THE AUSTENITE-MARTENSITE PHASE RELATIONSHIPS IN PRECIPITATION HARDENING STAINLESS STEELS

By

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B.S. in Met. Eng., Lehigh University

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Submitted in Partial Fulfillment of the

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ABSTRACT

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The austenite-martensite phase relationships in two precipitation hardening stainless steels were investigated after several heat treatments. The volume percentage of delta ferrite was obtained by means of a lineal analysis of the microstructure, and the contents of retained austenite, γ, and total ferrite, α, which included delta ferrite and martensite, M, were obtained from integrated intensity measurements of the x-ray diffraction lines, $\alpha(200)$ and $\gamma(200)$. Monochromatic chromium Kα radiation was used.

On aging a steel containing 17Cr-7Ni-1Al (weight percent) between 800° F and 1100° F, an increase in austenite content was observed even though the hardness increases, and it was concluded that a precipitation reaction occurs in this steel. A maximum hardness of Rockwell C 43 was obtained by aging between 900 and 1000° F. On the other hand, it was found that a steel containing 17Cr-4Ni-2.75Mo appears to rely primarily upon the martensite-to-austenite transformation for its strength, even after aging.

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I. INTRODUCTION

A. History and Theory of Precipitation Hardening Stainless Steels

The first precipitation hardening stainless steel, Stainless W, the composition of which is given in Table I, was developed during the latter part of World War II as a result of a systemmatic study by Smith, Wyche, and Gore(1) of the effect of additions of titanium and aluminum to standard austenitic steels of the 18 percent chromium - 8 percent nickel variety. The additions of titanium and aluminum raised the M_s or decreased the stability of the austenite by removing carbon and nitrogen from solid solution in the austenite during annealing. This produced at room temperature a structure which contained a high percentage of martensite. The titanium and aluminum also contributed to a precipitation reaction during a subsequent aging treatment at around 900° F.

The presence of high percentages of martensite produced from the decomposition of austenite is a necessary condition for effective precipitation hardening in these stainless steels. Smith et al attributed this to the relative solubilities of the precipitate forming elements in ferrite and austenite. The solubility is quite high in austenite but low in ferrite. Therefore, the martensite formed from the decomposition of austenite will be supersaturated with respect to these elements and precipitation will occur during the low temperature aging treatment.

Several other types of precipitation hardening stainless steels have been developed since the appearance of Stainless W. The Armco Steel

TABLE I

Nominal Compositions of Precipitation Hardening Stainless Steels(2)

	Composition, Weight Percent				
Type:	17Cr-7Ni-1Al-1Ti	18Cr-7Ni-1Al	18Cr-4Ni-4Cu	17Cr-4Ni-2.75Mo	17Cr-4Ni-2.75Mo
Trade Designation:	**Stainless W**	17-7PH	17-4PH	**AM350**	**AM355**
Carbon, max	0.12	0.09	0.07	0.10	0.17
Chromium	16.0 - 18.0	16.0 - 18.0	15.5 - 17.5	16.25 - 17.25	14.5 - 16.0
Nickel	6.0 - 8.0	6.5 - 7.75	3.0 - 5.0	4.0 - 4.5	4.0 - 4.5
Titanium	1.0 max.	--	--	--	--
Aluminum	1.0 max.	0.75 - 1.50	--	--	--
Copper	--	--	3.0 - 5.0	--	--
Molybdenum	--	--	--	2.5 - 3.0	2.5 - 3.0
Cb + Ta	--	--	0.25 - 0.45	--	--

Corporation has developed a 17 percent chromium - 4 percent nickel - 4 percent copper type, 17-4PH, and a 17 percent chromium - 7 percent nickel - 1 percent aluminum type, 17-7PH, and The Allegheny Ludlum Steel Corporation has produced two stainless steels of the 17 percent chromium - 4 percent nickel - 2.75 percent molybdenum type, AM 350 and AM 355. The compositions of these steels are given in Table I. 17-4PH is completely martensitic at room temperature and appears to depend upon the addition of approximately 4 percent copper for its precipitation reaction while 17-7PH, containing about 1 percent aluminum, has an M_s below room temperature, and must be transformed by special heat treatments to be described in the next section. The precipitate is postulated(3) to be nickel-aluminum in the 17Cr-7Ni-1Al alloy, but has not yet been positively identified in either this steel or the 17Cr-4Ni-4Cu alloy. The stainless steels containing nominally 2.75 percent molybdenum are also austenitic at room temperature and therefore also require special treatments. The producers(2) of these latter stainless steels do not believe that a precipitation reaction occurs during the aging treatment. Any increase in hardness during such a treatment is thought to be a result of a tempering reaction occurring in the martensite.

B. Heat Treatments of Precipitation Hardening Stainless Steels

1. Solution Treatment

The M_s temperatures of both the 17Cr-7Ni-1Al and 17Cr-4Ni-2.75Mo steels, those precipitation hardening stainless steels which may be austenitic at room temperature, are quite sensitive to annealing or solution temperature. Figure 2 shows the variation of M_s with solution temperature. At the high solution temperatures the austenite-stabilizing elements are in solution and the M_s is quite low. In this condition the austenite is very stable at room temperature and the alloy may be worked without difficulty. However, at low annealing temperatures, carbides precipitate, remove the stabilizing elements from solution, and raise the M_s.

2. Transformation

In order to produce the martensitic matrix which is necessary for the precipitation reaction, two alternative treatments are available. The alloys may be given an intermediate aging treatment between 1350° F and 1400° F or they may be refrigerated at -100° F. In the first case, the M_s has been raised because of the removal of carbon from solution in the austenite by the precipitation of carbides and as a result the austenite transforms to martensite during cooling to room temperature. The M_s of the stainless steels, if properly solution treated (around 1750° F) is just below room temperature and so by refrigerating at -100° F the austenite-to-martensite transformation occurs readily.

3. Aging Treatment

Following transformation the alloys may be aged in the temperature range from 750° F to 1050° F for 1 - 2 hours. The aging treatment produces a definite increase in hardness, tensile strength and yield strength. Yield strengths in excess of 150,000 psi may be obtained. Excellent summaries(2, 4-9) of the mechanical properties resulting from the various treatments of precipitation hardening stainless steels have been prepared.

C. Purpose of this Investigation

The previous discussions show that two strengthening reactions, the austenite-to-martensite transformation and a low temperature aging or tempering reaction, are superimposed to produce the very desirable strength properties in precipitation hardening stainless steels. It is the purpose of this investigation to study some aspects of the austenite-to-martensite transformation by establishing a technique for the determination of retained austenite in stainless steels. The aspects to be investigated are the extent of the austenite-to-martensite transformation after each of the standard treatments of the 17Cr-7Ni-1Al and 17Cr-4Ni-2.75Mo alloys and the variation in austenite content during aging.

Some thought has already been given to this latter aspect. Smith Wyche, and Gore(1) report that there is no change in the amount of austenite in the 17Cr-7Ni-1Al-1Ti alloy during aging while Armco(4) states that there is a slight reversion of martensite-to-austenite during aging of the 17Cr-7Ni-1Al steel at 950° F. This is substantiated by a slight contraction of the steel following the aging treatment indicating that some closely packed face centered cubic austenite is formed along with the precipitation reaction. Morely(10) investigating an alloy of the 17Cr-7Ni-1Al type reports that the reversion of martensite-to-austenite begins at 1076° F. Another possibility(7) is that some retained austenite transforms to martensite during aging and thereby adds to the hardness produced during aging. In order to evaluate these statements this investigation will attempt to disclose more accurately the austenite-martensite phase relations during aging.

D. Previous X-ray Investigations of Retained Austenite in Steel

Averbach and Cohen(11) determined the amount of austenite present in tool steel by comparing the integrated intensities of austenite and martensite obtained from film exposed to monochromatic cobalt radiation in a Debye camera. The x-ray values of retained austenite were in very good agreement with the results of lineal analysis on the same specimens, and the error in the determination was estimated to be ± 5 percent of the amount of retained austenite or ± 0.3 percent austenite, whichever is greater.

