WADC TECHNICAL REPORT 54-355
PART II

PRECIPITATION HARDENING AND EMBRITTLEMENT OF HIGH-STRENGTH TITANIUM ALLOYS

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FOREWORD

This report was prepared by Battelle Memorial Institute under USAF Contract No. AF 33(616)-445. The contract was initiated under Project No. 7351, " Metallic Materials" , Task No. 73510, " Titanium Metal and Alloys" , formerly RDO No. 615-11, " Titanium Metal and Alloys" and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt E. F. Erbin as project engineer. In addition to the authors, other Battelle personnel who contributed to this project were O. J. Huber, A. E. Austin, J. R. Doig, A. P. Young, H. W. Deem, and G. D. Calkins.

This report is the second part of WADC Technical Report 54-355. The first part of this report, dated December, 1954, was published under the basic report number only; it should be considered as Part I although it was not so marked.

This report covers the work conducted from April 1954 to 28 February 1955.

ABSTRACT

The structure of the metastable transition phase, omega, which is involved in the age hardening of titanium alloys, was determined. It is a complex body-centered-cubic cell of the gamma-brass type containing 54 atoms. The phase contains 3.7 atomic per cent of the alloying element. The [100] directions of the omega phase and the parent beta phase are parallel. A tentative mechanism for the age hardening of titanium alloys is proposed.

The formation of the omega phase during aging was found to be inhibited by increasing alloy content. Leaner alloys which transformed to alpha prime upon quenching exhibited some degree of age hardening.

Mechanical-property tests on quenched and aged Ti-4Fe and Ti-8Cr alloys confirmed the severe embrittling effect of the omega phase. Further aging to convert omega to alpha resulted in high strengths with recovery of some ductility.

Attempts to detect the omega phase by metallography or autoradiography were not successful.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS
(Continued)

SUMMARY

The research described in this report consisted of further study of the age-hardening reaction in beta-stabilized titanium alloys. Previous work on this investigation is described in WADC TR 54-355.

The structure of the metastable transition phase, omega, which is present in age-hardened alloys, was established. Weissenberg X-ray diffraction techniques on a single crystal of a Ti-8Cr alloy were used. The structure of omega was found to be in Space Group $I\bar{4}3m$ with 54 atoms per unit cell. It is a complex body-centered-cubic cell encompassing 27 of the original beta cells. Its parameter of 9.80 A was almost exactly three times that of the parent beta, which was 3.26 A. Atoms of the alloying element were found to be located at the center and corners of the cell, making a total of 2 atoms per cell. Thus, omega contains 3.7 atomic per cent of alloy. The omega phase is oriented with the parent beta by having the [100] directions parallel. Omega formation results in enrichment and contraction of the adjacent beta. Streaking of beta reflections indicated that this contraction may result in coherency strains in the beta which could contribute to hardening.

The study of the effect of alloy content on age hardening was broadened to include alloys both above and below the range of beta-stabilized alloys in which omega was known to form. Higher alloy contents in the Ti-Cr system inhibited omega formation and hardening effects diminished appreciably. Where the alloy content was too low to stabilize the beta phase upon quenching, the absolute values of hardness were somewhat lower than in an all-beta system. However, age-hardening effects were observed.

Electrical-resistivity measurements made on specimens during aging at 500 F confirmed earlier observations that resistivity decreases during the period of omega formation. This effect was very pronounced in the systems forming omega most rapidly. The decrease would be expected in a structure of the type proposed for omega phase.

A study was made of the effect of aging at 800 F on the mechanical properties of a Ti-4Fe and a Ti-8Cr alloy. Each alloy was aged after quenching from a temperature in the beta-phase region and the alpha-beta-phase region. Generally, the correlation of the mechanical properties with phase changes was good. Formation of the omega phase in the early stages of aging produced very brittle structures. As aging progressed and omega was replaced by alpha, some ductility was restored and very high strengths were attained. Compound precipitation during the later stages of aging resulted in decreased strength and in some increase in ductility, particularly in the case of the iron alloy. There was some evidence, however, that the early stages of compound formation in the chromium alloy severely embrittled this material.

Metallographic investigation of several omega-containing alloys did not show conclusively the presence of omega phase. A dark-etching phase was observed in a Ti-4Fe alloy, and the quantity of the phase appeared to increase with aging time. However, electron microscopy indicated that the structure was an etch-pit type and could have been caused by effects other than the presence of omega.

An attempt was made to show the distribution of alloying element in a Ti-4Fe alloy during the formation of omega by using high-resolution autoradiography. No evidence of segregation of the alloying element during omega formation could be detected, although X-ray studies showed that segregation must take place. However, when the aging was carried out to produce alpha and enriched beta, autoradiographic evidence of segregation of the iron atoms in the beta could be seen.

On the basis of the research described in this report and in WADC TR 54-355, a tentative mechanism for the age hardening of beta-stabilized titanium alloys is proposed. The proposed mechanism consists of two major stages:

(1) Initial hardening through the formation of an intrinsically hard transition phase, omega, in the parent beta phase in a sufficiently fine dispersion to prevent flow in the parent beta phase.

(2) During a later stage of aging, coherency hardening between larger omega particles and adjacent enriched beta. This effectively extends the time range over which hardening persists.

INTRODUCTION

The investigation described in this report on age hardening in titanium alloys is a continuation of the work undertaken under Contract No. AF 33(038)-3736(1, 2, 3, 4) and the earlier phases of the present Contract No. AF 33(616)-455(5). The report covers the period 15 April 1954 to 28 February 1955. The earlier work established the presence of a metastable transition phase, called omega, which appears in some beta-stabilized titanium alloys during the transition from beta to alpha phase. Age hardening has been associated with the formation of omega phase. As omega forms, the parent beta phase becomes richer in alloy content.

The current research program consisted of several major sections which were carried out concurrently. The crystallographic research was devoted to determining the structure of omega phase, its orientation relationship to the parent beta phase, and thus the mechanism of omega formation. The detection of coherency was also a part of the crystallographic work. Some specialized research techniques, as well as the more common tools of metallurgical research, have been used to define further the age-hardening phenomena. Metallography, both light and electron, autoradiography, electrical-resistivity measurements, and conventional mechanical testing were used in this phase of the program to study age hardening in high-purity titanium alloys.

FUNDAMENTAL CRYSTALLOGRAPHIC INVESTIGATION

The X-ray diffraction method was found very early to be a useful tool to study the mechanism of hardening and embrittlement in beta-stabilized alloys. First, a new transition phase named omega was found to be associated with a moderate hardening during isothermal transformation of a Ti-8Mn alloy. Later, the omega phase was found in alloys of Ti-4Fe, Ti-5Fe, Ti-5Cr, Ti-8Cr, Ti-10Cr, Ti-12Cr, Ti-10Mo, Ti-15V, and Ti-7.5Ni. The presence of omega was invariably found to be associated with hardening. In this work, a dip in the dilatometer curves of quenched and slowly heated samples was correlated with the presence of omega.

Attempts were made to determine the crystal structure of omega using polycrystalline samples, but these were not successful. The structure seemed complex, and it appeared necessary to use the more powerful single-crystal techniques for its solution.

The X-ray photograms obtained from polycrystalline but coarse-grained samples showed strong orientation relationships between beta and omega and between beta and alpha. This condition suggested that a single beta grain would retain its original orientation throughout a transformation process, so that the crystallography of omega and alpha precipitation could be studied. Accordingly, attempts were made to prepare single-crystal specimens for use in determining the relation of omega to beta, and the structure of omega.

Preparation of Single-Crystal Samples

The large beta grains used in this study were produced in high-purity sheet material by heating samples in vacuum for 4 hours or more at temperatures of 2400 F (1315 C) and above. These coarse-grained samples were then furnace cooled and sealed in capsules so that they could be given a betaizing solution treatment and quench.

A single beta grain suitable for examination in the Weissenberg camera was prepared from a coarse-grained Ti-4Fe alloy by etching after the sample had been solution treated at 1700 F and aged 2 hours at 800 F. This treatment developed considerable omega in this alloy. The grain from which this sample was made was chosen because it gave a satisfactory monocrystalline Laue pattern. It was about 3/16 inch in diameter and extended through a 1/8-inch sheet. This grain was sawed out and etched down to about 0.4-mm diameter in a solution of 50 parts nitric acid, 15 parts acetic acid, and about 4 parts hydrofluoric acid. The desired spheroidal shape was approached by applying Pyseal cement to one area or other of the sample at intermittent times to control the etching attack. The sample showed a pattern of TiH with a preferred orientation to the beta matrix, but this hydride did not seriously interfere with the subsequent crystallographic analysis. Initially, a diffraction pattern was obtained from this crystal, using simple rotation. Because of the diffuseness of the beta reflection and apparent complexity of the omega orientation in these photograms, this crystal was suspected to be too strained to justify further work. Therefore, it was decided that an unaged beta grain free of omega phase was needed. With such a grain, the development of the omega precipitation could be followed from the beginning of aging. However, when unaged grains of a Ti-8Cr alloy were extracted and examined with the Laue camera, the structure was distorted either as the result of hydrogen absorption or quenching strains.

In order to maintain the purity of the sample and to avoid mechanical strain from water quenching, a simultaneous degassing and beta-quenching treatment in a vacuum-bell jar was devised. In this method, the extracted grain rested on a strip of 5-mil molybdenum or tungsten sheet clamped between water-cooled electrical leads 1/4 inch apart. The strip was used as a resistance heater. The desired degassing-solution treating temperature was produced by adjustment of the heater current, and was read by means of an optical pyrometer. When the current was interrupted, the sample lost heat rapidly by conduction to the strip and water-cooled leads and radiation to the surroundings. Although this quench was not so rapid as a water quench, it was satisfactory in producing a sample free of hydride and mechanical strain. The specimen support system for the heat-treating equipment appears in Figure 1 with the bell jar removed. A piece of 30-mil wire, many times larger than the crystals, occupies the sample position.

The Ti-4Fe and Ti-8Cr samples of desired size were quenched in this manner. A Ti-4Fe sample was found to contain both alpha and omega, and was discarded. However, after several tries, one Ti-8Cr sample was found to be monocrystalline, free from alpha, and to show only faint diffuse reflections of omega.

This sample had been solution treated for 10 minutes at 975-1050 C (1787-1922 F) under a high vacuum. It was examined in the Weissenberg camera after each of the following successive treatments:

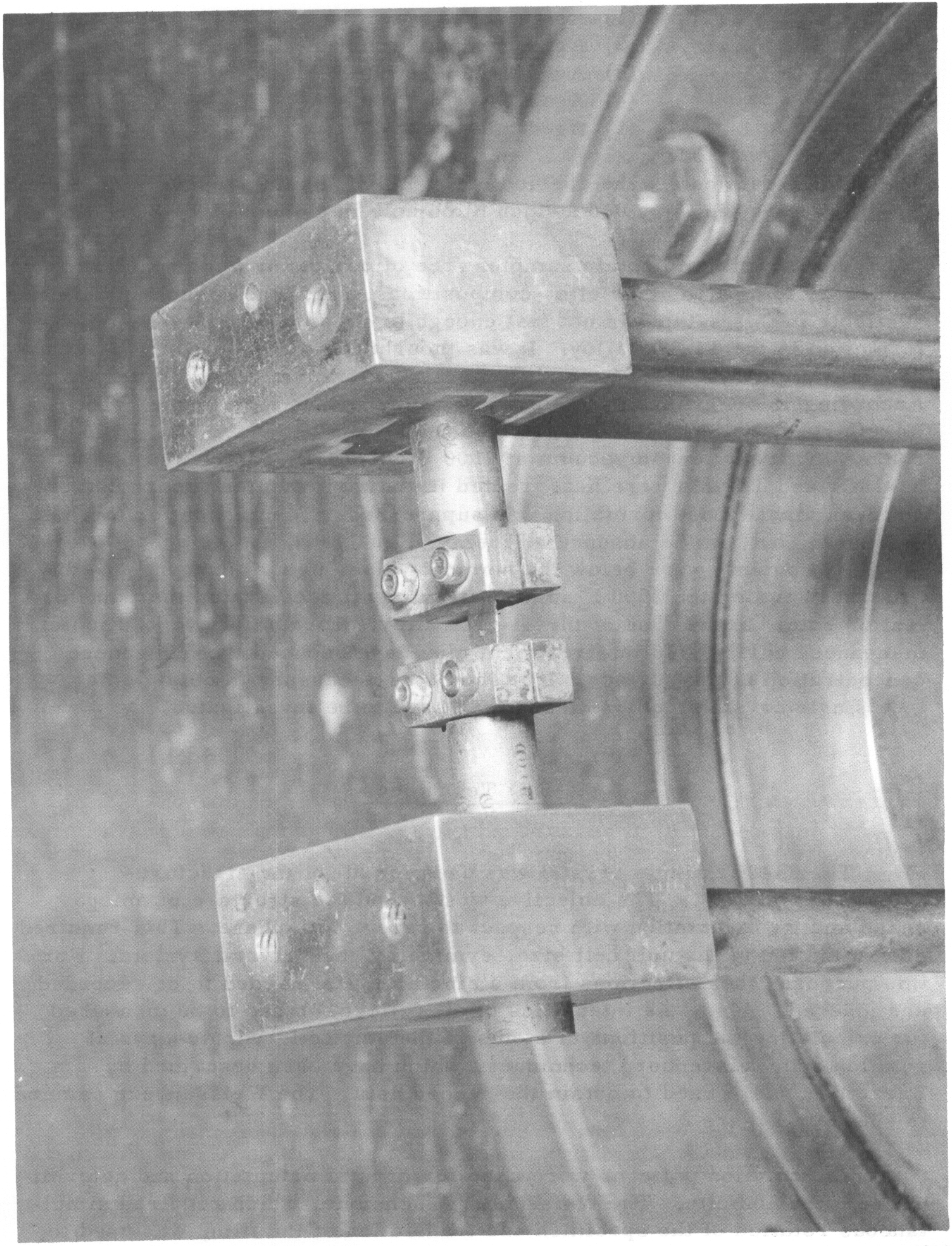

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FIGURE 1. SPECIMEN SUPPORT AND RESISTANCE-HEATING SYSTEM FOR VACUUM HEAT TREATMENT OF SMALL TITANIUM ALLOY CRYSTALS

(1) As quenched
(2) Aged 1/2 hour at 700 F
(3) Aged 1 hour at 700 F
(4) Aged 1 hour at 800 F
(5) Aged 5 hours at 800 F.

The aging treatments were carried out at 2 x 10^{-6} mm pressure while the sample was resting in a 0.050-inch blind hole in a sheet of Ti-8Cr alloy.

In attempting to obtain samples free of omega, it was considered necessary to look to other alloy compositions, since the quenching rate available in this setup was not fast enough to suppress completely omega formation in the Ti-8Cr alloy. It was thought that the Ti-10Cr, Ti-12Cr, and Ti-9Mn alloys would have sufficiently low critical cooling rates. Accordingly, 50-gram buttons of these compositions were made. They were forged, rolled to about 1/16 inch thick, and subjected to a grain-coarsening treatment in vacuum at 2600 F (1427 C). Samples of both Ti-10Cr and Ti-9Mn were heat treated in the strip-heater apparatus, but not even alpha-phase formation was suppressed. The reason for this is not known, but, in the absence of chemical analyses, it was suspected that the alloy contents were below the nominal values or that oxygen (possibly brought in during the 2500 F solution treatment) accelerated the transformation rate. In the case of the Ti-9Mn alloy, differential evaporation of manganese during solution treatment may have reduced the manganese concentration at the surface. If it should be necessary to obtain omega-free single crystals, other means may have to be investigated.

X-Ray Techniques

The Ti-8Cr single crystal was used for all of the structure-determination work. The objective was to find the structure of omega phase and its orientation with respect to parent beta phase. This required determination of the unit cell size, symmetry, and crystal system. For this purpose, the reflections from a single crystal needed to be recorded and indexed. Also, the intensities of all reflections had to be measured for calculating the positions of atoms in the unit cell. Single-crystal rotation and Weissenberg techniques, which have been described by Barrett(6), were used to obtain the needed data. The Weissenberg camera is shown in Figure 2.

The rotation patterns were used for crystal orientation and determination of periodicity. The Weissenberg technique, which required simultaneous rotation of the specimen and translation of the film, was used to determine the orientation of each reflection and its intensity. These data were used, in turn, for determining the orientation and structure of the omega phase.

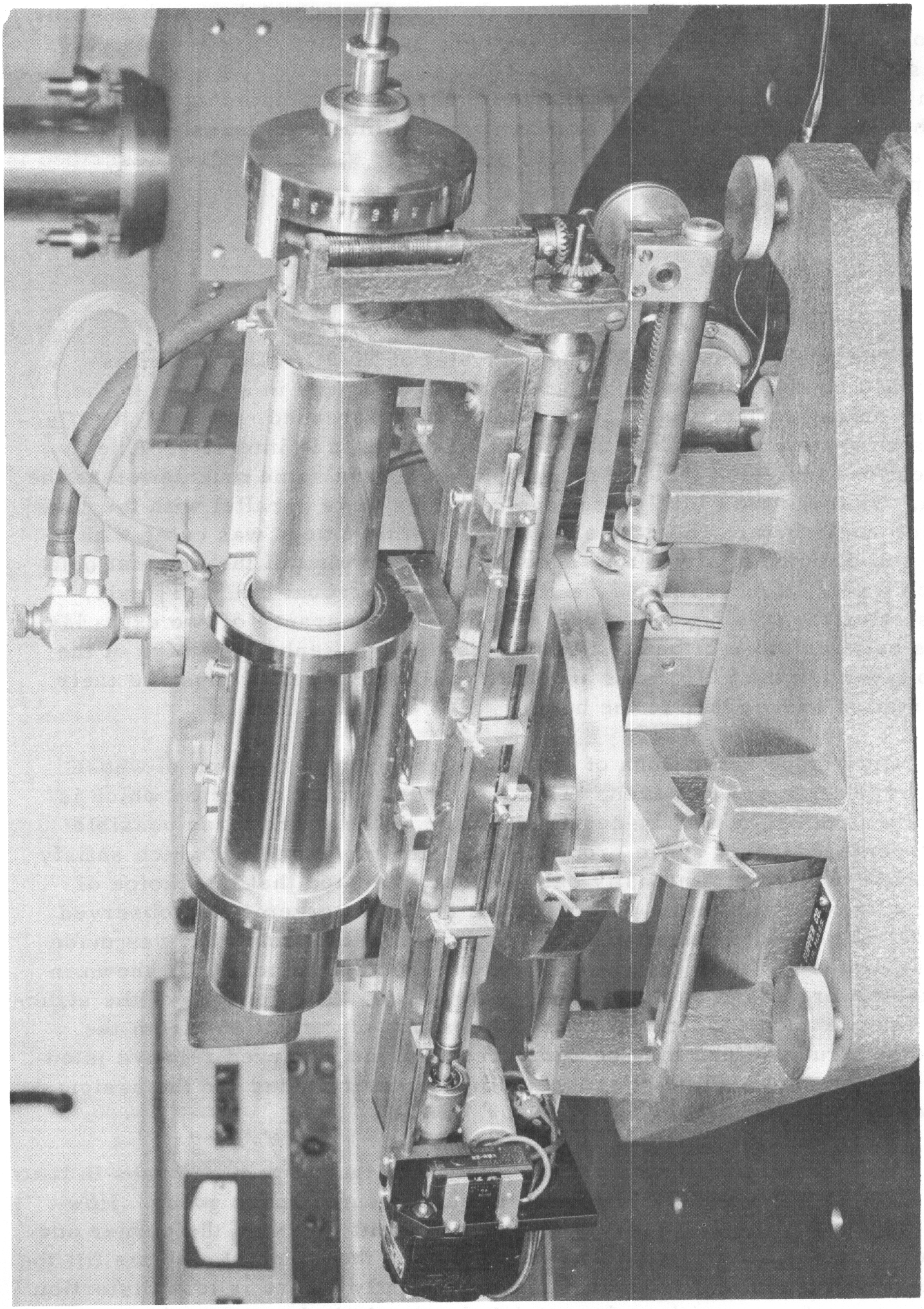

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FIGURE 2. THE WEISSENBERG X-RAY DIFFRACTION CAMERA

The rotation and Weissenberg photographs were taken with 24-hour exposures to unfiltered copper radiation. Intensities of reflection in the Weissenberg patterns were estimated by eye. Rotation patterns were taken with [110] and [111] axes of rotation. Weissenberg patterns were taken of each layer line for the [110] rotation axis. Similar patterns were taken in the as-quenched condition and after each of the stages of aging described in the preceding section.

Structure of the Omega Phase

The photograms of the single crystal of Ti-8Cr alloy in the as-quenched condition showed faint reflections of omega in addition to the main, strong reflections of beta. As aging progressed, the omega reflections increased and the beta reflections decreased in intensity. The reflections indicated that the omega phase had the same orientation as the beta. That is, the [100] directions in omega were parallel with the [100] directions in beta. The data also indicated that omega was cubic with a unit cell dimension of 9.80 A, about three times that of the original beta which was 3.26 A. Figure 3, a rotation pattern about the [111] axis, illustrates the tripling of the unit cell by the appearance of two extra layer lines between those of beta. Figure 4 is the Weissenberg pattern of the zero layer for the [110] axis and shows the omega reflections and their orientation with regard to the beta.

Only those reflections of omega were observed the sum of whose indices (h + k + l) were even. This is a space-group criterion which is definite evidence of a body-centered lattice. There are three possible body-centered-cubic space groups, $I\bar{4}3m$, Im3m, and I432, which satisfy the above criterion. Intensity calculations indicated that the choice of $I\bar{4}3m$ with 54 atoms in the unit cell gave the best agreement of observed and calculated intensities. The data upon which this selection was made are tabulated in Table 1. The calculated structure factors [F] shown in the table were based on the refined parameters. The squares of the structure factors are proportional to the intensities of reflections from the selected structure and may be compared with the observed relative intensities. The choice of point groups and parameter values for the assigned structure is given in Table 2.

This structure appeared to be similar to that of gamma brass in that it is a triple body-centered-cubic cell with the same space group. However, gamma brass has only 52 atoms in the unit cell with the corner and center atoms absent. In the omega structure, the chromium atoms fill the corners and the center of the cell. Consequently, there is less distortion of the atoms from positions for a tripled, simple body-centered cell than in the case of gamma brass.

