

CORROSION BEHAVIOR OF HEAT TREATED
18 PER CENT NICKEL MARAGING STEEL

by

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INTRODUCTION

In many instances, the desirable physical and mechanical properties of steels may determine their use, but it is generally true that one of their most important properties is their ability to withstand corrosion in a great many of the environments likely to be encountered by modern materials of construction. It is, therefore, necessary to make tests under these environments, investigate the processes involved and observe the corrosion behavior which is usually determined by the structure and composition. Structural alterations take place in steel when it is subjected to various heat treatments and as a result of these alterations, the magnitude of resistance to corrosion also changes.

PURPOSE

The purpose of this study was to investigate the effect of various heat treatments on the corrosion behavior of 18 per cent nickel maraging steel in one normal solution of sulfuric acid. Such a study should yield some information concerning the change in the corrosion resistance of the alloy that takes place due to change in heat treatments.

MARAGING STEELS

"Maraging steels" is the name given to a class of high-nickel, extra-low-carbon, iron-base alloys. These alloys have been termed "maraging" steels since their strength evolves primarily from the aging of a martensitic matrix. There are four major types of maraging steels containing 15 per cent, 18 per cent, 20 per cent and 25 per cent nickel. The 18 per cent nickel type is the most important at present, because of its advantageous use in large high-strength structures including pressure vessels, rocket motor cases, and large boosters. There are three popular grades in 18 Ni type arbitrarily based on yield strength i.e. the 200, 250, and 300 grades representing yield strength levels of 200,000, 250,000, and 300,000 psi, respectively which are achieved by varying the amounts of titanium, molybdenum, and cobalt present in the alloy.

The maraging steels have certain advantages over the low-alloy quenched-and-tempered martensitic steels. These advantages include good forming characteristics of the annealed alloy even though it is martensitic, attainment of high strengths with a relatively simple heat treatment at moderate temperatures, minimum dimensional change and distortion on heat treatment, and virtual immunity to decarburization. The fabrication characteristics and weldability by conventional techniques are other advantages of these steels.

LITERATURE REVIEW

The International Nickel Company, which originally developed the maraging series late in 1959, introduced the 18 per cent nickel member in 1961. Since then, a number of programs in the various grades of 18 per cent nickel type are being investigated which are in progress under governmental and private industrial sponsorship. A great deal of knowledge and understanding of the mechanical properties has been gained as a result of these programs. The International Nickel Company has investigated the stress corrosion cracking behavior of some of the members of the maraging series, the details of which have not yet been published. Decker, Eash and Goldman (2) gave some idea about the stress-corrosion resistance of 18 per cent nickel type.

Excellent stress-corrosion resistance.
Low alloy steel at the same yield and stress level failed in 2 days with 3-point loading in sea water. Furthermore, low alloy steels subjected to atmospheric stress corrosion at lower yield and stress levels failed.

Vanadium-Alloys Steel Company compared the 18 per cent nickel maraging steel with the beam type specimen of 300 M steel (4340 plus Silicon) for stress corrosion cracking in artificial sea water. 300 M steel failed in two days whereas the maraging 250 grade did not crack for more than 185 days.

Little work has been done in laboratories to study the change in the corrosion behavior of maraging steel when treated with different aging temperatures and times. This

is due to two reasons:

1. The laboratories engaged in research on maraging steels have focused their attention mostly on the investigation of the mechanical properties of the various members of the series.

2. The major obstacle encountered in the physical metallurgy of the maraging steels is in the aging studies. Cheney (1) discussed the aging process of 18 per cent nickel type.

We were not as successful in aging studies, however. Though we repeatedly attempted to observe structural alterations when aging the steel in the 900 to 1000 F range, none appeared. (This surprised us. Though we did not expect to see actual precipitation, we felt that structural modifications should be visible.)

The corrosion study of these alloys becomes very complicated without the understanding of the second point. The nature and kind of precipitate formed during the aging process is yet to be revealed by the investigators.

CORROSION THEORY AND METALLURGY

ELECTROCHEMICAL MECHANISM OF CORROSION

Metal surfaces are made up of a composite of electrodes, all of which are components of electrolytic cells, short circuited through the metal, and with the corrosive environment acting as an electrolyte (10). The electric current flows as soon as the metal is exposed to the electrolyte, and the resultant corrosion takes place at the electrodes called anodes. This is illustrated by the reaction for dissolution of iron:

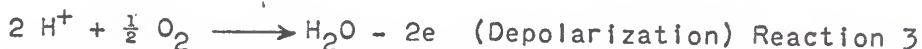


The following simultaneous reaction may take place at the electrodes called cathodes:



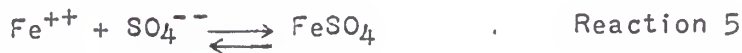
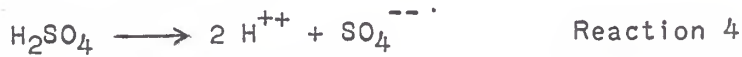
Since the precipitates present in the matrix of the steel constitute cathodic electrodes, their state of dispersion or particle size being the resultant of heat treatment, a relation between the nature of heat treatment and the corrosion behavior of steel is believed to exist.

The reaction 2 is fairly rapid in acids but becomes slower in alkaline or neutral aqueous media. The cathodic reaction can be accelerated by dissolved oxygen in accordance with the following reactions, a process called depolarization because it removes the cause of polarization.



The dissolved oxygen reacts with the adsorbed hydrogen atoms on the cathodic surfaces of steel, independent of the presence or absence of impurities. The cathodic reaction is called the controlling reaction since the polarization takes place at this electrode. Ferrous ions are highly soluble so the process of polarization is very slight in the anodic reaction.

When a solution of dilute sulfuric acid is used as an electrolyte, the ionic reactions are as follows:



In the case of acids, the reaction is the sum of both an appreciable rate of hydrogen evolution and oxygen depolarization. The hydrogen evolution depends on the structural phases present in a specific steel. These internal phases or the microstructure, which are much effected by the heat treatment, are very important when corrosion occurs due to the hydrogen evolution. Heat treatment, therefore, influences greatly the corrosion behavior of steel.

METALLURGY OF 18 PER CENT NI MARAGING STEEL

The phase relationships and their features, which control the behavior of maraging steels are controlled largely by the phase relationships prevailing in the binary iron-nickel system. (2) The normally observed transformation characteristics of the system are illustrated by figure 1, a diagram by Jones and Pumphrey. (6) This diagram shows that an 18 per cent nickel alloy must normally be heated to 1180°F or above to be completely transformed to austenite. The maraging steels contain substantial amounts of cobalt, molybdenum, and titanium in addition to nickel, so these must be heated to a minimum temperature of about 1350°F to assure complete transformation to austenite.

As a result of the studies of annealing cycles for the 18 per cent nickel maraging steels, the recommended annealing treatment, usually around 1500°F , dissolves precipitates and promotes relief of internal residual stresses developed during hot working, cold working, or joining.

