AN INVESTIGATION OF MARTENSITE FORMATION IN SOME AUSTENITIC STAINLESS STEELS

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Fulfillment of the Requirements
for the degree of
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SUMMARY

This investigation was initiated to determine the M_s (martensite start) temperature of some commercial austenitic stainless steels, and to study the effect of sensitization (heating in the carbide precipitation range) on the M_s temperature. The M_s temperature of most austenitic stainless steels is below the boiling point of liquid nitrogen and thus too low for practical applications of quenching for achieving high strength properties. However, the M_d temperature (temperature above which no martensite can be formed through plastic deformation) is believed to be some 600° F higher than M_s and is of great importance, for example in cold working operations and possibly under conditions leading to transgranular stress corrosion cracking.

Of twelve austenitic stainless steels studied, only AISI Types 304L and 309SCb were found to show some transformation to martensite at temperatures above -320° F. Magne Gage readings and metallography were used to determine amounts of martensitically-formed ferrite after various treatments.

M_s for Type 309SCb was above room temperature and no attempt was made to determine it precisely. M_s for Type 304L was found through extrapolation of Magne Gage data and metallography to be between -190° F and -170° F.

Sensitization of these steels by heating to 1200° F for two hours did not appear to affect the tendency toward spontaneous transformation to martensite. Moreover, it was shown that a similar sensitization treatment of Type 304 stainless steel is not sufficient to raise M_s to above -320° F.

AN INVESTIGATION OF MARTENSITE FORMATION IN SOME AUSTENITIC STAINLESS STEEL

Introduction

Martensite in stainless steel is considered to be a supersaturated solution of carbon, nitrogen, chromium, nickel, and other alloying elements in iron, having a body centered tetragonal lattice. It is formed by the diffusionless transformation of face centered cubic austenite on cooling below a temperature denoted as M_s (martensite start temperature). The M_s temperature is a function of austenite composition. The martensite transformation has been shown, in most cases at least, to be independent of time and a function of temperature alone. This suggests, therefore, that there is also an M_f (martensite finish) temperature where the transformation is complete. Such a temperature has been shown to exist in plain carbon and low-alloy steels. M_f temperatures for austenitic stainless steels, however, have not been reported.

The diffusionless martensitic transformation from the face centered cubic to the body centered cubic is believed to occur by a process involving homogeneous shear. Thus, it is not surprising that plastic straining can promote

such a transformation at temperatures up to about 200° C in 18Cr- 8Ni type stainless steels.

Eichelmann and Hull[1] have proposed the existence of an M_d temperature in austenitic stainless steels. This point is defined as that temperature above which martensite cannot be formed through plastic deformation. These authors have related the M_d temperature to the M_s temperature through the approximate equation:

$$M_d = M_s - 600^\circ F$$

However, Starrs, Reporter, and Dorn[2] in their study on the mechanism of the strain induced martensitic reaction found that the martensite reaction in 18-8 steels could be induced by a severe reduction in thickness by rolling at room temperature even though their data showed that the M_d of the material was well below room temperature. These authors thus concluded that a "plastic critical point" does not exist.

Completely stable austenitic stainless steels are desirable in many applications. They are readily work hardenable, and extremely shock resistant, that is, they have high impact strength and show no transition from ductile to brittle fracture. These steels are also satisfactorily machineable with the addition of small amounts of sulfer or selenium, although there are cases where these additions have a deliterous effect on corrosion

resistance. The absence of transformation during deformation gives these steels good cold forming properties. The stable austenitic stainless steels may also be welded without difficulty, and if the welding operation is controlled properly, the resistance to corrosion is not impaired.

On the other hand, Zeigler and Brace[3] have demonstrated that austenite instability can also have beneficial effects. In their work, these authors revealed that stainless steel alloys in which austenite transforms to martensite through cold working at sub-zero temperatures can be produced with tensile strengths far in excess of those cold worked at room temperature, particularly if the material is aged at 750° F after deformation. These authors, studying the commercial grades of austenitic stainless steels, observed that in all the steels the hardness values produced by plastic deformation were maintained or increased by aging at temperatures up to 750° F. At higher temperatures they found that softening commenced and at about 1000° F progressed fairly rapidly. No explanation of the increased hardness obtained by aging at 750° F was attempted by these authors. The authors did, however, state that the increased hardness obtained by cold rolling the steels at sub-zero temperatures was a result of the promotion of the austenite to martensite (gamma to alpha) transformation through plastic deformation.

It is obvious from the above considerations that there is a great need for data on the temperature at which the austenite to martensite transformation starts to occur in austenitic stainless steels. At present, very little such data exist. Eichelmann and Hull[4] have evaluated the effect of chromium, nickel, manganese, silicon, and carbon plus nitrogen on the M_s temperature of some 18-8 type stainless steels. From their investigation the authors derived the following empincal equation.

$$M_s(^{\circ}F) = 75\ (14.6 - Cr) + 110\ (8.9 - Ni) + 60\ (1.33 - Mn) + 50\ (0.47 - Si) + 3000\ (0.0068 - C + N)$$

In this expression, the compositions of the alloying elements are expressed directly in weight per cent. However, the authors point out that their equation is accurate only within 10 to 20° F and is applicable only to alloys that fall within the following composition range:

10 to 18 chromium

6 to 12 nickel

0.6 to 5.0 manganese

0.3 to 2.6 silicon

0.004 to 0.12 carbon

0.01 to 0.06 nitrogen

Eichelmann and Hull in this same work studied the effect of carbide precipitation (sensitization) on the M_s temperature.

They concluded that the precipitation of carbides results in an increase in the M_s temperature which varies with the amount of carbon and chromium removed from solid solution. In other words, the austenite stability is affected only by those alloying elements in solid solution with the iron.

Much work has been done by other investigators in areas paralleling the determination of the M_s in austenitic stainless steels. Uhlig[5] determined the influence of nitrogen on high purity carbon free alloys of the 18-8 type. From his study, the author concluded that an 18 chromium - 8 nickel steel melted in air or nitrogen contains nitrogen, is nonmagnetic and austenitic, but the nitrogen free alloy is ferromagnetic and ferritic. The author found that nitrogen, under certain conditions, readily diffuses into or out of 18-8, thereby converting the alloy to either the austenitic or ferritic structure.

Fiedler, Averbach, and Cohen[6] have reported the effect of plastic deformation on the transformation in high purity 18-8 type austenitic stainless steels both during the deformation and during subsequent cooling to subatmospheric temperatures. These investigators found that the M_s temperature decreases markedly with increasing carbon content, and the isothermal formation of martensite is observed at sub-zero temperatures. They also found that the amount of

martensite produced by plastic tensile strain increases as the temperature of deformation is lowered. This result concides with the findings of Ziegler and Brace[7] mentioned earlier in this paper.

Much work has been done in recent years on the mechanism of transgranular stress corrosion in austenitic 18-8 type stainless steels. Edeleanu [8] who did extensive research in this field, found metallegraphic evidence that a martensitic phase is produced on straining austenitic steels, and that this phase is corroded preferentially in certain aqulous environments. He also found that the austenitic stainless steels in which the austenite does not readily transform on straining are less susceptible to cracking. Through experimental steels he confirmed that transgranular cracking can be largely avoided either by a) increasing the alloy content of the normal steels and thus making the austenite more stable, or b) decreasing the alloy content and producing a partly martensitic steel in which the corrosion is less localized and therefore is less likely to cause cracking.

The investigation reported here was initiated to determine the M_s temperature in certain commercial austenitic stainless steels, and to study the effect of heat treatment (carbide precipitation) on the M_s temperature.

Materials and Equipment

A) Stainless Steels

Table I is a list of all the stainless steel alloys considered in this investigation, together with their compositions and their M_s temperature as calculated from the Eichelmann and Hull equation. The specimens were cylindrical pin-type samples 0.2" in diameter and 1.38" long.

B) Heat Treating Furnace

For heat treatment of the alloys, a muffle furnace capable of temperatures up to 2200° F was used. The furnace temperature was controlled by a Leads and Northrup Micromax which maintained the temperature within 10° F of the setting.