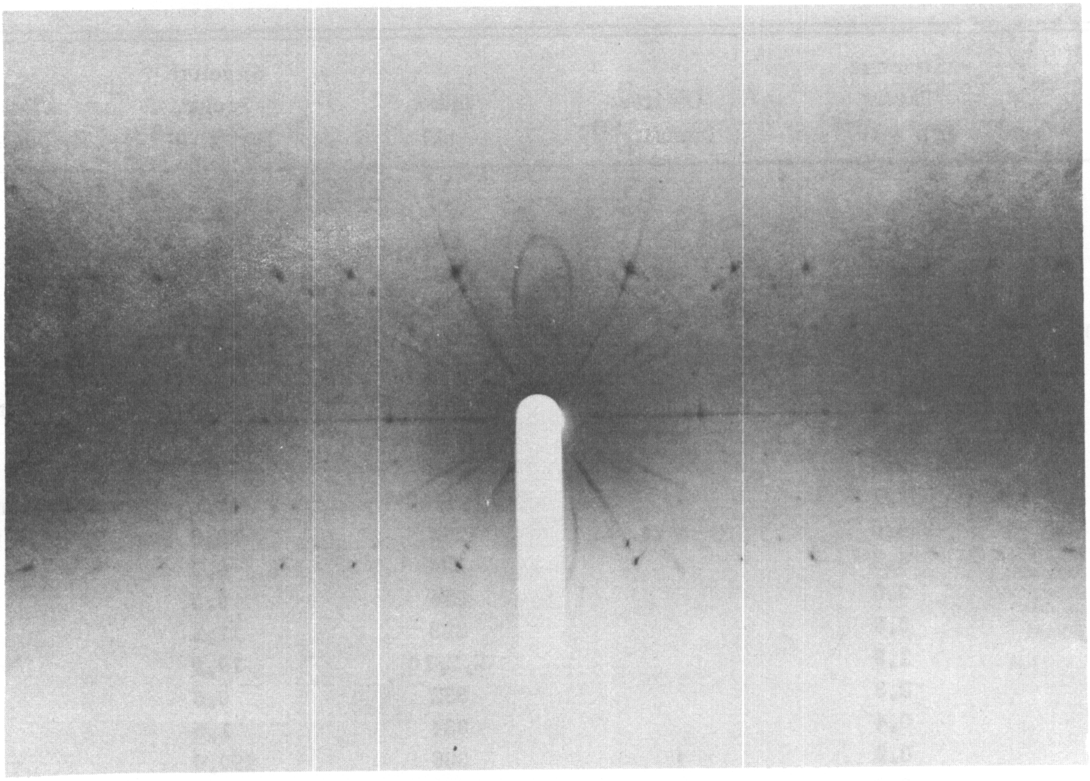

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FIGURE 3. X-RAY ROTATION PHOTOGRAPH OF Ti-8Cr BETA CRYSTAL ROTATED ABOUT [111] AXIS

Crystal Quenched From 1800 F and Aged 1 Hour at 700 F

This photograph shows the zero- and first-layer lines of the beta crystal with two additional omega-layer lines sandwiched between. This shows directly that the periodicity of omega is three times that of beta.

TABLE 1. COMPARISON OF THE CALCULATED STRUCTURE FACTORS AND THE OBSERVED

Index, hkl	Structure Factor, $[F]^2 \times 10^{-3}$	Observed Intensity[(a)]	Index, hkl	Structure Factor, $[F]^2 \times 10^{-3}$	Observed Intensity[(a)]
200	0.8		570	0.7	
400	2.0		590	0.3	
600	400.0	vvs	680	1.8	
800	5.5		6, 10, 0	1.0	
10, 0, 0	2.2		790	0.6	
110	0.3		112	0.0	
220	0.0		114	15.3	mf
330	620.0	vvs	116	0.4	
440	2.6		118	4.7	vvf
550	1.1		1, 1, 10	18.2	mf
660	224.0	vvs	222	12.9	f
770	4.5		224	0.2	
880	3.6		226	0.5	
130	0.3		228	11.1	
150	1.9		2, 2, 10	19.9	vf
170	2.3		332	0.6	
190	0.4		334	1.5	
240	0.2		336	290.0	vvs
260	0.0		338	3.4	
280	0.3		3, 3, 10	1.6	
2, 10, 0	1.9		442	8.8	f
350	4.6		444	33.3	m
370	2.0		446	1.6	
390	173.0	vs	448	1.3	
460	2.9		4, 4, 10	32.3	m
480	0.0		552	14.8	
4, 10, 0	4.4		554	3.0	
			556	0.8	
			558	12.2	vvf

(a) s = strong; m = medium; f = faint; v = very.

RELATIVE INTENSITIES OF REFLECTIONS FOR THE PROPOSED OMEGA STRUCTURE

Index, hkl	Structure Factor, $[F]^2 \times 10^{-3}$	Observed Intensity$^{(a)}$	Index, hkl	Structure Factor, $[F]^2 \times 10^{-3}$	Observed Intensity$^{(a)}$
662	2.9		235	0.3	
664	2.8		237	0.8	
666	142.0	vvs	239	1.7	
668	1.7		246	0.3	
772	15.6	mf	248	3.2	
774	39.6	m	2, 4, 10	15.6	mf
776	4.4		257	1.6	
882	14.4	vf	259	0.4	
884	8.1		2, 5, 11	7.1	vf
123	0.2		268	0.9	
125	4.7	vvf	279	1.6	
127	7.5	vf	345	2.3	
129	0.3		347	3.4	
134	1.1		349	1.0	
136	0.9		356	2.1	
138	0.2		358	1.3	
1, 3, 10	3.1	vvf	3, 5, 10	1.4	
145	0.8		367	0.5	
147	26.3	m	369	116.5	vvs
149	0.5		378	0.1	
156	0.6		457	5.1	vf
158	9.2		459	0.3	
1, 5, 10	7.7	vvf	468	0.3	
167	1.6		479	2.5	
169	4.3				
178	1.5				
1, 7, 10	20.0	m			

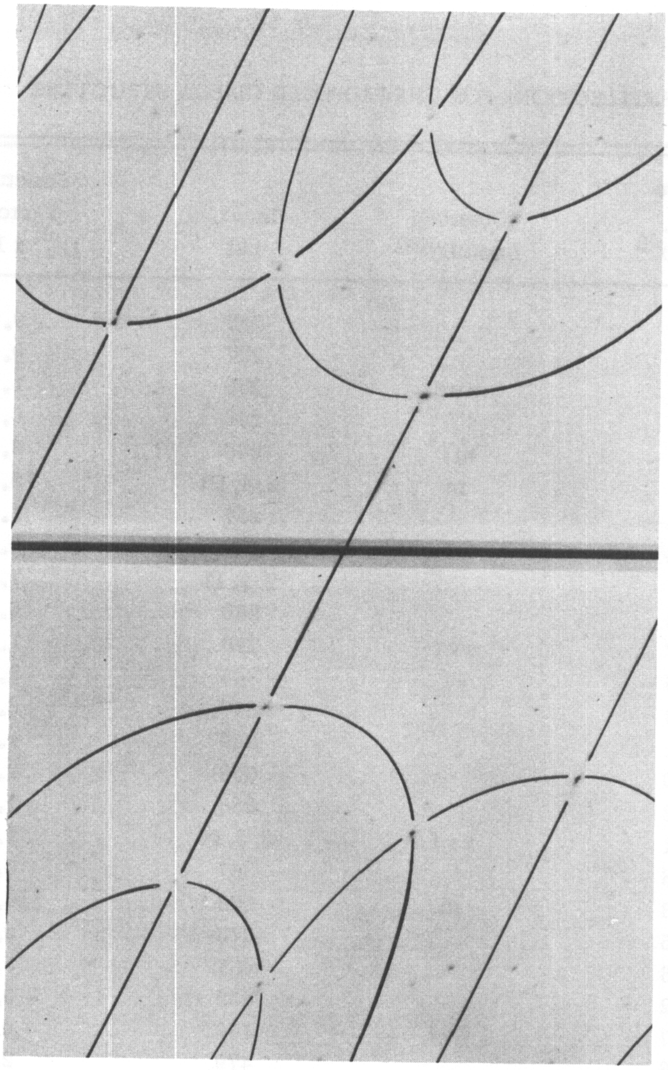

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FIGURE 4. WEISSENBERG X-RAY PHOTOGRAPH OF THE Ti-8Cr ALLOY CRYSTAL QUENCHED FROM 1800 F AND AGED 1/2 HOUR AT 700 F

Zero layer of beta and omega is shown. The beta reflections are at the intersections of the inscribed beta-row lines. All other reflections are omega.

TABLE 2. EQUIVALENT POSITIONS AND PARAMETERS OF ATOMS IN THE STRUCTURE OF OMEGA PHASE

Atom	Equivalent Position	Number of Atoms	Coordinates (000, 1/2 1/2 1/2)+	Parameters
Cr	(a)	2	000	0
Ti	(c)	8	xxx	x = .158
Ti	(c)	8	xxx	x = -.170
Ti	(e)	12	x00	x = .340
Ti	(g)	24	xxz	x = .320 z = .020

Figure 5 shows schematically the atomic positions in the triple body-centered cell of omega. The eight nearest titanium atoms around each chromium atom are displaced, with four moving closer to the chromium atom and four moving outward. The actual displacements from the original positions in the beta phase are small, being about 0.07 or 0.15 A. Since this is small, only the directions of displacements are shown by arrows and these are shown only for the eight titanium atoms about the central chromium atom. The next nearest titanium atoms are displaced by varying amounts, from 0.07 to 0.26 A. In order to simplify Figure 5 these displacements are not shown.

A single grain of a Ti-4Fe alloy quenched from 1700 F and aged for 1 hour at 800 F was also examined. Although the grain was not a single crystal, all reflections in the Weissenberg pattern could be indexed as either beta or omega according to their interplanar spacings. This indicated that the omega phase had the same structure in this alloy as in the Ti-8Cr alloy.

Density measurements on quenched and aged alloys supported the omega structure derived from the X-ray data. The results of these measurements are given in Table 3. The density increase with aging was the result of enrichment of the beta phase. The calculated density for beta Ti-8Cr was 4.64, which is about 1 per cent less than the measured density. The calculated density for the omega structure was 4.62. The mean density of a sample with omega and enriched beta may be calculated by the relation

$$\rho = 4.64 + 0.066x \quad , \qquad (1)$$

where

x = fraction of omega.

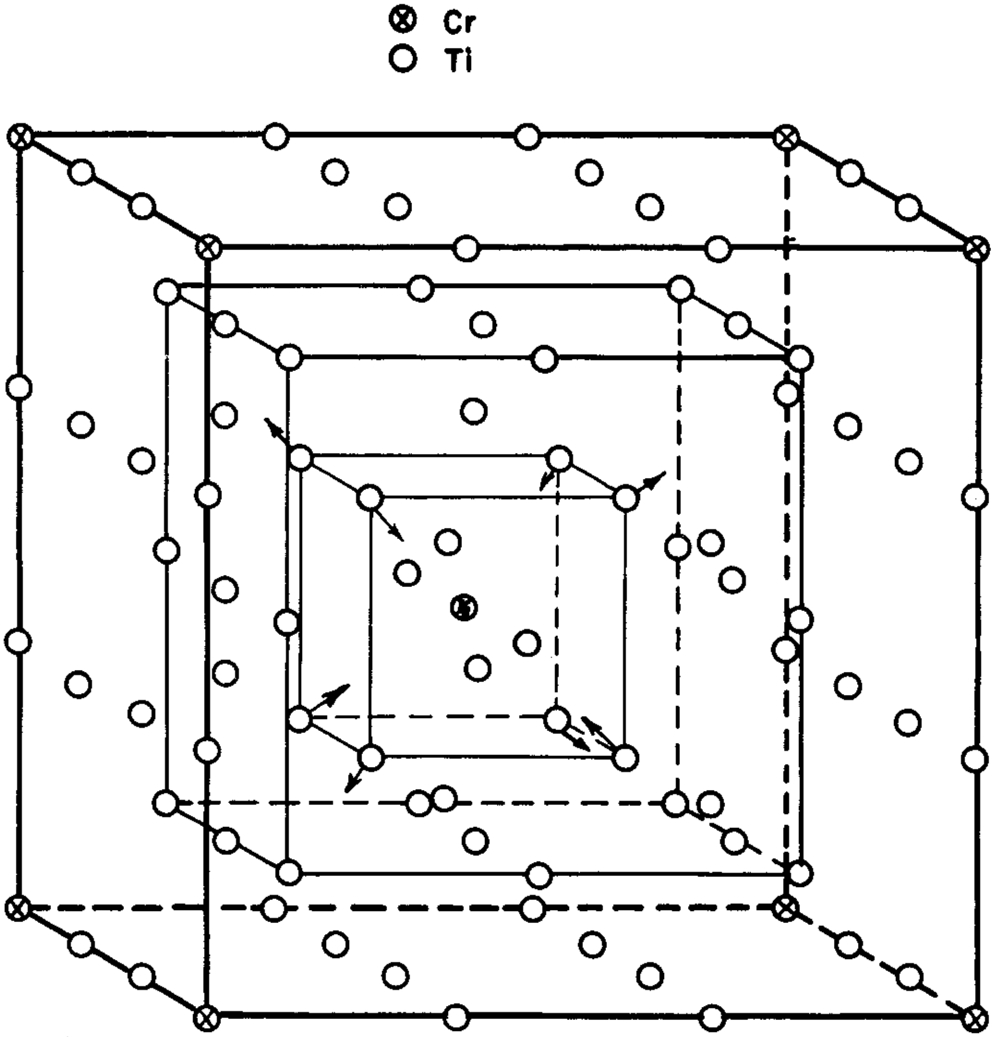

FIGURE 5. SCHEMATIC DIAGRAM OF THE ATOMIC POSITIONS IN TRIPLE-BODY-CENTERED UNIT CELL OF OMEGA PHASE

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TABLE 3. MEASURED DENSITY OF TITANIUM ALLOYS

Composition, weight per cent	Heat Treatment	Density(a), grams per cm^3
Ti-4Fe	Solution treated 1/2 hr at 1700 F	4.660 at 70.0 F
Ti-4Fe	Solution treated 1/2 hr at 1700 F, aged 8 hours at 800 F	4.665 at 68.4 F
Ti-8Cr	Solution treated 1/2 hr at 1700 F	4.684 at 70.2 F
Ti-8Cr	Solution treated 1/2 hr at 1700 F, aged 8 hours at 800 F	4.763 at 71.2 F

(a) Accuracy of density is ±0.1 per cent.

This equation indicates that the density increases with formation of omega, as observed. The derivation of this equation and Equation (2) is given in the Appendix. Calculated densities for a 52-atom omega structure the same as gamma brass gave the relation

$$\rho = 4.64 - 0.13x. \qquad (2)$$

This would indicate a marked density decrease for formation of an omega structure with less than 54 atoms per unit cell. Thus, the density data on Ti-8Cr alloy offer confirming evidence for the omega structure derived from the X-ray data. In the case of the Ti-4Fe alloy much less density change would be expected, because the initial composition is very close to that of the proposed omega structure. The observed data showed practically no density change with aging in the Ti-4Fe alloy.

Further Observations on the Aging Reaction

As previously mentioned, the intensity of the omega reflections increased as aging of the Ti-8Cr crystal progressed. After heating for 1 hour at 700 F, a marked decrease in intensity of beta reflections occurred with the corresponding increase in intensity of omega reflections. The temperature was raised to 800 F to hasten the aging. After 1 hour at 800 F, diffuse streaking of beta reflections appeared, while the omega reflections remained relatively sharp. The streaking of the beta reflections was examined in detail by taking longer exposures of both Weissenberg and oscillation patterns. The streaking was prominent in the [100] direction for the (200) reflection. The (110), (220), and (112) reflections also were diffuse in [100], [010], and [001] directions. There was apparently no streaking from (200) reflections in the [010] or [001] directions. The diffuse streaking is interpreted as the result of directional strain in regions of the beta crystal immediately adjacent to the omega to produce local tetragonality. This strain is apparently the result of contraction of the beta phase as it becomes richer in chromium, combined with the tendency of the beta to remain coherent with the omega. It could contribute toward increasing hardness during aging. From the development of strain in the beta lattice during aging, it is clear that in the as-quenched specimen, where no diffuse streaking is observed, the omega and beta structures were fully coherent without strain.

With further aging for 5 hours at 800 F, the omega reflections remained strong and the beta reflections were separated from omega spots, with diffuse streaking observed in the [100] direction. Also, there appeared faint (11.0) and (00.2) reflections of alpha titanium. The (11.0) alpha reflection was oriented parallel to the (444) omega reflection, thus the (11.0) alpha planes are parallel to (444) omega and (111) beta planes. Also, the (00.2) alpha reflection was parallel to the (110) beta and/or (330) omega reflections. The (00.2) alpha reflection showed diffuse streaking the same as the (110) beta reflection. Since the omega and beta structures are oriented the same, the orientation of alpha does not indicate whether it forms from the omega or beta phases. The observed orientation is the same as that reported for the beta-to-alpha transformation.(8) However, it seems reasonable that alpha would nucleate from the omega because of the lower alloy content of the latter phase.

Conclusions From Crystallographic Investigations

Age hardening of beta-quenched titanium-chromium and titanium-iron alloys proceeds by several steps. The first is the precipitation of omega phase. This phase is a body-centered structure, triple the size of the beta-titanium lattice, with an alloy content of 3.71 atomic per cent. It is oriented with the beta phase, the [100] directions being parallel. As aging proceeds, the amount of omega phase increases and there is enrichment of the alloy content of the beta phase. This growth of omega and beta enrichment produces directional strains in the beta phase, which could cause continued hardening. With further aging, the alpha phase is formed. The alpha phase is oriented with the beta and omega phases the same as in the martensitic formation of alpha from beta. That is, the (00.2) alpha planes are parallel to (110) beta and omega and (11.0) alpha is parallel to (111) beta or omega.

The possibility of the omega phase being an ordered beta structure has been considered throughout the investigation, but it has now been eliminated. Although it is true that the alloy atoms occupy specific positions in the omega cell, the necessary relocation of surplus alloy content within the beta phase cannot be considered a part of simple ordering.

The structure of the omega phase suggests that it may be an electron-atom ratio compound just as the similar gamma-brass structures are. The low alloy content is rather puzzling in this regard. However, very little is known about the valencies in a compound consisting of two transition metals.

Proposed Mechanism for the Age Hardening of Titanium Alloys

Based on the foregoing structural studies and the mechanical properties of age-hardened alloys presented in a later section of this report, a mechanism for the age hardening of beta-stabilized alloys may be postulated. It has been established that the high hardnesses and extreme brittleness of age-hardened titanium alloys are associated with the presence of the omega phase. This implies (1) that the omega phase itself is intrinsically very hard, or (2) that its formation, as a phase coherent with the beta matrix, produces strains in the matrix which would result in hardening. The latter possibility does not seem likely during the early stages of aging, in view of the lack of X-ray evidence of strain and the close similarity in parameter values between the omega phase and the parent beta phase from which it formed. On the other hand, the complex structure of omega suggests that it would be intrinsically hard since it would contain no short-slip vectors such as exist in simple body-centered-cubic structures. The absence of these vectors would make the movement of dislocations, hence slip, difficult. Also, during the early stages of aging, a fine dispersion of the omega phase would severely limit the movement of dislocations in the parent beta phase, thus further increasing hardness and brittleness.

As aging progresses, the amount of omega increases, which tends to maintain hardness. However, one would expect that some softening could occur prior to alpha precipitation as the particle size of the omega phase increases by a natural process of diffusion and coalescence. This in fact, did occur in a Ti-10Mo alloy aged at 800 F as pointed out in WADC TR 54-355. However, at this stage in the aging process, a secondary hardening reaction occurs. The beta phase immediately adjacent to the omega particles becomes sufficiently enriched in alloying element that its parameter changes significantly. This results in coherency hardening of the beta phase from the strains engendered in the enriched beta lattice as it attempts to maintain registry with the omega. The effect of this coherency type of hardening is to extend further the time interval over which high hardness and embrittlement are observed. The aforementioned drop in hardness of the Ti-10Mo alloy during this stage of aging was probably due to the larger atomic diameter of the molybdenum as compared with chromium or iron. Enrichment of the beta phase in molybdenum would result in less contraction of the beta lattice and, consequently, less hardening effect due to coherency during this stage of aging. Further aging, of course, results in the precipitation of the alpha phase with consequent softening and restoration of ductility.

In addition to the aging mechanisms previously discussed, there may be a third mechanism operative during later stages of aging, but this is highly speculative. A secondary hardness peak has been observed during aging in many alloys at a time considerably longer than that necessary to form alpha. This peak may be due to a coherency-hardening phenomenon between the alpha and enriched beta or omega similar to that which occurs between omega and enriched beta. Of course, in eutectoid systems, this secondary peak also may be associated with compound formation.

To summarize briefly, there seem to be two major hardening mechanisms operative in the age hardening of titanium alloys:

(1) The formation of an intrinsically hard transition phase, omega, in the parent beta phase in a sufficiently fine dispersion to prevent flow in the parent phase

(2) During later stages of aging, coherency hardening between larger omega particles and adjacent enriched beta, which extends the time range over which hardening persists.

EFFECT OF AGING ON MECHANICAL PROPERTIES

An important phase of the investigation of any aging phenomenon is an evaluation of its effects upon mechanical properties. The relative usefulness or potential dangers in commercial use of age-hardening alloys can be evaluated only by extensive testing programs. In this portion of the project, only a cursory survey was undertaken on two binary alloys, Ti-4Fe and Ti-8Cr. A third alloy, Ti-10Mo, was originally included in the mechanical-test program, but was discarded because of tungsten contamination during melting and inhomogeneity revealed by radiography after rolling.

The melts made for the mechanical testing program were 1 pound in size and contained iodide titanium and high-purity alloying elements. The melts were rolled to 3/8-inch-square rods and then swaged to 1/4-inch rounds. The rods were then cut to length for micro impact specimens and 1/8-inch-diameter tensile specimens. Solution treatment in the beta or alpha-plus-beta region and iced-brine quenching was followed by aging at 800 F. The aging times were selected to cover the interesting regions indicated by the earlier hardness and resistivity data. The results of the tests are shown in Tables 4, 5, 6, and 7, and the tensile and hardness data are plotted in Figures 6, 7, 8, and 9.

The tensile properties and hardnesses of the Ti-4Fe alloy, shown in Figures 6 and 7, correlate very well with the phase changes which occurred during aging at 800 F. Consider the specimens quenched from the beta-phase region (Figure 6). In the as-quenched condition and after short

TABLE 4. MECHANICAL PROPERTIES OF A Ti-4Fe ALLOY QUENCHED FROM 1700 F AND AGED AT 800 F

Aging Time, hr	Vickers Hardness Number (10-Kg Load)	Reduction of Area, per cent	Yield Strength, psi	Tensile Strength, psi	Impact Energy, inch-pounds	Phases Present(a)
As quenched	548		Sample broke in shop		1.5	$\beta + \omega$
1/2	566		Ditto		.75	Ditto
4	490	0	--	124, 000	1.0	"
7	429	0.8	--	145, 000	2.0	"
10	383	--	--	154, 000	2.0	"
40	351	4.0	152, 000	158, 000	4.0	$\alpha + \beta$
125	330	2.4	135, 500	143, 500	3.75	Ditto
250	309	4.9	120, 500	129, 500	4.75	"
506	218	19.2	56, 000	87, 500	7.25 1	α + compound

(a) The phases present were estimated from X-ray diffraction data on a different heat of the same alloy which had the same thermal history.