Gilbert and Owen have shown that, at nickel content of 18 per cent, the transformation temperature is sufficiently depressed that martensite forms, rather than ferrite, under all conditions of cooling. (5) The transformed martensite is not disturbed by adding such other elements as molybdenum, cobalt, and titanium, the presence of which provides the 18 per cent nickel maraging steels with their distinguishing characteristics. The M_s temperature of these steels is in the vicinity of 310°F , while their M_f temperature is about

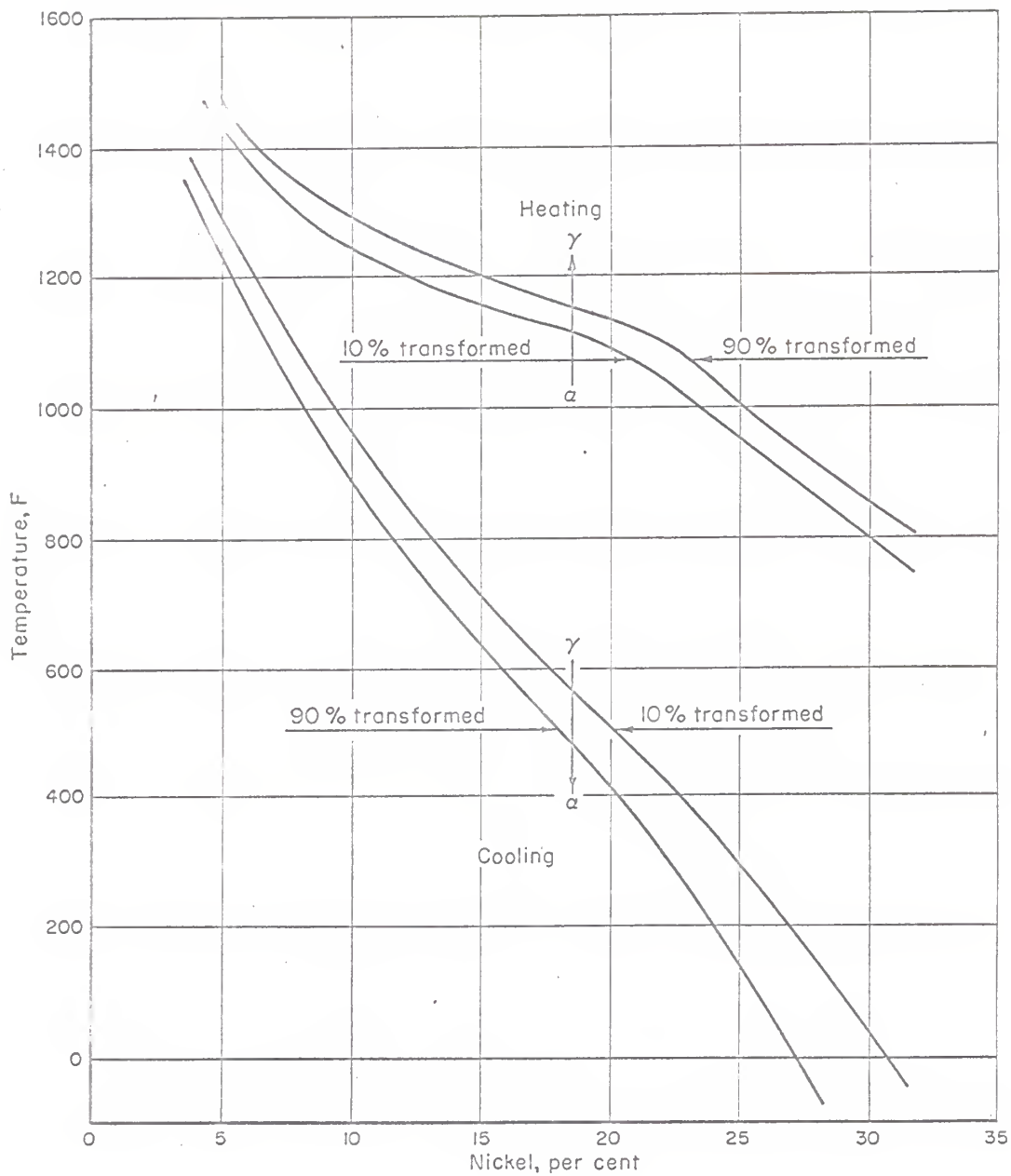


FIGURE 1. IRON-NICKEL TRANSFORMATION DIAGRAM⁽⁶⁾

210°F. (2) The martensitic structure cooled to room temperature is a homogeneous phase at this stage and resists corrosion as has been explained later in the discussion.

The aging treatment of 18 per cent nickel maraging steel consists of reheating to the elevated temperatures to below that at which reversion to austenite sets in. Figure 1 shows that it is possible to do it up to a fairly high temperature. This, in turn, provides considerable opportunity to develop aging and precipitation reactions within the martensite and it starts changing to an inhomogeneous structure. The mechanisms and precipitates formed during the aging treatment have not yet been definitely identified. The Applied Research Laboratory of the United States Steel Corporation, under an Air Force contract, has been engaged for some time in investigating this subject.

The heat treatment cycle of the 18 per cent nickel maraging steel is shown in figure 2. In the annealed martensitic condition, as supplied by the producer, the alloy has 28 to 32 Rockwell "C" hardness. In this condition the alloy is best suited for any machining and forming operations. Subsequent aging at 900°F for three to six hours, followed by air cooling, produces a Rockwell "C" hardness of 50 to 54 with corresponding high strength properties. The best balance of strength and ductility is usually obtained by aging at about 900°F for three or four hours after annealing at 1500°F. The rest of the physical metallurgy of the maraging steel not covered here is not much related with this discussion.

