic Moment Degradation Rate as a Function of Temperature, Humidity and 0.95% Silicon in Iron Particles

Figure 33. Contour Plots of Magnetic Moment Degradation Rate as a Function of Temperature, Humidity and 1.12% Silicon in Iron Particles

By definition, relative humidity is the ratio of the vapor pressure of water in air at some temperature divided by the partial pressure of water at that same temperature at saturation. This is also an expression of activity which is the driving force of the degradation reaction. If the temperature increases, the relative humidity decreases as does the activity and the over-all effect at high temperature is for the degradation rate to decrease. Special precautions should be taken when attempting to predict long term low temperature behavior based on high temperature data with a system that is humidity sensitive such as this one. Actual archival stability could be less than expected unless humidity control is maintained during high temperature exposure.

CHAPTER IV

CONCLUSIONS

This study has shown the effects of percent silicon content, temperature and percent relative humidity on pre-passivated fine iron particles used for magnetic recording. It was observed that silicon had very little effect on the specific magnetic moment of the as-received iron between 0.81 and 0.95% by weight. However, at 1.12% silicon content the magnetic moment was much lower than would be expected by dilution alone. X-ray diffraction revealed a greater degree of oxidation in the as-received powder sample probably due to greater reactivity of the α -Fe during the pre-passivation step. The nature of the oxide was determined by X-ray diffraction and ESCA to be primarily magnetic γ -Fe₂O₃.

When the iron particles were exposed to various temperatures between 50 and 120°C at very low humidity it was observed that the degradation rates were not affected by either the silicon content or the initial value of the magnetic moment. The mechanism of degradation was attributed to diffusion of iron ions through the oxide matrix via short circuit paths such as grain boundaries or other defects. The activation energy of this process was determined to be an order of magnitude less than that for normal lattice diffusion. X-ray diffraction indicated the oxide structure was the same as the as-received samples. TEM micrographs revealed that the oxide layer grew thicker leading to a condition of passivity.

It was shown that for a given temperature there exists a critical relative humidity value above which the degradation rate of magnetic moment increases markedly. The presence of silicon appears to increase the critical humidity value at which rapid degradation occurs. When the magnetic moment degrades to 50-60 EMU/gram it subsequently remains constant for any additional exposure time. The degradation is due to the two processes of chemical oxidation via thermal ionic transport and electrochemical corrosion occurring simultaneously. TEM reveals that a large fraction of the iron particles completely oxidize while others are relatively unaffected. X-ray diffraction indicates the presence of non-magnetic α -Fe₂O₃ which may explain magnetic moment values less than expected if the oxidation product was all γ -Fe₂O₃. The formation of α -Fe₂O₃ is attributed to a change in mechanism from chemical oxidation to electrochemical corrosion for the higher relative humidity exposures. The electrochemical processes result in complete oxidation of some of the iron particles rather than a gradual growth of the oxide shell.

A parametric expression has been proposed to relate silicon content, temperature and humidity to the initial rate of specific magnetic moment degradation for the iron particles used in this study.

CHAPTER V

SUGGESTIONS FOR FUTURE STUDY

Among the areas that should be studied in the future are:

- a. The effect of a wider range of silicon levels in iron particles to more completely characterize the effect silicon has on both the initial magnetic properties and on the oxidation resistance of the particles.
- b. The effect of other elements (i.e., Al) on the stability of iron particles.
- c. The effect of absolute humidity on the stability of iron particles, through a more balanced experimental design, in order to develop a better parametric expression for observed behavior.
- d. Use X-ray powder techniques (i.e., Debye-Scherrer) to accumulate enough radiation for higher order lines to be resolved such that more accurate identification of the oxide structure can be made.
- e. Study those particles that did not degrade completely at high humidity to determine what is different about them.

Investigation into the above areas listed should provide insight into the fundamental changes that are occurring when fine iron particles are exposed to various environmental conditions. This would lead to more accurate prediction of long term behavior.