TABLE 5. MECHANICAL PROPERTIES OF A Ti-4Fe ALLOY QUENCHED FROM 1425 F AND AGED AT 800 F

Aging Time, hr	Vickers Hardness Number (10-Kg Load)	Reduction of Area, per cent	Yield Strength, psi	Tensile Strength, psi	Impact Energy, inch-pounds
As quenched	300	12	95, 500	149, 000	8
1/2	370	4.6	122, 000	170, 000	1.75
6	336	0.5	94, 500	151, 000	2.25
8	333	4.9	91, 500	162, 500	3.0
15	319	7.2	98, 500	151, 500	4.0
45	287	18.7	88, 000	135, 000	4.0
125	279	15.3	84, 000	125, 000	4.75
260	254	9.5	73, 000	116, 000	5.25
600	251	34.9	40, 500	91, 000	10.0

TABLE 6. MECHANICAL PROPERTIES OF A Ti-8Cr ALLOY QUENCHED FROM 1700 F AND AGED AT 800 F

Aging Time, hr	Vickers Hardness Number (10-Kg Load)	Reduction of Area, per cent	Yield Strength, psi	Tensile Strength, psi	Impact Energy, inch-pounds	Phases Present[(a)]
As quenched	117	--	--	167,000	11.25	$\beta + \omega$
1/2	548	0.8	--	112,500	1.0	Ditto
1-1/2	508	Sample broke during machining			1.0	"
4	514	0.8	--	104,000	1.25	"
8	442	0.8	--	229,000	7.0	$\alpha + \beta + \omega$
48	433	--	--	165,500	Broke during machining	α
100	425	Sample broke during machining			Ditto	α
506	254	2.4	92,000	105,000	2.0	α + compound
800	266	2.3	96,000	105,500	2.0	Ditto

(a) The phases present were estimated from X-ray diffraction data on a different heat of the same alloy which had the same thermal history.

TABLE 7. MECHANICAL PROPERTIES OF A Ti-8Cr ALLOY QUENCHED FROM 1400 F AND AGED AT 800 F

Aging Time, hr	Vickers Hardness Number (10-Kg Load)	Reduction of Area, per cent	Yield Strength, psi	Tensile Strength, psi	Impact Energy, inch-pounds
As quenched	433	8.1	179,000	182,000	11.0
1/2	554	0.8	--	138,500	2.0
1-1/2	530	0.8	109,500	134,000	1.75
4	525	1.6	163,000	179,500	1.5
8	483	0	--	210,500	2.0
48	421		Sample broke in shop		2.0
100	421	1.6	--	206,500	2.0
506	262	13.7	--	120,500	4.0
800	270	6.5	86,500	120,000	2.25

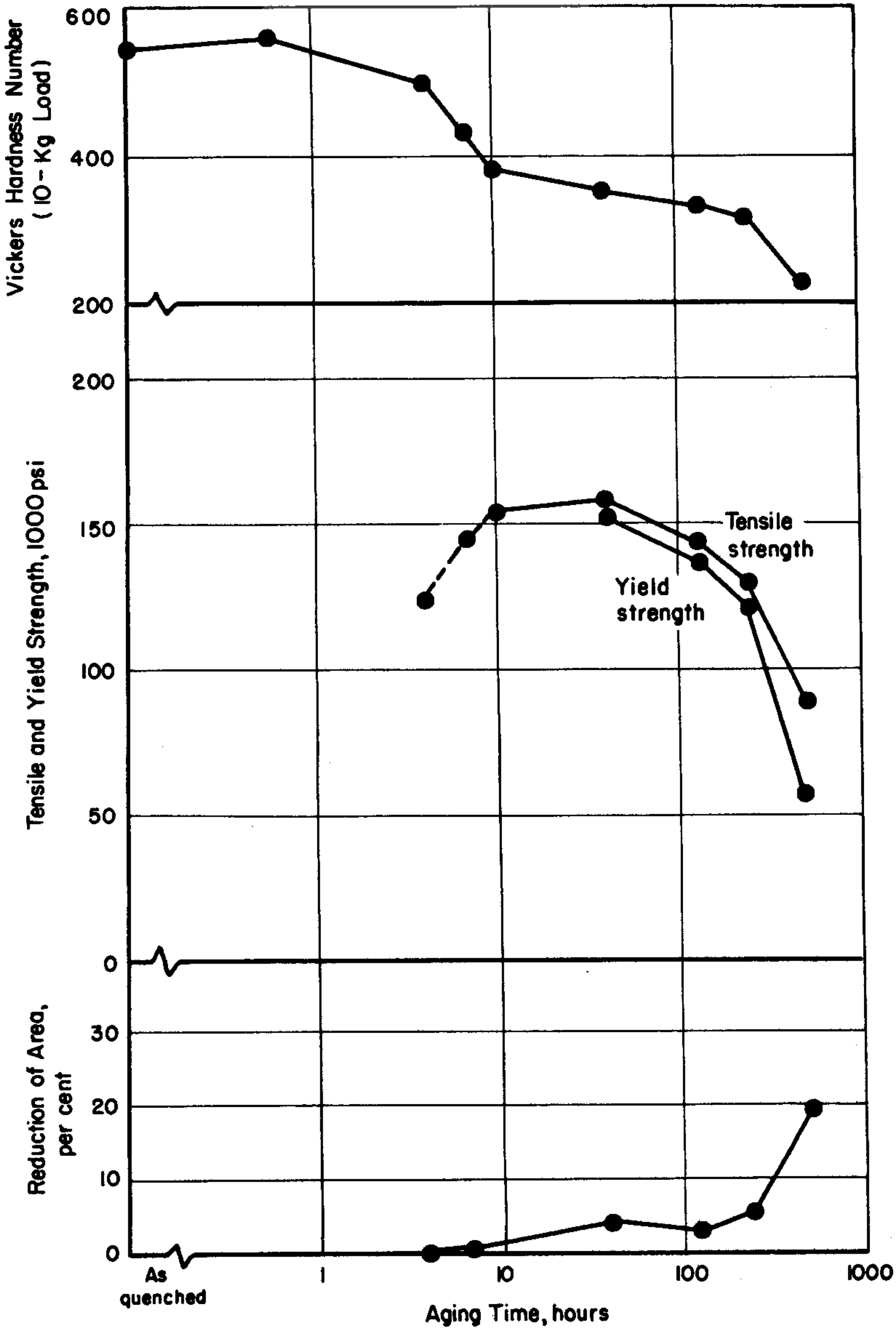

FIGURE 6. EFFECT OF AGING AT 800 F ON THE MECHANICAL PROPERTIES OF A Ti-4Fe ALLOY QUENCHED FROM 1700 F

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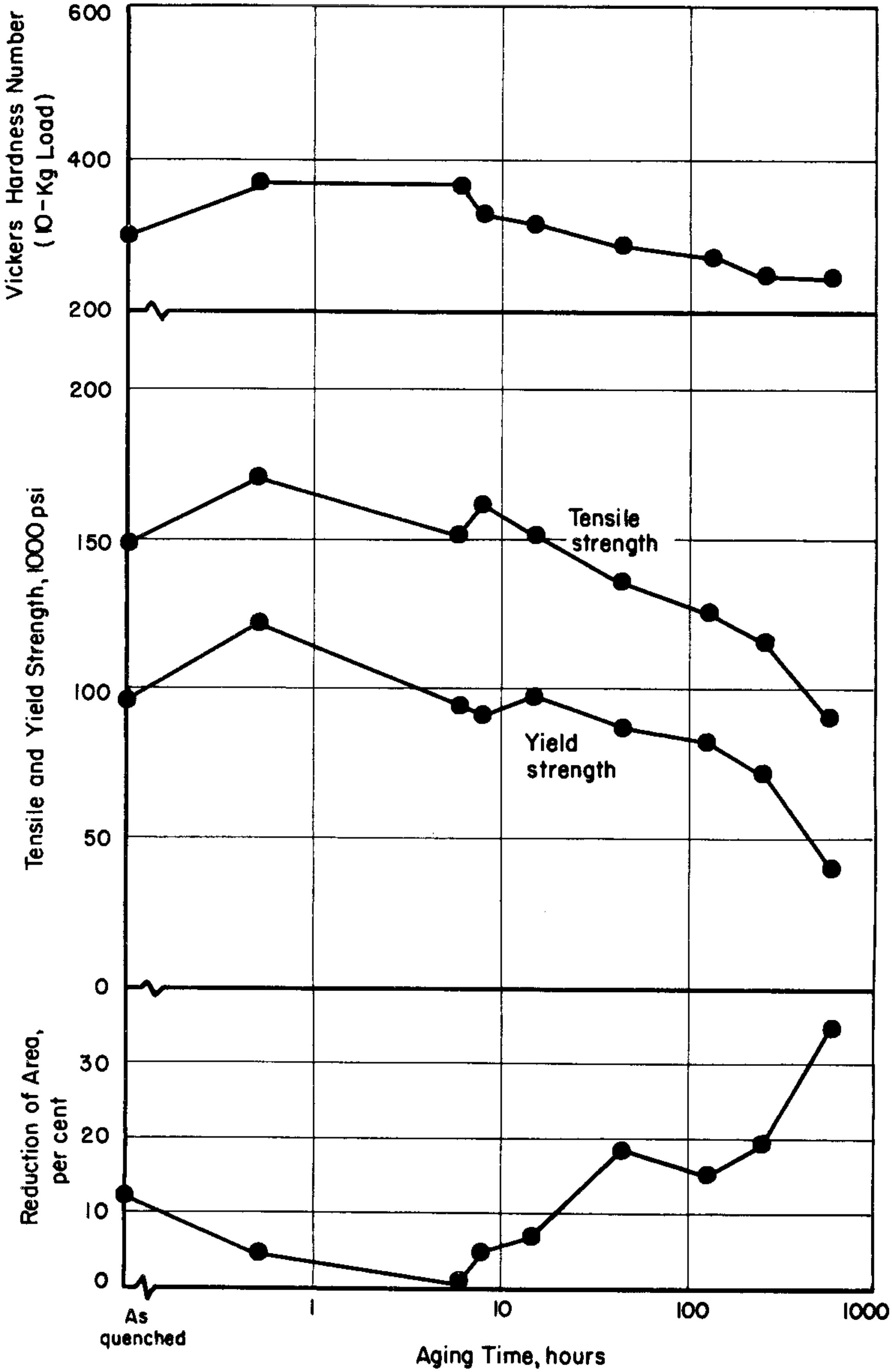

FIGURE 7. EFFECT OF AGING AT 800F ON THE MECHANICAL PROPERTIES OF A Ti-4Fe ALLOY QUENCHED FROM 1425 F A-13706

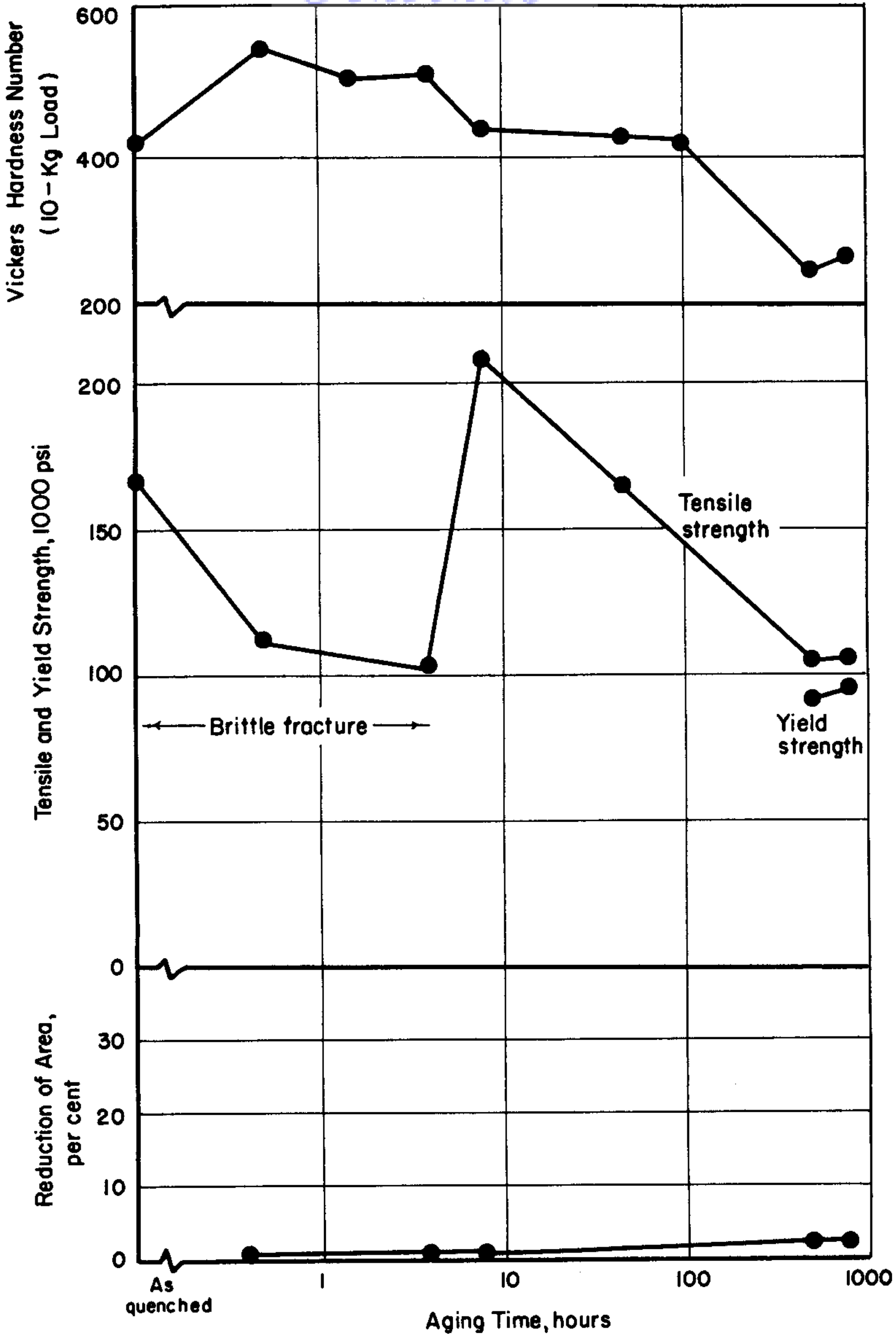

FIGURE 8. EFFECT OF AGING AT 800 F ON THE MECHANICAL PROPERTIES OF A Ti-8Cr ALLOY QUENCHED FROM 1700 F

A-13707

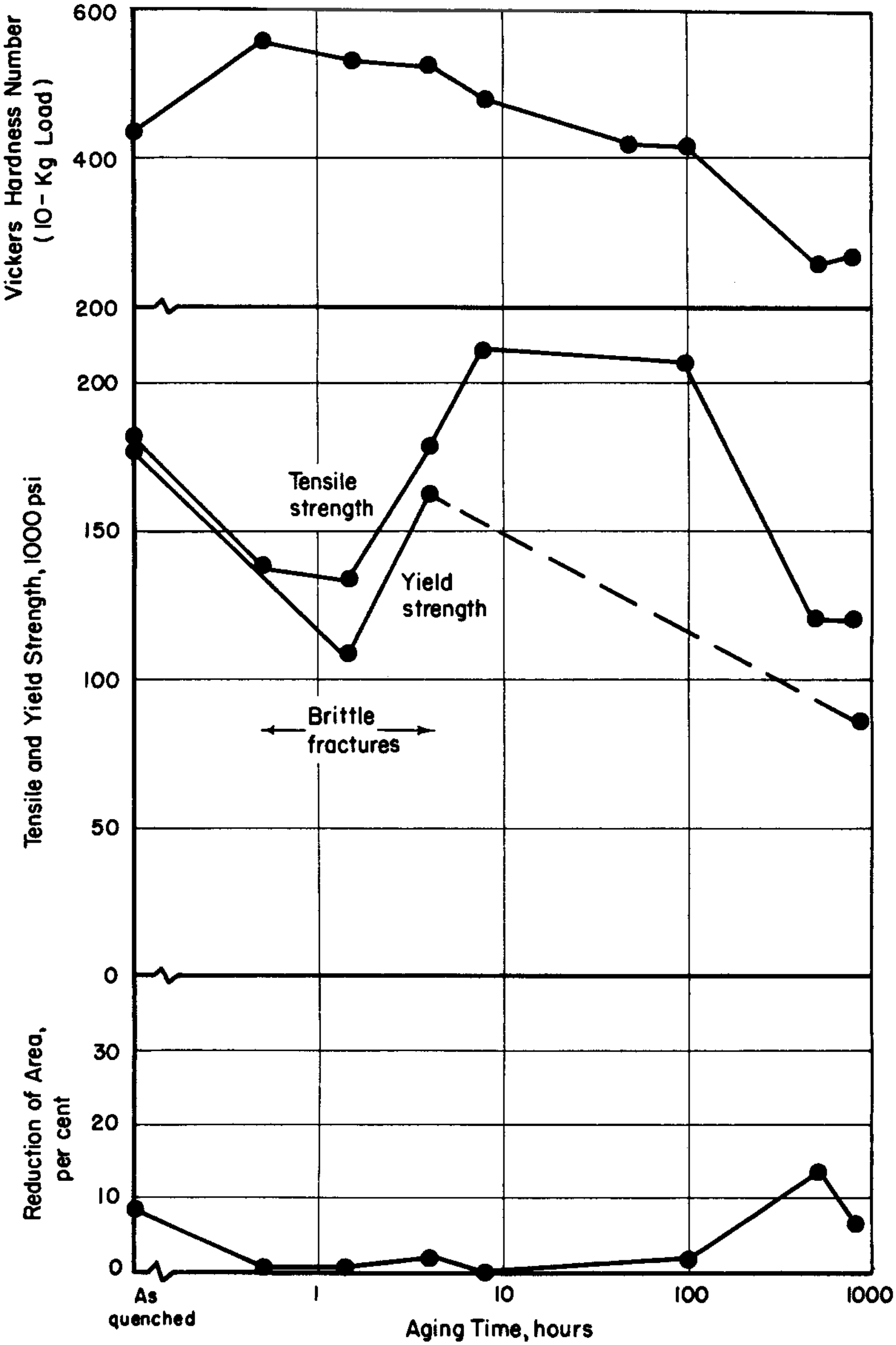

FIGURE 9. EFFECT OF AGING AT 800 F ON THE MECHANICAL PROPERTIES OF A Ti-8Cr ALLOY QUENCHED FROM 1400 F A-13708

periods of aging, these specimens were extremely brittle. It is known from X-ray diffraction and resistivity data that the omega phase was present in the as-quenched specimen and increased in amount during the early stages of aging. After about 10 hours of aging, the specimens attained some ductility. This is coincident with the appearance of the alpha phase in diffraction photograms and the disappearance of the omega phase. As aging progressed further, the ductility continued to increase and strength and hardness to decrease. Further precipitation and coalescence of the alpha phase and precipitation of the Ti-Fe compound from the enriched beta phase were responsible for these changes.

The specimens of the Ti-4Fe alloy quenched from the alpha-beta field and aged show much the same general trends as the beta-quenched specimens (Figure 7). However, in this case, the as-quenched specimen showed appreciable ductility, and the ductilities developed after relatively long periods of aging were much higher than those of the beta-quenched specimens. These differences in behavior are characteristic of beta-stabilized titanium alloys. They are associated largely with the inherently lower ductility of beta-quenched material for reasons not fully understood at present. Although there is no actual X-ray diffraction data available on this alloy quenched from the alpha-beta field, hardness and resistivity data which were presented in WADC TR 54-355 indicate that the phase changes which occurred during aging were essentially the same as those in beta-quenched material.

The degree of ductility exhibited by the Ti-4Fe alloy after the Ti-Fe compound precipitated was unusual. In the past, it has generally been assumed that the eutectoidal decomposition of titanium alloys resulted in severe embrittlement. The spread between the yield and ultimate strengths in this alloy, solution treated in the alpha-beta field and aged, was also unusual.

The Ti-8Cr alloy quenched from the beta-phase region (Table 6 and Figure 8) was extremely brittle except after very long aging times of 500 hours or more at 800 F. Ductility even after these long aging times was very low. Likewise, the ductility of the material solution treated in the alpha-beta-phase region was low after all aging treatments (Figure 9). This behavior implied that the compound precipitation in this alloy did adversely affect ductility. Although the X-ray diffraction data in WADC TR 54-355 did not show $TiCr_2$ until 500 hours of aging at 800 F, it is very possible that the precipitation of this compound began much sooner in the present specimens. Therefore, the recovery of ductility usually associated with the disappearance of the omega phase in favor of alpha could have been masked by the effects of the early stages of compound formation. There was some evidence of increased ductility in this alloy associated with the appearance of alpha after about 10 hours of aging. Tensile strengths increased sharply at this point. The lower tensile strengths exhibited by specimens aged for shorter times were believed to be the result of a completely brittle structure and not an indication of the true strength of the material.

The changes in mechanical properties during the various stages of the decomposition of the beta phase may be summarized as follows:

(1) A sharp decrease in ductility occurs as the omega phase forms. This may or may not be accompanied by an increase in apparent strength, since the embrittlement can be so severe that brittle fracture occurs at low stresses.

(2) An increase in ductility occurs as the omega phase disappears and is replaced by alpha. Useful high-strength properties are developed during this stage. If aging is continued over long periods of time, the strength will progressively decrease, and ductility increase as the alpha particles coalesce, provided there are no additional reactions such as compound precipitation.

(3) In the eutectoid systems, a further decrease in strength occurs as the compound precipitates. The effect of this precipitation on ductility may vary with the alloy system. The results presented in this report indicate that ductility increases considerably in Ti-Fe alloys, but only slightly, if at all, in the Ti-Cr system.

The temperature range over which the full sequence of these reactions occurs is not well defined as yet. It will probably vary somewhat with alloy composition. However, past experience with the heat treatment of beta-stabilized alloys has indicated that the full sequence occurs at temperatures of about 800 to 1000 F. Above 1000 F, the omega reaction, if it occurs at all, is of very short duration.