C) Thermocouple and Potentiometer

Sub-zero temperatures were obtained with liquid nitrogen which has a boiling point of -320.8° F.[9] For measurement of the sub-zero temperatures a copper-constantan thermocouple, which covers the range from 700° F to -330° F, was used. The thermocouple was constructed from B and S 20 gage copper wire and B and S 24 gage constantan wire. Copper leads, also B and S 20 gage, were attached to the thermocouple wires to provide for extension from the ice water reference junction to the potentiometer.

TABLE I

AISI Type	COMPOSITIONS												
	% Cr	% Ni	% Ma	% C	% Mo	% Si	% Cu	Cb&Ta	% Ti	% P	% S	% Fe	Calculated Ms*
302B	17.66	9.05	0.44	0.11		2.42				0.019	0.014	Bal.	-416.6° F
304	18.0	9.0		0.078								Bal.	-192° F
304L	19.3	9.3	0.60	0.022								Bal.	-211° F
309SCB	22.92	13.42	1.79	0.035	0.1	0.59		1.38		0.015	0.018	Bal.	-1064° F
310S	25.0	19.7	1.96	0.024		0.56						Bal.	-1708° F
316	16.55	11.76	1.13	0.10	2.32	0.56						Bal.	-549.5° F
316L	17.6	13.4	1.66	0.29	2.32	0.45						Bal.	-1405° F
318	17.9	14.6	1.86	0.16	2.69	0.50		0.95				Bal.	-1184° F
321	17.68	10.79	1.85	0.064		0.69			0.56	0.023	0.011	Bal.	-469° F
347	17.9	10.42	1.90	0.056		0.59		0.89		0.027	0.013	Bal.	-418° F

* Several of the alloys fall outside the composition range covered by the Eichelmann and Hull equation (see equation ? in text).

TABLE I (continued)

AISI Type	COMPOSITIONS												Calculated Ms
	% Cr	% Ni	% Ma	% C	% Mo	% Si	% Cu	Cb&Ta	% Ti	% P	% S	% Fe	
Carpenter 20	20.00	29.0		0.27	2.0	1.00	3.00					Bal.	-2567° F
Incoloy	21.39	31.94	0.53	0.04		0.47	0.20				0.007	Bal.	-2917° F

The output from the copper-constantan thermocouple was read on a Leads and Northrup null balance potentiometer capable of reading down to 0.01 millivolts.

D) Magne Gage

For measuring the amount of martensite present in the partially transformed stainless steel alloys, an Aminco-Brenner Magne Gage was used. The Magne Gage is a relatively simple and inexpensive instrument, consisting of a permanent bar magnet on a piveted arm, with a calibrated knob connected to the first bar through a spiral spring. The magnet is quiet small and has a hemispherical point. To use the instrument, the calibrated knob is turned counterclockwise until the magnet remains in contact with the specimen. The knob is turned clockwise to apply an increasing torque at the first. When the torque becomes sufficiently high, the magnet breaks free from the specimen. The dial reading can be used directly or can be converted to a zero base. The gage can be used with magnets of different strengths. All data were obtained with magnet number four which is usable from 1 % to approximately 15 % ferrite in the specimens.

The Magne Gage is shown in Figure 1. In order to show some of the details of the bar magnet, a plastic housing which normally covers the working mechanism has been removed.

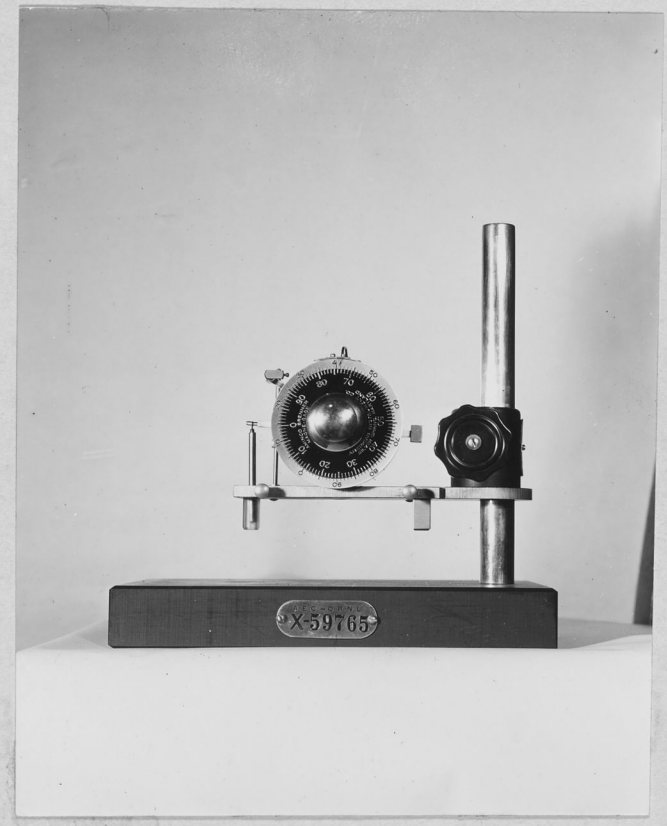

Figure 1. Aminco Brenner Magne Gage.

E) Metallographic Equipment

Standard mounting equipment, including a Beuhler Press and lucite powder, were used to prepare specimens for metallographic study. For polishing the mounted specimens, the following equipment was used; rough belt grinder, emory paper of fineness #1, 1/0, 2/0, and 3/0, and three lap wheels with alumina, Linde A and Linde B abrasives. Mounted and polished specimens were studied and photographed in a Bausch and Lombe Research Metallograph.

F) Micro Hardness Tester

A Tukon Micro-hardness Tester built by the Wilson Mechanical Instrument Company was used with a diamond pyramid indenter and a 0.1 kilogram load for determining the DPN (diamond pyramid hardness number) of the martensitic and austenitic areas in the partially transformed specimen.

Experimental Procedure

A) Calibration of Thermocouple

Before accurate temperature measurements could be made, it was first necessary to calibrate the copper-constantan thermocouple. This was done with a series of three standards ranging from 32° F down to -320.8° F. The three standards were: 1) ice water at 32° F, 2) the freezing point of mercury at -37.97° F, and 3) the boiling point of

liquid nitrogen at -320.8° F. Figure 2 is the cooling curve taken in determining the freezing point of mercury. In order to obtain these data, the copper-constantan thermocouple was placed in a long glass tube about 1/8" in diameter. The tube was filled with oil to minimize any temperature gradient which might exist between the wall of the tube and the thermocouple. The tube containing the thermocouple was then immersed in a test tube of pure distilled mercury, and the test tube was placed in a beaker containing liquid nitrogen. The thermocouple cold junctions were placed in a thermos containing ice and water in equilibrium at 32° F. The thermocouple leads were connected to the Leads and Northrup potentiometer. A kodak timer was used to measure the length of time required for the mercury to cool o.2 millivolt. These data were recorded from 3° F down to -190° F. Table in the appendix gives the data taken for the cooling curve obtained on the mercury.

The output from the thermocouple at the ice point and the liquid nitrogen point were obtained simply by placing the glass tube containing the oil immersed thermocouple into the two baths and reading the output indicated on the potentiometer. Three readings were taken at each of the two points and the three were then averaged to give the millivolt output from the copper constantan thermocouple at the ice point and liquid nitrogen point.