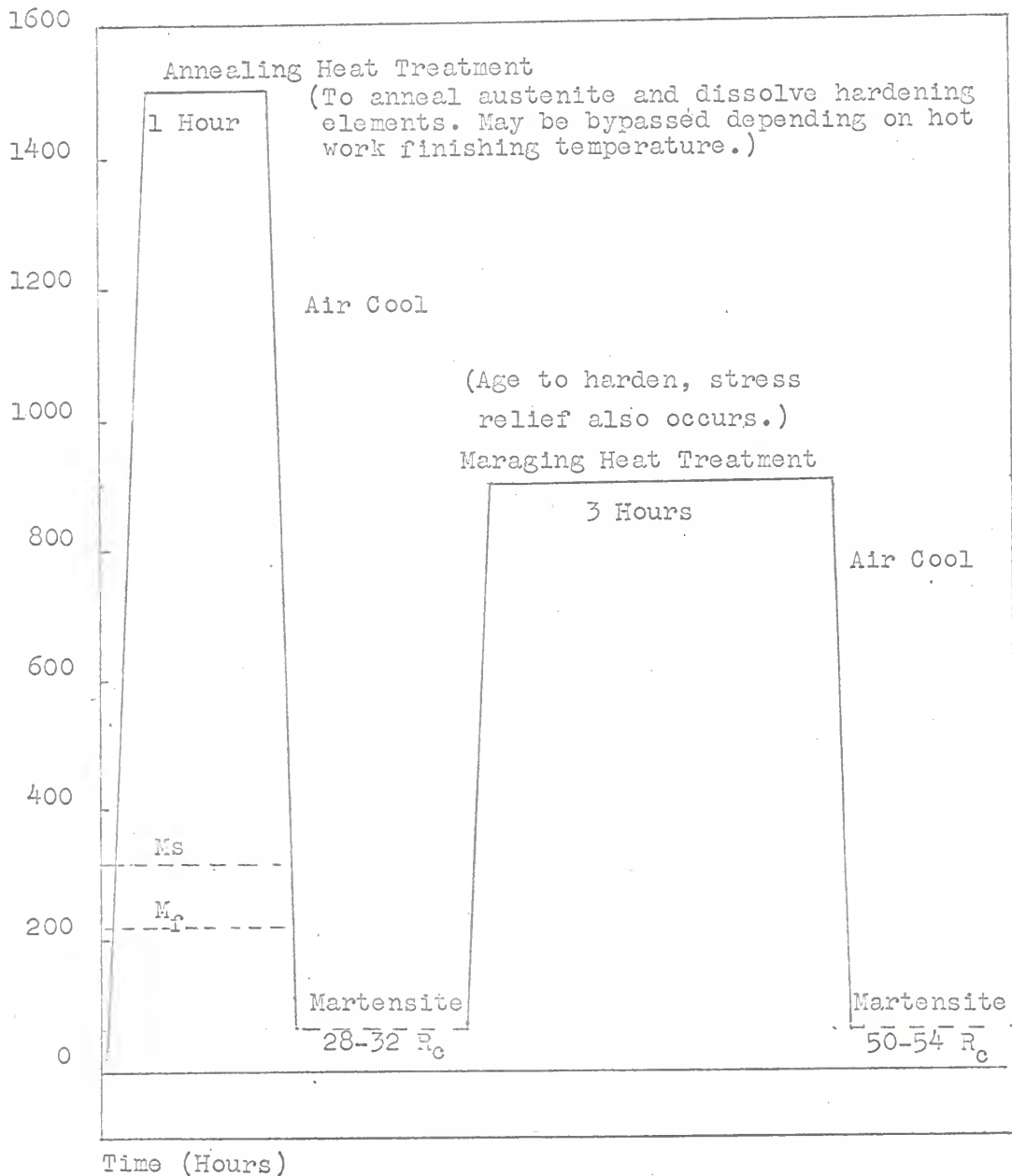


Figure 2. Normal Heat Treatment for 18%Ni Maraging Steel.

EXPERIMENTAL PROCEDURE

The experimental study was undertaken to collect the quantitative data on the corrosion behavior of 18 per cent nickel, 250 grade, maraging steel when aged at 900°F for various aging times. The data was also collected by keeping the aging time constant, but varying the aging temperature.

The experiment involved:

1. Preparation of Samples.
2. Design and Setup of the Apparatus.
3. Equipment and Material Used.
4. Cleaning Process of Samples.
5. Procedure to Run the Experiment.

PREPARATION OF SAMPLES

All samples were prepared from 5/8 inch diameter round bar of CVM Vasco Max 250. As indicated before, the number incorporated into the name indicates the approximate yield strength of the alloy. This bar had the following chemical analysis:

Carbon-----	.02
Silicon-----	.10
Manganese-----	.08
Sulfur-----	.010
Phosphorus-----	.004
Nickel-----	18.200
Cobalt-----	7.72
Molybdenum-----	4.78
Aluminum-----	0.10
Titanium-----	0.50
Boron-----	0.002
Zirconium-----	0.01
Calcium-----	0.05 added

Circular discs of about $3/16$ inch thickness were cut from the round bar on the abrasive cutter in the Materials Laboratory of the Industrial Engineering Department. The samples were drilled at the center with $9/64$ inch holes and marked for further identification.

All the samples were annealed for one hour at 1500° F and left overnight to air cool to room temperature. A set of three samples was then given the same aging treatment i.e. aged at the same temperature and for the same period of time simultaneously. All the faces of the samples were then ground on the Duo-Belt wet surfaces principally used for preliminary surface preparation of a specimen for microstructural examination. These surfacers were equipped with the mechanism to keep the samples cool while grinding by maintaining a constant flow of coolants on the surfacing belt in order not to alter superficially the structure of the metal undergoing grinding, particularly if it was fully hardened, as was the case here. Every care was taken not to use excessive pressure during surfacing, as well as during hand grinding on the emery papers for the circular portions of the specimen because it would promote the formation of disturbed metal on the surface of the specimen. This disturbed or distorted metal might, in many cases, extend inward from the surface to a very considerable depth and it would bring some change in the initial rate of corrosion at the surface of samples when allowed in contact with the corrosive environment. (8)



Figure 3. Glass hanger of 3 m.m. solid rod to immerse the test specimens in 1 N sulfuric acid.

DESIGN AND SETUP OF THE APPARATUS

The apparatus was designed with the following points in mind:

1. The temperature of the solution should remain constant throughout the experiment.
2. All the samples should have the same volume of solution available and there should not be any stagnation in the solution around the specimens.
3. The whole surface area of a sample should be in contact with the solution.
4. The test metal should be the only metal in contact with the solution.
5. The electrolyte used should be the least volatile and non-injurious to health.

EQUIPMENT AND MATERIAL USED

The following equipment and material was used for the setup of the apparatus which satisfied the above-mentioned points.

1. A 2' x 3' x 1' steel tank was filled with $4\frac{1}{2}$ inches water.
2. An electric heating coil was kept in the tank to raise the temperature of water, if needed.
3. A thermostat was put into the circuit of the heating coil to regulate the temperature of the environment in the tank.

4. A thermometer was fixed to keep a constant watch of the temperature of the weight loss panels.

5. An electric pump was used to keep the water in the tank rotating in order to keep the temperature uniform.

6. Glass beakers of 1000 milliliters each contained the corrosive medium i.e. dilute sulfuric acid solution.

7. Hook-shaped glass hangers were specially constructed for the experiment from 3 m.m. solid glass rods. The design of the hangers is shown in figure 3. Small weights were hung at the side arms of the hangers so as to avoid the tilting of the beakers in the water.

8. One normal solution of sulfuric acid was used as a corrosive medium. The solution was prepared by taking 26.652 c.c. chemically pure, concentrated sulfuric acid of specific gravity 1.846 grams per c.c. and bringing it to one liter with distilled water. 500 ml solution was taken in each 1000 ml glass beaker and was used as weight loss panels by exposing six corrosion specimens in each.

The most natural environment for corrosion tests is the atmosphere or water. Sulfuric acid was used as an environment for the corrosion test because it gave an accelerated test. That does not mean that the results obtained from this test would be applicable in general but it would give some idea about the environment where corrosion is mainly controlled by cathodic reaction. Hydrochloric acid could also have been used instead of the sulfuric acid solution but because it was a highly volatile acid, it created many impractical implications. Figure 4 shows one of the weight loss panels used and figure 5 shows the complete setup of the apparatus.

9. Soft bristle brush or a soft nylon brush, alcohol and a few glass plates to clean the corrosion samples.

10. Chemical balance and a standardized set of weights.



Figure 4. Weight loss panel containing 1 N acid, hanger and test specimens.

CLEANING OF THE CORROSION SPECIMENS

The method used in cleaning the corroded specimens depends upon the procedure adopted to measure the corrosion. The method used in this experiment was one of loss of weight in the specimens after every eight hour period, so it was necessary to thoroughly clean every specimen of practically all corrosion products without loss of any sound metal. Uhlig (11) discusses the method of cleaning corrosion specimens:

The removal of the corrosion product may not be a simple procedure as no one method can be relied upon. No hard and fast rules can be laid down; consequently it is necessary for the individual to study the problem and select the most suitable procedure.

The method of wet scrubbing by hand with a soft nylon brush was the one selected for this study after trying a few different types of brushes as a pilot run for some samples of maraged steel. Alcohol used in the cleaning process was collected in different glass discs and allowed to evaporate in order to check the amount of sound metal particles being removed while cleaning. The particles picked by magnet were so few for the method selected that it was not possible to weigh them on an ordinary chemical balance.