EFFECT OF ALLOY CONTENT ON AGE-HARDENING CHARACTERISTICS

The work in the early phases of this contract had indicated that the formation of omega phase was accompanied by localized enrichment of the parent beta phase in the solute element. This led to the speculation that a relatively high alloy content might inhibit omega formation and the rate of formation might differ from that previously observed in leaner alloys. The initial phases of the work on higher alloy materials were described in WADC TR 54-355. Resistivity and hardness determinations made on a Ti-12Cr and a Ti-16Cr alloy quenched from 1700 F and aged at 700 F indicated that the rate of the aging reaction did decrease with increasing alloy content. This work was continued under the present contract extension.

Selected specimens of both the Ti-12Cr and Ti-16Cr alloys aged for periods up to 1000 hours were examined by X-ray diffraction to determine the phases present. The results appear in Table 8 and the relative intensities of the phase patterns are presented graphically in Figures 10 and 11, along with the hardness and resistivity data from the earlier work. In both the tables and the figures, the observed diffuseness or broadness of the diffraction lines have been indicated since they are an important part of the X-ray data in this case.

TABLE 8. X-RAY-DIFFRACTION STUDY OF Ti-12Cr AND Ti-16Cr ALLOYS QUENCHED FROM 1700 F AND AGED AT 700 F

Chromium Content, per cent	Aging Time, hr	Phase Patterns Observed				
		Untransformed Beta, β_0	Enriched Beta, β_r	Omega, ω	Alpha, α	TiH
12	1/2	ms	vs, br	mf-m	0	vf, d
12	4	0	s, vbr	mf	0	vf, d
12	200	0	m, vd	f, d	f, d	f, d
12	600	0	f-mf, vd	0	ms, d	0
12	1000	0	vf	0	m	0
16	1/2	s	0	0	0	0
16	4	s	0	0	0	0
16	24	s(a), d	0	0?	0	0
16	200	s(a), vd	0	0?	0	m, vd
16	400	0	ms, vd	0	0	mf, vd
16	600	0	ms, vd	0	0	mf, vd
16	1000	0	ms, vd	0	0	m, vd

(a) The beta here is called β_0 because no important change in lattice constant was observed. However, the diffuseness of the pattern indicates that some kind of transformation was occurring.

Key to abbreviations: s = strong, m = medium, f = faint, v = very, d = diffuse, br = broad in direction of Bragg angle θ.

The 12Cr alloy appeared to have passed through phase changes during aging similar to those of the 8Cr alloy described in WADC TR 54-355. The omega phase formed during the early stages of aging and, as aging progressed, this phase gradually disappeared as alpha phase formed. The rate of omega formation in the 12Cr alloy could not be accurately determined from the X-ray diffraction photograms, but the hardening in this alloy was somewhat slower than in the Ti-8Cr alloy. Also, the maximum hardness attained by the Ti-12Cr alloy was lower. If it is assumed that hardness is an indication of the amount of omega present, then the phase must have formed more slowly and in smaller amounts in the system with the higher alloy content.

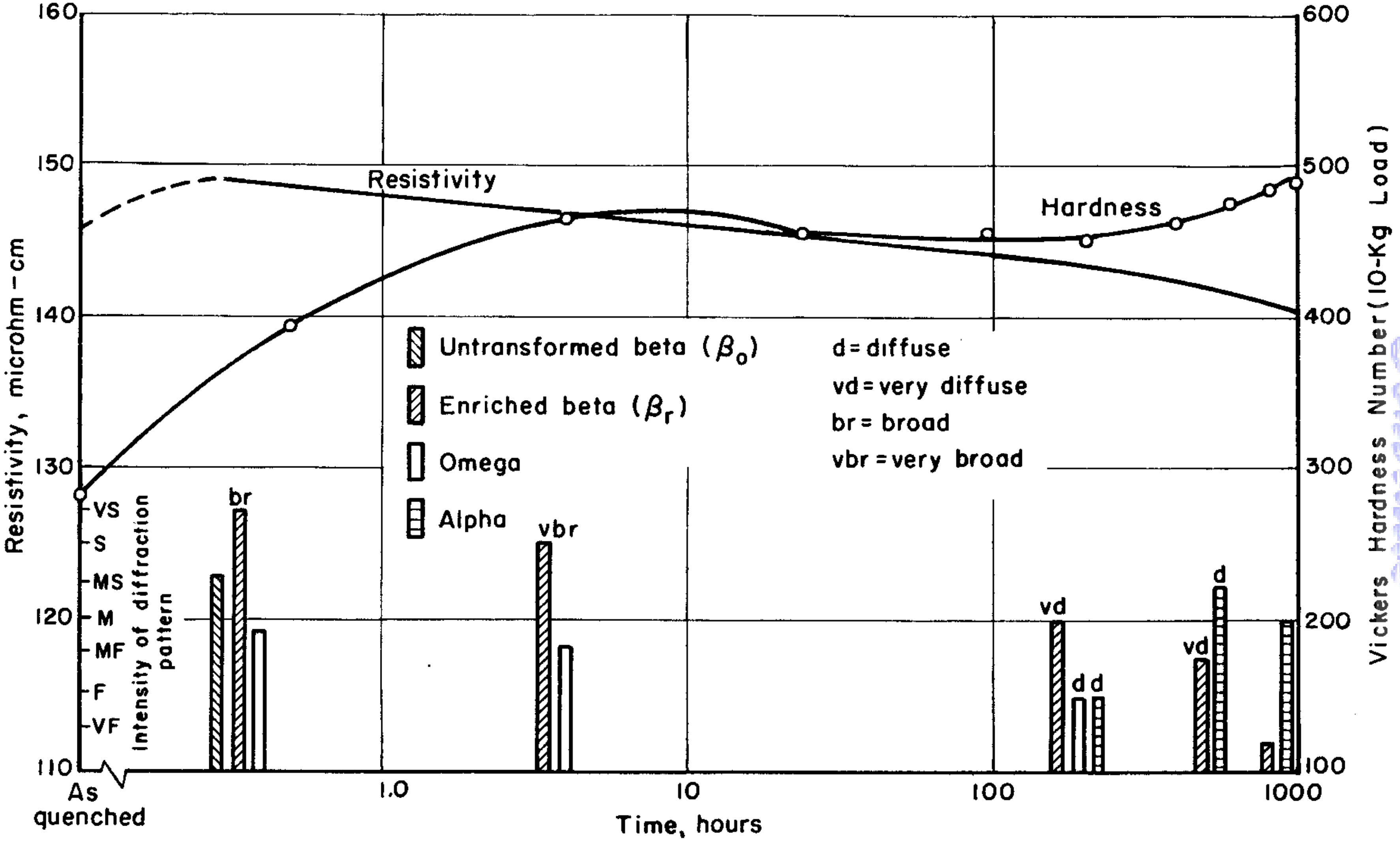

FIGURE 10. EFFECT OF AGING AT 700F ON THE RESISTIVITY, HARDNESS, AND X-RAY PATTERN INTENSITIES OF A Ti-12 Cr ALLOY QUENCHED FROM 1700 F

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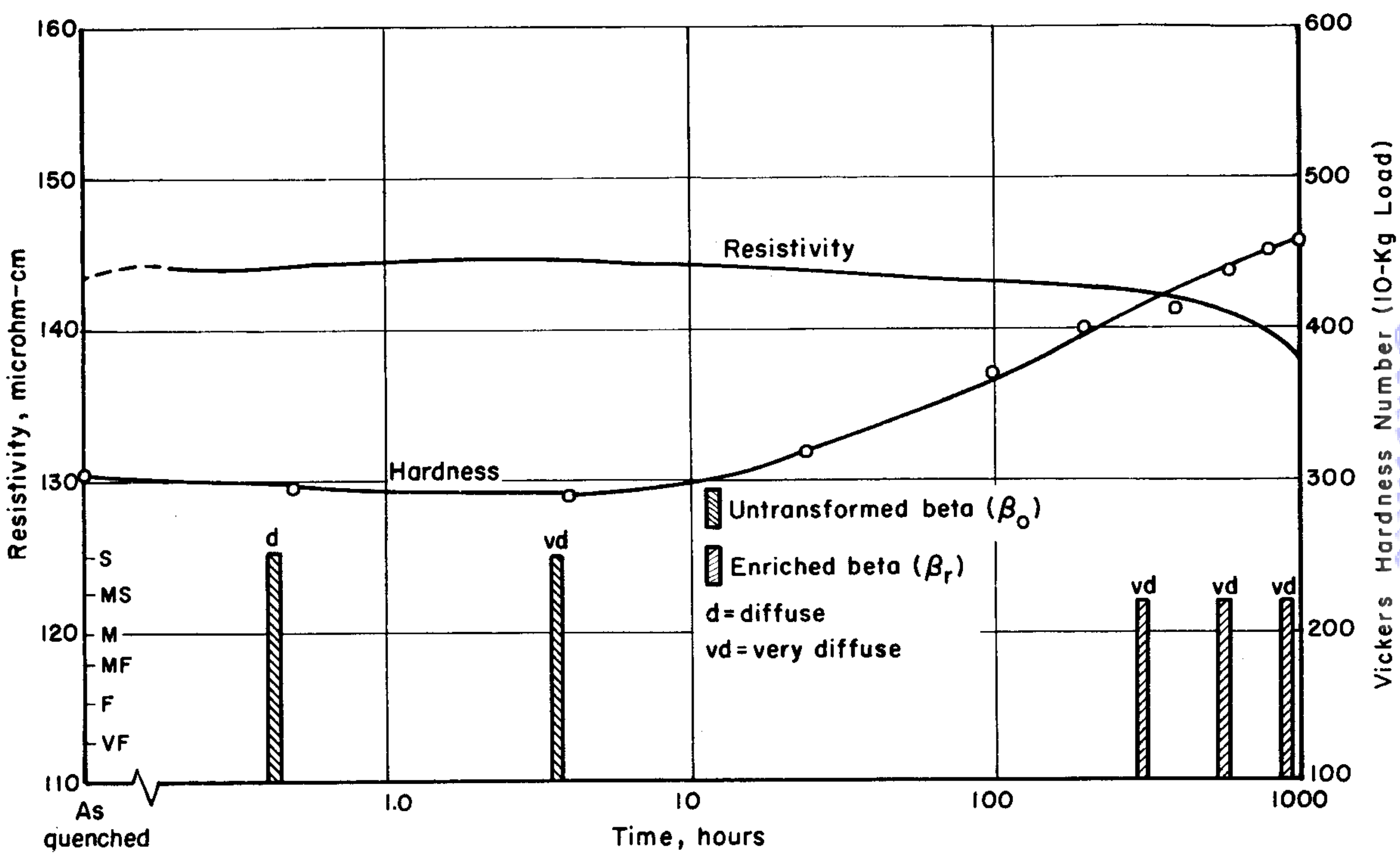

FIGURE 11. EFFECT OF AGING AT 700F ON THE RESISTIVITY, HARDNESS, AND X-RAY PATTERN INTENSITIES Ti-16 Cr ALLOY QUENCHED FROM 1700 F

A-11954

The Ti-12Cr alloy exhibited unusual behavior with respect to both hardness and resistivity in the later stages of aging. It may be seen in Figure 10 that there was no decrease in hardness accompanying the appearance of alpha in the diffraction photograms. In fact, at very long aging times (600 to 1000 hours), the hardness actually increased. Likewise, there was no pronounced change in resistivity with the appearance of alpha. Similar behavior with respect to resistivity was observed in earlier work on a Ti-4Fe alloy aged at 700 F, as described in WADC TR 54-355. On the other hand, several alloys aged at 800 F showed a sharp decrease in resistivity prior to or coincident with the detection of alpha by X-ray diffraction. These resistivity and hardness anomalies observed in the different alloys aged at 700 F suggest either a coherency between the alpha and omega or beta, or a high degree of dispersion hardening by the alpha particles precipitating at this temperature. Also, these data indicate that resistance changes are not reliable criteria of alpha precipitation at temperatures below 800 F.

No direct evidence of the omega phase was found in specimens of the Ti-16Cr alloy. However, after the specimens had been aged for 24 hours or more, the diffraction lines of the beta phase became diffuse, indicating that a reaction was occurring. After aging for 400 or more hours, the beta-phase lines indicated a reduced lattice constant similar to that observed during omega formation in lower alloys. No reflections corresponding to the 2.83, 1.78, or 1.41 A reflections of omega were found in any of the specimens examined. Reflections of the alpha and compound phases were also absent even after the 1000-hour aging period.

Age hardening in the Ti-16Cr alloy correlated well with the appearance of the diffuse beta lines in the X-ray photograms. As shown in Figure 11, the first increase in hardness was detected after 24 hours at 700 F. Hardening proceeded slowly and maximum hardness was not attained during the 1000-hour aging period. Thus, it appears that the aging characteristics change considerably with increasing alloy content. The rate of the aging reaction is decreased and there is some indication that the mechanism of hardening, particularly after long times, may be somewhat different than in the case of the lower alloy contents.

It was also considered desirable to study, to a limited extent at least, the age hardening of alloys containing less than the nominal 4Fe, 8Cr, and 10Mo compositions used heretofore. The ability of most of these leaner alloys to be age hardened was expected to be limited because of their inability to retain the beta phase upon quenching. Nevertheless, definition of the aging potential of the alloys would provide useful information.

A series of binary high-purity titanium alloys was prepared for this work. The nominal compositions of the small melts were as follows:

Ti-1Fe
Ti-2Fe
Ti-3Fe
Ti-4Fe
Ti-2Cr
Ti-4Cr
Ti-6Cr
Ti-8Cr
Ti-2Mo
Ti-4Mo
Ti-6Mo
Ti-8Mo
Ti-10Mo
Ti-2Mn
Ti-4Mn
Ti-6Mn
Ti-8Mn

The highest alloy content in each series was investigated in earlier work, but was included as a control.

The 10-gram melts were made in a tungsten-electrode arc furnace, using iodide titanium and high-purity alloy materials. They were subsequently rolled at 1450 F to 0.064-inch sheet and cut into small coupons for heat treatment. The solution treatment was 1/2 hour at 1700 F while sealed in Vycor with argon atmosphere. This was followed by a rapid iced-brine quench. The quenched specimens were aged at 700 F for periods of time up to 24 hours. The average hardness readings obtained from these specimens, using a diamond penetrator and 10-kg load, are plotted against aging time in Figures 12 through 15.

Generally, the as-quenched hardness and the degree of hardening due to aging increased with increasing alloy content. This trend was least pronounced in the Ti-Mo alloys which showed only slight increases in the quenched and aged hardnesses as the alloy content increased from 2 to 10 per cent. The Ti-10Mo alloy of this series did not harden to the extent that previous alloys of this composition did. This was probably due to an alloy content lower than the nominal, since this alloy exhibited a transformed alpha-prime structure instead of the expected retained beta after quenching.

With the exception of the highest alloy compositions in each series, the remaining alloys all had an alpha-prime structure which did not change significantly during aging. Figure 16, which shows the structure of the Ti-3Fe alloy aged 24 hours at 700 F, is representative of this type of structure. In view of the apparent transformation of the beta in these leaner alloys during quenching, the degree of age hardening shown by the Ti-3Fe, Ti-6Cr, and Ti-6Mn compositions was surprising. It implies that a considerable amount of the beta phase was retained in these alloys which was not visible in the microstructure. It is also possible that the hardening of these alloys was due to a hitherto unknown reaction which is not dependent on the retention of beta. It was not possible to pursue this investigation further to define the mechanism of hardening in these alloys.

ELECTRICAL RESISTIVITY CHANGES DURING AGING

Changes in electrical resistivity have been used throughout the project to help define phase transformations. Resistivity changes during aging at