REFERENCES

- (1) John J. Newman, "Magnetic Measurements for Digital Magnetic Recording", IEEE Transactions on Magnetics, Vol. MAG-14, No. 4, (July 1978), p. 154.
- (2) L. A. Marusak, P. L. Walker, Jr. and L. N. Mulay, "The Magneto-kinetics of Oxidation of Pyrite (FeS_2)", IEEE Transactions on Magnetics, Vol. MAG-12, No. 6, (November 1976), p. 889, hereafter cited as Marusak.
- (3) Lawrence S. Darken, Robert W. Gurry, Physical Chemistry of Metals, McGraw-Hill Book Company, Inc., New York (1953), p. 351.
- (4) Richard A. Swalin, Thermodynamics of Solids, John Wiley and Sons, London (1962), p. 84.
- (5) Paul Nylon and Edward Sunderland, Modern Surface Coatings, John Wiley and Sons, London (1965), p. 479.
- (6) Marusak, p. 889.
- (7) O. Toft Sorensen, Nonstoichiometric Oxides, Academic Press, New York, (1981), p. 220.
- (8) A. Bruckman and G. Simkovich, "Concerning the Mechanism of Scale Growth Due to Cation Diffusion in Fe_2O_3 and CuS ", Corrosion Science, Vol. 12 (1972), p. 595.
- (9) N. Birks and G. H. Meier, Introduction to High Temperature Oxidation of Metals, Edward Arnold Ltd, London, (1983), p. 74.
- (10) V. V. Struminskii, V. M. Gremyachkin and E. M. Gokhmin, "The Model of High Temperature Oxidation of a Spherical Iron Particle in Water Vapor", Oxidation Communications 4, Nos. 1-4 (1983), p. 317.

- (11) Mars G. Fontana and Norbert D. Green, Corrosion Engineering, McGraw-Hill, New York (1967), p. 356.
- (12) Chihiro Kaito, Kazuo Fujita and Toshio Naiki, "Electron Microscopic Observation of Fine Iron Smoke Particles", Japan Journal of Applied Physics, 9 (1970), p. 151; hereafter cited as Kaito.
- (13) Ting-Ho Dan Lee, Sidney Hu and Nerisa Madulid, "Stability Studies of Iron Particle", IEEE Transactions on Magnetism, Vol. MAG-23, No. 5 (September 1987), p. 2881.
- (14) A. M. van Diepen, H. J. Vledder and C. Langereis, "The Nature of the Passivating Oxide Layer on Iron Powder", Applied Physics, 15 (1977), p. 164.
- (15) D. E. Davies, and V. R. Evans, "The Identity of the Cubic Oxide Present in Films on Iron", Journal of the Chemical Society (1956), p. 4373.
- (16) M. Kishimoto, S. Kitahata and M. Amemiya, "Morphology and Magnetic Properties of the Iron Oxide Layer Formed on Iron Acicular Particles", IEEE Transactions on Magnetism, Vol. MAG-22, No. 5 (September 1986), p. 732; hereafter cited as Kishimoto.
- (17) Walter James Sherwood, Jr., "The Effect of Water Vapor on the Oxidation Behavior of Dilute Iron-Silicon Alloys", PhD Thesis, Rensselaer Polytechnic Institute, Troy New York (Dec. 1986), p. 1; hereafter cited as Sherwood.
- (18) I. Svedung and N.-G. Vannerberg, "The Influence of Silicon on the Oxidation Properties of Iron", Corrosion Science, Vol. 14 (1974), p. 391.
- (19) T. Ban, K. Bohnenkamp and H.-J. Engell, "The Formation of Protective Films on Iron Silicon Alloys", Corrosion Science, Vol. 19 (1979), p. 283.

- (20) Sherwood, p. 134.
- (21) Kimiteru Tagawa et al., "Annealing Effect of Oxidized -Fe Particles", IEEE Transactions on Magnetics, Vol. MAG-22, No. 5 (September 1986), p. 730.
- (22) Kaito, p. 151.
- (23) Kishimoto, p. 733.
- (24) Herbert H. Uhlig, Corrosion and Corrosion Control, 3rd ed., John Wiley and Sons Inc., New York, p. 173.