Precautions were taken to treat all the specimens uniformly while cleaning. As the aim of the experiment was to collect the data in order to find the qualitative nature of the corrosion behavior and compare the relative corrosion rates, the uniformity of the treatments given to specimens at different stages of the experiment was very important. To find the exact rate of corrosion a much more sophisticated cleaning equipment would be needed.

PROCEDURE TO RUN THE EXPERIMENT

The type of steel was verified by a strength test performed in the Laboratory of the Department of Applied Mechanics and the hardness test performed in the Materials Laboratory of the Department of Industrial Engineering. A test specimen, according to the standard specification of the pulling machine, was prepared in the machine shop and passed through the heat treatment cycle as given in figure 2 (page 10). The stress-strain curve obtained on the pulling machine gave the following information which was very close to the properties for the 18 per cent nickel 250 grade maraging steel.

Ultimate tensile strength-----	$\frac{54,400 \text{ lbs.}}{0.2 \text{ sq. in.}}$
	----- 272,000 psi
Yield strength	----- $\frac{50,000 \text{ lbs.}}{0.2 \text{ sq. in.}}$
	----- 250,000 psi
Modulus of elasticity	----- $\frac{5,000}{0.001}$
	----- 25×10^6

The hardness tests were carried out on the Rockwell hardness tester, the results of which, given in tables No. 1, 2, and 3, further verify the identity of the type of steel.

Table 1

<u>Reading No.</u>	<u>Hardness "Rc"</u>
1.	49
2.	50
3.	50
4.	51
5.	50
6.	50

While performing the Rockwell hardness tests, the three necessary precautions were taken e.g. (1) parallel faces i.e. top and bottom of the sample, (2) tests kept far apart so that the indentation not at the same point and (3) thickness of the sample at least 10 times the indentation.

Table 2Hardness of Sample I

No.	Hardness R_c
1.	32
2.	33
3.	33
4.	34
5.	33
6.	33
7.	34
8.	31

Table 3Hardness of Sample II

No.	Hardness R_c
1.	30
2.	31
3.	31
4.	30
5.	30
6.	31
7.	31
8.	30
9.	30
10.	30

Sample I was the piece from the 5/8 inch round bar from which the test specimen was taken.

Sample II was the piece from the same bar annealed with the test specimen.

Sample III was also from the same bar and maraged with the test specimen. Hardness for this sample is given in table 5.

After verifying the material by the above two tests, the corrosion specimens were prepared and heat treated according to the procedure explained earlier. They were made free of any scale by surfacing on the Duo-Belt wet surfacers and weighed on the chain-o-matic analytical balance up to four decimal places of accuracy. The weights and heat treatments for the different sets of specimens are given in tables No. 5, 6 and 7. The weight loss panels were set up and the specimens were allowed to corrode. (The reduced weights were recorded for each specimen at an 8 hour interval.) Not all the specimens were started at the same time as it would have been very difficult to clean and weigh them simultaneously.

The data collected was as given in tables No. 5, 6 and 7. This data was standardized to 8 gram original weight of the specimen. The converted data was entered in tables No. 8, 9 and 10. It was then plotted on the graph as shown in figures 7 and 10 for further interpretation and discussion.

Every care was taken, while conducting the experiment, to implement all the points mentioned for the design and set-up of the apparatus. The temperature of the acid was maintained $30^{\circ}\text{C} \pm 0.5$ throughout the experiment. There was sufficient stirring of the solution due to the chemical reaction and the evolution of gas. No other reactant material was in contact with the test solution except the test specimens. The volume of solution per sample was very nearly the same. The electrolyte used i.e. 1 N acid was much less volatile than some other acids like HCl.



Figure 5. Setup of the apparatus for the weight loss method of corrosion.

CORROSION DATA

Table 4WEIGHT LOSSES IN ANNEALED SAMPLES EXPOSED TO 1 N H₂SO₄

Annealing Temperature: 1500°F. (1 hr.)

Exposure Time in Hours	Sample 1		Sample 2		Sample 3	
	Sample	Weight	Sample	Weight	Sample	Weight
	Weight	Loss	Weight	Loss	Weight	Loss
	in Grams	in Grams	in Grams	in Grams	in Grams	in Grams
0	8.2692	--	8.2827	--	8.2968	--
8	8.0714	0.1978	8.0934	0.1893	8.0977	0.1991
24	7.8777	0.3915	7.9088	0.3739	7.8979	0.3995
48	7.7116	0.5576	7.7396	0.5431	7.7330	0.5638
72	7.6395	0.6297	7.6846	0.5981	7.6663	0.6305

Table 5

WEIGHT LOSSES IN MARAGED SAMPLES FOR VARYING AGING TIME

Annealing Temperature: 1500°F.(1 hr.)

Aging Temperature: 900°F.

Aged: 1 hr.	Sample 4		Sample 5		Sample 6	
Exposure Time in Hours	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams
0	8.7693	--	8.0497	--	8.6800	--
8	7.4818	1.2875	6.7535	1.2960	7.3156	1.3644
24	7.3186	1.4507	6.6189	1.4308	7.1713	1.5087
48	7.2982	1.4711	6.6037	1.4460	7.1624	1.5176
72	7.2918	1.4775	6.5965	1.4532	7.1593	1.5207

Aged: 2 hrs.	Sample 7		Sample 8		Sample 9	
Exposure Time in Hours	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams
0	8.5963	--	8.2710	--	8.6120	--
8	7.0830	1.5133	6.8928	1.3782	7.1217	1.4903
24	6.6171	1.9792	6.6904	1.5806	6.6371	1.9749
48	6.5866	2.0097	6.6674	1.6036	6.6165	1.9955
72	6.5798	2.5965	6.6633	1.6079	6.6104	2.0016

Aged: 3 hrs.	Sample 10		Sample 11		Sample 12	
Exposure Time in Hours	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams
0	7.9574	--	8.7621	--	8.0120	--
8	6.3956	1.5618	7.0924	1.6697	6.4693	1.5427
24	5.8986	2.0588	6.6104	2.1517	6.0245	1.9875
48	5.8734	2.0840	6.5878	2.1743	5.9696	2.0424
72	5.8676	2.0898	6.5809	2.1812	5.9620	2.0500

Table 5
(Continued)

Aged: 4 hrs. Sample 13			Sample 14		Sample 15	
0	8.6716	--	8.8570	--	8.9646	
8	6.8212	1.8504	7.0129	1.8441	7.0649	1.8997
24	6.3153	2.3563	6.5326	2.3244	6.5892	2.3754
48	6.2948	2.3768	6.5110	2.3460	6.4963	2.4683
72	6.2832	2.3884	6.5064	2.3506	6.4824	2.4822
Aged: 6 hrs. Sample 16			Sample 17		Sample 18	
0	8.2153	--	8.1640	--	8.8107	--
8	6.5805	1.6348	6.4990	1.6650	7.0357	1.7750
24	6.0395	2.1758	5.9504	2.2136	6.4655	2.3452
48	6.0236	2.1917	5.9406	2.2234	6.4453	2.3654
72	6.0106	2.2047	5.9255	2.2385	6.4318	2.3789
Aged: 12 hrs. Sample 19			Sample 20		Sample 21	
0	9.0202	--	8.1056	--	8.8896	--
8	6.9132	2.1070	6.2106	1.8950	6.8162	2.0774
24	6.2239	2.7963	5.5840	2.5216	6.1322	2.7574
48	6.2099	2.8103	5.5695	2.5361	6.1172	2.7724
72	6.1953	2.8249	5.5532	2.5524	6.1037	2.7859

Table 6

WEIGHT LOSSES OF THE SAMPLES AGED AT VARYING TEMPERATURE

Annealing Temperature: 1500°F(1 hr.)