Littmann(12) measured the line energies in 52100 and 1045 steels by using a Geiger counter spectrometer and vanadium-filtered chromium radiation. The chromium radiation was necessary to reduce the high background resulting from iron fluorescence when cobalt and iron radiation were used. The values of retained austenite obtained were estimated to be within 0.5 - 2 percent of the true value.

The above techniques used for carbon and low-alloy steels are applicable to stainless steels, but difficulty is encountered in the determination of retained austenite in the latter due to the high background produced by chromium K α fluorescence when diffraction is attempted with almost all of the commonly used radiations. There are two approaches to the problem of increasing the peak-to-background ratio. One method is to use a diffracted beam monochromator set to reflect only the characteristic radiation diffracted from the sample. Such a technique was used by Comerford(13) when confronted with high background radiation in an investigation on a high strength titanium alloy. The other alternative is to use chromium radiation, the only commonly used radiation with a wave length greater than that of the absorption edge of chromium. This latter approach was taken by Littman(12) and Erbin, Marshall, and Backofen(14) recently used this method to follow the martensitic transformation during the machining of austenitic stainless steel. In the Stainless W investigation(1), quantitative x-ray diffraction was performed using standards containing known amounts of austenite and ferrite. The accuracy here was given as ± 5 percent austenite.

II. EXPERIMENTAL PROCEDURE

A. Material Description

Two precipitation hardening stainless steels, a 17Cr-7Ni-1Al type and a 17Cr-4Ni-2.75Mo type, were investigated. The former was received as 3/4-inch diameter rod and the latter as 5/8-inch diameter rod and 1/16-inch diameter wire. The composition of the heats received are given in Table II.

1. Segregation in 17-4 Mo

During the course of carrying out the standard heat treatments for the 17Cr-4Ni-2.75Mo stainless steel, a very large variation in hardness over the cross-section of the rod was observed after transformation. Hardness readings varied from Rockwell C 20 to Rockwell C 36. Microscopic investigation showed that a structure in which some areas were completely untransformed austenite existed. This banded structure is probably the result of segregation of the austenite stabilizing elements during solidification and the subsequent elongation of the segregated areas during breakdown and rolling operations.

B. Specimen Preparation

1. Resistance Samples

The 17Cr-4Ni-2.75Mo wire was centerless ground from .0625 inch diameter to .050 inch diameter to remove an undesirable case that had formed during processing. The wire was cut into 3.5 inch lengths

TABLE II

Compositions of Heats Used in this Investigation

Element	Composition, percent	
	17Cr-7Ni-1Al *	17Cr-4Ni-2.75Mo**
Carbon	0.068	0.083
Manganese	0.60	0.66
Phosphorus	0.021	0.017
Sulfur	0.014	0.018
Silicon	0.45	0.32
Chromium	17.08	16.93
Nickel	7.43	4.30
Aluminum	1.16	--
Molybdenum	--	2.75

* Armco 17-7PH Heat No. 46878

** Universal-Cyclops 17-4MO Heat No. C-9625 and four pure nickel lead wires, two current leads (one on either end of the specimen) and two voltage leads, were then spot welded to each sample. The distance between the voltage leads (the two inner wires) was 2.75 inches.

2. X-ray and Hardness Samples

The bar stock was cut into cylindrical discs and these discs were cut in half along a diameter. The longitudinal face was used for x-ray analysis and one of the transverse faces was used for the hardness readings. This shape made it possible to perform many treatments and hardness tests on the same sample without disturbing the area used for x-ray examination. All samples prior to solution treatment were sealed in evacuated vycor.

3. Electropolishing and Electroetching

All electropolishing and electroetching was performed in an electrolyte(15) containing 25 grams of chromium oxide, 133 milliliters of glacial acetic acid, and 7 milliliters of water. The current density used for polishing was between 4-5 amperes per square inch and that used for etching was between 0.3 and 0.4 amperes per square inch. All samples were electropolished between 20 and 30 minutes prior to x-ray examination. A layer of metal approximately 0.005 inch thick was removed after polishing for this length of time.

C. Lineal Analysis

Quantitative metallographic analysis employing the Hurlbut electric semiautomatic counter technique described by Howard and Cohen(16) was used to determine the volume percent ferrite in the 17Cr-7Ni-1Al and 17Cr-4Ni-2.75Mo samples. Four 5000 count traverses were made at 500X for each sample. The estimated error is ±1 percent delta ferrite.

D. Resistance Measurements for M_s Determinations

A Kelvin double bridge was used to measure the resistance of the samples described in Section II-B. The procedure followed during a run to determine the M_s corresponding to a given solution temperature is as follows:

1. Solution treatment for 1 hour
2. Quench into boiling water bath
3. Attach leads to bridge leads with brass connectors taking care to keep samples immersed in bath
4. Measure resistance as sample and water cool; use ice to cool
5. Transfer sample to acetone and dry ice bath if M_s is not reached at 32° F

The resistance dropped linearly with temperature until the M_s point was reached. At this temperature a sharp increase in resistance was observed. A copper-constantan thermocouple was used to measure temperature during these low temperature resistance runs.

E. X-ray Measurements

The output of a chromium line focus x-ray tube operated at 40 kilovolts and 10 milliamperes was diffracted from the (200) planes of a bent and ground lithium fluoride focusing crystal to produce monochromatic chromium Kα radiation. The x-rays diffracted from the sample were received by a Geiger-Mueller counter whose pulses were received and recorded by a scaler with a resolving time of only 0.8 microseconds. The use of this radiation produced a low background and eliminated chromium fluorescence.

The long wave length of the chromium Kα x-rays, however, caused a large loss of intensity due to air absorption. Calculations show that a chromium x-ray beam is halved after travelling 8 inches in air and is reduced 75 percent after travelling 16 inches through air. For this reason, the focusing geometry and spectrometer arrangement were selected to minimize the air path through which the x-ray beam would have to travel. The spectrometer geometry is shown in Figure 1. The total air path from tube to counter is 10.2 inches, and the resulting decrease in intensity was not prohibitive to accurate measurement of peak intensities. In fact, a sheet of aluminum foil 0.002 inch thick had to be inserted just in front of the receiver slit to avoid counting rates that would flood the counter.