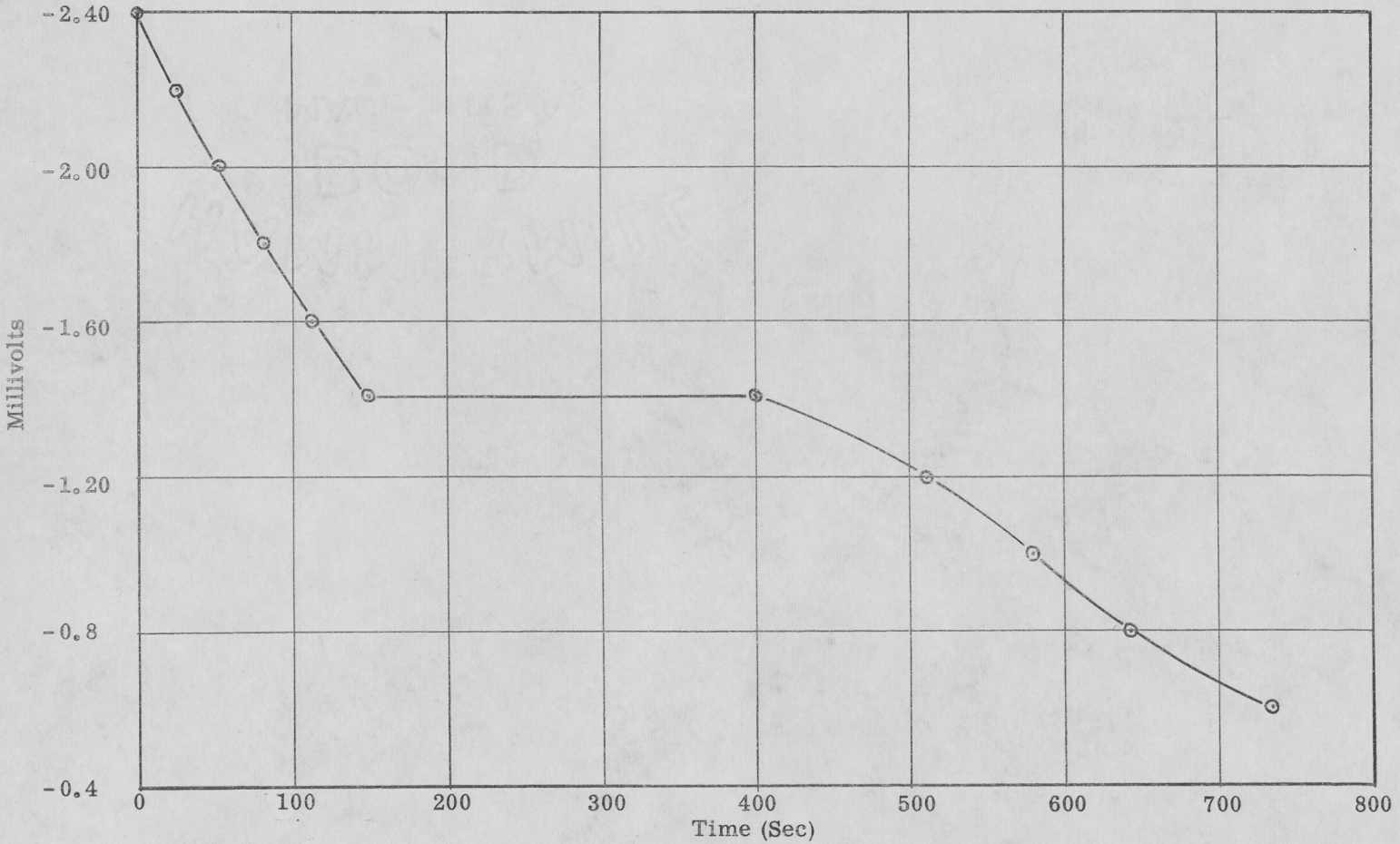

Figure 2. Melting Curve For Hg, With Millivolts Output From Cu-Constantan Thermocouple Plotted Vs Time. Plot Indicates Thermal Arrest For Hg at -1.405 Millivolts.

Figure 3 is the calibration curve for the copper-constantan thermocouple obtained by plotting the output of the thermocouple at the ice point, mercury point, and liquid nitrogen point against the known temperature at these three points. Figure 4 is a plot of data taken from the thermocouple tables for the copper-constantan thermocouple. A comparison of Figures 3 and 4 shows that there is only a slight variation in the output of the copper-constantan thermocouple from the accepted thermocouple tables. The variation, at the liquid nitrogen point, is actually less than the experimental accuracy. Thus, the copper-constantan thermocouple tables were used to convert millivolts output to temperature.

B) Heat Treatments

The heat treatment of the stainless steel alloys was carried out in an evacuated atmosphere to prevent decarburization and oxidation of the outer surface. For this purpose, the specimen was placed in a 1/4" I.D. vycor tube which was closed off at one end. The tube was then necked down in a gas flame at a distance of about 2" from the specimen. When the tube was almost closed at the point of necking, it was removed from the flame. The ofla end of the tube was then attached to a mechanical vaccucan pump through a rubber hose and evacuated. The tube was then sealed off at the point of necking and the evacuated portion of the tube

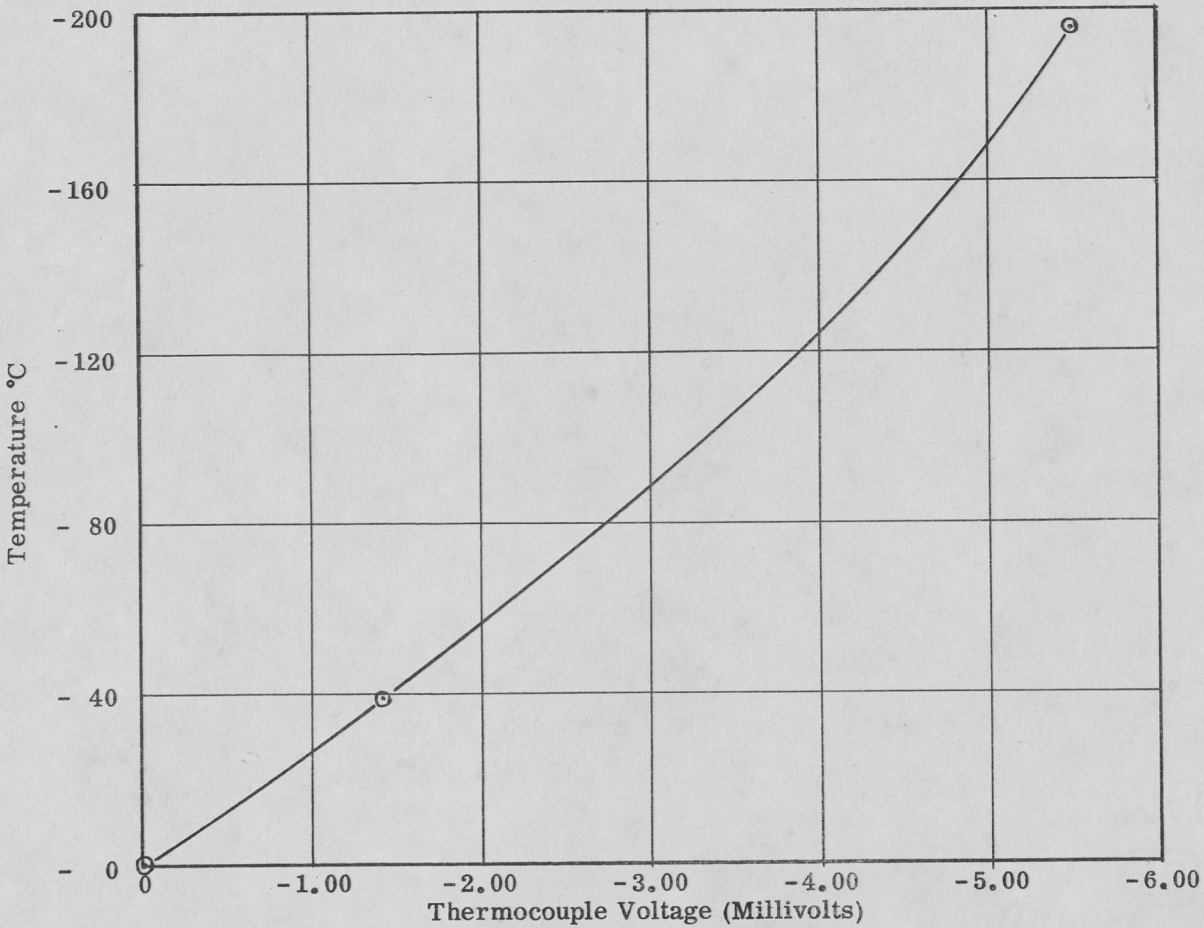

Figure 3. Calibration Curve Obtained For Copper-Constantan Thermocouple, Using 1) Ice Point, 2) Mercury Point and 3) Liquid Nitrogen Point.