APPENDIX A

Experimental Data

EXPOSURE DATA

TEMP (°C)	HUMIDITY (% RH)	SILICON (Wt. %)	TIME (Hours)	SIGMA (EMU/Gr)	SQUAR. -	COERCIV (Oersteds)
50	18	0.81	0	127.70	0.402	975
50	18	0.81	63	129.74	0.404	970
50	18	0.95	0	125.01	0.448	1123
50	18	0.95	63	119.79	0.435	1100
50	18	1.12	0	95.43	0.493	1263
50	18	1.12	63	92.05	0.496	1280
50	52	0.81	0	127.70	0.402	975
50	52	0.81	63	97.82	0.409	950
50	52	0.95	0	125.01	0.448	1123
50	52	0.95	63	106.67	0.445	1110
50	52	1.12	0	95.43	0.493	1263
50	52	1.12	63	93.61	0.491	1265
50	66	0.81	0	127.70	0.402	975
50	66	0.81	1	125.25	0.406	970
50	66	0.81	24	115.00	0.405	960
50	66	0.81	48	109.49	0.403	960
50	66	0.95	0	125.01	0.448	1123
50	66	0.95	1	119.80	0.418	1110
50	66	0.95	2	120.89	0.456	1125
50	66	0.95	5	118.20	0.458	1110
50	66	0.95	24	110.99	0.449	1120
50	66	0.95	48	110.97	0.445	1115
50	66	1.12	0	95.43	0.493	1263
50	66	1.12	1	94.85	0.460	1220
50	66	1.12	2	93.97	0.481	1260
50	66	1.12	5	94.55	0.476	1230
50	66	1.12	24	92.62	0.503	1290
50	66	1.12	48	91.96	0.470	1250
50	89	0.81	0	127.70	0.402	975
50	89	0.81	1	123.25	0.406	970
50	89	0.81	2	120.70	0.415	990
50	89	0.81	3	114.38	0.403	980
50	89	0.81	7	93.89	0.360	920
50	89	0.81	24	55.97	0.344	860
50	89	0.81	48	55.78	0.263	860
50	89	0.81	168	53.35	0.336	810
50	89	0.81	318	50.26	0.361	790
50	89	0.95	0	125.01	0.448	1123
50	89	0.95	1	114.82	0.451	1125
50	89	0.95	2	105.69	0.451	1140
50	89	0.95	3	94.49	0.451	1095
50	89	0.95	5	86.69	0.450	1110
50	89	0.95	24	64.23	0.439	1050
50	89	0.95	168	68.21	0.400	1045
50	89	1.12	0	95.43	0.493	1263
50	89	1.12	1	90.60	0.469	1260

EXPOSURE DATA

TEMP (°C)	HUMIDITY (% RH)	SILICON (Wt. %)	TIME (Hours)	SIGMA (EMU/Gr)	SQUAR. -	COERCIV (Oersteds)
50	89	1.12	7	88.50	0.496	1280
50	89	1.12	24	87.23	0.492	1260
50	89	1.12	48	87.04	0.498	1240
50	89	1.12	168	84.91	0.486	1260
50	89	1.12	318	81.17	0.499	1270
70	7	0.81	0	127.70	0.402	975
70	7	0.81	1	129.91	0.419	970
70	7	0.81	2	128.70	0.412	930
70	7	0.81	3	129.24	0.328	960
70	7	0.81	5	128.98	0.420	980
70	7	0.81	24	128.13	0.410	940
70	7	0.81	48	126.84	0.422	990
70	7	0.81	168	120.70	0.398	996
70	7	0.81	336	119.88	0.388	960
70	7	0.95	0	125.01	0.448	1123
70	7	0.95	1	122.14	0.383	1110
70	7	0.95	2	120.97	0.446	1120
70	7	0.95	3	120.40	0.434	1110
70	7	0.95	5	120.30	0.445	1140
70	7	0.95	21	119.97	0.416	1120
70	7	0.95	72	116.75	0.446	1145
70	7	1.12	0	95.43	0.493	1263
70	7	1.12	2	93.86	0.485	1260
70	7	1.12	3	94.32	0.500	1250
70	7	1.12	24	92.66	0.484	1245
70	7	1.12	48	88.60	0.479	1190
70	7	1.12	168	85.57	0.479	1245
70	7	1.12	336	80.69	0.495	1270
70	47	0.81	0	127.70	0.402	975
70	47	0.81	3	130.77	0.412	1000
70	47	0.81	5	124.62	0.396	975
70	47	0.81	24	122.11	0.394	990
70	47	0.81	72	111.67	0.417	1000
70	47	0.95	0	125.01	0.448	1123
70	47	0.95	3	119.28	0.438	1140
70	47	0.95	5	122.82	0.462	1135
70	47	0.95	24	116.20	0.433	1125
70	47	0.95	72	110.28	0.426	1120
70	47	1.12	0	95.43	0.493	1263
70	47	1.12	3	91.89	0.481	1220
70	47	1.12	5	95.99	0.490	1280
70	47	1.12	24	93.46	0.481	1280
70	47	1.12	72	88.48	0.499	1290
70	59	0.81	0	127.70	0.402	975
70	59	0.81	1	126.74	0.413	1000
70	59	0.81	2	129.57	0.401	1000