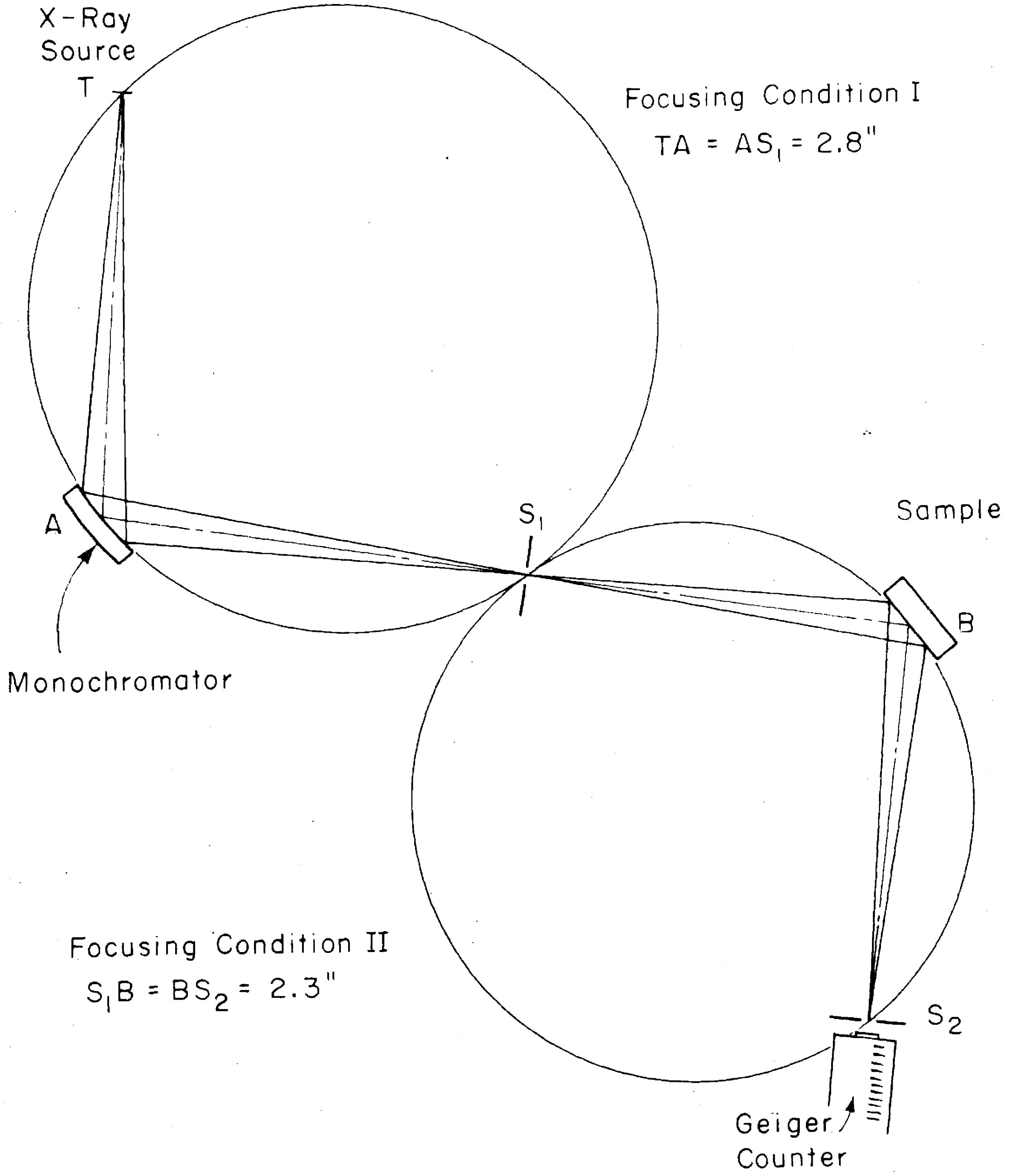

FIGURE I - SCHEMATIC DIAGRAM OF SPECTROMETER ARRANGEMENT

2. Method of Obtaining Peak Intensities

The 2θ positions of the austenite and martensite peaks were calculated using the unit cell dimensions of these phases in stainless steel of the 18 percent chromium - 8 percent nickel type determined by Fiedler, Averbach and Cohen(17). The peak profiles were then determined to check the position and the breadth of the lines. The (200) martensite and the (200) austenite peaks were found to by symmetrical and free from interference from other lines and it is these peaks which were used for the determination of the volume percentages of martensite and austenite.

The peak intensities were obtained by opening the Geiger counter receiver slit wide enough to take in all the diffracted intensity from a peak when the counter was set at the peak center. A slit opening of 0.30 inch corresponding to a 2θ value of approximately 7.5 degrees was found to be wide enough to take in the martensite (200) peak, the broadest peak. The background level of radiation was subtracted from the peak intensities and was obtained by counting the same 2θ increment at a position between the austenite (200) and martensite (200) peaks. Each peak and the background was counted for five minutes.

III. RESULTS AND DISCUSSION

A. M_s Determination

The change in M_s with solution temperature as determined by resistance measurements on the 17Cr-4Ni-2.75Mo precipitation hardening stainless steel is shown in Figure 2. The results of this investigation are compared with those of dilatometric determinations of M_s for the 17Cr-7Ni-1Al and for the 17Cr-4Ni-2.75Mo types of stainless steels. The very sharp decrease in M_s resulting from solution treating above 1800° F is noticeable in all the steels, and good agreement between the 17Cr-4Ni-2.75Mo and 17Cr-7Ni-1Al curve exists. Up to solution temperatures of 1800° F, however, the M_s temperatures for 17Cr-4Ni-2.75Mo stainless determined by dilatometric measurements are consistently higher than those for the same type of steel determined by resistance measurements. This discrepancy might be explained by slight variations of chemical composition in different heats.

B. Microstructure

After solution treatment the microstructure of the precipitation hardening steels contained 10 - 20 percent delta ferrite in a matrix of austenite. Some martensite was present if the M_s was close to room temperature or if the surface of the steel had been deformed or worked. Figure 3 shows the structure of a 17Cr-4Ni-2.75Mo sample solution treated for one hour at 1800° F. Equiaxed austenite with annealing

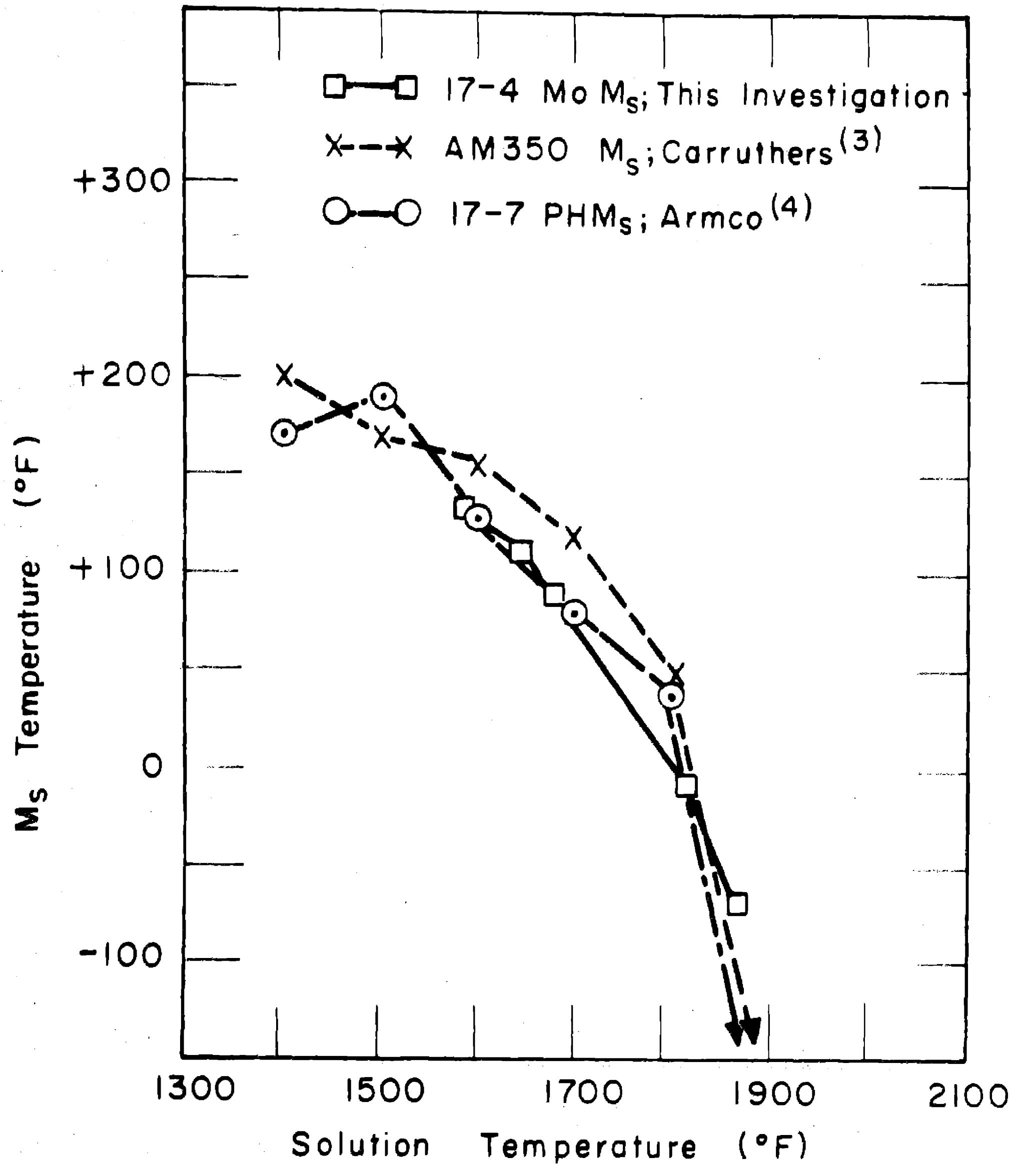

FIGURE 2 VARIATION IN M_s OF PRECIPITATION HARDENING STAINLESS STEELS WITH SOLUTION TEMPERATURE

twins, stringers of delta ferrite, and dark needles of martensite are present. Lineal analysis established the volume percent delta ferrite at 13.7 percent and x-ray analysis showed the volume percent of martensite to be 4.5 percent.