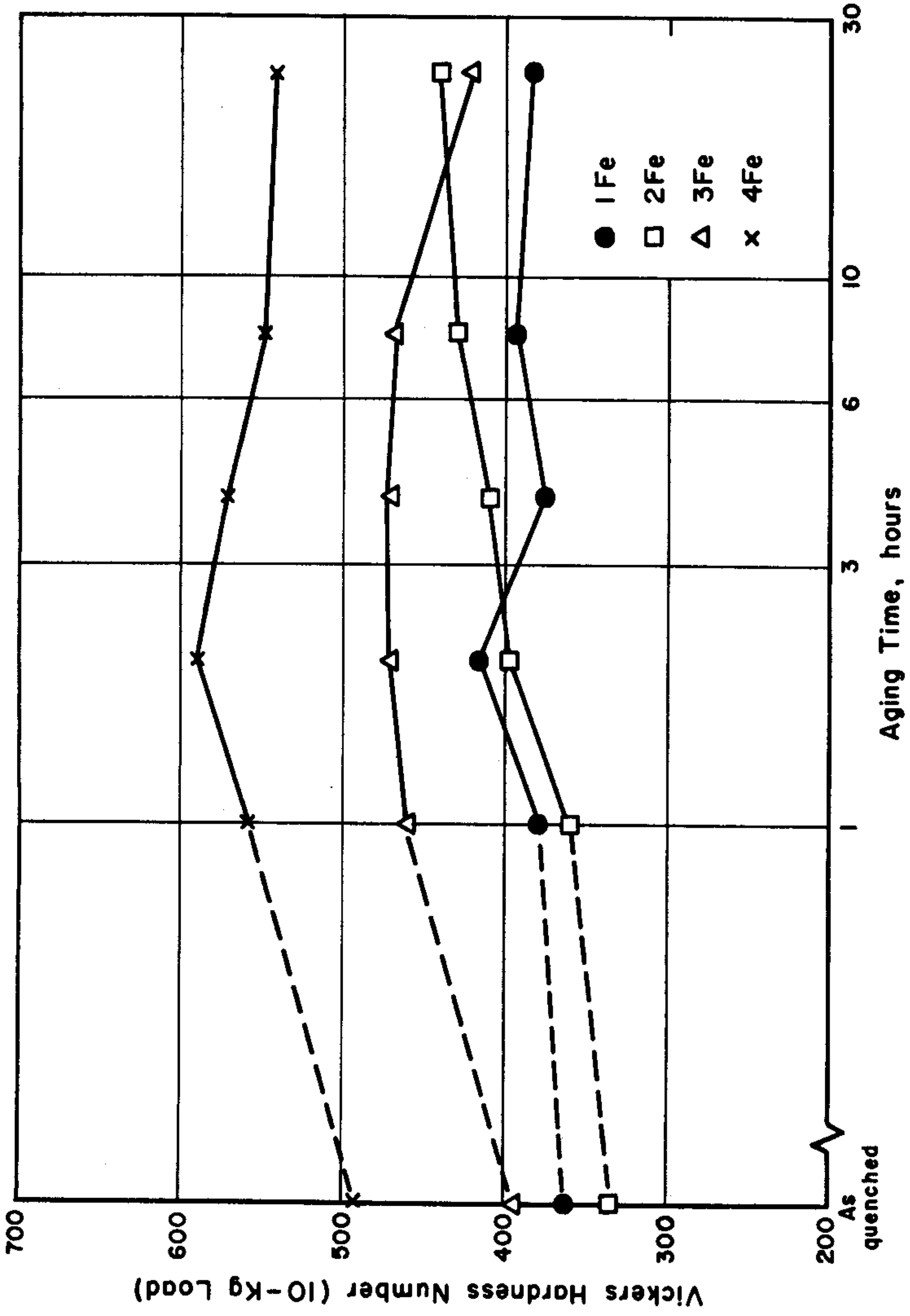

FIGURE 12. EFFECT OF AGING AT 700 F ON THE HARDNESS OF TITANIUM-IRON ALLOYS QUENCHED FROM 1700 F

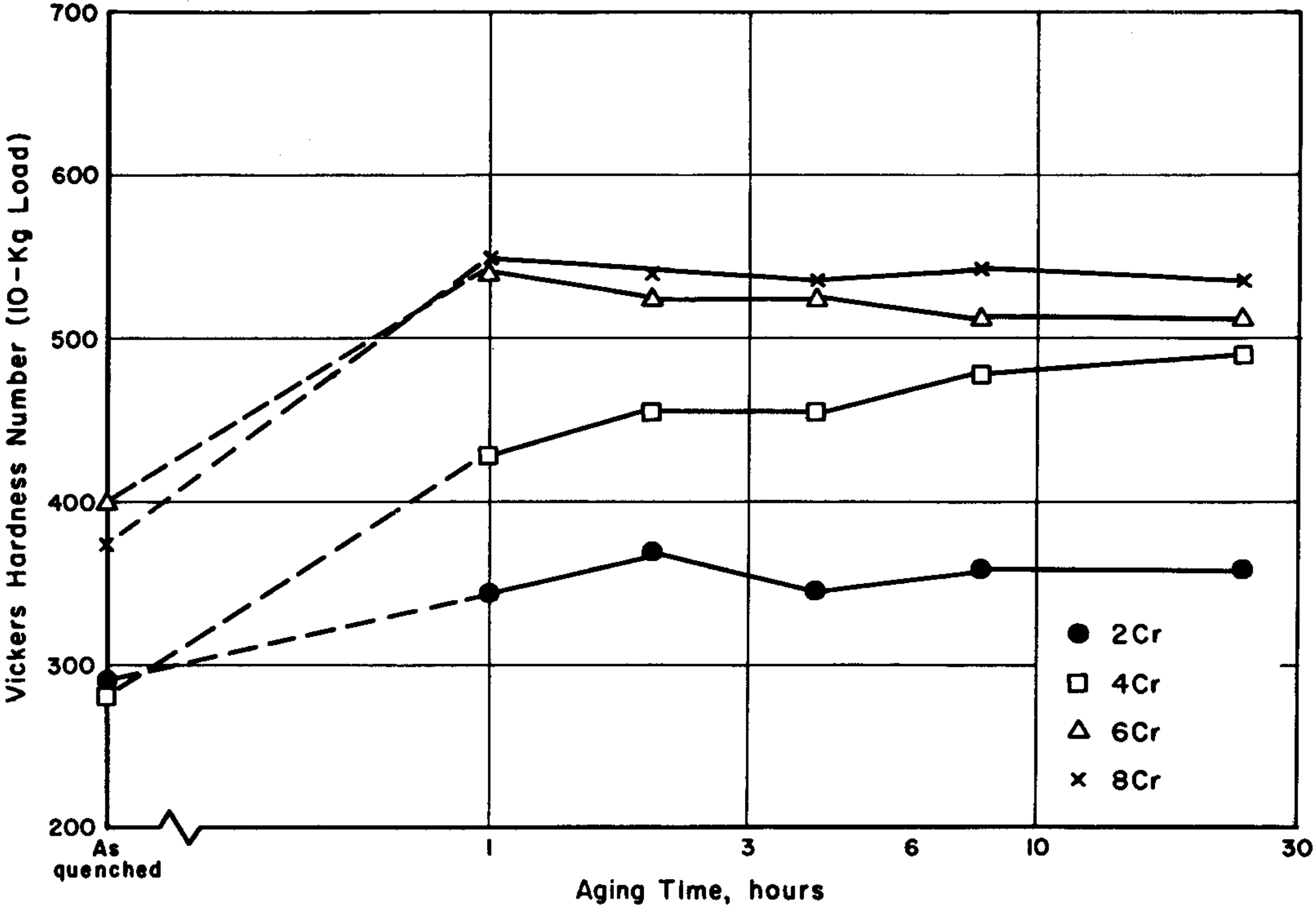

FIGURE 13. EFFECT OF AGING AT 700 F ON THE HARDNESS OF TITANIUM-CHROMIUM ALLOYS QUENCHED FROM 1700 F

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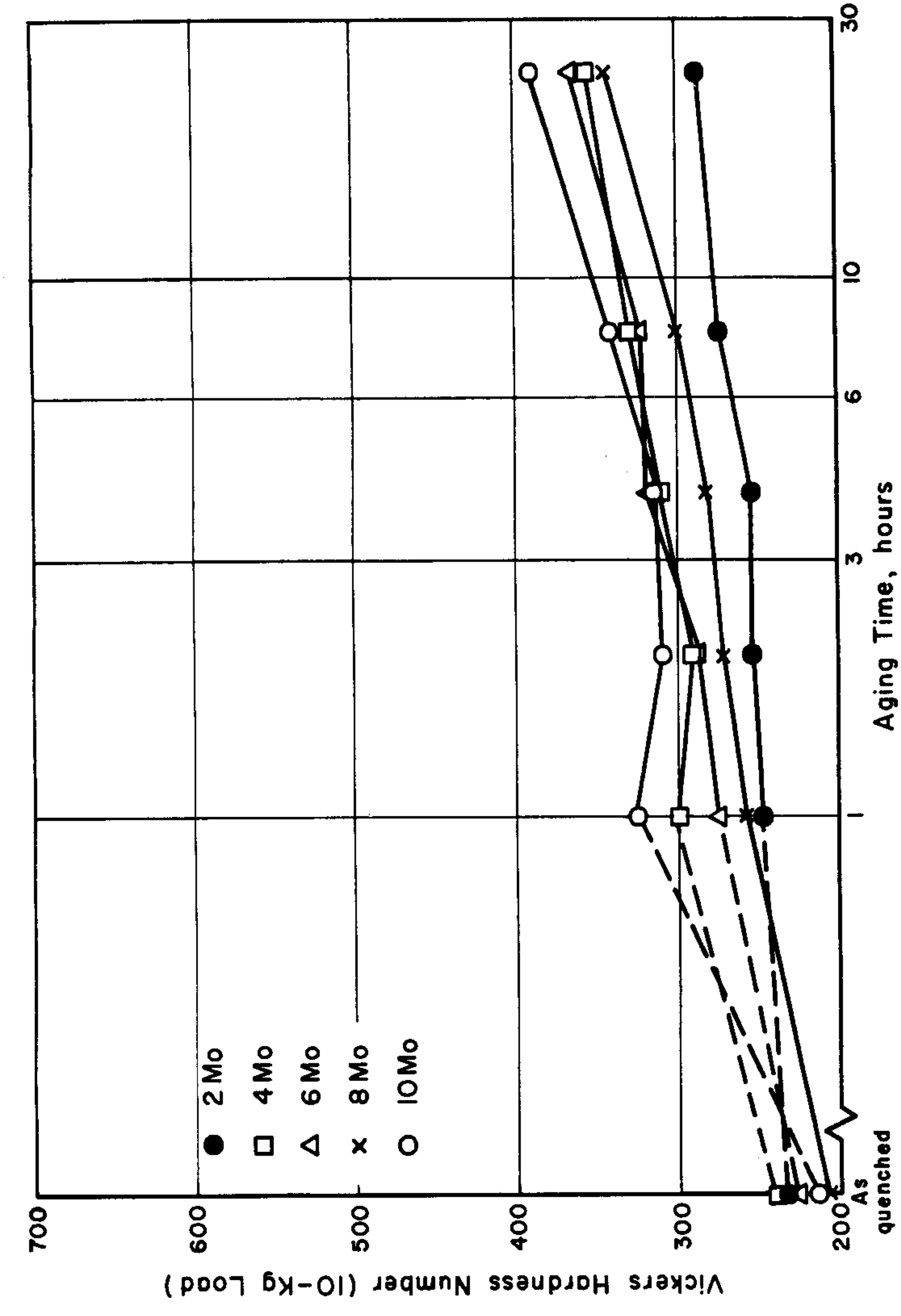

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FIGURE 14. EFFECT OF AGING AT 700 F ON THE HARDNESS OF TITANIUM-MOLYBDENUM ALLOYS QUENCHED FROM 1700 F

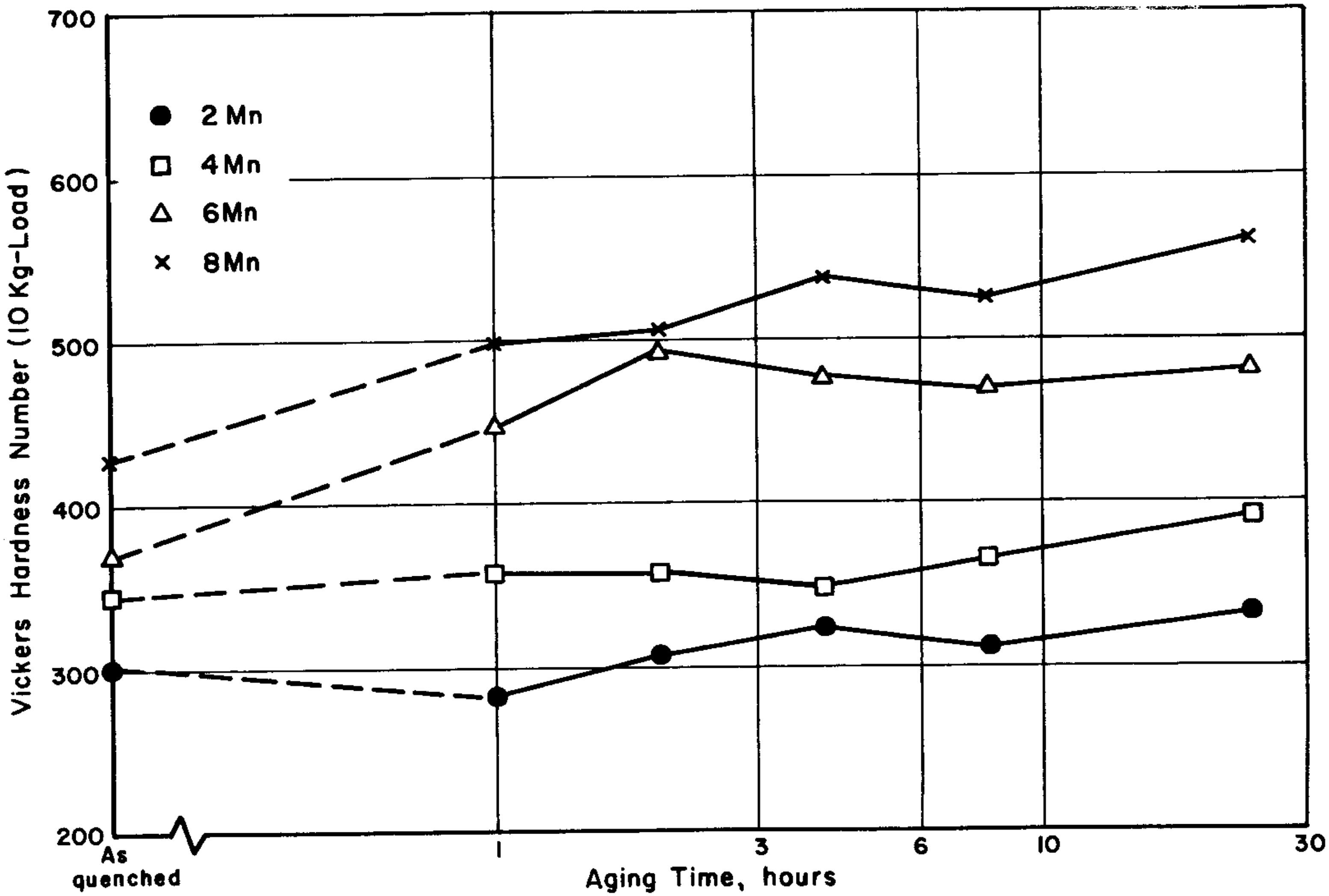
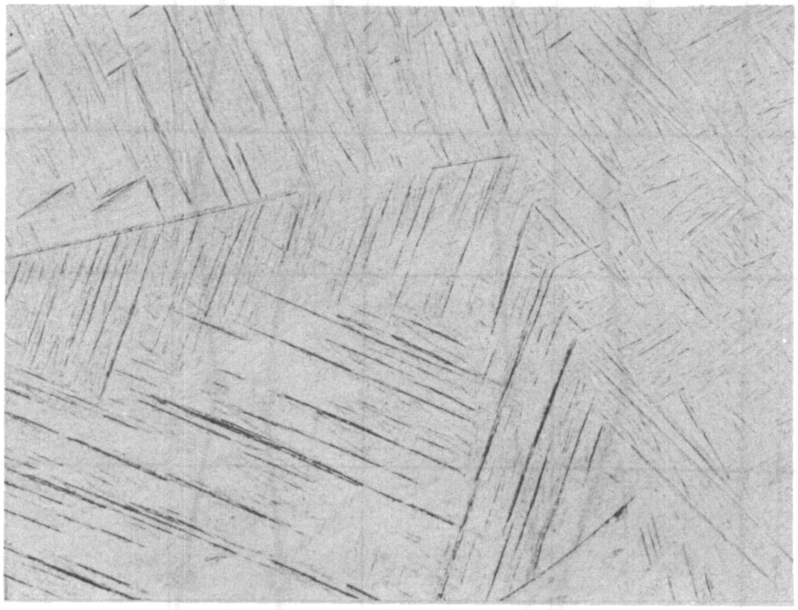


FIGURE 15. EFFECT OF AGING AT 700 F ON THE HARDNESS OF TITANIUM-MANGANESE ALLOYS QUENCHED FROM 1700 F

A-13712



250X N19160

FIGURE 16. Ti-3Fe ALLOY SOLUTION TREATED 1/2 HOUR AT 1700 F, QUENCHED IN ICED BRINE, AND AGED 24 HOURS AT 700 F

Structure: Alpha Prime

700 and 800 F were measured on the following high-purity alloys by methods described in WADC TR 54-355:

Ti-4Fe
Ti-8Cr
Ti-12Cr
Ti-16Cr
Ti-10Mo
Ti-3Mn-1Cr-1Fe-1Mo-1V.

The changes which occurred during heating to the aging temperature were not known. Stable temperature conditions were attained after about 10 minutes and resistivity measurements were begun at that time. Considering the measured room-temperature resistivities and assuming a positive coefficient of resistance, there appeared to be a large drop in resistivity during the initial heating period.

Direct determination of the resistivity of the alloys at zero time at the aging temperature would be very difficult. The rapidity with which the omega phase forms during aging would require almost instantaneous heating to temperature and measurement of resistance. Consequently, two alternative methods of defining the initial changes in resistivity were used. The first involved estimating the resistivity at zero time from temperature-resistance data obtained at low temperatures. The second consisted of studying the changes in resistivity of selected alloys at a lower aging temperature (500 F). The latter method, in effect, slowed down the aging reaction so that the initial phases could be more easily observed.

Estimation of Resistivity at Zero Time

The resistivity of the various alloys in the as-quenched condition was determined at temperatures of -90, 86, and 203 F. It is believed that no phase changes occur at these temperatures. The results of these measurements are given in Table 9.

Two alloys, Ti-4Fe and Ti-10Mo, quenched from the alpha-beta-phase region showed an appreciable positive coefficient of resistivity. The Ti-12Cr, Ti-16Cr, and Ti-3Mn-complex alloys showed negative coefficients of resistivity. The latter behavior is somewhat unusual but has been observed in other alloy systems. In the other alloys, the resistivity varied only slightly as the temperature was changed.

The curve determined by plotting resistivity at these three temperatures was then extrapolated to the aging temperature. These extrapolated values were incorporated in the resistivity curves presented in WADC TR 54-355. The revised curves are shown in Figures 10 and 11, and 17 through 23, along with the hardness and X-ray data. The accuracy of the extrapolated resistivity values is open to question; hence, the early portions of the curves are shown as dotted lines.

TABLE 9. RESISTIVITY OF AS-QUENCHED TITANIUM ALLOYS AT -90 F, 86 F, AND 203 F

Sample	Nominal Composition, per cent	Solution Temp, F	Resistivity, microhm-centimeters, at -90 F	86 F	203 F
1	4Fe	1700	182	182	182
2	8Cr	1700	169	168	168
3	10Mo	1700	156	157	157
4	12Cr	1700	156	151	149
5	16Cr	1700	149	146	145
6	4Fe	1425	130	143	148
7	8Cr	1325	160	161	162
8	10Mo	1325	123	129	132
9	3Mn complex	1700	177	173	171
10	3Mn complex	1400	169	166	166

In some cases (Figures 11, 17, 18, and 19), the change in resistivity with temperature was very small, so that the original curves based on the room-temperature values were only slightly changed. With the exception of the Ti-4Fe alloy quenched from 1425 F, the revised curves show a rather interesting relation between resistivity and alloy content. The leaner alloys (Ti-8Cr, Ti-4Fe, Ti-10Mo, and Ti-3Mn complex) quenched from the beta-phase region all show an initial sharp drop in resistivity during aging. The richer alloys (Ti-12Cr and Ti-16Cr alloys) or the leaner alloys quenched from the alpha-beta-phase region generally show either no change or an actual increase in resistivity during the early stages of aging. Of course, quenching the leaner alloys from the alpha-beta region effectively increases the alloy content of the beta phase present, and this would be expected to slow down any reaction that would cause a change in resistivity.

The significance of the apparent rapid changes in resistivity in some of the alloys at the beginning of the aging period is not known.

Aging at 500 F

The resistivity changes during aging were also measured on a number of alloys at 500 F by the voltage-drop method described in detail in WADC TR 54-355. The results are shown in Figures 24 through 28. Where available from earlier work, hardness and X-ray diffraction data have also been plotted.

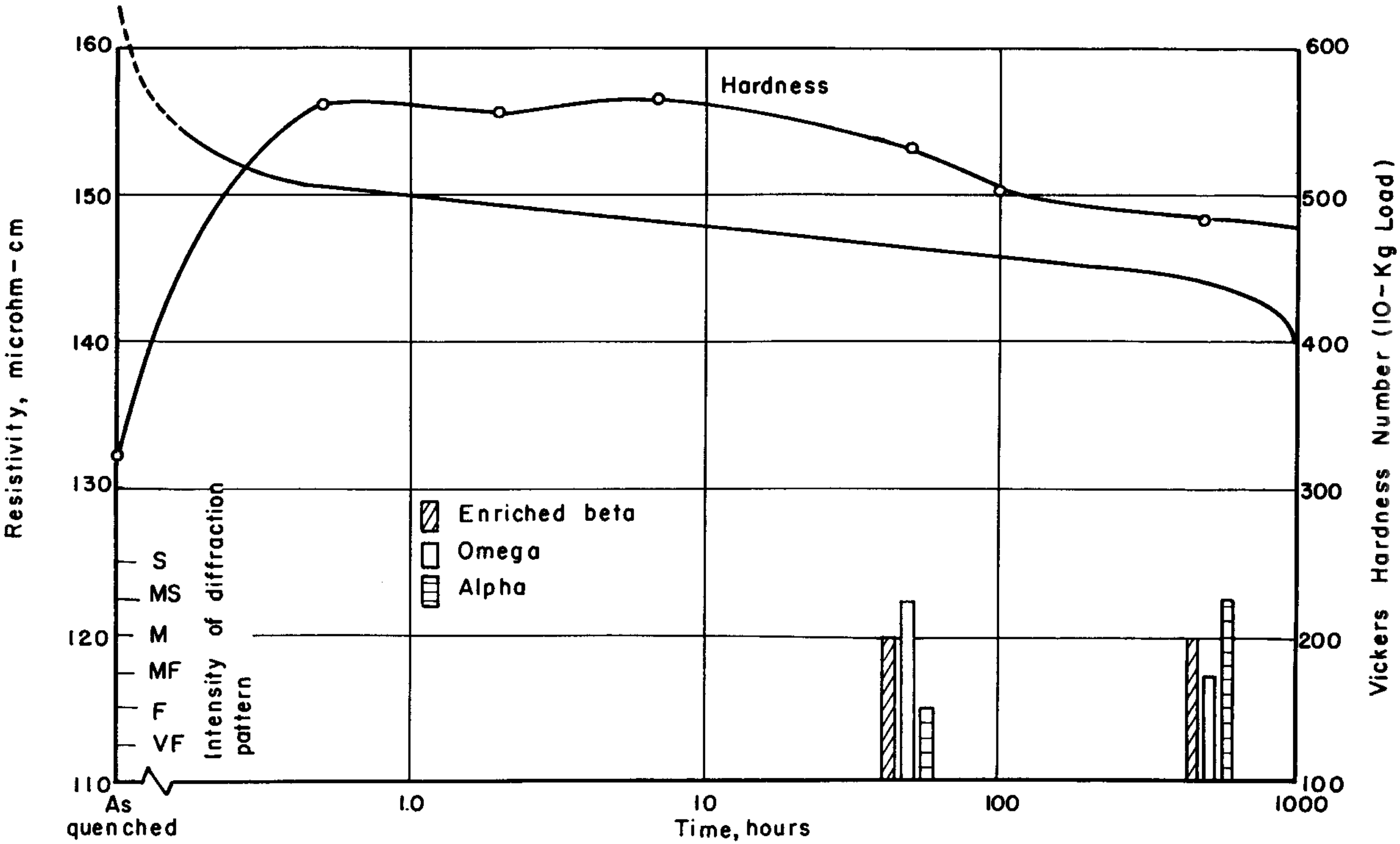


FIGURE 17. EFFECT OF AGING AT 700F ON THE RESISTIVITY, HARDNESS, AND X-RAY PATTERN INTENSITIES OF A Ti-8Cr ALLOY QUENCHED FROM 1700 F

A-12359

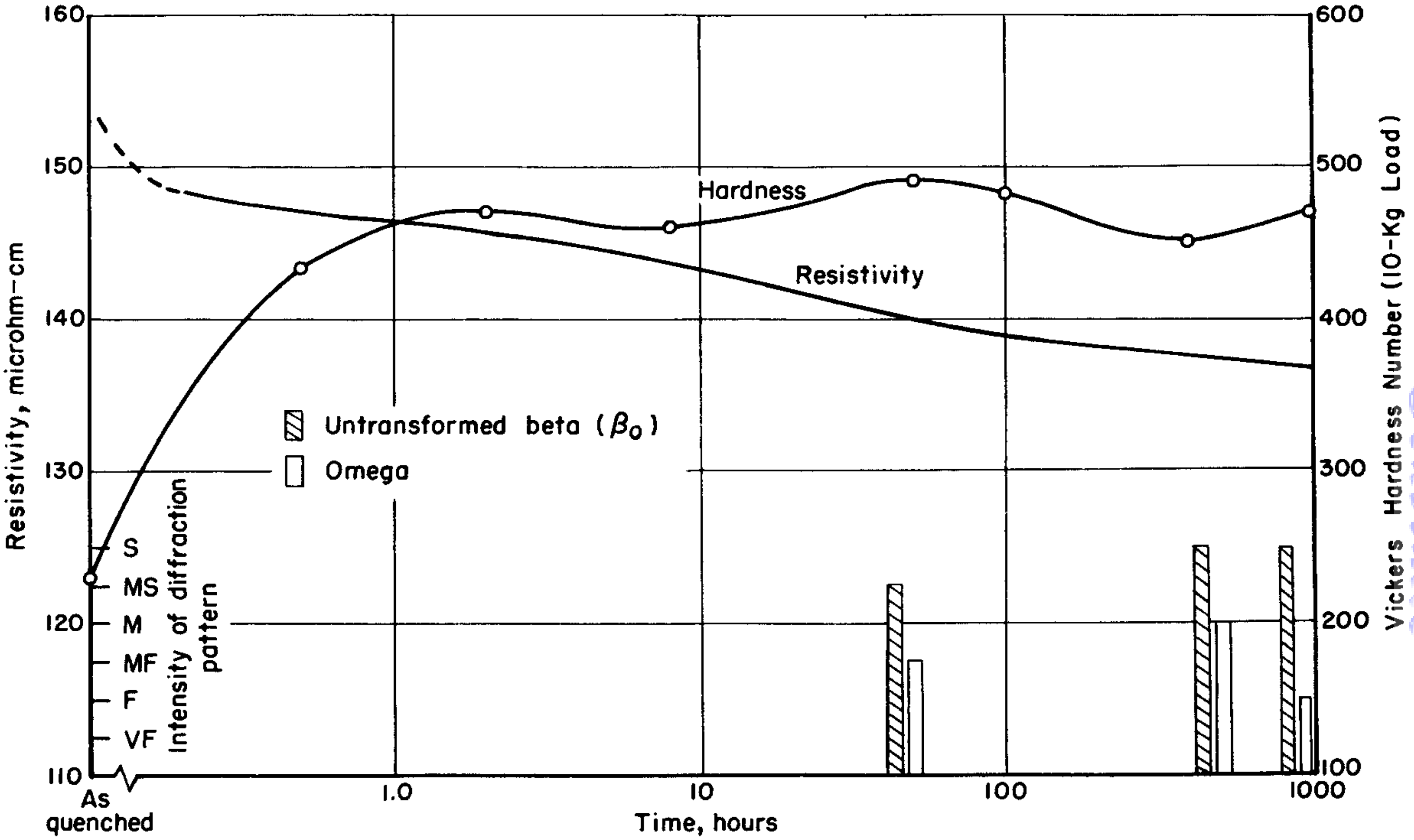


FIGURE 18. EFFECT OF AGING AT 700F ON THE RESISTIVITY, HARDNESS, AND X-RAY DIFFRACTION-PATTERN INTENSITIES OF A Ti-10 Mo ALLOY QUENCHED FROM 1700 F