Aging Time: 4 hrs.

Aged: 500F	Sample 22	Sample 23	Sample 24
Exposure Time in Hours	Sample Weight in Grams	Sample Weight in Grams	Sample Weight in Grams
0	8.7420	8.5892	8.6291
8	7.6203	7.5249	7.5628
24	7.4795	7.3992	7.4430
48	7.3759	7.3227	7.3746
72	7.3568	7.3052	7.3480

Aged: 700F	Sample 25	Sample 26	Sample 27
0	8.7642	8.4998	8.1541
8	8.4310	8.1711	7.8458
24	8.1163	7.8610	7.5507
48	7.9620	7.7122	7.4007
72	7.9481	7.6996	7.3897

Aged: 800F	Sample 28	Sample 29	Sample 30
0	7.8229	7.9665	7.8316
8	6.9296	7.0391	6.9525
24	5.3444	5.7684	5.7226
48	4.4609	4.5731	4.5441
72	4.2352	4.3173	4.3092

Table 6
(Continued)

Aged: 900F	Sample 31	Sample 32	Sample 33
0	8.6716	8.8570	8.9646
24	6.5153	6.5326	6.6035
48	6.2948	6.5110	6.4852
72	6.2832	6.5064	6.4264
Aged: 1000F	Sample 34	Sample 35	Sample 36
0	8.7594	8.6432	8.2822
24	6.5933	6.4291	6.1626
48	6.5808	6.4157	---
72	6.5756	6.4111	---
Aged: 1100F	Sample 37	Sample 38	Sample 39
0	8.8810	8.3238	8.6655
24	6.6135	6.1945	6.4495
48	6.5302	6.1120	6.3664
72	6.5263	6.1074	6.3607

Table 7

WEIGHT LOSSES IN MARAGED SAMPLES FOR VARYING AGING TIME
(Data converted from table 5 for 8 grams original weight)

Annealing Temperature: 1500°F.(1 hr.)

Aging Temperature: 900 F.

Aged: 1 hr.						
Sample 4			Sample 5		Sample 6	
Exposure Time in Hours	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams
0	8.0000	--	8.0000	--	8.0000	--
8	6.8254	1.1745	6.7118	1.2880	6.7425	1.2575
24	6.6765	1.3234	6.5780	1.4220	6.6095	1.3905
48	6.6579	1.3421	6.5664	1.4371	6.6013	1.3987
72	6.6521	1.3479	6.5557	1.4442	6.5984	1.4016

Aged: 2 hrs.						
Sample 7			Sample 8		Sample 9	
Exposure Time in Hours	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams
0	8.0000	--	8.0000	--	8.0000	--
8	6.5917	1.4083	6.6669	1.3331	6.6156	1.3844
24	6.1581	1.8419	6.4712	1.5288	6.1654	1.8346
48	6.1297	1.8703	6.4489	1.5511	6.1463	1.8537
72	6.1234	1.8766	6.4449	1.5552	6.1406	1.8594

Aged: 3 hrs.						
Sample 10			Sample 11		Sample 12	
Exposure Time in Hours	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams
0	8.0000	--	8.0000	--	8.0000	--
8	6.4298	1.5707	6.4755	1.5245	6.4596	1.5404
24	5.9302	2.0698	6.0354	1.9646	6.0155	1.9845
48	5.9124	2.0876	6.0225	1.9775	5.9919	2.0081
72	5.8990	2.1010	6.0085	1.9915	5.9521	2.0471

Table 7
(Continued)

Aged: 4 hrs.						
Sample 13			Sample 14		Sample 15	
0	8.0000	--	8.0000	--	8.0000	--
8	6.2929	1.7071	6.3343	1.6657	6.3047	1.6953
24	5.8262	2.1738	5.9005	2.0995	5.8802	2.1198
48	5.8073	2.1927	5.8810	2.1190	5.7973	2.2027
72	5.7966	2.2036	5.8768	2.1232	5.7849	2.2151
Aged: 6 hrs.						
Sample 16			Sample 17		Sample 18	
0	8.0000	--	8.0000	--	8.0000	--
8	6.4080	1.5920	6.3684	1.6316	6.3883	1.6117
24	5.8812	2.1188	5.8309	2.1691	5.8706	2.1294
48	5.8657	2.1343	5.8213	2.1787	5.8522	2.1478
72	5.8531	2.1469	5.8065	2.1935	5.8400	2.1600
Aged: 12 hrs.						
Sample 19			Sample 20		Sample 21	
0	8.0000	--	8.0000	--	8.0000	--
8	6.1312	1.8687	6.1297	1.8703	6.1341	1.8695
24	5.5200	2.4800	5.5113	2.4887	5.5185	2.4815
48	5.5075	2.4925	5.4969	2.5031	5.5050	2.4950
72	5.4946	2.5054	5.4809	2.5191	5.4929	2.5071

Table 8

WEIGHT LOSSES FOR VARYING MARAGING TEMPERATURE

Annealing Temperature: 1500°F.(1 hr.)

Aging Time: 4 hrs.

Aged: 500F Sample 22			Sample 23		Sample 24	
Exposure Time in Hours	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams
0	8.0000	--	8.0000	--	8.0000	--
8	6.9735	1.0265	7.0087	0.9913	7.0115	0.9887
24	6.8446	1.1554	6.8916	1.1084	6.9004	1.0996
48	6.7498	1.2502	6.8203	1.1797	6.8370	1.1630
72	6.7324	1.2676	6.8041	1.1959	6.8124	1.1876

Aged: 700F Sample 25			Sample 26		Sample 27	
Exposure Time in Hours	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams
0	8.0000	--	8.0000	--	8.0000	--
8	7.6958	0.3042	7.6906	0.3094	7.6975	0.3025
24	7.4086	0.5914	7.3988	0.6012	7.4080	0.5920
48	7.2677	0.7323	7.2587	0.7413	7.2608	0.7392
72	7.2550	0.7450	7.2469	0.7531	7.2500	0.7500

Aged: 800 Sample 28			Sample 29		Sample 30	
Exposure Time in Hours	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams	Sample Weight in Grams	Weight Loss in Grams
0	8.0000	--	8.0000	--	8.0000	--
8	7.0864	0.9136	7.0687	0.9313	7.0984	0.9116
24	5.4654	2.5346	5.7926	2.2073	5.8457	2.1503
48	4.5619	3.4381	4.5923	3.4077	4.6418	3.3587
72	4.3310	3.6689	4.3352	3.6645	4.4018	3.5982

Table 8
(Continued)