The nature of the martensitic transformation in 17Cr-7Ni-1Al stainless steel is shown in Figure 4. The sample was electrolytically polished prior to transformation at -100° F and then photographed at 500X under oblique lighting without polishing or etching after transformation. The resulting photomicrograph shows the surface upheavals produced as the martensite platelets form from the austenite. In some areas the inert delta ferrite has been deformed due to the formation of martensite plates beneath and around the ferrite islands.

No precipitate has as yet been identified or observed metallographically. Figures 5 and 6, taken at 1000X and 2000X respectively, show the microstructure of a 17Cr-7Ni-1Al sample that has been solution treated at 1750° F for one hour, transformed at -100° F for one hour, and aged at 900° F for 5 3/4 hours. The rather heavy grain boundary attack at the interface between the delta ferrite and the matrix is in part due to the depletion of chromium by carbide precipitation in these areas. This grain boundary attack by the etchant was much more severe in the samples transformed by annealing at 1350° F, and in these samples extended to the prior austenite grain boundaries. In Figure 6, austenitic areas can be seen, but no distinction between untransformed austenite

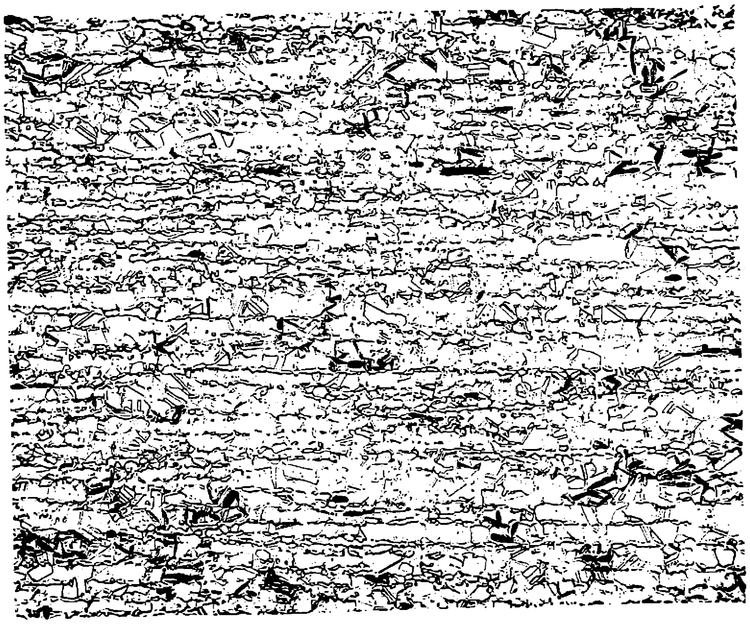

FIGURE 3. 17C-4Ni-2.75Mo sample solution treated at 1800° F. Note stringers of delta ferrite, equiaxed grains of austenite containing annealing twins, and dark needles of martensite. 100X. Electropolished and electroetched in chrome-acetic electrolyte.

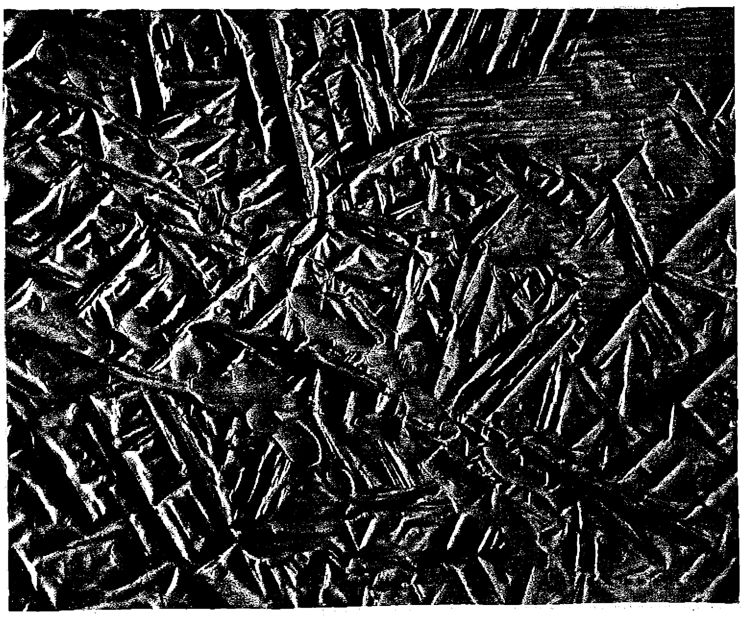

FIGURE 4. 17Cr-7Ni-1Al alloy transformed at -100° F. Surface was electropolished prior to but not after transformation. The surface upheaval due to the formation of the martensite plates is apparent. 500X. Oblique lighting.

FIGURE 5. 17Cr-7Ni-1Al alloy aged for 5 3/4 hours at 900° F after transformation at -100° F. Note heavy attack at interface between ferrite and matrix. 1000X. Electropolished and electroetched in chrome-acetic electrolyte.

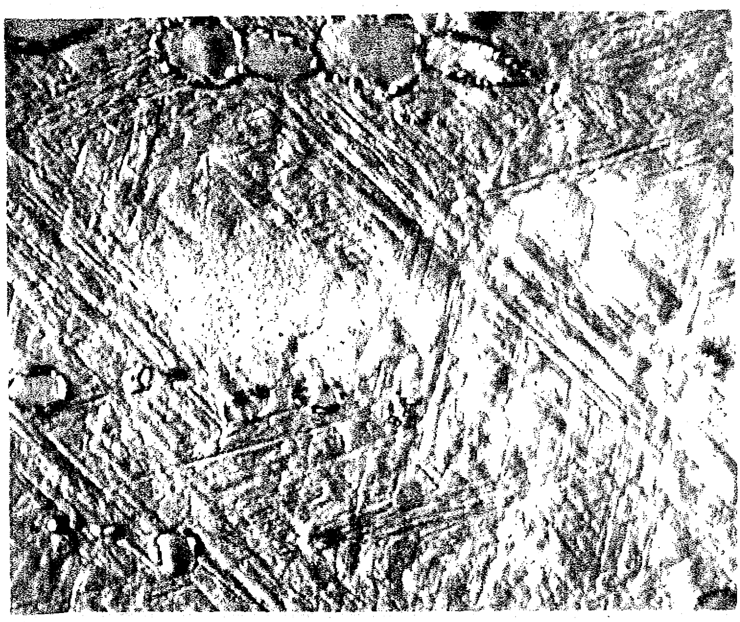

FIGURE 6. Same structure as in Figure 5 but now shown at 2000X. No precipitate can be distinguished even at this magnification. Note that surface upheavals make angles of 60 degrees with one another. 2000X by oil immersion.

and austenite formed during aging can be made. It is also interesting to note that the surface contours and lines indicating the presence of martensite make angles of 60 degrees with one another, the angle between (110) planes in a cubic crystal, and in some cases almost form complete equilateral triangles.

C. Determination of Volume Percent Austenite by X-ray Analysis

The total energy, $P_{(hkl)_\gamma}$, diffracted from a given set of planes, (hkl), of a phase γ in a polycrystalline specimen with randomly oriented grains is given by:

$$P_{(hkl)_\gamma} = K \frac{1}{v_\gamma^2} \quad m_{(hkl)_\gamma} (L.P.) F^2_{(hkl)_\gamma} \quad e^{-2M} V_\gamma A \qquad (1)$$

where: K = a constant independent of type of quantity of diffracting material.

v_γ = volume of unit cell of phase

$m_{(hkl)_\gamma}$ = multiplicity

L.P. = Lorentz-polarization factor

$F_{(hkl)_\gamma}$ = Structure factor per unit cell

V_γ = Volume of diffracting phase

e^{-2M} = Debye temperature factor

A = Absorption factor; it is assumed to be constant in this investigation.

Let:

$$R_{(hkl)_\gamma} = \frac{1}{v_\gamma^2} \quad m_{(hkl)_\gamma} (L.P.) F_{(hkl)_\gamma} \; e^{-2M} \tag{2}$$

All of the quantities in the right-hand side of the above equation are either tabulated or may be calculated. Appendix I describes in detail the calculation of the R factors and a list of R values for this investigation is given in Table A-I.