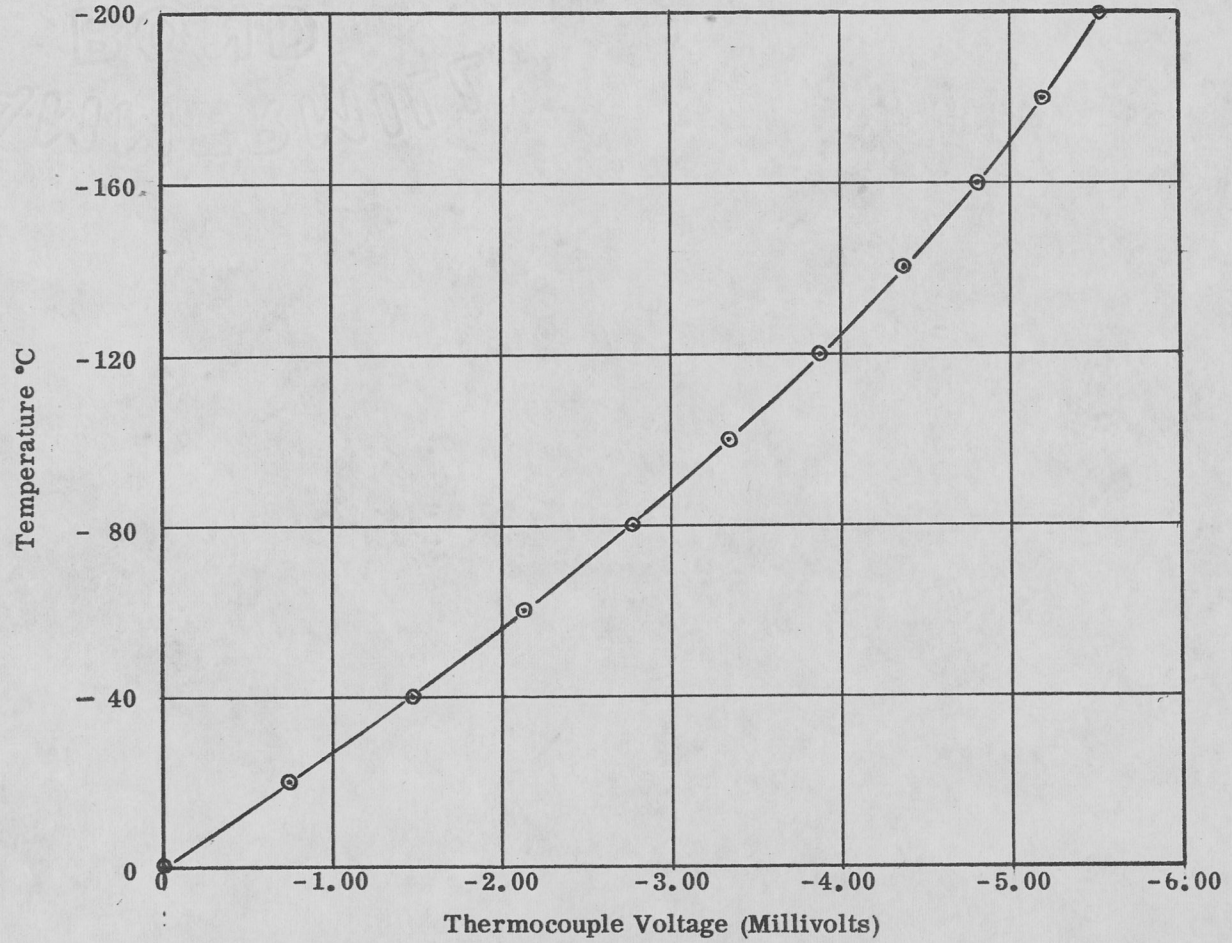

Figure 4. Data Taken From Copper-Constantan Thermocouple Tables.

containing the specimen was melted free of the rest of the vycor tube.

One specimen of each of the twelve stainless steel alloys was sealed in an evacuated tube as described above. These specimens were then placed in the muffle furnace for solution annealing at 2000° F for a period of one hour. This treatment has been found[9] to be totally adequate to redissolve any precipitation carbides and to eliminate any effects due to partial transformation to martensite on previous coolings.

At the end of the solution annealing period, the specimens were removed from the furnace and quenched to room temperature in a water bath. This quench was made to prevent any chromium carbides from precipating in the temperature range from 1500° F down to 1050° F. Upon reaching room temperature, the specimens were removed from the nycor tube and further quenched in liquid nitrogen to a temperature of -320.8° F. After the liquid nitrogen quench, each specimen was checked with both a bar magnet and the Magne Gage to determine whether the M_s temperature was above or below the boiling point of liquid nitrogen (-320.8° F).

From the twelve original stainless steel alloys, three were chosen to study the effect of a sensitizing heat treatment on back of paper. These were, 304, 304L and 309SCB. One specimen of each of the three alloys, in

the solution annealed condition, was sealed in an evacuated nycor tube. The tubes, containing the specimens were then placed in the muffle furnace at 1200° F for a period of two hours. The tubes were then removed from the furnace and allowed to air cool to room temperature. Each of the three specimens was then checked with the Magne Gage to determine the effect of the sensitizing heat treatment on the M_s temperature of the alloys.

C) M_s Determination

From the first solution anneal and liquid nitrogen quench of the twelve alloys, type 304L was chosen for an M_s determination. A specimen of the type was solution annealed, as described above, and water quenched to room temperature. The specimen was then placed in a 3/16" quartz tube and rested on a quartz plug used to close one end of the tube. A small hole was cut in the side of the tube half way between the ends of the specimen. The copper-constantan thermocouple was placed in the hole and secured with a short length of asbestos string such that it was held firmly against the specimen. The thermocouple junctions were then placed in an ice water bath and the leads connected to the potentiometer. The quartz tube containing the specimen was then placed in a Dewar flask containing liquid nitrogen so that the specimen was cooled by the vapor from the boiling nitrogen. In this manner, the specimen was

cooled in 10° C (18° F) increments from room temperature down to -320° F. At the end of each 10° C (18° F) increment, the specimen was removed from the cooling medium and checked with the Magne Gage to determine the per cent of martensitically-formed ferrite present.

As a means of correlating Magne Gage readings with the actual amount of ferrite present, compacts of electrolytic iron in copper were made which contained per centages of iron powder, by volume, within the range of 2.0 to 25.0%. The compacts were then cut in half in the longitudinal direction, and readings were taken with the Magne Gage both on the end and on the longitudinal section of the compacts in order to allow for the particle size effect on the readings. From the data obtained, two curves of per cent ferrite versus Magne Gage reading were plotted. One curve is for the readings taken on the longitudinal section, and the other is for the readings on the end section. Photomicrographs were taken of each compact at different magnifications and are used along with the calibration curves.

In order to convert a Magne Gage reading to per cent ferrite, it is first necessary to match the grain size of the ferrite particles in the specimen under study with that of one of the photomicrographs included with the calibration curves for the Magne Gage. In this manner,

the operator of the instrument determines whether the end section curve or the longitudinal section curve is to be used. After this has been determined, it is simply a matter of reading from the plot the per cent ferrite corresponding to the Magne Gage reading obtained.

D) Metallography

The results obtained by the Magne Gage were substantiated by a metallographic study. Samples of the three alloys were cut from the specimens at various stages to show the presence or absence of the martensitically-formed ferrite. In the case of the 304L alloy, metallographic specimens were taken at room temperature immediately following the solution anneal, and after cooling to -120° C (-184° F), -150° C (-238° F), -196° C (-320° F). For the 304 and 309SCB alloy, metallographic specimens were taken after cooling to room temperature immediately following the solution anneal, after quenching in liquid nitrogen to -196° C (-320° F), after cooling to room temperature following the sensitizing heat treatment, and again after quenching the sensitized specimen in liquid nitrogen.