Aged: 900F Sample 31			Sample 32		Sample 33	
0	8.0000	--	8.0000	--	8.0000	--
24	5.8262	2.1738	5.9005	2.0995	5.8829	2.1171
48	5.8073	2.1927	5.8810	2.1190	5.7874	2.2126
72	5.7966	2.2034	5.8768	2.1232	5.7349	2.2651
Aged: 1000F Sample 34			Sample 35		Sample 36	
0	8.0000	--	8.0000	--	8.0000	--
24	6.0217	1.9783	5.9507	2.0493	5.9525	2.0475
48	6.0103	1.9897	5.9377	2.0623	5.9341	2.0659
72	6.0055	1.9945	5.9340	2.0660	5.9271	2.0729
Aged: 1100F Sample 37			Sample 38		Sample 39	
0	8.0000	--	8.0000	--	8.0000	--
24	5.9574	2.0426	5.9535	2.0465	5.9542	2.0458
48	5.8824	2.1176	5.8742	2.1258	5.8775	2.1225
72	5.8789	2.1211	5.8698	2.1302	5.8722	2.1278

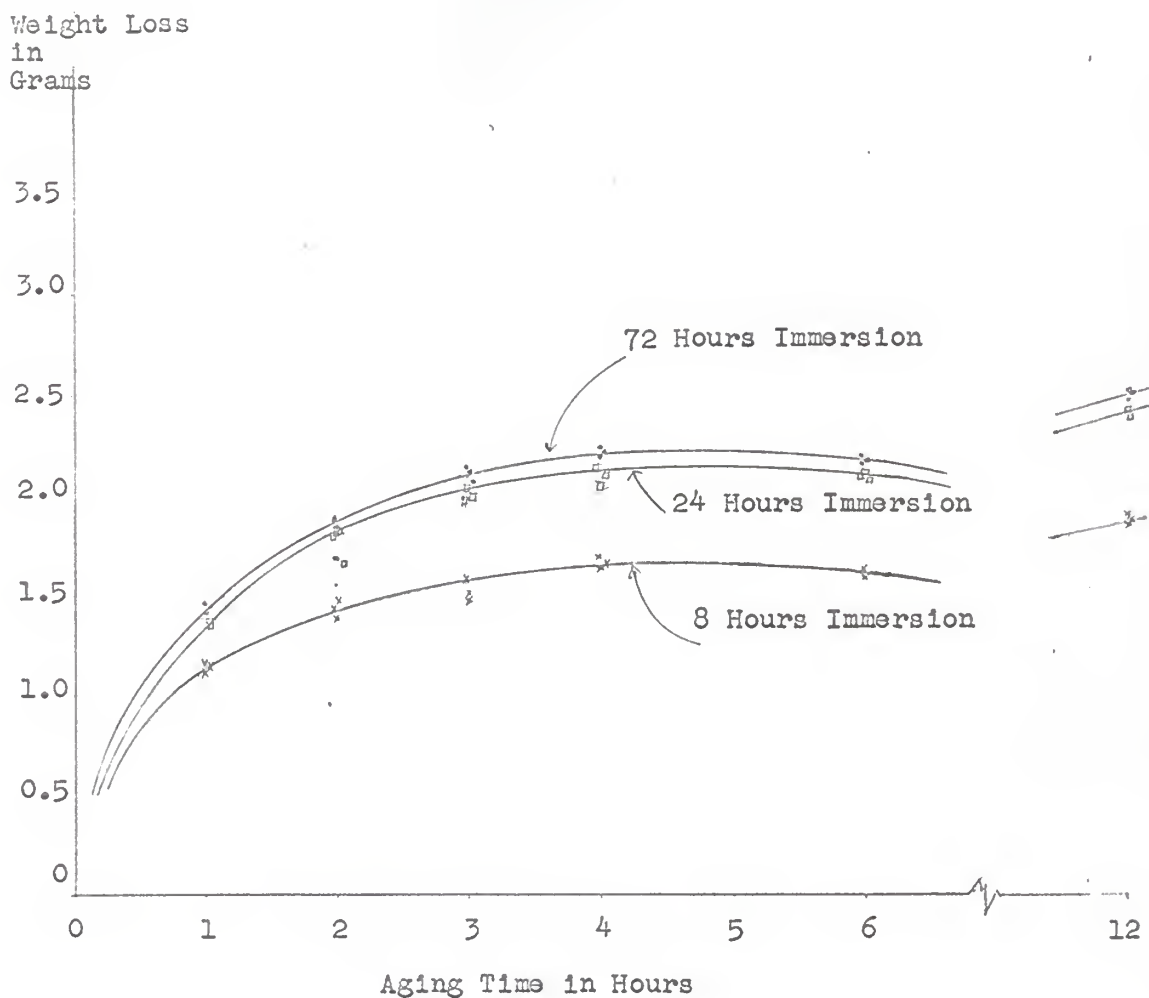


Figure 7. Effect of maraging time on the corrosion of 18% Ni maraging steel. Specimens annealed at 1500°F and maraged at 900°F for the indicated times. Samples were immersed in 1 normal sulfuric acid.

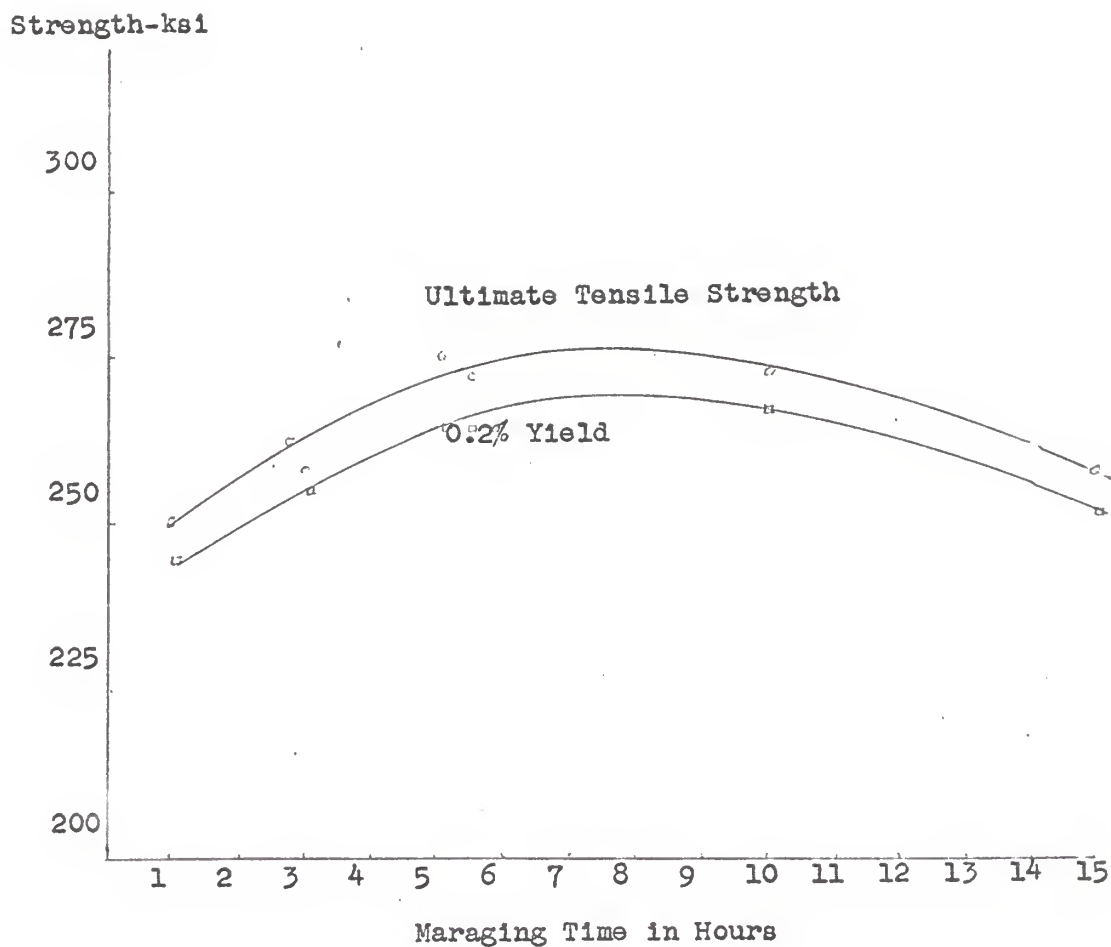


Figure 8. Effect of maraging time on the tensile strength of 18% Ni maraging steel aged at 900°F.