A-11948

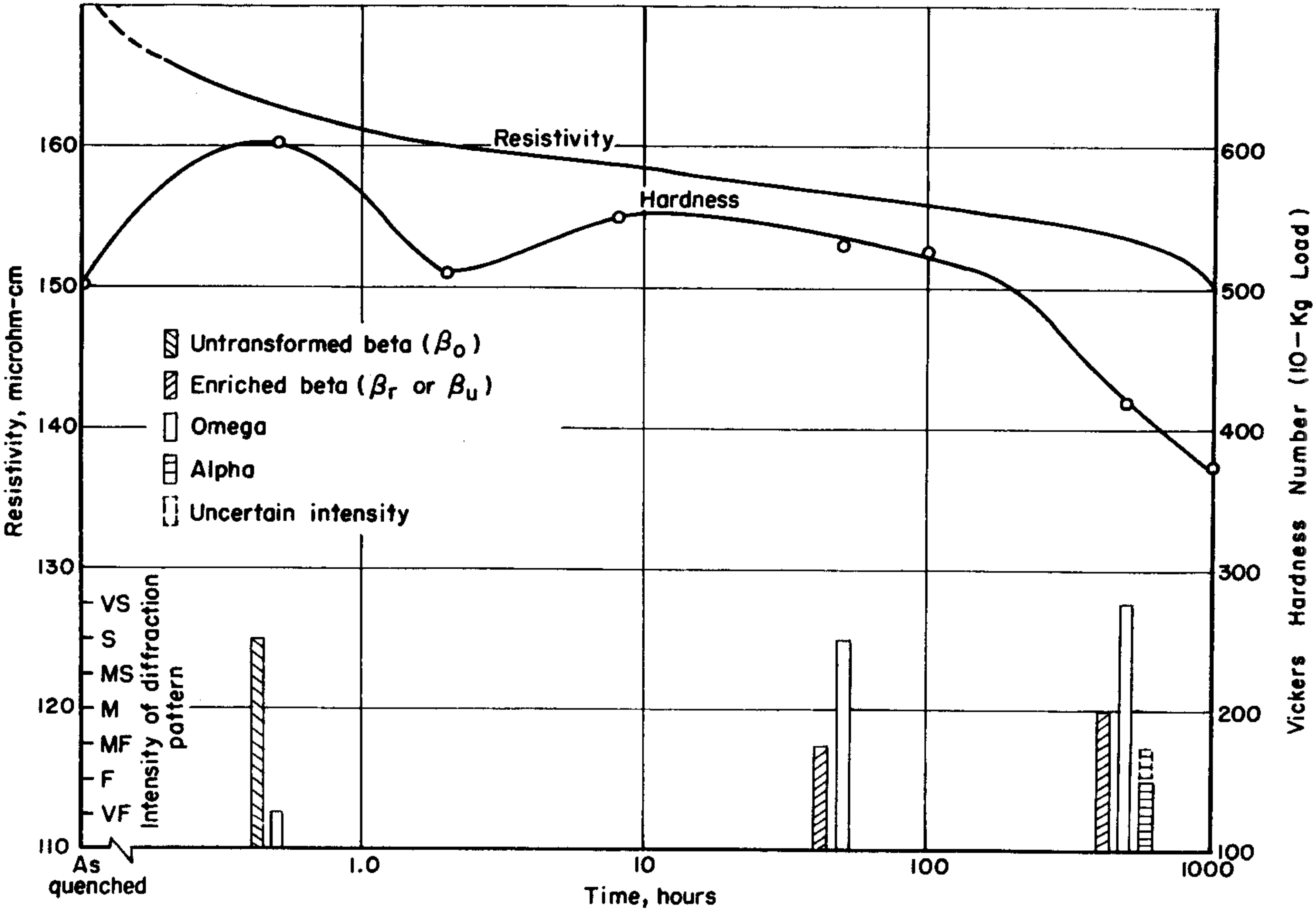


FIGURE 19. EFFECT OF AGING AT 700F ON THE RESISTIVITY, HARDNESS, AND X-RAY DIFFRACTION-PATTERN INTENSITIES OF A Ti-4 Fe ALLOY QUENCHED FROM 1700 F

A-11946

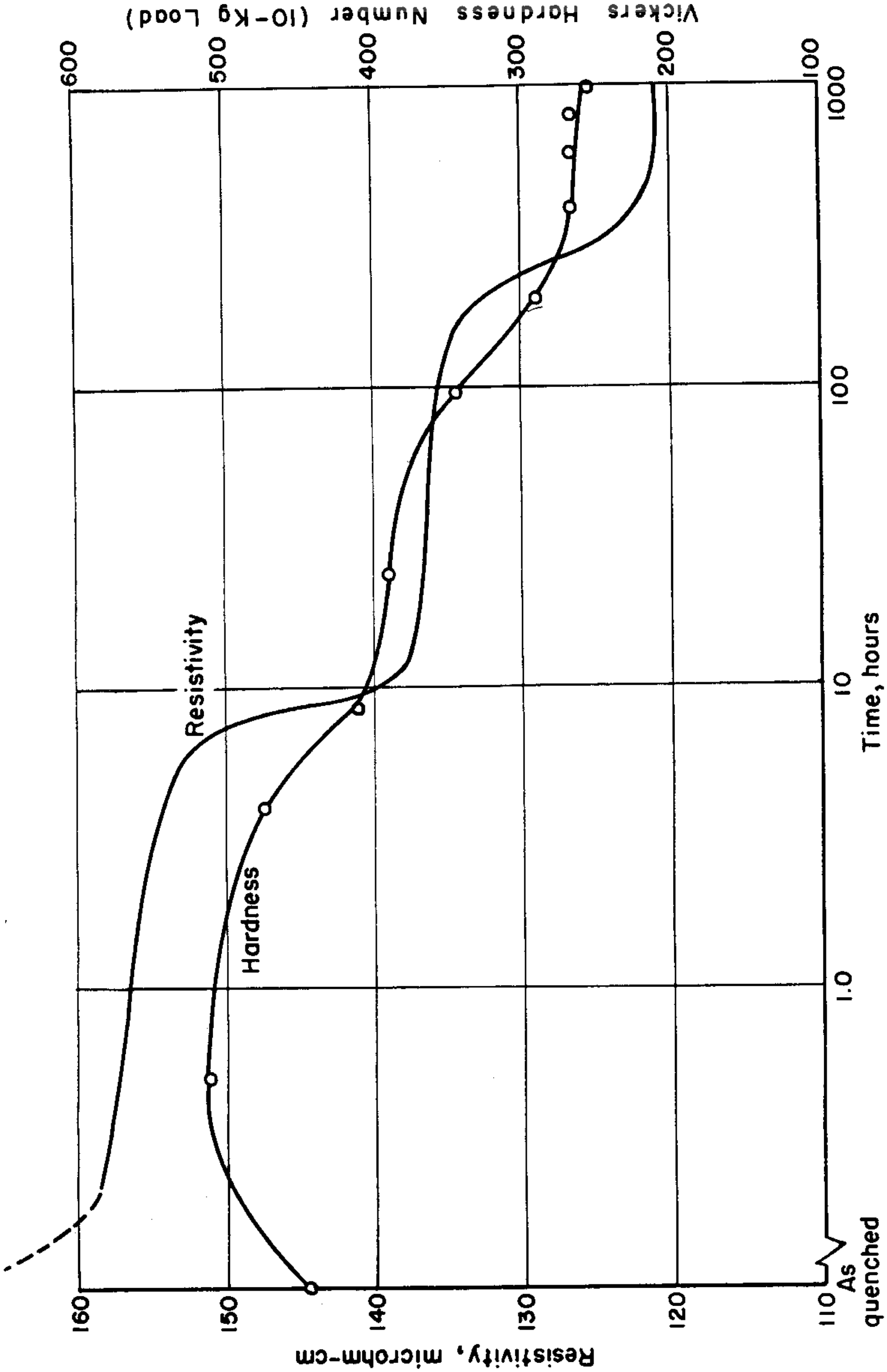


FIGURE 20. EFFECT OF AGING AT 800F ON THE RESISTIVITY AND HARDNESS OF A Ti-4Fe ALLOY QUENCHED FROM 1425 F

A-11949

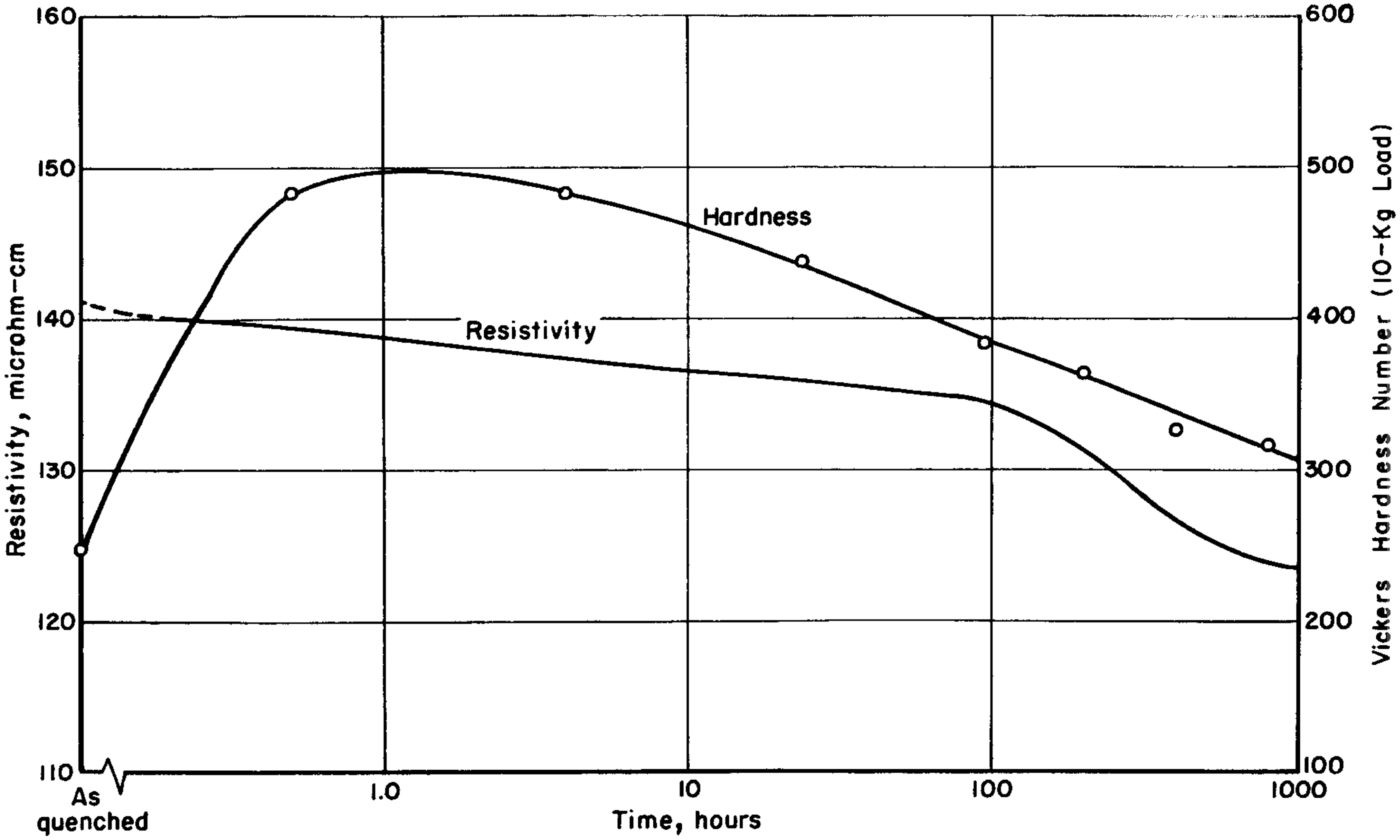


FIGURE 21. EFFECT OF AGING AT 800F ON THE RESISTIVITY AND HARDNESS OF A Ti-10 Mo ALLOY QUENCHED FROM 1325 F

A-11951

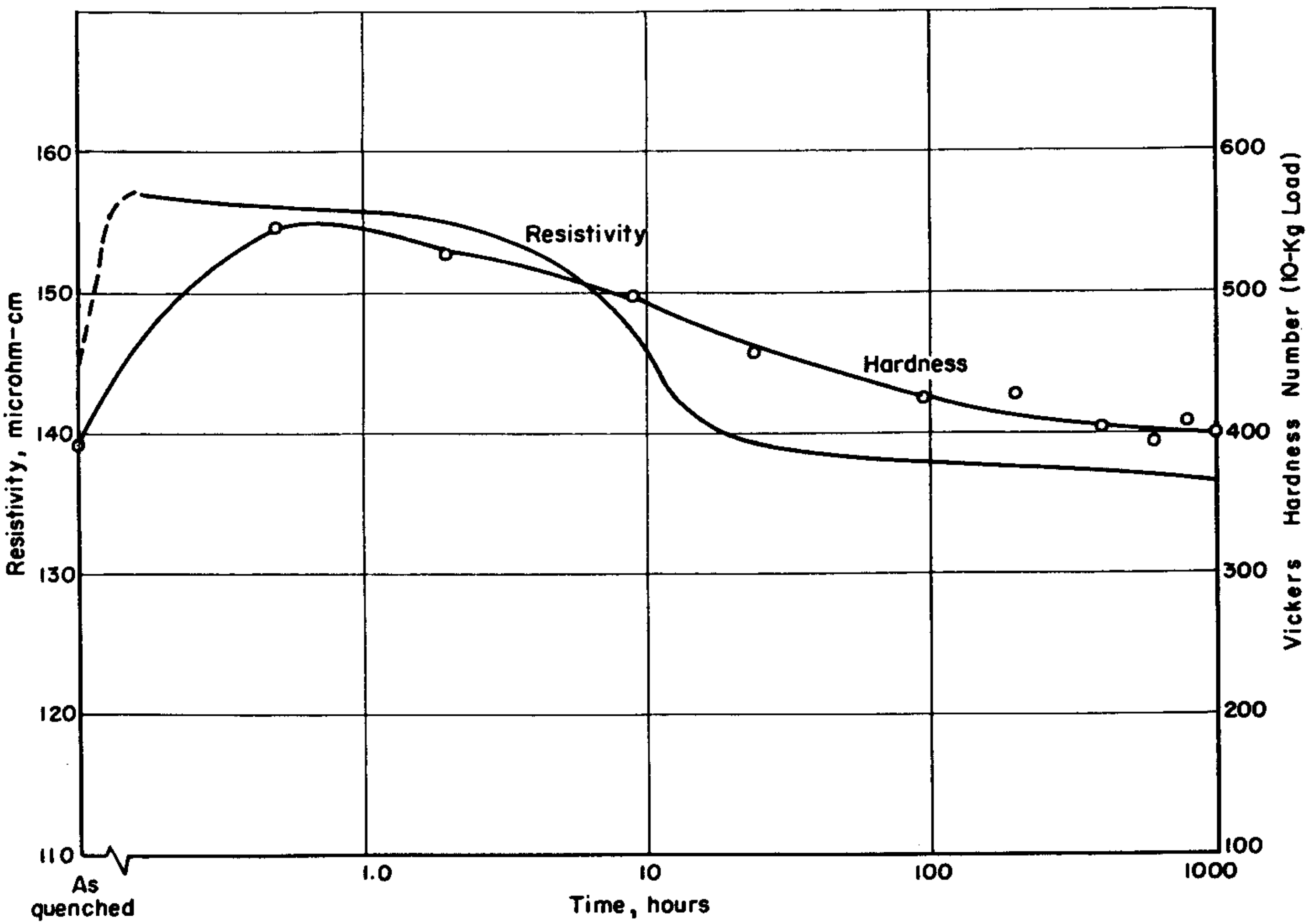


FIGURE 22. EFFECT OF AGING AT 800F ON THE RESISTIVITY AND HARDNESS OF A Ti-3Mn-1Cr-1Fe-1Mo-1 V ALLOY QUENCHED FROM 1400F

A-11962

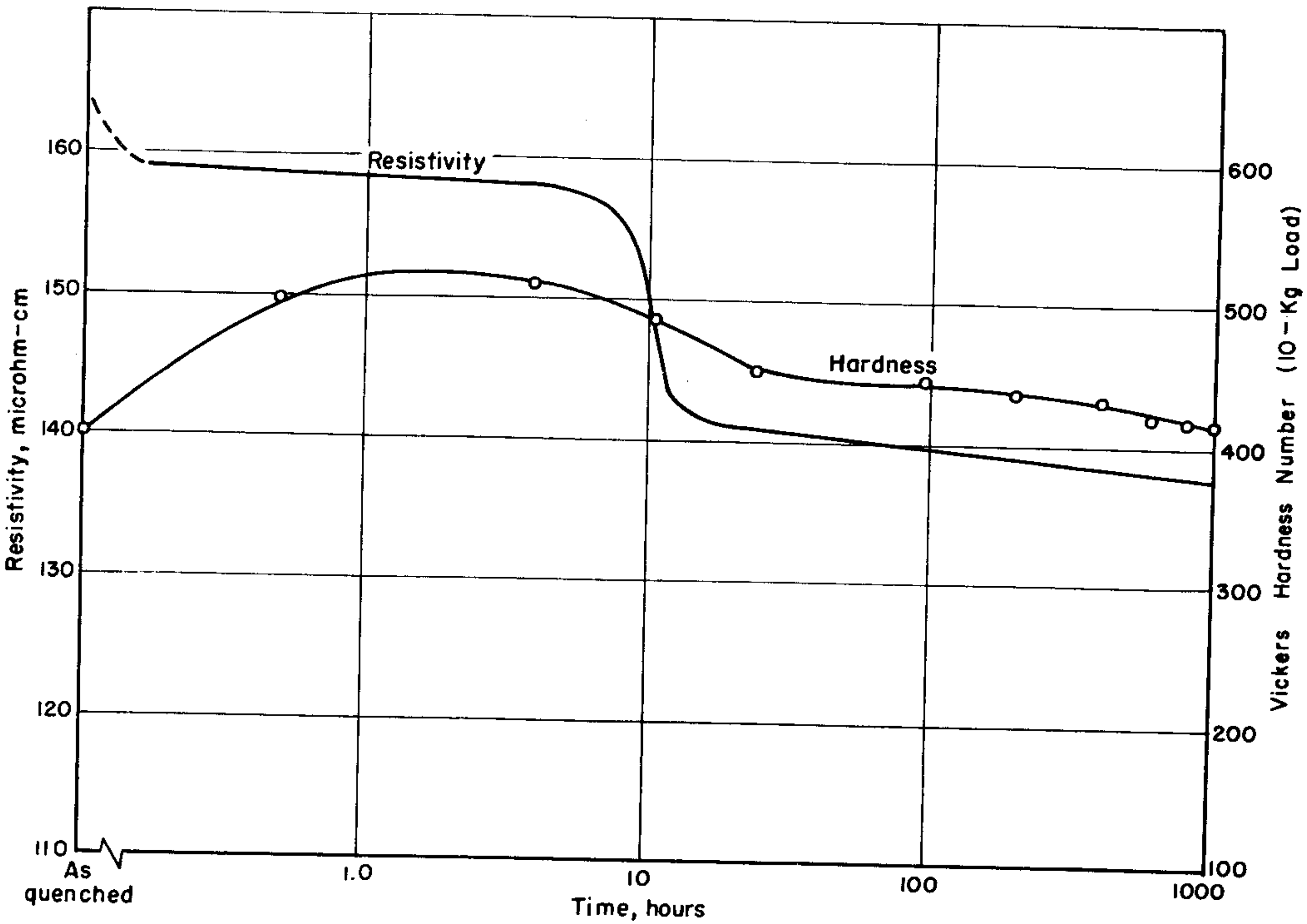


FIGURE 23. EFFECT OF AGING AT 800F ON THE RESISTIVITY AND HARDNESS OF A Ti-3 Mn-1 Cr-1 Fe-1Mo-1V ALLOY QUENCHED FROM 1700 F

A-11951

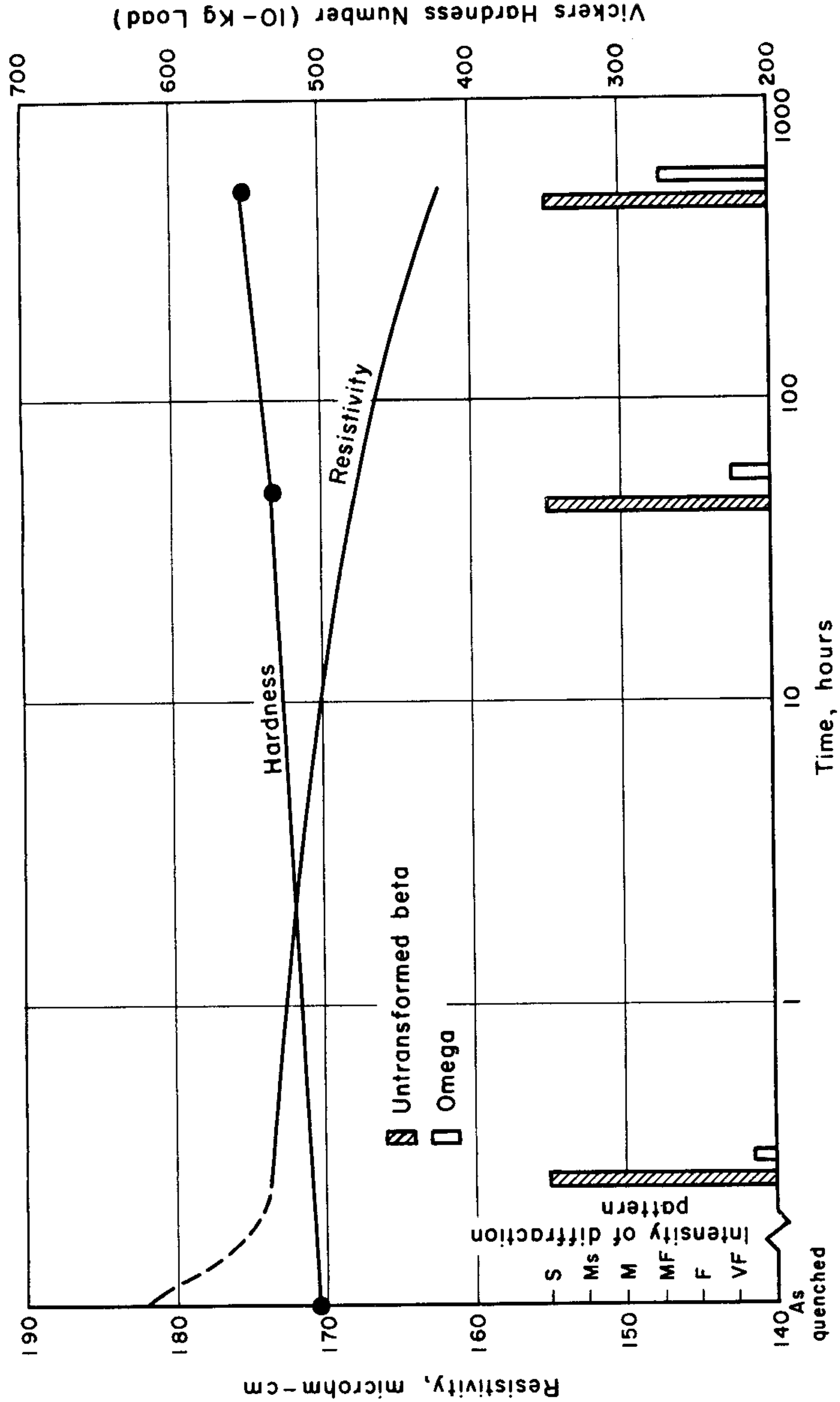


FIGURE 24. EFFECT OF AGING AT 500 F ON THE RESISTIVITY, HARDNESS, AND X-RAY DIFFRACTION-PATTERN INTENSITIES OF A Ti-4Fe ALLOY QUENCHED FROM 1700 F