Standard mounting and polishing procedures were used to prepare the metallographic specimens. The samples chosen for study were mounted in lucite on the Beuhler Press. They were then taken through a series of rough polishes including the belt grinder, #1, 1/0, 2/0,

and 3/0 emory paper in that order. Following the emory papers, the specimens were then polished on a series of three electrically driven polishing wheels using alumina, Linde A, and Linde B abrasives in that order.

In all cases the etchant used was 20% nitric, 40% hydrochloric, and 40% glycerol, by volume as recommended by the Metals Handbook.[10]

RESULTS

A) Initial Solution Anneal and Liquid Nitrogen Quench

Of the twelve austenitic stainless steels originally solution annealed and subsequently quenched in liquid nitrogen, only the 304L was found suitable for an M_s determination. After the initial quench from the solution annealed condition, the 304L alloy was found by Magne Gage measurement to contain approximately 4 per cent martensite.

Type 309 SC_b contained approximately 11 per cent ferrite after the solution anneal and liquid nitrogen quench; however, on closer examination it was found that this alloy contained some 3 per cent ferrite even after slow cooling to room temperature from the annealing temperature.

Type 304 was found to be non-magnetic after the liquid nitrogen quench from the solution annealed condition. Thus, the temperature of spontaneous transformation for this alloy occurs below the temperature of liquid nitrogen (-320° F). However, because of its relatively high carbon content and lack of stabilizing elements, such as columbium or titanium), this alloy was chosen to study the effect of sensitization (carbide precipitation) on the M_s temperature.

In principle, the 309 SCb is stabilized against chromium carbide precipitation, and type 304L is low enough in carbon content so that carbide precipitation at 1200° F is not regarded as a problem. Nevertheless, the effect of

heating these two alloys in the sensitizing range was studied also.

Table II lists the three alloys chosen for study, along with the various heat treatments, types of quenches used, and the results of Magne Gage measurements following the quenches.

TABLE II

MAGNE GAGE READINGS FOLLOWING VARIOUS HEAT TREATMENTS AND QUENCHES

	Treatment*	Magne Gage Reading Type 304	Type 304L	Type 309SCb
1	SA / SC	0	0	85**
2	SA / Wa	0	0	85**
3	SA / Wa / WNQ	0	23	100**
4	SA / SC / Sens	175**	0	27**
5	SA / SC / Sens / LNQ	0	18	96**

* Definition of symbols:
SA - Solution anneal at 2000° F for one hour
WA - Water quench to room temperature
SC - Slow cool to room temperature
LNQ - Quenched in liquid nitrogen (-320° F)
Sens - Held at 1200° F for two hours followed by slow cool to room temperature

** Martensite not identifiable by metallography.

B) M_s Determination of Type 304L

Figure 5 is a plot of the results obtained in the M_s determination of Type 304L. The temperature to which the specimen was cooled is plotted on the abscissa, while the per cent ferrite from the converted Magne Gage readings is plotted on the ordinate. The curve was extrapolated to zero per cent martensite to obtain the approximate temperature at which the transformation began.

Mecrohardness readings were taken in both austenite and martensite areas on the partially transformed 304L specimen. Table III gives the results of the microhardness tests in diamond pyramid (DPH) values and in Rockwell B or C values as converted from the DPH numbers.

TABLE III

HARDNESS OF AUSTENITE AND MARTENSITE IN PARTIALLY TRANSFORMED TYPE 304L STAINLESS STEEL

Phase	DPH	Rockwell By Conversion
Austenite	135	B 74
Martensite Type 1*	247	C 22
Martensite Type 2*	299	C 29

*For explanation of "types" of martensite, see text.

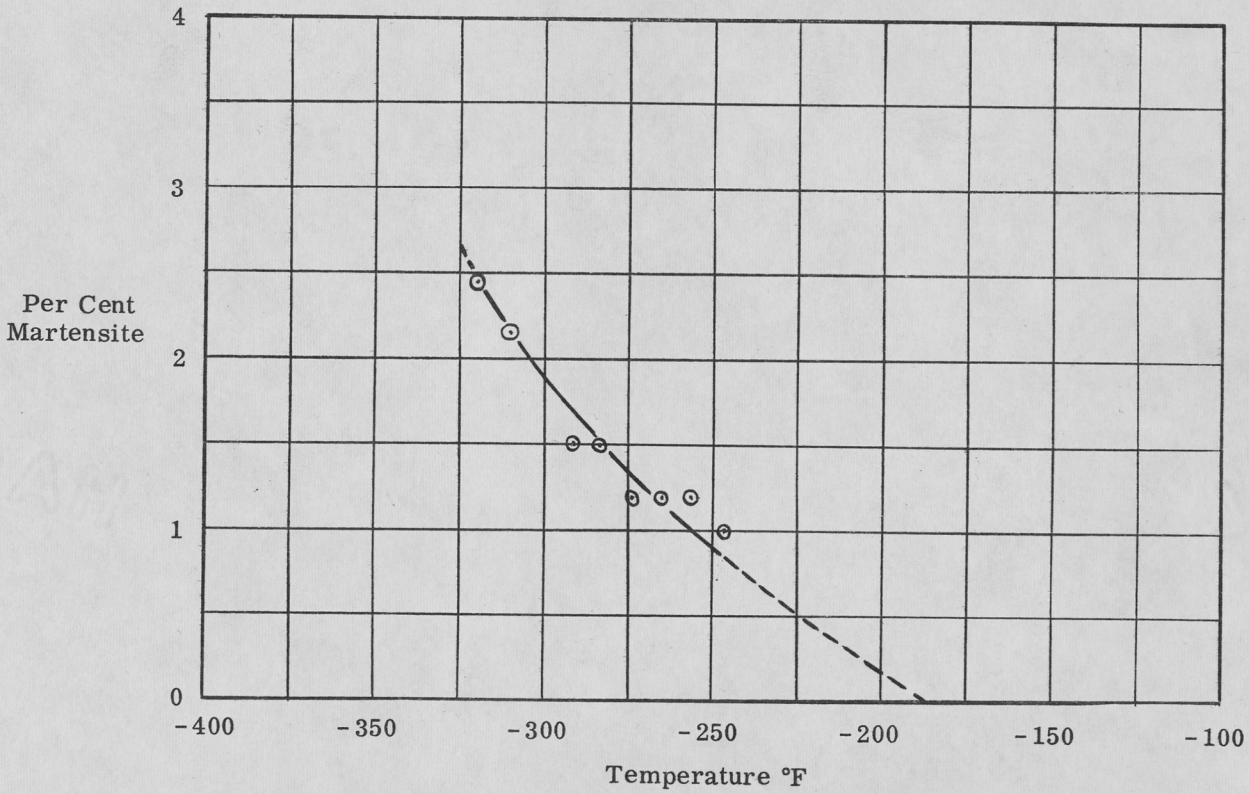

Figure 5. Curve of Spontaneous Formation of Martensite on Cooling AISI Type 304L Austenitic Stainless Steel Below the M_s Temperature.

Hardness values for two types of martensite are listed in Table III because readings were taken in different martensite areas, and the readings were about evenly distributed between averaged values of 247 and 299 DPH.

Figures 6 through 9 are photomicrographs of the Type 304L specimen which was partially transformed on cooling. The metallographic samples were cut from the specimen being transformed at various stages of the transformation between room temperature and -320° F. These photomicrographs are included to show the correlation between microstructure and Magne Gage measurements used in determination of Ms for Type 304L.

C) Type 304

Figures 10 through 12 are photoimicrographs of the Type 304 alloy included to show the microstructures after various treatments. These photomicrographs show evidence which offers an explanation of the anomalous Magne Gage readings shown in Table II. This matter is considered under Discussion of Results. The photomicrographs also show the grain boundary carbide precipitation resulting from the sensitizing treatment at 1200° F.

D) Type 309SCb

Figures 13 through 16 are photomicrographs of Type 309SCb stainless steel showing the microstructures resulting



Figure 6. Type 304^{L} stainless steel (19.3 Cr, 9.3 Ni, 0.022C); solution annealed at 2000° F and water quenched to room temperature. The structure consists of austenitic grains showing numerous annealing twins. Some of the black spots are undissolved carbides and others are exide inclusions or pits from polishing and etching. X525; Glyceregia etch.