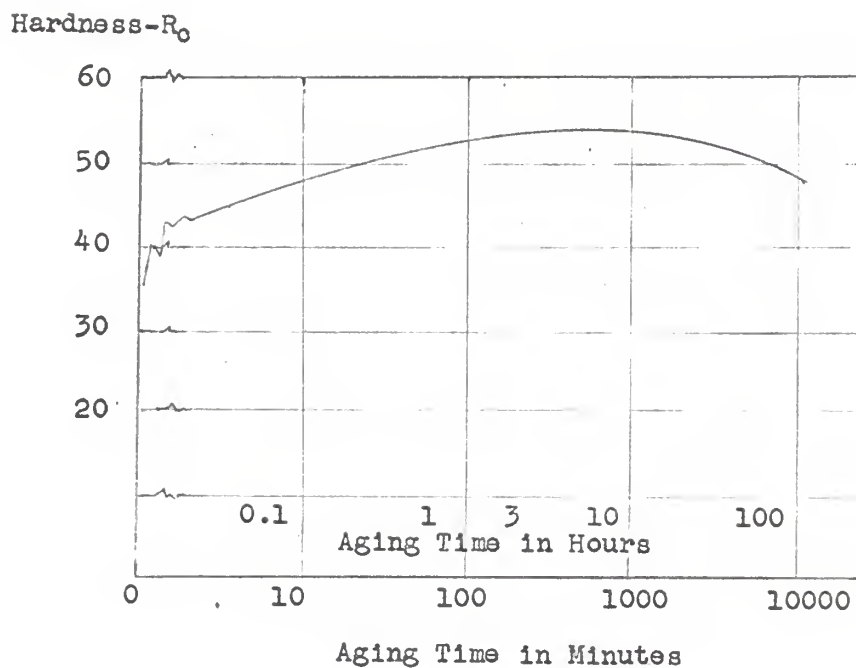


Figure 9. Hardness vs. maraging time at 900°F .
for a 19 Ni, 7 Co, 4.9 Mo, 0.4 Ti-Fe alloy.
Annealed 1 hour at 1500°F , air cooled.(2)

Weight Loss
in
Grams

3.5

3.0

2.5

2.0

1.5

1.0

0.5

0

600

700

800

900

1000

1100

Aging Temperature in °F.

72 Hours Immersion

48 Hours Immersion

24 Hours Immersion

Figure 10. Effect of maraging temperature on the corrosion of 18% Ni maraging steel exposed to 1N H_2SO_4 . Specimens annealed at 1500° for 1 hour and maraged for 4 hours at the indicated temperatures.

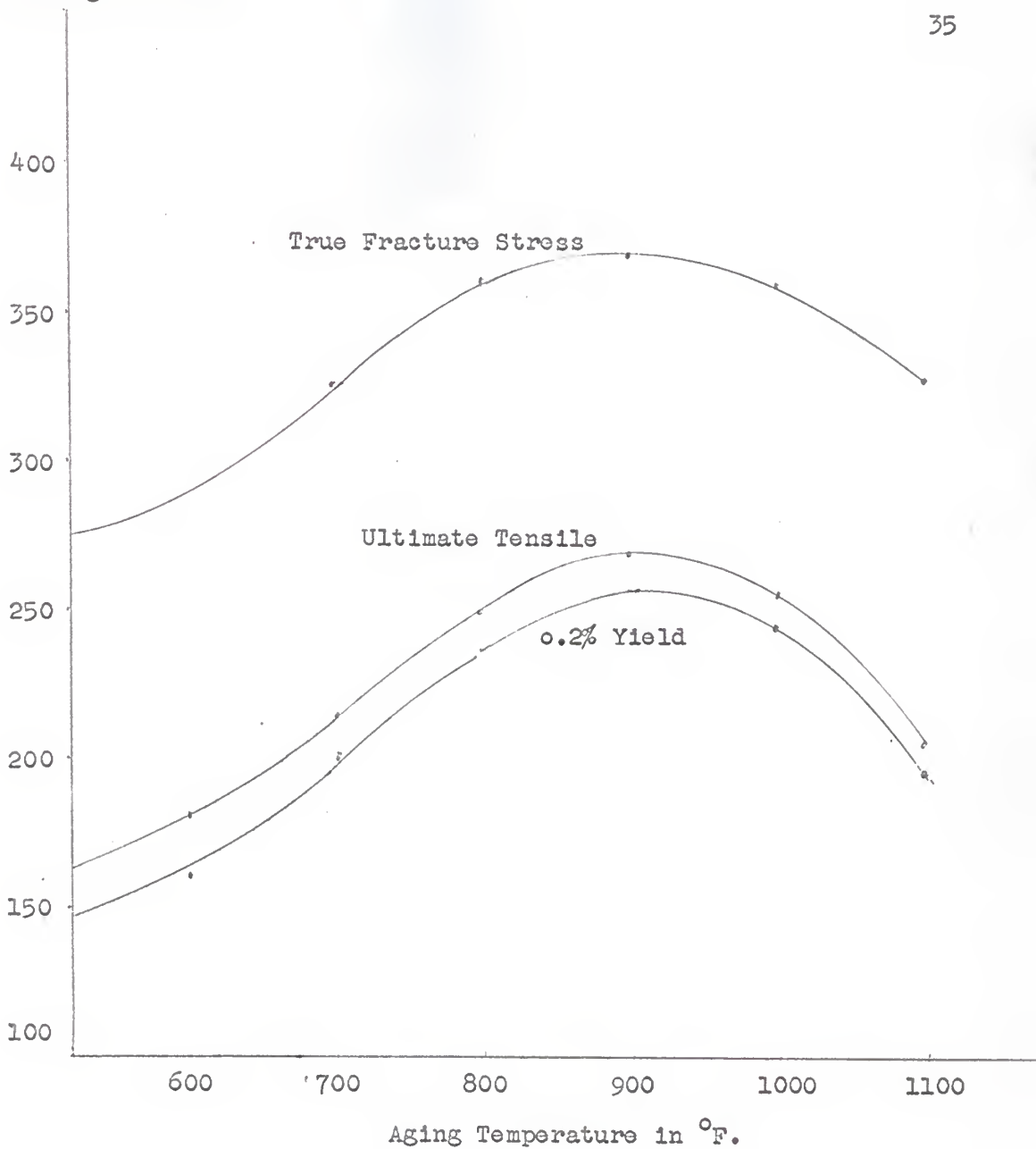


Figure 11. Effect of maraging temperature on the tensile properties of 18% Ni maraging steel.(13)

Annealed Structure



Figure 12. Martensitic microstructure of 18 percent nickel maraging steel produced by annealing 1 hour at 1500°F; 100% body center cubic phase.