With the aid of equation (2), equation (1) may now be rewritten as:

$$P_{(hkl)_\gamma} = K \, R_{(hkl)_\gamma} \, V_\gamma \tag{3}$$

If this relationship is determined for another reflection in another phase, the ratio of the volume percentages of the two phases present can be determined as shown below in equation (4).

$$\frac{V_\alpha}{V_\gamma} = \frac{P_{(hkl)_\alpha} \; R_{(hkl)_\gamma}}{P_{(hkl)_\gamma} \; R_{(hkl)_\alpha}} \tag{4}$$

V_α and V_γ are the only unknowns since the R values are known and the P values are determined experimentally by x-ray diffraction. If α is the ferrite and γ is the austenite in the stainless steel, and if no other diffracting phases are present, V_α and V_γ may be calculated from the additional relationship:

$$V_\alpha + V_\gamma = 100 \tag{5}$$

D. Determination of Volume Percent Martensite

In the precipitation hardening stainless steels studied, both the delta ferrite and martensite resulting from the decomposition of austenite contributed to the $\alpha(200)$ reflection used to obtain integrated intensities for the ferrite phase, and it is the summation of these two phases that the V_α of equation (5) yields. Therefore, a more accurate relationship between the phases in precipitation hardening stainless steels may be written as:

$$V_{\text{delta ferrite}} + V_{\text{martensite}} + V_{\text{austenite}} = 100 \qquad (6)$$

This relationship assumes that the volume percent of carbides, and other precipitates, if present, is negligible.

Once $V_{\text{austenite}}$ has been determined with aid of equations (4) and (5), and $V_{\text{delta ferrite}}$ has been independently obtained by lineal analysis, the volume percent martensite may be determined by difference from equation (6).

E. Comparison of X-ray Results with Lineal Analysis

In order to check the accuracy of the x-ray determinations of austenite in stainless steel, five samples of 17Cr-4Ni-2.75Mo steel were solution treated at 1890° F for one hour and quenched to produce a microstructure at room temperature which would consist entirely of austenite and delta ferrite. Table III compares the volume percentages of austenite obtained by the x-ray method and by lineal analysis. It can be seen that there is very good agreement between these independent tests and on the basis of this experiment the error in x-ray determination is estimated to be ± 1percent austenite.

F. Standard Treatments and Retained Austenite

Tables IV and V show the phase relationships in the 17Cr-7Ni-1Al and 17Cr-4Ni-2.75Mo stainless steels respectively, after the standard heat treatments described in Section I-B. The 30.7 percent martensite in the 17Cr-7Ni-1Al affirms that the M_s after solution treating at 1750° F must have been close to room temperature as shown in Figure 2.

The hardness of the 17Cr-4Ni-2.75Mo samples was consistently higher than the hardness of the 17Cr-7Ni-1Al after all treatments but the final low-temperature aging. This is true even though the 17Cr-7Ni-1Al samples contained equal (as after the subzero cooling treatment) or greater (as after the intermediate aging treatment) percentages of martensite. It appears, therefore, that the martensite of the stainless with the molybdenum addition is harder than that of the stainless with the aluminum addition, and that because of this already high level of hardness after transformation, the hardness increase after aging is less for the 17Cr-4Ni-2.75Mo than for the 17Cr-7Ni-1Al stainless.

The austenite content of both the 17Cr-4Ni-2.75MO and 17Cr-7Ni-1Al specimens which had been transformed by subzero cooling increased after aging, but the change in both the hardness and austenite content

TABLE III

Comparison of X-ray Results with Lineal Analysis

Sample Number(*)	Volume Percent X-ray Ferrite	Volume Percent Metallographic Ferrite
13	16.5	18.4 ± 1
14	18.5	19.1 ± 1
15	17.3	18.5 ± 1
16	19.5	18.2 ± 1
17	21.0	18.9 ± 1

(*) All samples are solution treated at 1890° F for 1 hour. The samples are 17Cr-4Ni-2.75Mo.

TABLE IV

Phase Relationships in 17-7 Al after Standard Treatments

Treatment	Temperature*	Volume Percent Delta Ferrite	Volume Percent Martensite	Volume Percent Austenite	Hardness
Solution	1750° F	10.6	30.7	58.7	R_B 87
Intermediate Transformation	1750° F 1425° F	11.4	82.0	6.6	R_C 29
Intermediate Transformation plus Aging	1750° F 1425° F 950° F	11.4	81.6	7.0	R_C 44
Subzero Cooling Transformation	1750° F -100° F	10.6	76.5	12.9	R_C 31
Subzero Cooling Transformation plus Aging	1750° F -100° F 900° F	10.6	71.4	18.0	R_C 42

* All times at temperature are one hour.

TABLE V

Phase Relationships in 17-4 Mo after Standard Treatments

Treatment	Temperature*	Volume Percent Delta Ferrite	Volume Percent Martensite	Volume Percent Austenite	Hardness
Solution	1800° F	14.3	3.9	81.8	R_B 97
Intermediate Transformation	1800° F 1350° F	14.1	67.3	18.6	R_C 37
Intermediate Transformation plus Aging	1800° F 1350° F 850° F	14.1	74.8	11.1	R_C 42
Subzero Cooling Transformation	1800° F -100° F	15.1	76.2	8.7	R_C 44
Subzero Cooling Transformation plus Aging	1800° F -100° F 750° F	15.1	74.4	10.5	R_C 45

* All times at temperature 1 hour.

of the 17Cr-7Ni-1Al alloy was much more significant. Aging the 17Cr-4Ni-2.75Mo sample transformed by heating at 1350° F, however, results in a definite decrease in austenite. This fact, together with the small hardness increment, adds weight to the argument that no precipitation occurs in this steel and that an increase in martensite might cause the additional hardening after aging.

G. Aging Series

Samples of 17Cr-7Ni-1Al which had been solution treated at 1750° F and transformed at -100° F were aged at 700° F, 800° F, 900° F, 1000° F, and 1100° F. The volume percent austenite and hardness were obtained from each sample after 15 minutes, 1 hour, 2 hours, and 4 hours, at the aging temperature. The results of these determinations are presented in Figures 7 through 11.

The volume percent austenite was found to increase from the as-transformed value at all aging temperatures but 700° F. This evidence of the increase in austenite during aging supports the hypothesis used to explain the contraction of 0.0003 inch per inch observed during dilatometric tests in 17Cr-7Ni-1Al after aging at 950° F(4).

At 700° F the austenite decreased to a minimum of 13.5 percent after one hour and then slowly increased toward the initial amount as aging time increased. Hardness increased very little after four hours at this temperature, and even after the shorter aging times at which an increase in martensite was observed, no significant hardness change