Figure 7. Same stainless 304^{L} as Figure 6. Solution annealed at 2000° F and water quenched to room temperature, then cooled to -184° F. The structure is the same as in Figure 6, except for the appearance of the martensitic area in the upper right hand corner. This was the only martensite area on the entire polished surface. X525; Glyceregia etch.

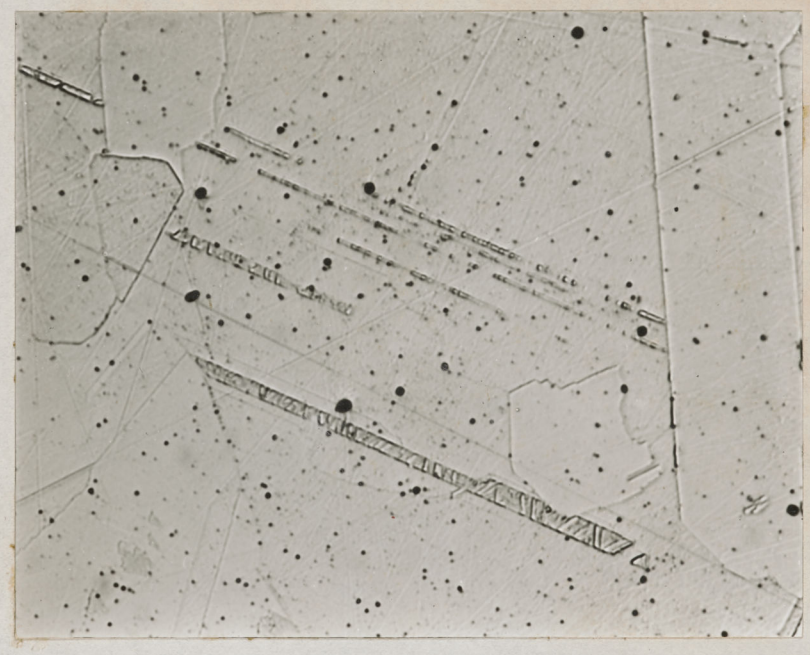

Figure 8. Same stainless 304L as Figures 6 and 7. Solution annealed at 2000° F and water quenched to room temperature, then cooled to -238° F. Several martensite areas similar to the ones shown were present on the polished surface. X525; Glyceregia etch.

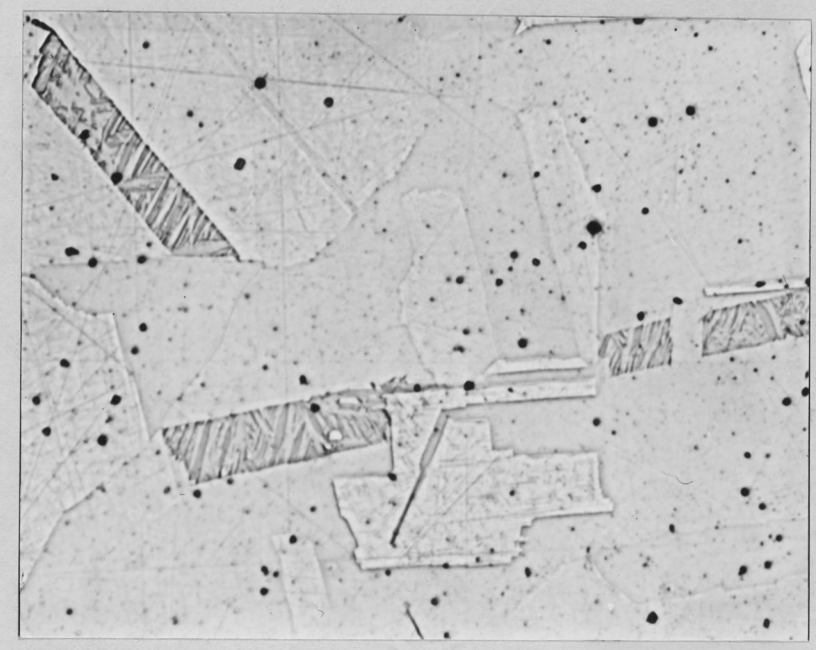

Figure 9. Same stainless 304L as Figures 6, 7, and 8. Solution annealed at 2000° F and water quenched to room temperature, then cooled to -320° F. Numerous martensitic areas such as the one shown here were present on the polished surface. The martensite formed always between annealing twins. The martensite patches were larger at this temperature than at -184° F and -238° F. X525; Glyceregia etch.

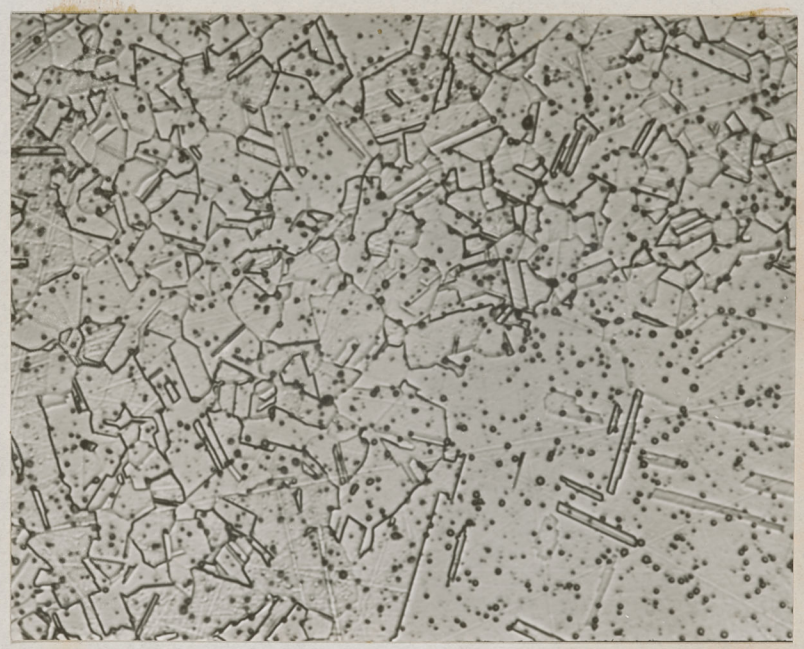

Figure 10. Type 304 stainless steel (18.0 Cr, 9 Ni, 0.078C); solution annealed at 2000° F and water quenched to room temperature. The structure consists of austenitic grains showing numerous annealing twins, and containing some carbides and oxide inclusions. The major portion of the specimen consisted of the small grains; however, three large grain areas similar to the one shown, were present at the outer edge of the specimen. X525; Glyceregia etch.

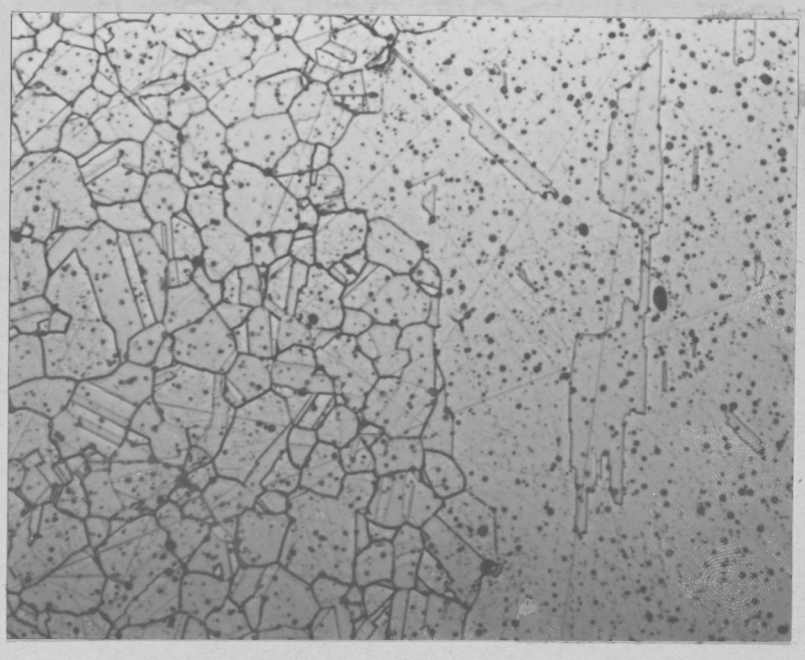

Figure 11. Same stainless 304 as Figure 10. Solution annealed at 2000° F and water quenched to room temperature, then sensitized at 1200° F for two hours and slow cooled to room temperature. The structure is the same as in Figure 10, except for numerous carbides present in the grain boundaries. The carbides are not resolved at this magnification. X525; Glyceregia etch.