A-13713

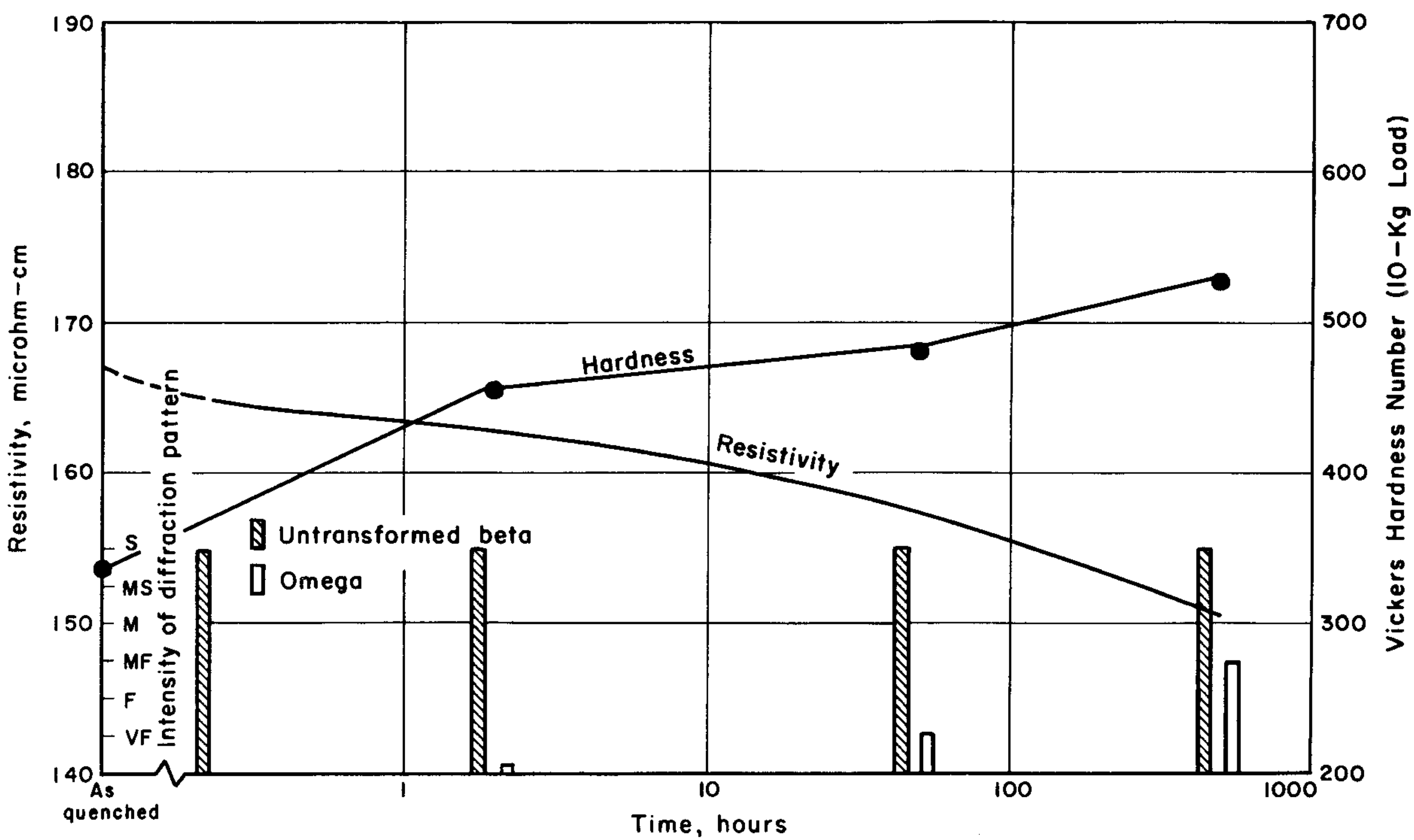


FIGURE 25. EFFECT OF AGING AT 500 F ON THE RESISTIVITY, HARDNESS, AND X-RAY DIFFRACTION-PATTERN INTENSITIES OF A Ti-8Cr ALLOY QUENCHED FROM 1700 F A-13714

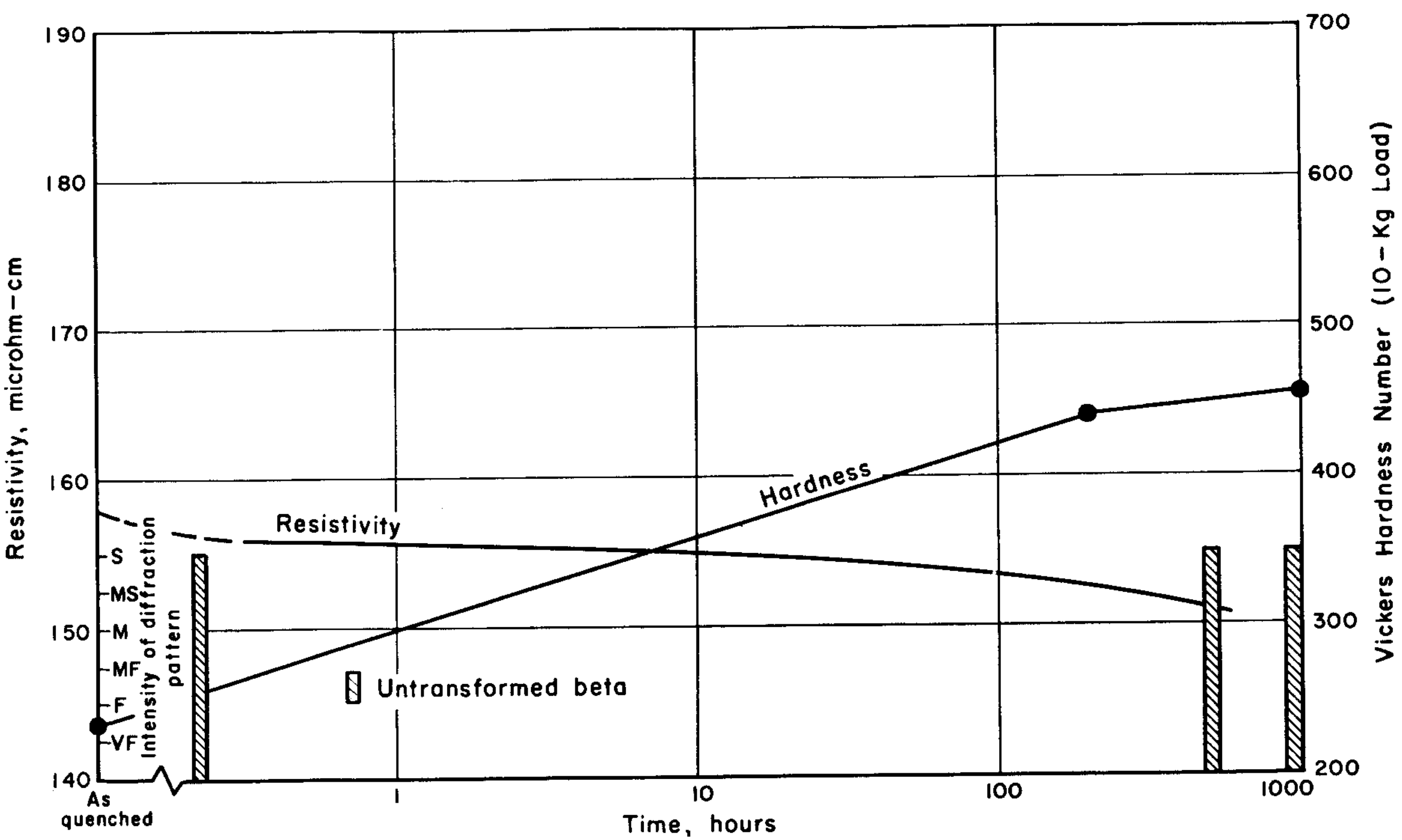


FIGURE 26. EFFECT OF AGING AT 500 F ON THE RESISTIVITY, HARDNESS, AND X-RAY DIFFRACTION -PATTERN INTENSITIES OF A Ti-10Mo ALLOY QUENCHED FROM 1700 F

A-13715

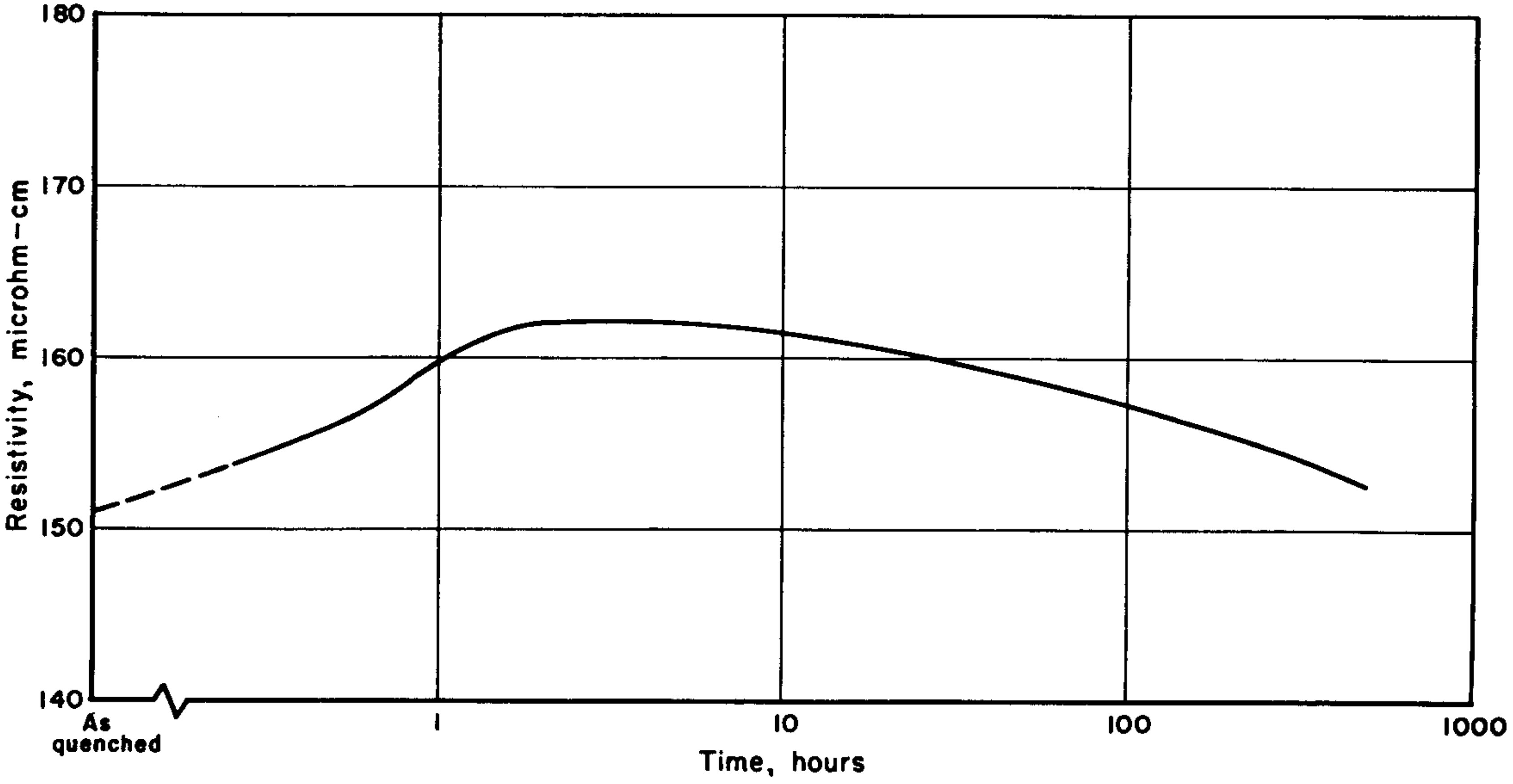


FIGURE 27. EFFECT OF AGING AT 500 F ON THE RESISTIVITY OF A Ti-12Cr ALLOY QUENCHED FROM 1700 F

A-13716

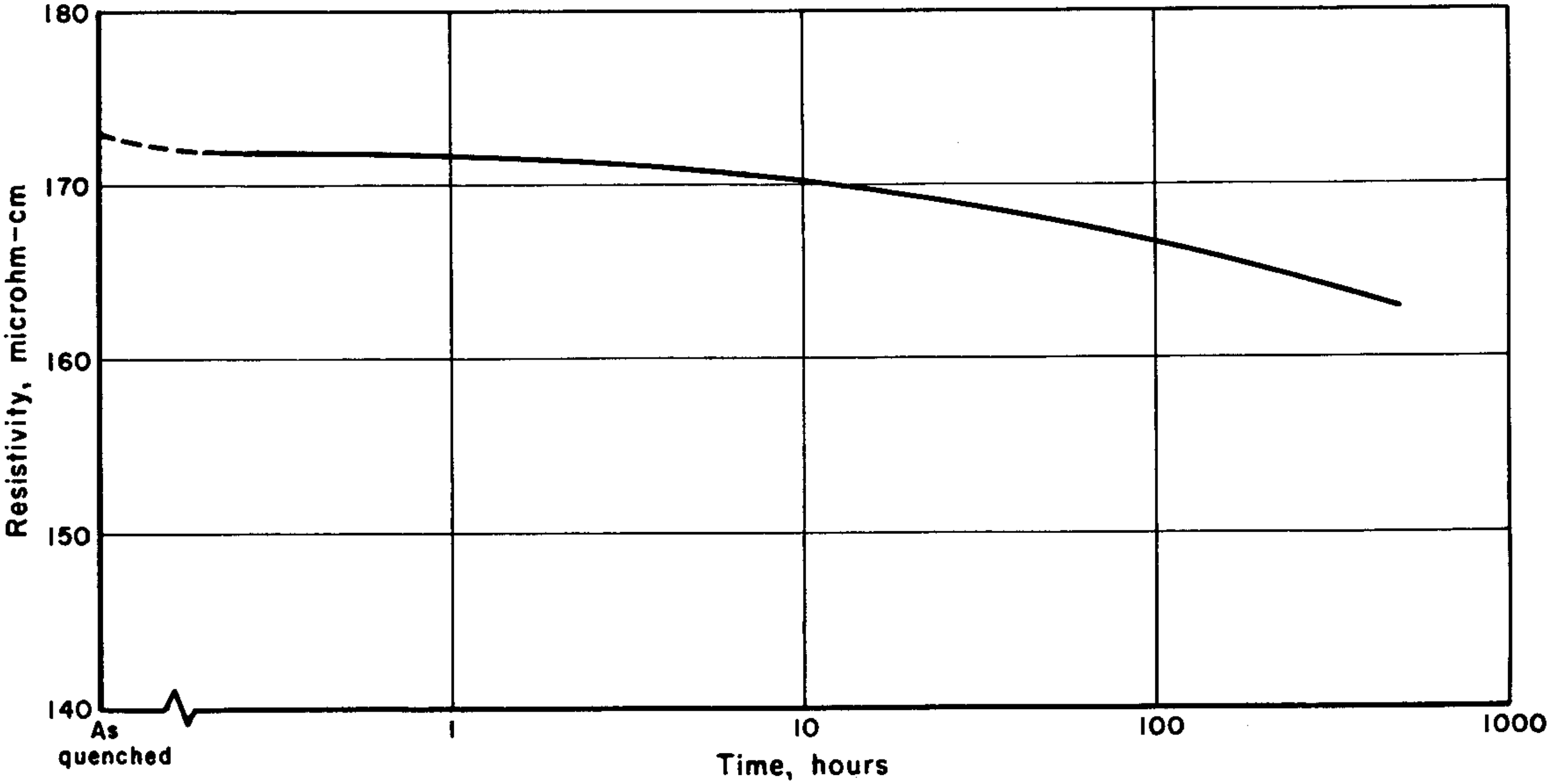


FIGURE 28. EFFECT OF AGING AT 500 F ON THE RESISTIVITY OF A Ti-3Mn-1Fe-1Cr-1Mo-1V ALLOY QUENCHED FROM 1700 F

A-13717

Where 500 F resistivity, hardness, and X-ray diffraction data are available, the results bear out the conclusions drawn from similar tests at 700 and 800 F. The resistivity begins to drop more quickly in the alloys which form omega phase rapidly. In no case did a sharp resistivity change occur during aging at 500 F. Omega-phase formation and the accompanying increase in hardening were still in process at the end of the 500-hour test period for the Ti-4Fe and Ti-8Cr alloys. Omega phase was not detected in the Ti-10Mo alloy after 1000 hours of aging.

The trend of decreasing resistivity with omega-phase formation seems generally established, in spite of the very flat portions of some curves and an indicated increase in the case of the Ti-12Cr alloy. The reason for this initial increase is not evident. However, the high-chromium alloys apparently do not form omega phase as rapidly as the leaner alloys, and the initial increase in resistivity may be an indication of a very early stage of omega formation which cannot be detected in other alloys because of the high reaction rate.

Although the structure of omega phase cannot be considered a simple ordering of the beta phase, its specific atom positioning would probably lead to a lowering of the resistivity of the more random beta phase. However, there are other factors to be considered in the resistivity and the above is probably an oversimplification of the case. The resistivity of beta phase, for example, would increase as it becomes enriched, since impurities generally increase specific resistivities.

METALLOGRAPHIC STUDIES

There has been no definite metallographic evidence of omega phase, although several attempts have been made to secure it. Photomicrographs showing a dark-etching intragranular structure were presented in WADC TR 54-355 as being a possible indication of omega phase. In the present contract, it appeared advisable to review the metallographic work to determine the validity of the identification. A number of specimens in the quenched and in the quenched and aged conditions were selected for examination.

The metallography of titanium has been the subject of some controversy and it seemed advisable to compare a few of the recommended etchants on the type structures encountered in age-hardened alloys. A high-purity Ti-4Fe alloy was examined in both quenched and quenched and aged conditions, using the four etchants listed below:

1.5 per cent HF, 3.5 per cent HNO_3 in H_2O
20 per cent HF, 20 per cent HNO_3 in glycerine
3 cc HF, 1 cc HNO_3, 0.8 g $NaNO_3$ in 100 cc H_2O
50 per cent HF in ethylene glycol.

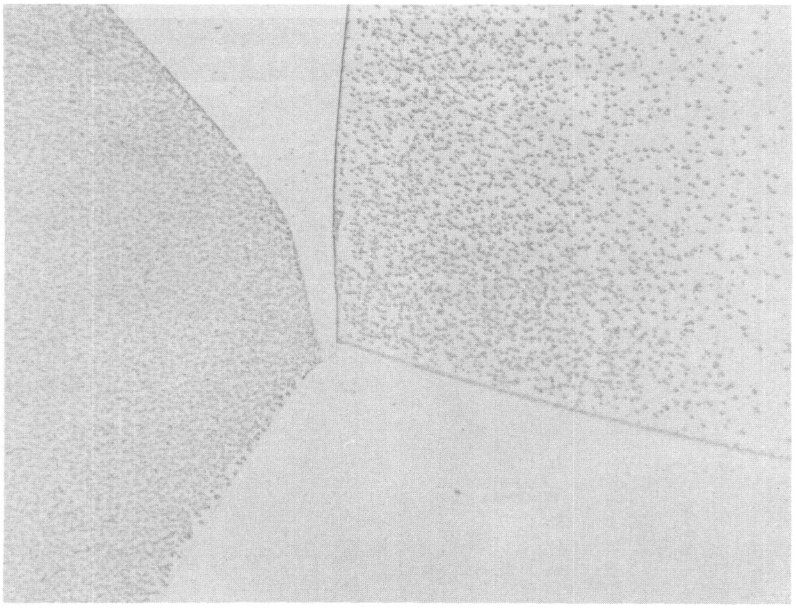
The results are shown in Figures 29 through 32. The etching structure reported earlier was revealed by all four etchants. The 1.5 per cent HF, 3.5 per cent HNO_3 in H_2O etchant appeared to show the dark intragranular structure with the greatest clarity, and it was selected for the remainder of the metallographic program.

Although it was possible to find areas in both as-quenched and quenched and aged specimens of the Ti-4Fe alloy which show the dark-etching structure, the proportion of such areas did increase with the aging time. Since the omega phase was known to be present in this alloy in the as-quenched condition, and to increase in amount with aging, it seemed possible that the observed structure was associated with or dependent upon the formation of the omega phase. However, a series of specimens of a Ti-8Cr alloy quenched from 1700 F, aged at 700 F, and subjected to the same etching procedures showed no evidence of the dark-etching structure, even though omega was known to be present. This is illustrated in Figure 33, which shows the structure of the specimen aged for 24 hours at 700 F. On the other hand, this same alloy aged at 500 F showed the dark-etching structure strongly, as in Figure 34. This photomicrograph was reproduced from WADC TR 54-355. The as-quenched specimen of the Ti-8Cr alloy also showed some evidence of this structure, although no evidence of omega was found in X-ray diffraction work.

A number of specimens which were known to contain omega and had shown the dark-etching structure were subsequently examined by electron microscopy. Initial results indicated that the dark-etching areas were caused by etch pits. The existence of etch pits was confirmed by using a double-shadowing technique on silica replicas made from the etched surfaces of the specimens. The replicas were obliquely shadowed with metal from opposite directions. This resulted in structures of the type shown in Figure 35, which is an electron micrograph of a Ti-8Cr alloy which had been quenched from 1700 F and aged for 1000 hours at 500 F. The light areas are double "shadows" cast during the metal-shadowing process. They indicate that the structures shown are actually ridges in the replica which correspond to pits in the original specimen surface. The etching structure shown in Figure 35 gave rather strong indications of a fine lamellar structure. This type structure was frequently evident but, in many areas, the etch pits did not fall into a discernible pattern.