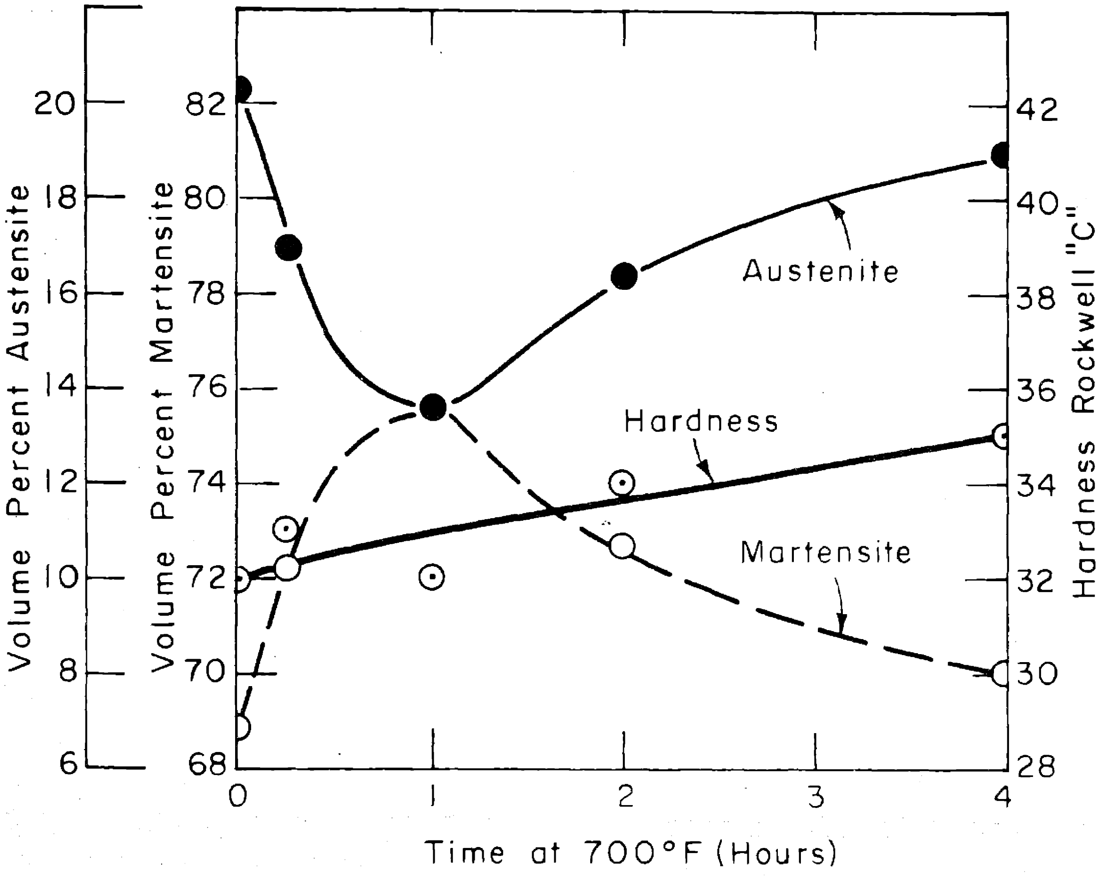

FIGURE 7 - VARIATION IN VOLUME PERCENT AUSTENITE, VOLUME PERCENT MARTENSITE, AND HARDNESS OF 17% Cr - 7% Ni - 1% Al STAINLESS STEEL WITH TIME AT 700°F
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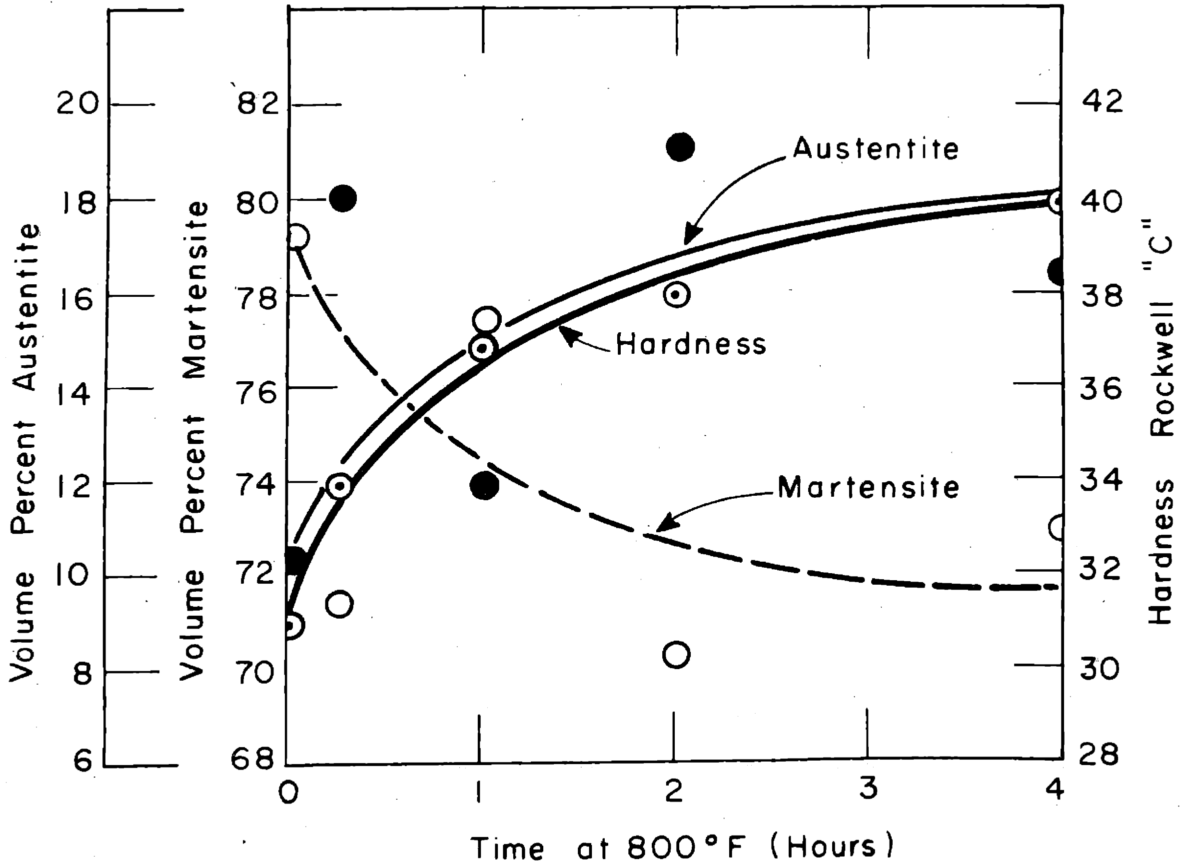

FIGURE 8 VARIATION IN VOLUME PERCENT AUSTENTITE, VOLUME PERCENT MARTENSITE, AND HARDNESS OF 17% Cr-7% Ni-1% Al STAINLESS STEEL WITH TIME AT 800°F

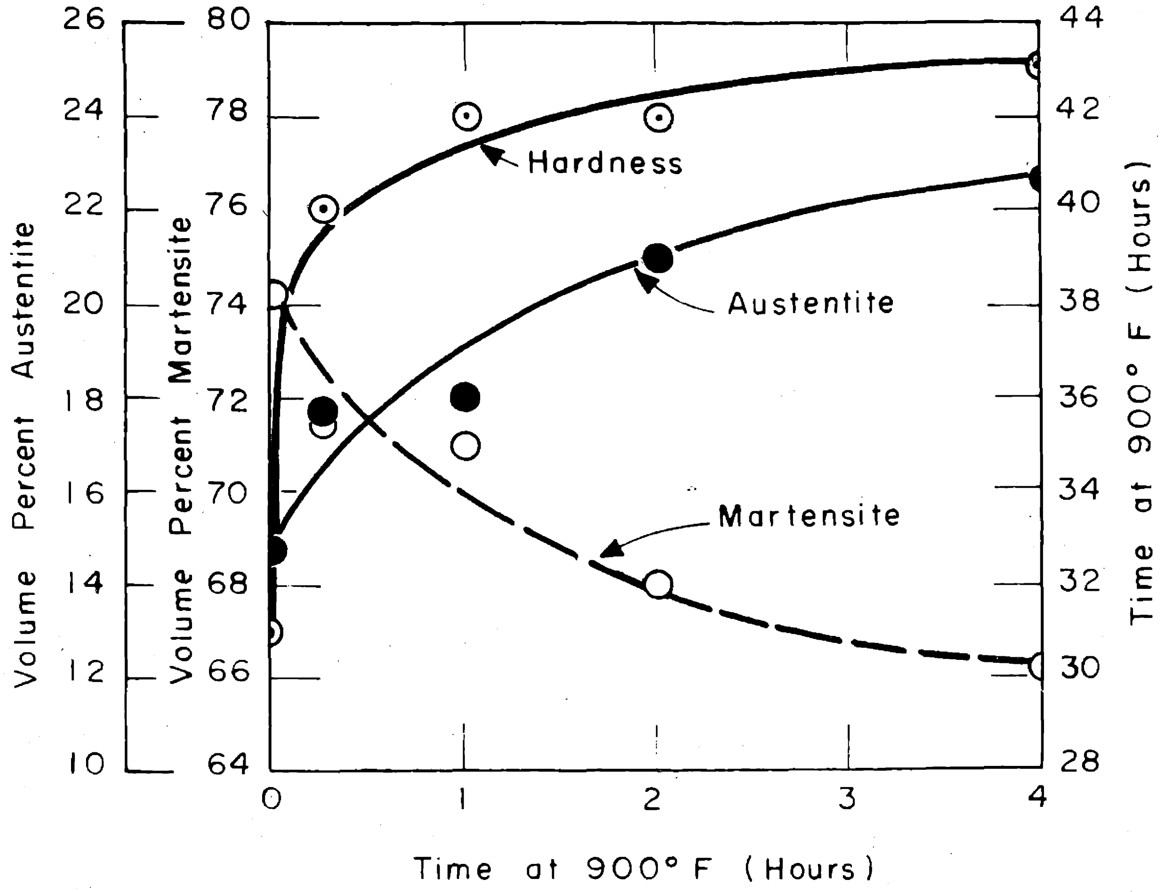

FIGURE 9 VARIATION IN VOLUME PERCENT AUSTENTITE, VOLUME PERCENT MARTENSITE, AND HARDNESS IN 17% Cr – 7% Ni – 1% Al STAINLESS STEEL WITH TIME AT 900°F