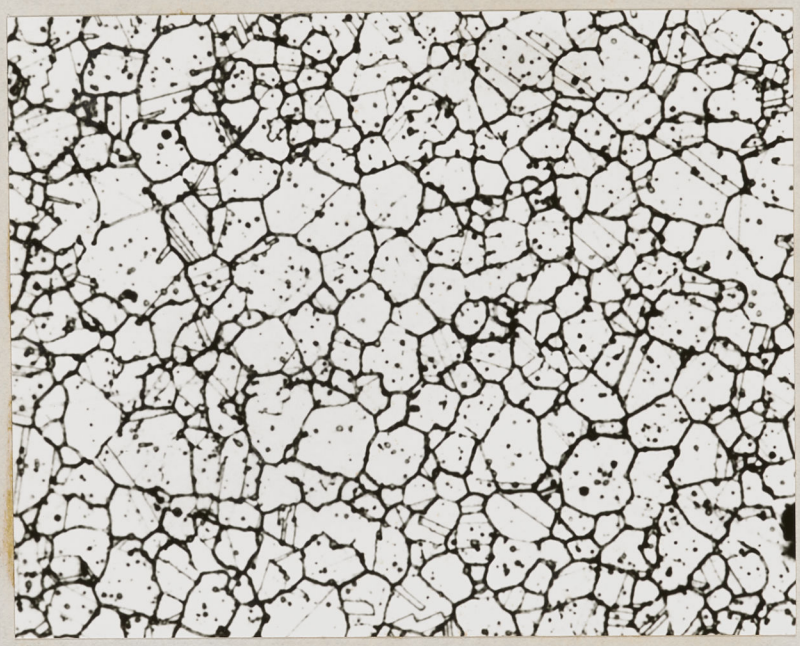

Figure 12. Same stainless 304 as in Figures 11 and 12, solution annealed at 2000° F and water quenched to room temperature, then sensitized and cooled to -320° F. Same structure as Figure 12, except that the large grain areas are no longer present. No martensite was identifiable in any of the 304 microstructures. X525; Glyceregia etch.

from various heat treatments. These photomicrographs offer no evidence of the ferrite indicated by the Magne Gage readings on these specimens.

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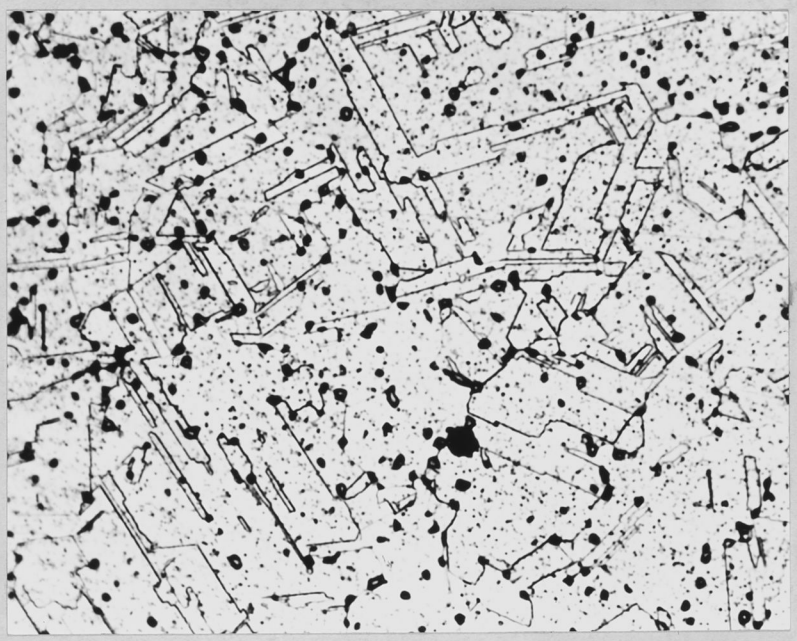

Figure 13. Type 309SCb stainless steel (22.92 Cr, 13.42 Ni, 0.035 C); solution annealed at 2000° F and water quenched to room temperature. The structure consists of austenitic grains containing numerous annealing twins. The dark spots are columbium carbides. Though a Magne Gage reading of 85 was obtained on this specimen, no martensite areas could be identified. X525; Glyceregia etch.

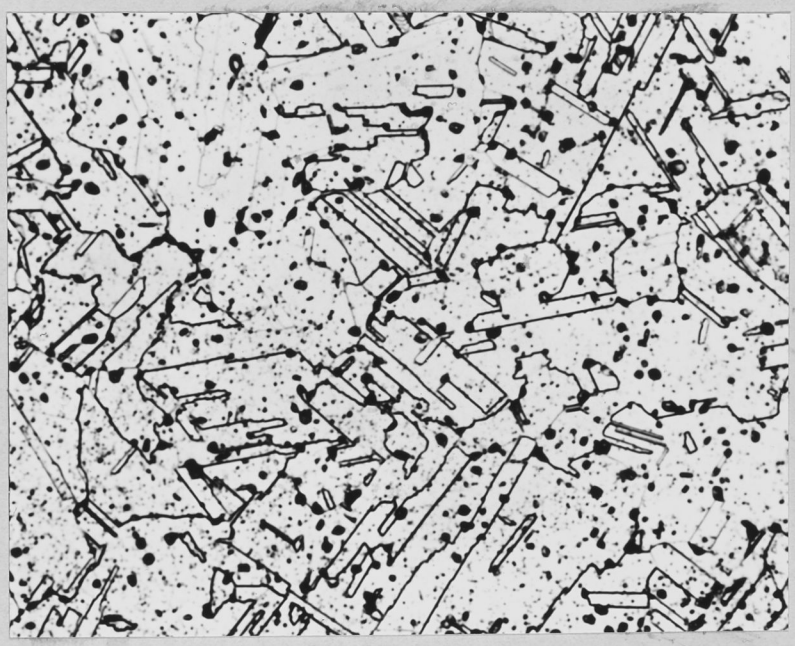

Figure 14. Same stainless 309SCb as Figure 13, solution annealed at 2000° F and water quenched to room temperature, then quenched liquid nitrogen. The structure is the same as that observed in Figure 13. No change in microstructure occured due to the liquid nitrogen quench. X525; Glyceregia etch.

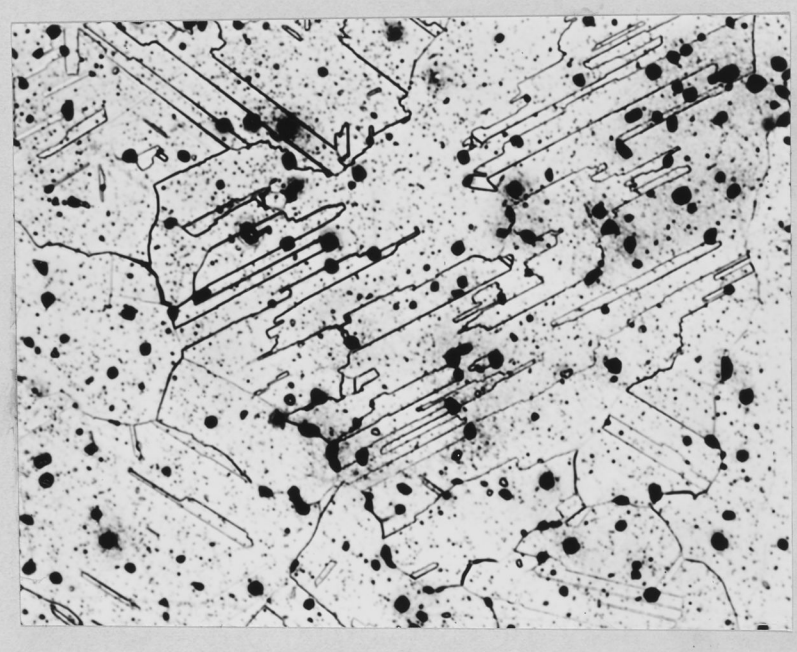

Figure 15. Same stainless 309SCb as Figures 13 and 14, solution annealed at 2000° F and water quenched to room temperature, then sensitized to 1200° F and slow cooled to room temperature. The structure is very nearly the same as that in Figure 13. No martensite structure is visible. X525; Glyceregia etch.