EXPOSURE DATA

TEMP (°C)	HUMIDITY (% RH)	SILICON (Wt. %)	TIME (Hours)	SIGMA (EMU/Gr)	SQUAR. -	COERCIV (Oersteds)
70	59	0.81	3	126.18	0.399	1005
70	59	0.81	5	127.34	0.398	990
70	59	0.81	21	113.75	0.404	980
70	59	0.95	0	125.01	0.448	1123
70	59	0.95	1	120.84	0.447	1100
70	59	0.95	2	121.89	0.455	1145
70	59	0.95	3	119.39	0.448	1130
70	59	0.95	5	120.73	0.419	1120
70	59	0.95	21	114.82	0.439	1130
70	59	1.12	0	95.43	0.493	1263
70	59	1.12	1	92.40	0.491	1260
70	59	1.12	2	93.58	0.488	1290
70	59	1.12	3	94.62	0.500	1270
70	59	1.12	5	94.11	0.457	1250
70	59	1.12	21	91.80	0.487	1260
70	74	0.81	0	127.70	0.402	975
70	74	0.81	1	117.10	0.412	980
70	74	0.81	2	99.31	0.375	940
70	74	0.81	3	98.77	0.409	900
70	74	0.81	24	56.18	0.382	840
70	74	0.81	48	50.90	0.367	850
70	74	0.81	168	51.23	0.344	760
70	74	0.81	336	53.31	0.353	800
70	74	0.95	0	125.01	0.448	1123
70	74	0.95	1	113.86	0.448	1140
70	74	0.95	2	104.15	0.449	1120
70	74	0.95	3	95.83	0.448	1130
70	74	0.95	5	92.25	0.434	1110
70	74	0.95	21	71.53	0.437	1075
70	74	0.95	72	57.37	0.392	990
70	74	1.12	0	95.43	0.493	1263
70	74	1.12	1	90.91	0.503	1290
70	74	1.12	2	89.97	0.507	1325
70	74	1.12	3	88.24	0.492	1250
70	74	1.12	5	88.42	0.486	1260
70	74	1.12	24	84.21	0.484	1270
70	74	1.12	48	82.81	0.489	1225
70	74	1.12	168	69.48	0.486	1220
70	74	1.12	336	62.11	0.483	1190
80	7	0.95	0	125.01	0.448	1123
80	7	0.95	1	123.18	0.454	1130
80	7	0.95	3	121.96	0.454	1120
80	7	0.95	5	121.66	0.454	1125
80	7	0.95	24	118.10	0.432	1110
80	7	0.95	48	112.37	0.395	1090
80	7	0.95	168	107.75	0.452	1100