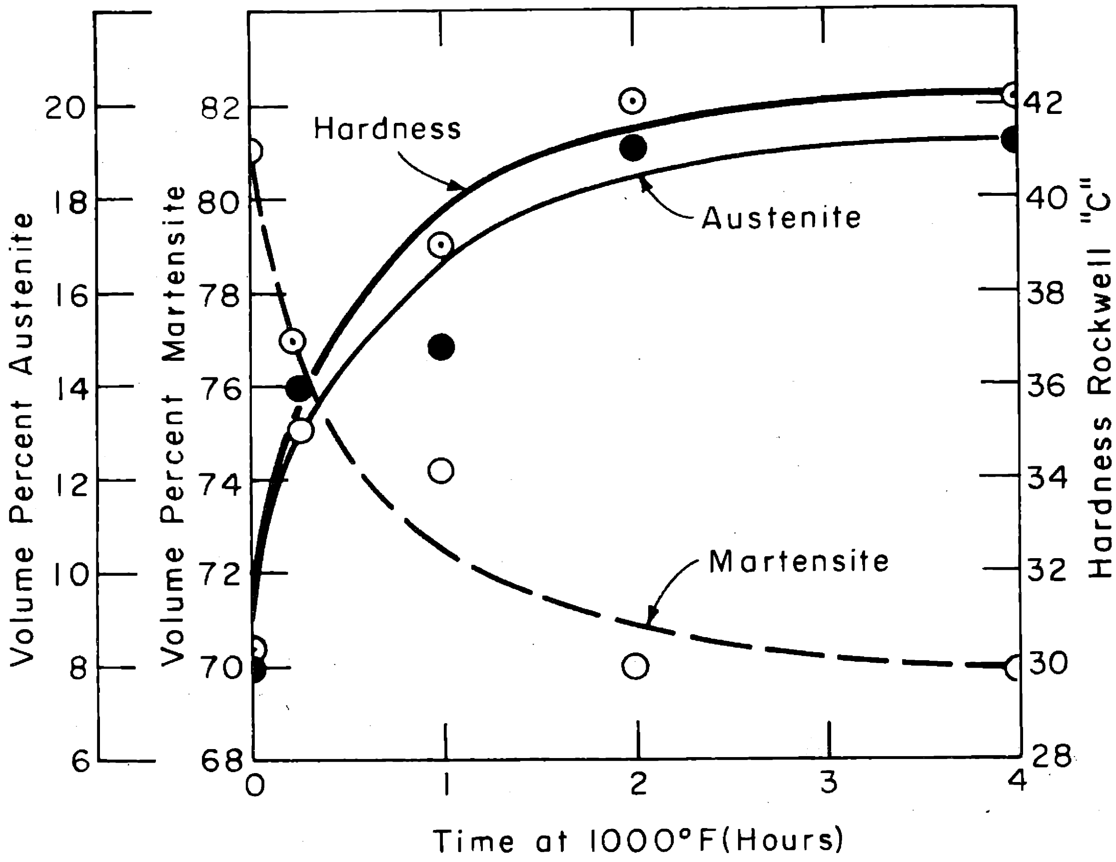

FIGURE 10 VARIATION IN VOLUME PERCENT AUSTENITE, VOLUME PERCENT MARTENSITE, AND HARDNESS IN 17% Cr-7% Ni-1% Al STAINLESS STEEL WITH TIME AT 1000°F

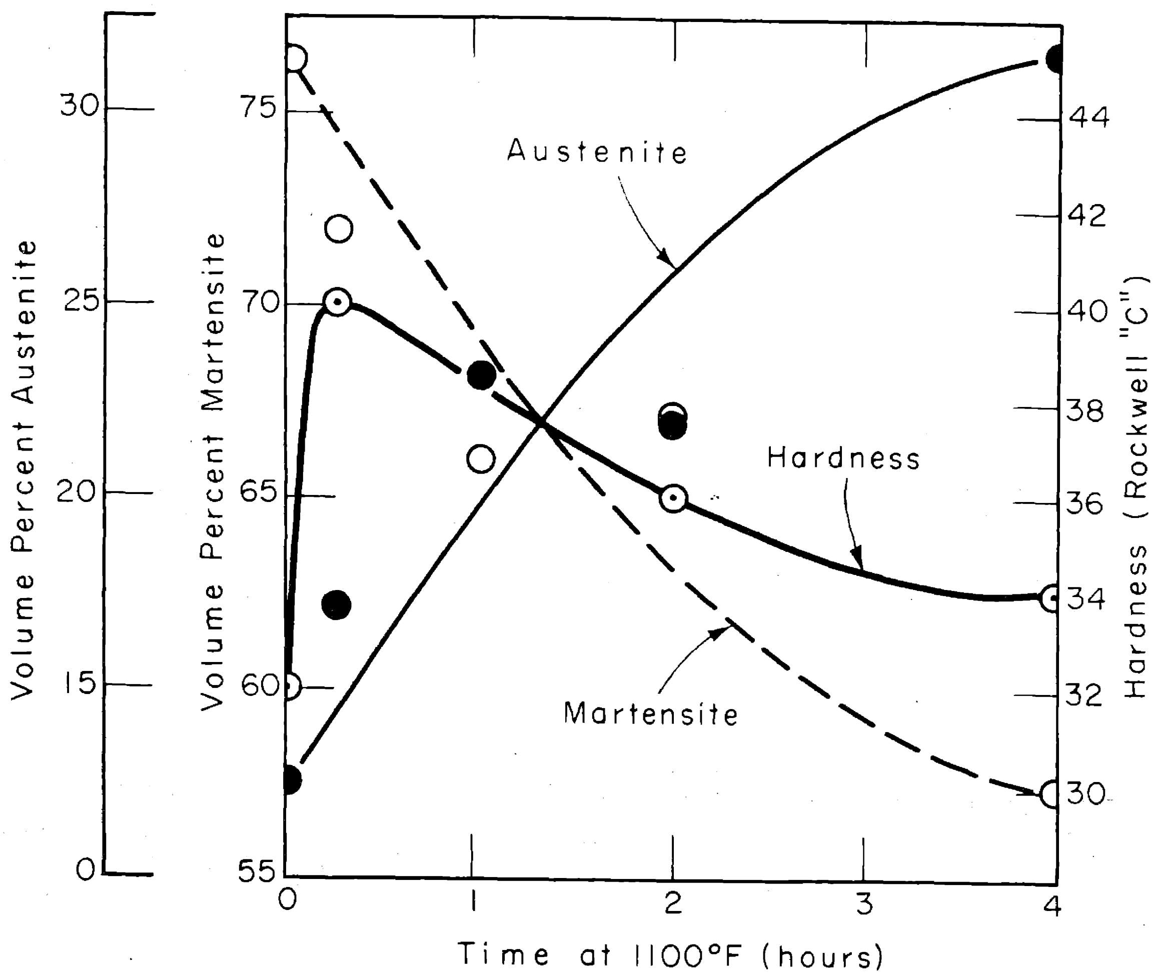

FIGURE 11 – VARIATION IN VOLUME PERCENT AUSTENITE, VOLUME PERCENT MARTENSITE, AND HARDNESS OF 17%Cr – 7% Ni – 1% Al STAINLESS STEEL WITH TIME AT 1100 °F

was noted. This observation strengthens the statement made in the previous section concerning the relative insensitivity of 17Cr-7Ni-1Al hardness to changes in quantity of martensite when compared to the 17Cr-4Ni-2.75Mo alloy.