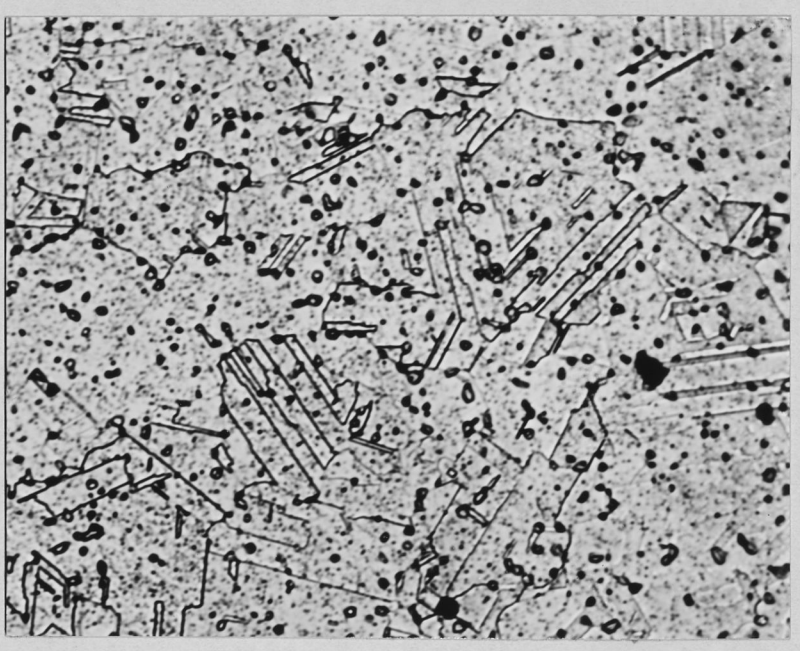

Figure 16. Same stainless 309SCB as Figures 13, 14, and 15. Solution annealed at 2000° F and water quenched to room temperature, then sensitized at 1200° F and quenched in liquid nitrogen (-320° F). The structure is essentially the same as in Figures 13, 14, and 15. Only austenitic grains containing columbium carbides are visible. X525; Glyceregia etch.

DISCUSSION OF RESULTS

A) Type 304L

Troiano and Cresinger have shown that the amount of martensite formed per degree of decrease in temperature is not a constant. The amount of martensite produced at first is small. As the temperature continues to decrease, the amount of martensite increases; and finally, near the end, it decreases again. A curve of this nature was fitted to the plot of per cent martensite versus temperature for the Type 304L stainless steel (Figure 5) to serve as a guide for extrapolation to zero per cent martensite. This extrapolation indicates an M_s temperature of -180° F which seems reasonable in view of the results of the metallographic study (Figures 6, 7, 8, and 9). One very small patch of martensite was present after cooling to -184° F (Figure 7). Increasing amounts of martensite were visible after cooling to temperatures of -238° F and -320° F (Figures 8 and 9).

The presence of martensite in the partially transformed specimen was confirmed by nicro-hardness measurements on the austenite areas and the areas suspected of being martensite (Table III). The two hardness values obtained and listed in Table III may be due to a difference in the density of the martensite platelets in different transformed areas.

The martensite formed in the partially transformed

304L specimen was found only between annealing twins (Figures 7, 8, and 9). No explanation of this phenomenon can be drawn from the present study, nor was any found in the literature survey.

B) Type 304

The results indicate that Ms for Type 304 stainless steel, in the solution annealed condition, is below -320° F (Table II). No Magne Gage reading was obtained, and no magnetism could be detected with a stronger bar magnet after quenching the specimen in liquid nitrogen.

The Magne Gage reading obtained on the Type 304 specimen after sensitizing and cooling to room temperature indicates that M_s has been raised to above room temperature (Table II). However, an examination of the microstructure of this specimen reveals no martensite (Figure 11). A further study of Table II shows that after the sensitized specimen was quenched in liquid nitrogen, no magnetism could be detected with the Magne Gage. A possible explanation for this anomalous behavior may be derived from a review of the experimental procedure. The specimen was chucked in a drill press and polished with an emory cloth to a size small enough for the quartz tube. It was then solution annealed and water quenched to room temperature. It had been determined previously that the M_s was below -320° F. A

sample was cut from the specimen, mounted and polished to show the microstructure of the Type 304 in the solution annealed condition (Figure 10). The remainder of the specimen was then sensitized and cooled to room temperature. When checked with the Magne Gage it gave a reading of 175. Another metallographic sample was cut from the specimen, mounted and polished to show the microstructure of the Type 304 in the sensitized condition (Figure 11). Finally, the remainder of the specimen was quenched in liquid nitrogen and when checked with the Magne Gage gave no indication of being magnetic. It is believed, therefore, that one end of the specimen became cold worked when chucked in the drill press, and the subsequent heat treatment was sufficient to transform the ferrite, formed during cold working, back to austenite. Thus, a Magne Gage reading of 175 was obtained from the martensite formed through deformation at the cold worked end.

The microstructures of the three samples cut from the specimen lend support to the above theory (Figures 10, 11, and 12). Figures 10 and 11 show evidence that recrystallization and grain growth had taken place in a portion of the specimen. An examination of these two specimens at a lower magnification revealed three such areas corresponding to the position of the three jaws of the drill chuck. Figure 12, showing no evidence of recrystallization, was apparently cut

from the specimen at a point which was not in contact with the drill chuck.

The overall evidence indicates that even though carbide precipitation occurred in the grain boundaries (Figures 11 and 12), the M_s temperature was still below -320° F.

C) Type 309SCb

Results from Magne Gage readings on the Type 309SCb stainless steel indicate that the M_s temperature is above room temperature (Table II). No martensite could be identified in the microstructure of the specimen which was solution annealed and cooled to room temperature (Figure 13). However, if the Magne Gage reading is converted to per cent martensite using the same curve that was used for the Type 304L, it corresponds to 3 per cent martensite.

Cooling the solution annealed specimen to -320° F only slightly increased the Magne Gage reading from 85 to 100 (Table II).

After sensitization of the Type 309SCb and cooling to -320° F, the Magne Gage reading was essentially the same as that obtained after cooling the solution annealed specimen to -320° F. Thus, the sensitization had no effect on the Type 309SCb stainless steel. The microstructure of this specimen is consistent with these results, in that no carbides can be seen in the austenite grain boundaries

(Figure 16).

Conclusions

The following conclusions may be drawn from these limited studies:

1) The M_s temperature of the AISI Type 304L stainless steel is between -190° and -170° F.

2) Sensitization by heating to 1200° F for two hours does not affect the M_s temperature of the Type 304L stainless steel.

3) The M_s temperature of the AISI Type 304 stainless steel is less than -320° F.

4) Sensitization of the Type 304 stainless steel by holding for two hours at 1200° F is not sufficient to raise the M_s to above -320° F.

5) The M_s temperature of the AISI Type 309SCb appears to be above room temperature.

6) Sensitization by holding at 1200° F for two hours has no observable effect on M_s for Type 309SCb.

Recommendations

The following recommendations are made for further study of the M_s temperature of austenitic stainless steels:

1) A more extensive study into the effect of

sensitization on the M_s temperature.

2) An attempt to identify the martensite phase in the 309 SCb stainless steel.

3) An investigation into the cause of the formation of martensite exclusively between annealing twins in the Type 304L stainless steel.

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BIBLIOGRAPHY

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APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein but approves the thesis only for the purpose for which it is submitted.

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