Etchant: 50 c.c. HCl, 25 c.c. HNO₃
1 gm. CuCl₂, 150 c.c. H₂O

Magnification: 1000X

No difference in chemical composition between the dark platelets and light background. Microhardness measurements showed no difference between these faces.

DISCUSSION

It was pointed out earlier that the structure of 18 per cent nickel maraging steel when annealed by air cooling from 1500°F to room temperature is the body centered cubic martensite which is in a single phase homogeneous form. (Fig. 12) The samples of this structure showed the greatest resistance to corrosive attack in one normal sulfuric acid. The losses in weight, in grams, at the end of every eight hours immersion in the acid are shown in table 4.

On comparing the losses in weight for the samples, it could be observed that the corrosion was at a minimum for the annealed samples. This is due to the fact that if the corrosion reaction was controlled at the metal surface, a single phase or homogeneous metal resisted the attack better than a multiphase or inhomogeneous metal.

According to the electrochemical theory, the annealed maraging steel, being a single phase structure, had almost a negligible cathodic area at the surface which was a controlling factor so the electrochemical corrosive attack was minimum. In the case of the acid, factors within the metal rather than oxygen depolarization became more important.

An analogy might be found in the case of a carbon steel, water quenched from about 1600°F, the corrosion rate of martensite in 1 per cent sulfuric acid was very small as compared to the corrosion rate of a finely dispersed cementite in a ferrite matrix. It had usually been considered that

cementite made up the cathodes, and ferrite the anodes of active corrosion cells. Maximum corrosion representing a five to seven-fold increase over martensite or pearlite occurred at a tempering temperature between 570° and 750° F, a range in which the amount of cementite would be maximum and in the finest state of dispersion.

The loss in weight in the case of maraging steel in acid increased due to maraging. From the recent investigations (1,2) it was assumed that during the aging process fine particles of the hardening precipitate developed which were assumed to be the complex of nickel-cobalt-molybdenum-titanium. It was very likely that these precipitate particles acted as cathodes and the fineness of dispersion and their size controlled the corrosion behavior of the maraged specimens in 1 N acid.

There were two kinds of tests I and II conducted on the maraging samples. Test I was to change the time of maraging and find its relation with the weight loss due to corrosion in 1 N acid. The test specimens given in table 5 and subsequently in table 7 were tested according to the procedure explained in the earlier discussion. The periods, for which the samples were maraged, were 1, 2, 3, 4, 6 and 12 hours.

The losses in weight in the corroded specimens, in grams, at an eight hour interval in the acid were recorded both in table 7 and figure 7. It could be observed that the weight loss due to corrosion increased with an increase in maraging time. This relationship was quite comparable with that of the maraging time to the strength of the alloy which could be seen in figures 7 and 8.

It is believed that a very fine precipitate formed during maraging heat treatment. (2) It is proposed that these particles increased in size, and perhaps in number also, gradually by increasing the period of maraging heat treatment. It is, therefore, possible that the cathodic area at the surface of the steel was enlarged due to the change in the total peripheral area of the precipitate particles when the aging time increased. This increase in the amount of particles might be limited to a certain optimum. During the experiment there was a marked difference in the activity of the reaction with the different samples.

The increase in the cathodic area and, therefore, faster electrochemical reaction might be the reason for the stimulation in the corrosive attack, so the increase in loss in weight. The weight loss and maraging time relationship is shown in figure 7 as plotted from the data obtained.

Test II was to find the effect of a changing maraging temperature on the loss in weight in 1 N sulfuric acid for the 18 per cent nickel maraging steel. The annealed test specimens were maraged for four hours at 500, 700, 800, 900, and 1000 and 1100° F and allowed to corrode in the acid in the same way as explained for test I. The data for losses in weight of the test specimens was recorded as given in table 6. This data was then converted for 8 grams of the original weight of a specimen. This was done because the original weights of all the specimens were not exactly 8 grams. The corrected data for this test appeared in table 8 and the corresponding graph in figure 10.

The curves obtained for the weight loss in the acid for the different periods of immersion were again quite similar to the relationship between the aging temperature and the tensile strength of the alloy. One important difference in the two curves was that the hump or peak which appeared in both the curves was not at the same temperature. It was at about 800°F maraging temperature in the case of the corrosion rate but at 900°F in the case of the strength. This difference remained to be further investigated. Without the knowledge and understanding of the exact hardening mechanism and the nature and the kind of development of the precipitate, if any, it might be very difficult to reveal the exact cause of the above difference.

The explanation for the corrosion behavior in the case of test II remained the same as for test I i.e. cathodic area exposed to electrolyte controlled the electrochemical reaction by forming the tiny cells on the surface of the alloy. It was possible that this cathodic area had increased due to an increase in the amount or size of the precipitates which developed during the maraging heat treatment.

It was explained before that after maraging treatment at temperatures within a certain aging temperature range, the maraging steel changed to an inhomogeneous structure and it is generally an accepted fact (10) that inhomogeneous structures are less resistant to corrosion.

CONCLUSIONS

The purpose of this experimental study was to find the qualitative nature of the corrosion behavior of 18 per cent nickel maraging steel with respect to heat treatment. The following conclusions were derived from the study for corrosion in one normal sulfuric acid:

1. The corrosion rate of the maraging steel increased with the maraging time. The rate of increase was rapid for the first three to four hours but then slowed down for longer periods.
2. The curves showing relationships between the maraging time and the corrosion rate, and that with the strength were quite similar in shape. The curve for hardness versus aging time also resembled the above two curves.
3. For four hours maraging time, the corrosion rate was maximum at 800°F aging temperature. The weight loss due to corrosion was almost four times that obtained at 700°F and nearly doubled that obtained at 900 or 1000°F maraging temperatures.
4. The curves showing the relationship between the aging temperature and the amount of corrosion; and the aging temperature and the strength were similar in shape except that the hump in the curve was at 800°F in the former and at 900°F aging temperature in the latter.

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CORROSION BEHAVIOR OF HEAT TREATED
18 PER CENT NICKEL MARAGING STEEL.

by

Vishesh Chander Wadhwa
B.S., Kansas State University, 1964

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Manhattan, Kansas

1965

ABSTRACT

The purpose of the research was to determine the effect of aging time and temperature on the corrosion rate of maraging steel in one normal sulfuric acid. Aging time varied between 1 and 12 hours while the aging temperature remained at 900°F. and with time held constant the aging temperature varied from 500 to 1100°F.

The weight loss method was used to find the amount of corrosion. Specimens were immersed in acid by hook shaped hangers made of 3 m.m. glass rods in order to allow the maximum surface area of the test pieces in contact with the solution. The temperature was thermostatically controlled at $85 \pm 0.5^\circ\text{F}$. In order to give a true comparison of corrosion rate, care was taken to maintain the uniformity in the processes involved. The study yielded the following results:

1. The corrosion rate increased with the maraging time. For the first 3 to 4 hours maraging time, increase in corrosion rate was rapid but then slowed down for longer periods.

2. The corrosion rate versus the maraging time relationship was quite similar to the relationship between the strength and the maraging time.

3. The corrosion rate was maximum at 800°F maraging temperature.

4. The curves for corrosion rate and strength versus the maraging temperature were similar in shape except that the humps were at 800 and 900°F respectively.