Hardness increased significantly at all other aging temperatures, with the optimum aging temperature being bounded by 900° F and 1000° F. Because of the very definite increase in austenite content observed in the samples during aging, the increase in hardness cannot be attributed to additional martensitic transformation, and so a precipitation reaction must account for the difference.

Overaging is first observed at 1100° F when the hardness drops after aging for times greater than 15 minutes. At this temperature the austenite increases by almost 20 percent.

IV. CONCLUSIONS

A precipitation reaction occurs in stainless steels containing 1 percent aluminum when aged between 800° F and 1100° F. Accompanying the increase in hardness resulting from this reaction, there is a significant increase in austenite content.

The M_s temperature of the precipitation hardening stainless steels investigated is strongly dependent upon solution temperature.

The martensitic transformation appears to be the primary source of strength in the stainless steel containing molybdenum. The slight increase in hardness following aging could in one case be attributed to an increase in martensite during aging.

An x-ray diffraction method using chromium radiation monochromated by a bent and ground lithium fluoride crystal provides sufficient intensity and low enough background to make possible determination of austenite in stainless steels to an accuracy estimated to be ±1 volume percent austenite.

V. SUGGESTIONS FOR FUTURE WORK

Many aspects of the physical metallurgy of precipitation hardening stainless steels remain to be investigated and clarified. These aspects resolve themselves into two groups: those associated with the austenite-to-martensite transformation, and those connected with the precipitation reaction. The formation of isothermal martensite and investigation of the tempering reactions in these stainless steels are two of the aspects of the austenite-to-martensite transformation which would deserve study, while identification of the precipitates and mechanism of precipitation would be some aspects of the aging reaction worthy of investigation.

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APPENDIX I

Calculation of R Factors

A. Atomic Scattering Factor

The expression for the scattering factor, f, is given by

$$f = f_o + \Delta f' + i\Delta f'' \qquad \text{(I-1)}$$

where Δf' and Δf'' are the real and imaginary parts of the correction applied to the scattering factor necessary to account for dispersion by the K, L, and M electrons.

Rewriting (I-1) as

$$f = (f_o + \Delta f') + i\Delta f'' \qquad \text{(I-2)}$$

and multiplying this expression by its complex conjugate, we obtain

$$f^2 = (f_o + \Delta f')^2 + (\Delta f'')^2 \qquad \text{(I-3)}$$

or

$$f = [(f_o + \Delta f')^2 + (\Delta f'')^2]^{1/2} \qquad \text{(I-4)}$$

The above equation was used to obtain the scattering factor for each element in the stainless steel for the angular position of the Bragg reflection being considered. The values of Δf' and Δf'' were those determined by Dauben and Templeton(18).

To determine an average scattering factor for the stainless steel, the following procedure was used:

1. The scattering factor for each element was divided by its atomic number. In symbolic form, $\frac{f_i}{Z_i}$ was obtained.
2. The average of the summation of the above expressions for all the elements in the alloy was calculated. This gave an average scattering factor, $<\bar{f}>$, of the form

$$<\bar{f}> = \frac{f_1}{Z_1} + \frac{f_2}{Z_2} + \ldots . \frac{f_n}{Z_n} /n \qquad \text{(I-5)}$$

3. This average structure factor was then multiplied by $(x_1 Z_1 + x_2 Z_2 + \ldots . x_n Z_n)$, a new effective atomic number for the alloy which balances the composite atomic number in (I-5).

Several assumptions had to be made in order to make the calculation of a scattering factor possible. It was assumed that the compositions of the austenite and ferrite are identical, and that the elements are randomly distributed in each according to their weight fraction in the alloy. The assumption introduces some error into the calculation since the compositions of the delta ferrite and austenite would be expected to vary, the ferrite formers and austenite formers tending to concentrate in their respective phases during solution treatment. However, the assumption is good when the martensite formed from the decomposition of austenite is considered.

B. Structure Factor

For the FCC austenite cell,

$F = 4\,(x_1 Z_1 + x_2 Z_2 + \ldots . x_n Z_n)\ \langle \bar{f} \rangle$ if hkl are unmixed

$F = 0$ if hkl are mixed

For the BCC ferrite shell,

$F = 2\,(x_1 Z_1 + x_2 Z_2 + \ldots x_n Z_n) \langle \bar{f} \rangle$ if $(h + k + l)$ is even

$F = 0$ if $(h + k + l)$ is odd

C. Lorentz Polarization Factor

The **Lorentz Polarization** factor is given by the expression

$$\mathbf{L.P.} = \frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin\theta \sin 2\theta} \tag{I-6}$$

when an unpolarized beam is first diffracted from a monochromating crystal set at an angle θ_m and then reflected from the sample at an angle θ. θ_m was 34.8° for chromium Kα diffracted from the (200) planes of the lithium fluoride crystal monochromator used in this investigation.

D. Temperature Factor

The term M of the Debye temperature factor e^{-2M} is given by James[19] as

$$M = \frac{6h^2 T}{mk\,\Theta_m^2} \left\{ \phi(x) + \frac{x}{4} \right\} \frac{\sin^2\theta}{\lambda^2} \tag{I-7}$$

Where: h = Planck's constant

T = Temperature °K

m = Average atomic mass (g/atom)

k = Boltzman's constant

Θ_m = Debye characteristic temperature as applied to the temperature factor

λ = wave length of incident radiation

$x = \frac{\Theta}{T}$; the function $\left\{ \phi(x) + \frac{x}{4} \right\}$ is tabulated for values of x in James(19)

θ = Bragg angle of reflection

let

$$B = \frac{6 h^2 T}{m k \Theta_m^2} \left\{ \phi(x) + \frac{x}{4} \right\} \qquad \text{(I-8)}$$

then

$$M = \frac{B \sin^2 \theta}{\lambda^2} \qquad \text{(I-9)}$$

where B is a constant for a given material and a given temperature, and $\frac{\sin^2 \theta}{\lambda^2}$ depends upon the angular position of the line investigated.

In order to use this expression to obtain the temperature factor for stainless steel, an average characteristic temperature was calculated assuming that the Debye temperatures of the alloying elements contributed to the Debye temperature of the alloy in proportion to their atomic percentages. This average characteristic temperature for the 17Cr-4Ni-2.75Mo steel was 437.5° K.

TABLE A-I

Tabulation of R Factors for Chromium $K\alpha$ Radiation

Material	Line	Phase	θ	R Factor
17Cr-4Ni-2.75Mo	(111)	Austenite	33.6	32.2
17Cr-4Ni-2.75Mo	(110)	Ferrite	34.3	40.8
17Cr-4Ni-2.75Mo	(200)	Austenite	39.6	16.25
17Cr-4Ni-2.75Mo	(200)	Ferrite	53.0	9.59
17Cr-7Ni-1Al	(200)	Austenite	39.6	15.0
17Cr-7Ni-1Al	(200)	Ferrite	53.0	8.85

APPENDIX II

Preparation of Lithium Fluoride Monochromating Crystal

The lithium fluoride crystal used as a monochromator was prepared by plastically bending the crystal by heating under pressure in a matching set of steel dies machined to a 5-inch radius. The temperature was maintained at 850° F for 1 1/2 hours and weights up to a total of 9 pounds were added in 4 increments during this period. After the last weight was added, the temperature was lowered to 750° F and the crystal kept at this temperature for two hours.

This treatment was based upon other efforts to bend lithium fluoride crystals. At higher temperatures excessive polygonization resulted, while at lower temperatures the crystals didn't bend or broke when the load was applied.

After bending, the crystal was ground to a 2 1/2 inch radius. Comparison of exposures of the beam diffracted from the crystal when etched in a 1:1.6:1 HF: HNO_3: acetic acid bath for 16 hours and from the same crystal with an as-ground surface, showed that a more uniform diffracted beam resulted from the ground surface. Striations in the beam are visible and are due to the polygonization or formation of low angle grain boundaries that could not be avoided during the bending of the crystal.

For the etched crystal, these striations were more intense, but the intensity between them dropped considerably, therefore producing a diffracted beam with large variations in intensity.

The diffracted beam came to a focus 2.85 inches from the crystal.