EXPOSURE DATA

TEMP (°C)	HUMIDITY (% RH)	SILICON (Wt. %)	TIME (Hours)	SIGMA (EMU/Gr)	SQUAR. -	COERCIV (Oersteds)
80	7	0.95	336	102.96	0.435	1090
80	77	0.95	0	125.01	0.448	1123
80	77	0.95	1	109.78	0.455	1130
80	77	0.95	2	93.12	0.413	1100
80	77	0.95	3	86.01	0.375	1050
80	77	0.95	5	70.37	0.419	1070
80	77	0.95	24	59.35	0.389	980
80	77	0.95	48	56.41	0.401	1000
80	77	0.95	168	51.77	0.382	910
80	77	0.95	336	43.83	0.379	890
90	9	0.81	0	127.70	0.402	975
90	9	0.81	3	126.80	0.337	976
90	9	0.81	5	125.48	0.409	979
90	9	0.81	22	122.31	0.345	952
90	9	0.81	48	116.00	0.410	964
90	9	0.81	332	108.35	0.403	995
90	9	0.95	0	125.01	0.448	1123
90	9	0.95	1	120.45	0.445	1100
90	9	0.95	5	119.31	0.458	1095
90	9	0.95	72	107.96	0.429	1090
90	9	1.12	0	95.43	0.493	1263
90	9	1.12	1	93.15	0.501	1255
90	9	1.12	2	91.92	0.494	1255
90	9	1.12	3	91.73	0.500	1240
90	9	1.12	5	91.79	0.369	1240
90	9	1.12	22	84.12	0.467	1240
90	9	1.12	48	81.43	0.477	1225
90	9	1.12	170	75.51	0.483	1225
90	9	1.12	332	68.89	0.492	1250
90	74	0.81	0	127.70	0.402	975
90	74	0.81	1	100.38	0.404	945
90	74	0.81	2	94.18	0.390	948
90	74	0.81	3	60.85	0.315	738
90	74	0.81	48	56.64	0.326	728
90	74	0.81	170	58.62	0.305	682
90	74	0.81	332	54.94	0.280	644
90	74	0.95	0	125.01	0.448	1123
90	74	0.95	1	98.31	0.448	1125
90	74	0.95	2	87.21	0.421	1075
90	74	0.95	3	74.89	0.428	1030
90	74	0.95	5	76.24	0.416	1010
90	74	0.95	72	60.57	0.359	910
90	74	1.12	0	95.43	0.493	1263
90	74	1.12	1	86.61	0.498	1260
90	74	1.12	5	82.33	0.451	1240
90	74	1.12	22	69.64	0.450	1200

EXPOSURE DATA

TEMP (°C)	HUMIDITY (% RH)	SILICON (Wt. %)	TIME (Hours)	SIGMA (EMU/Gr)	SQUAR. -	COERCIV (Oersteds)
90	74	1.12	48	60.60	0.444	1170
90	74	1.12	170	46.90	0.445	1125
90	74	1.12	332	40.47	0.413	1070
105	4	0.81	0	127.70	0.402	975
105	4	0.81	6	121.98	0.414	988
105	4	0.81	24	115.57	0.404	968
105	4	0.81	120	106.25	0.391	964
105	4	0.81	168	101.97	0.397	968
105	4	1.12	0	95.43	0.493	1263
105	4	1.12	2	91.12	0.479	1260
105	4	1.12	4	85.98	0.470	1245
105	4	1.12	6	84.37	0.479	1215
105	4	1.12	24	75.95	0.466	1225
105	4	1.12	120	67.41	0.459	1240
105	4	1.12	168	63.27	0.484	1220
120	3	0.81	0	127.70	0.402	975
120	3	0.81	2	119.06	0.398	955
120	3	0.81	4	116.60	0.415	957
120	3	0.81	6	115.32	0.413	957
120	3	0.81	72	97.82	0.405	944
120	3	0.81	120	92.52	0.388	918
120	3	1.12	0	95.43	0.493	1263
120	3	1.12	2	81.58	0.474	1235
120	3	1.12	4	76.96	0.486	1230
120	3	1.12	6	74.54	0.476	1225
120	3	1.12	24	65.45	0.458	1195
120	3	1.12	100	52.99	0.457	1225

APPENDIX B

Statistical Data

```

Menu0> Load thesta3
Menu0> fit log_rate
LOG_RATE:
  standard deviation about the regression = 0.1331
  explained variation about the mean (R-squared) = 96.03%
  condition of design matrix = 539.5
  model = EXPLICIT 1.0,
    SILICON,
    REL_HUMID,
    TEMP*REL_HUMID,
    SILICON*REL_HUMID,
    TEMP^2.0,
    SILICON^2.0,
    REL_HUMID^2.0
Menu0> residual log_rate

```

Table of Residuals for LOG_RATE

RUN	Controlled Factors			Characteristic LOG_RATE			Residuals		
	TEMP	REL_HUMID	SILICON	Observed	Predicted	Residuals	MIN	0	MAX
1	50.00	66.00	0.8100	-1.358	-1.306	-0.0518		x	
2	50.00	18.00	0.9500	-1.959	-1.928	-0.0311		x	
3	50.00	52.00	0.9500	-1.415	-1.656	0.2417			x
4	50.00	66.00	0.9500	-1.345	-1.397	0.0523			x
5	50.00	89.00	0.9500	-0.676	-0.785	0.1094			x
6	50.00	18.00	1.1200	-2.149	-2.210	0.0613			x
7	50.00	66.00	1.1200	-2.086	-2.166	0.0801			x
8	50.00	89.00	1.1200	-1.987	-1.787	-0.2000	x		
9	70.00	7.00	0.8100	-2.027	-2.123	0.0963			x
10	70.00	7.00	1.1200	-1.876	-1.893	0.0168		x	
11	70.00	74.00	0.8100	-0.614	-0.666	0.0521			x
12	70.00	74.00	1.1200	-1.544	-1.675	0.1309			x
13	80.00	7.00	0.9500	-1.693	-1.609	-0.0833		x	
14	80.00	77.00	0.9500	-0.386	-0.520	0.1339			x
15	90.00	9.00	0.8100	-1.735	-1.863	0.1277			x
16	90.00	9.00	0.9500	-1.504	-1.478	-0.0260		x	
17	90.00	9.00	1.1200	-1.620	-1.670	0.0499			x
18	90.00	74.00	0.8100	-0.245	-0.225	-0.0193		x	
19	90.00	74.00	0.9500	-0.327	-0.384	0.0570			x
20	90.00	74.00	1.1200	-1.308	-1.234	-0.0743		x	
21	50.00	89.00	0.8100	-0.578	-0.501	-0.0769		x	
22	70.00	47.00	0.8100	-1.511	-1.490	-0.0214		x	
23	70.00	59.00	0.8100	-1.270	-1.163	-0.1067		x	
24	70.00	47.00	1.1200	-1.959	-1.999	0.0408			x
25	70.00	59.00	1.1200	-2.000	-1.894	-0.1055		x	
26	70.00	7.00	0.9500	-1.893	-1.722	-0.1708	x		
27	70.00	47.00	0.9500	-1.551	-1.423	-0.1284		x	
28	70.00	59.00	0.9500	-1.466	-1.196	-0.2696	x		
29	70.00	74.00	0.9500	-0.710	-0.824	0.1148			x

```

          x
          x
        x x x
      x x x x
    xx x x xx
  x xx xxxxx xxxxx x
|-----|-----|
MIN          0          MAX

```

Menu0> anova log_rate

Analysis of Variance for LOG_RATE

Source	df	SS	MS	F-Ratio
Total (corrected)	28	9.3793		
Regression	7	9.0074	1.28677	72.66 (1)
Residual	21	0.3719	0.01771	

(1) Implies 99.9% confidence regression equation is nonzero.
Menu0> coefficient log_rate

Regression Coefficients for LOG_RATE

Coefficient	Term	Standard Error	T-Value	Confidence Coef <> 0
-14.76	1.000	2.069	7.136	99.9%
25.26	SILICON	4.180	6.043	99.9%
0.04176	REL_HUMID	0.0108	3.877	99.9%
0.000150	(TEMP*REL_HUMID)	0.0001	2.384	98.1%
-0.05963	(SILICON*REL_HUMID)	0.0073	8.193	99.9%
0.000068	(TEMP^2.000)	0.0000	2.487	98.5%
-12.49	(SILICON^2.000)	2.131	5.859	99.9%
0.000219	(REL_HUMID^2.000)	0.0000	4.512	99.9%

Confidence figures are based on 21 degrees of freedom
Coefficients 1 and 2 and 7 provide similar information (condition index = 539.5)
Menu0> map log_rate vary temp,rel_humid section na,na,0.81

LOG_RATE

SILICON = 0.8100
Menu0> map log_rate vary temp,rel_humid section na,na,0.95

SILICON = 0.9500
Menu0> map log_rate vary temp,rel_humid section na,na,1.12

SILICON = 1.120
Menu0> set pwidth 135
Replaces 80