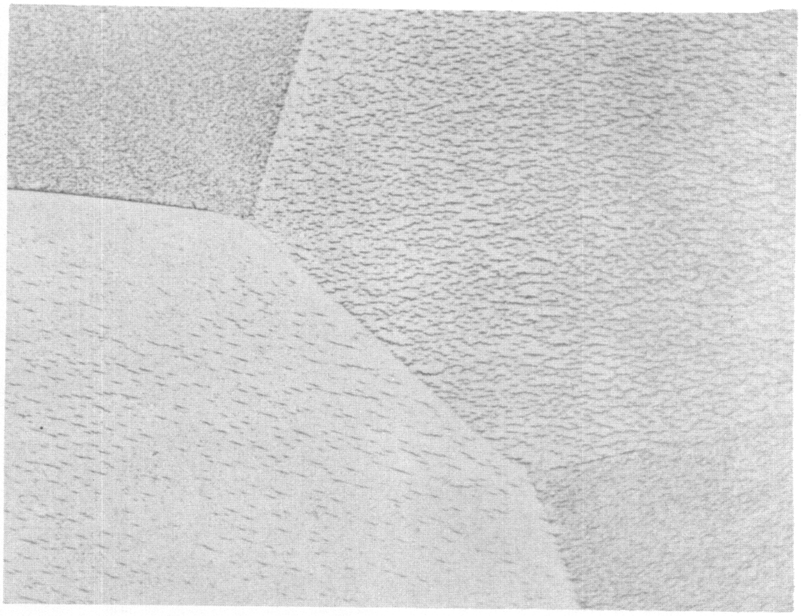
It is evident that the results of the metallographic examinations were, as a whole, inconclusive so far as the identification of omega phase is concerned. There was evidence in the Ti-4Fe alloy that could be associated with omega formation. However, the results of the examination of the Ti-8Cr alloy were inconsistent. The investigation was not an extensive one, and it is possible that other techniques could produce more consistent results.

The identification of the omega phase by metallography could be very difficult, taking into consideration the structure as determined by X-ray



500X N19151

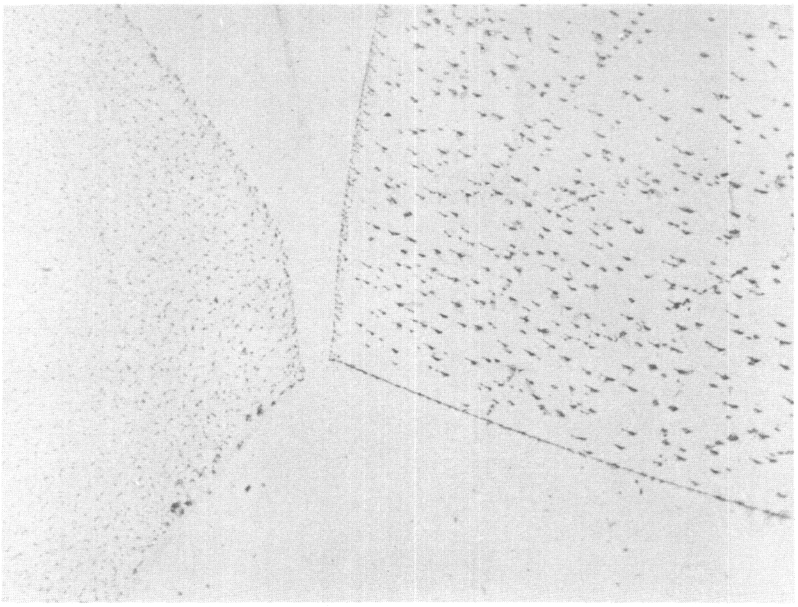
Heated 1/2 Hour at 1700 F and Quenched in Iced Brine



500X N19152

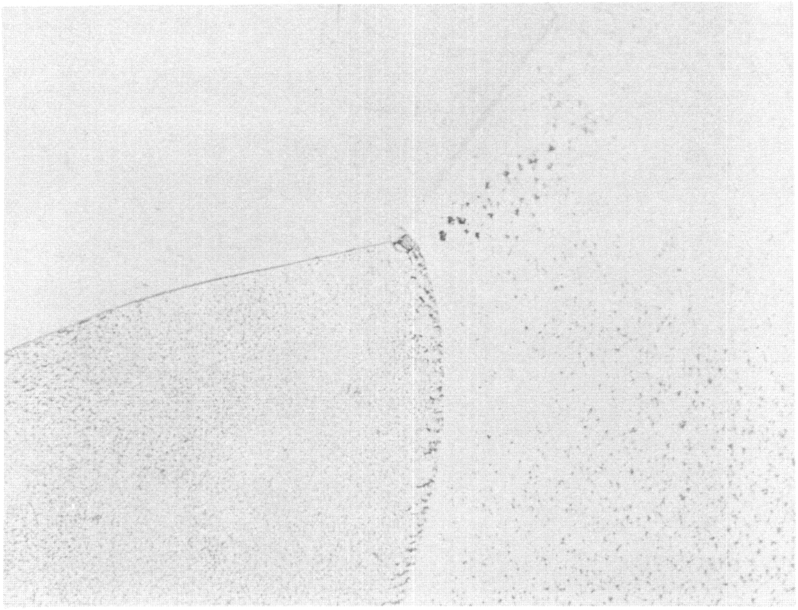
Heated 1/2 Hour at 1700 F, Quenched in Iced Brine, and Aged 24 Hours at 700 F

FIGURE 29. Ti-4Fe ALLOY ETCHED IN 1.5 PER CENT HF, 3.5 PER CENT HNO_3 IN H_2O ETCHANT



500X N19153

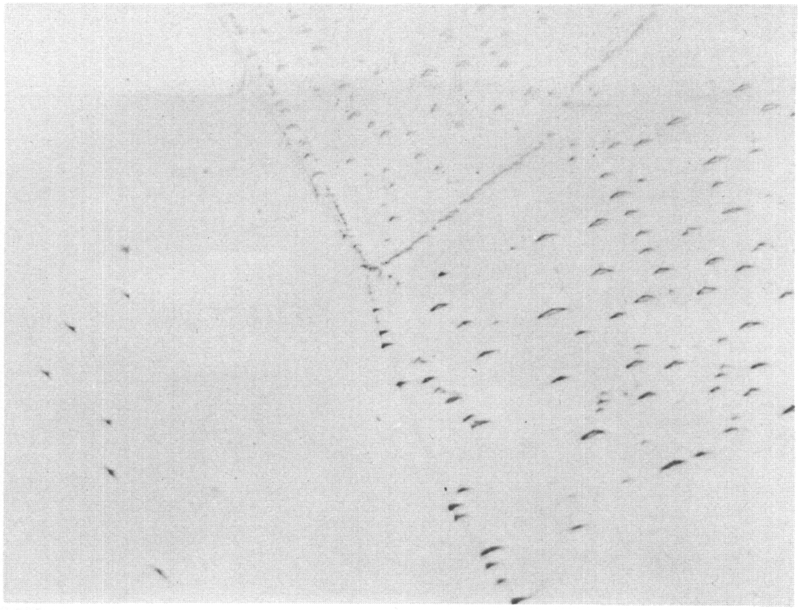
Heated 1/2 Hour at 1700 F and Quenched in Iced Brine



500X N19154

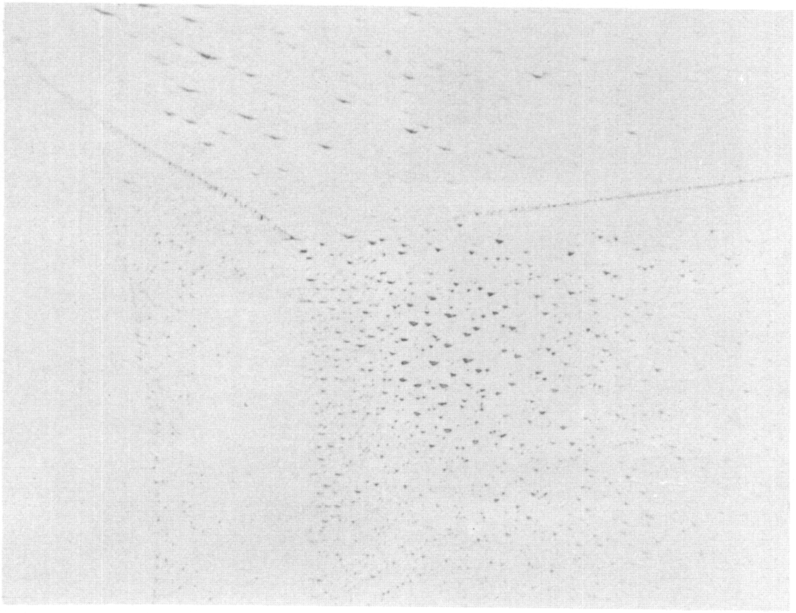
Heated 1/2 Hour at 1700 F, Quenched in Iced Brine, and Aged 24 Hours at 700 F

FIGURE 30. Ti-4Fe ALLOY ETCHED IN 20 PER CENT HF, 20 PER CENT HNO_3 IN GLYCERINE ETCHANT



500X N19155

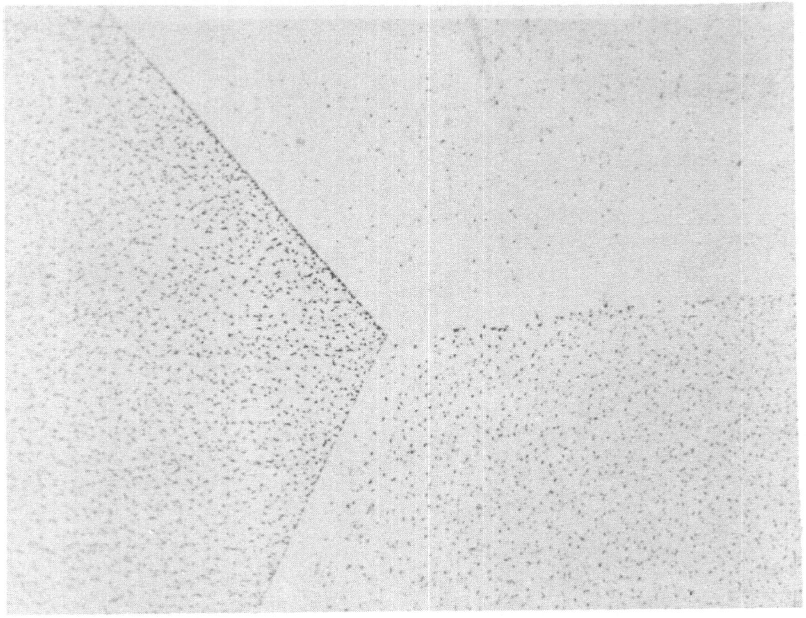
Heated 1/2 Hour at 1700 F and Quenched in Iced Brine



500X N19156

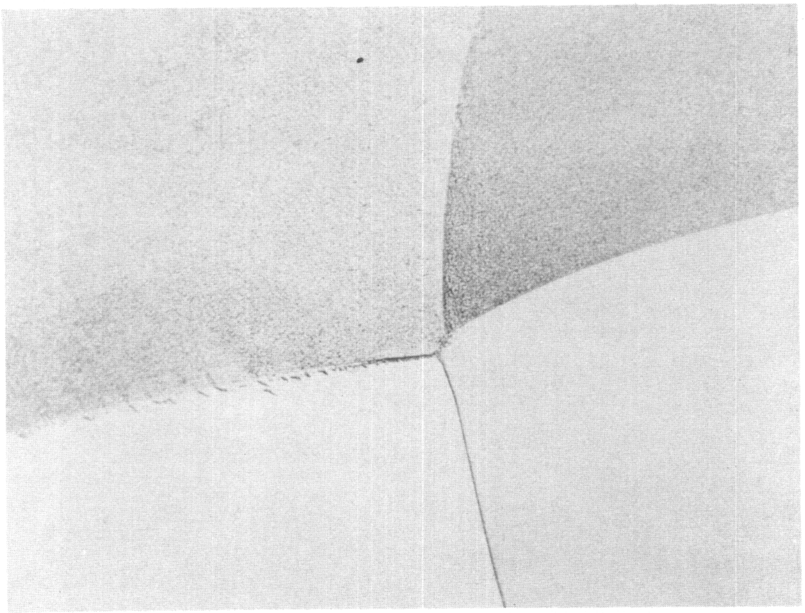
Heated 1/2 Hour at 1700 F, Quenched in Iced Brine,
and Aged 24 Hours at 700 F

FIGURE 31. Ti-4Fe ALLOY ETCHED IN 3 CC HF, 1 CC HNO_3, 0.8 G $NaNO_3$ IN 100 CC H_2O ETCHANT



500X N19157

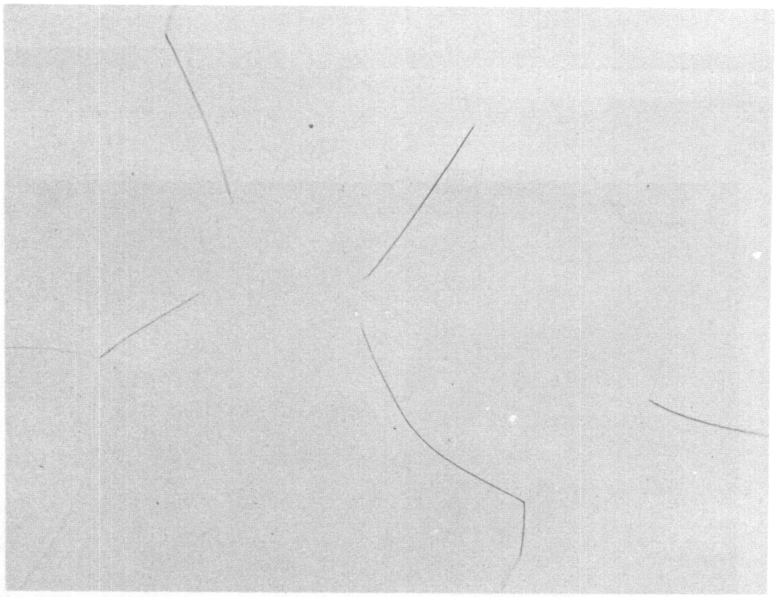
Heated 1/2 Hour at 1700 F and Quenched in Iced Brine



500X N19158

Heated 1/2 Hour at 1700 F, Quenched in Iced Brine, and
Aged 24 Hours at 700 F

FIGURE 32. Ti-4Fe ALLOY ETCHED IN 50 PER CENT HF IN ETHYLENE GLYCOL ETCHANT

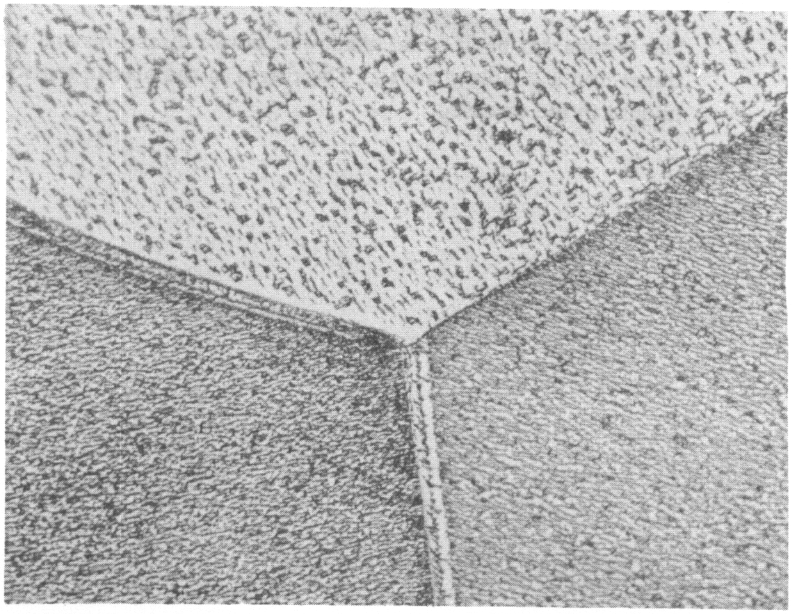


250X

N19171

FIGURE 33. Ti-8Cr ALLOY SOLUTION TREATED 1/2 HOUR AT 1700 F, QUENCHED IN ICED BRINE, AND AGED 24 HOURS AT 700 F

Etched in 1.5 per cent HF, 3.5 per cent HNO_3 in H_2O etchant. The same lack of structure is obtained when many other etchants, including 50 per cent HF-50 per cent ethylene glycol, are used on the alloy in this condition. Compare lack of structure with the etching effect obtained with HF-ethylene glycol etch on same alloy aged at 500 F, Figure 34.



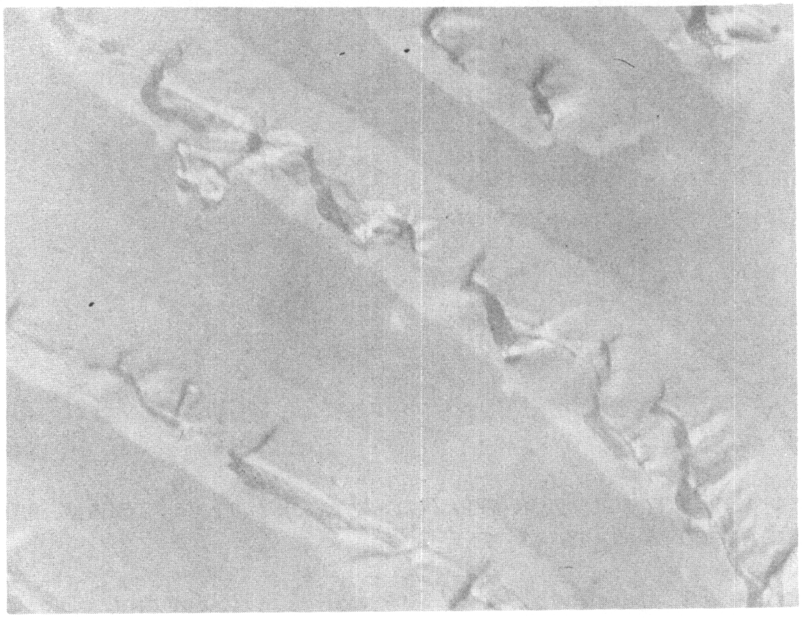
500X

N5772

50 Per Cent HF - 50 Per Cent Ethylene Glycol Etch

FIGURE 34. Ti-8Cr ALLOY, ICED-BRINE QUENCHED FROM 1700 F AND AGED 8 HOURS AT 500 F

Dark-etching areas may be associated with the omega phase.



7500X N20675

FIGURE 35. SILICA REPLICA OF Ti-8Cr ALLOY, SOLUTION TREATED AT 1700 F, QUENCHED, AND AGED 1000 HOURS AT 500 F

The replica has been metal shadowed in two directions and the long ridges cast a double shadow. The ridges in the plastic replica indicate troughs in the sample.

diffraction. Because of the basic similarities in structure and orientation, the etching characteristics of the beta phase and the omega phase may be similar to the point that the phases are indistinguishable. The comparison of omega phase with gamma brass may extend into metallography. Although it has been the subject of considerable research over recent years, there is no reliable metallographic means of showing gamma brass.

AUTORADIOGRAPHY

The X-ray diffraction work throughout the study on omega-phase formation has indicated an accompanying alloy enrichment of the parent beta phase. Radioactive tracers in autoradiography would offer a means of confirming the observation if the crystallographic units were sufficiently large. The resolution of autoradiography under ideal conditions is of the order of 2 to 5 microns.

The radioactive tracer materials may be introduced in the original melt or the alloy may be bombarded to produce radioactivity. Neutron irradiation of the fabricated and aged alloys offered very definite advantages and was possible in high-purity binary alloys, since the titanium isotopes produced decay to low levels in several days. One isotope of iron, Fe^{59}, has a half life of 47 days and was ideal for use up to approximately 4 months after irradiation.

The nominal composition of the alloy selected for autoradiographic examination was 4 per cent iron. The irradiated specimens were 1/8-inch disk sections from the Ti-4Fe alloy which had been rolled and swaged to 1/4-inch rod. The disks were given a solution treatment at 1700 F and subsequently aged at 800 F for periods up to 72 hours. Unirradiated samples were used for controls throughout the work. The specimens were given a 7-day neutron irradiation by the Oak Ridge National Laboratories. The series of irradiated and control specimens are listed in Table 10. The odd-numbered specimens were neutron bombarded and the even-numbered specimens were used as controls.

All specimens were mounted in Bakelite metallographic mounts after irradiation. Preliminary experiments indicated a tendency for chemical reaction between the titanium alloy and the photographic emulsion during processing. It was, therefore, necessary to place a protective plastic film, approximately 1 micron thick, on the metal surface. Since the resolution of the technique depends upon closeness of contact between the metal and photographic emulsion, the plastic coating resulted in a resolution reduction to approximately 10 to 20 microns.

TABLE 10. AGING TIMES OF Ti-4Fe SPECIMENS USED FOR AUTORADIOGRAPHY AND CONTROLS[(a)]

Specimen[(b)]	800 F Aging Treatment
1	As quenched
2	As quenched
3	1 hour
4	1 hour
5	4 hours
6	4 hours
7	8 hours
8	8 hours
9	24 hours
10	24 hours
11	72 hours
12	72 hours

(a) Specimens solution treated at 1700 F and ice-brine quenched.

(b) Odd-numbered specimens were irradiated and the even-numbered specimens served as controls.

A small portion of one specimen was not mounted in Bakelite but was used for a radioactivity assay. There was an unknown contaminating radioisotope present which had a half life of approximately 3 days. The decay of this material was followed until the activity dropped to an insignificant level in approximately 25 days. The autoradiographs prepared after this time were produced almost entirely by the beta radiation emitted by Fe^{59}.

The details of autoradiographic procedures for high-resolution work have been developed by H. J. Gomberg at the University of Michigan(8). Minor modifications are often necessary to produce the best results in a particular case. The process as used in this work is outlined below. All emulsion manipulations were performed in a darkroom:

(1) The Bakelite mount was immersed for 10 seconds in a 1 per cent solution of Vinylite plastic in methyl ethyl ketone. The solution was allowed to drain from the specimen surface held vertically for 30 seconds. After a 2-minute air dry, the mount was heated for 30 minutes at 18 inches from a heat lamp.

(2) The coated specimens were then immersed in a water bath held at 68 F and containing 1 per cent by weight of alkyl aryl sodium sulfonate (Wyandotte Chemicals designation: Krelon 8-G Wetting Agent 1). A piece of Kodak permeable base autoradiographic stripping film was cut somewhat smaller than the mount face. The emulsion was stripped from its cellulose backing and floated emulsion side down on the surface of the water. After the film was allowed to swell for 1 minute, the specimen, tilted at an approximately 45-degree angle, was brought gently up under the emulsion until both were clear of the bath.

(3) With the film thus attached, the 3-hour exposure began in a desiccator. Approximately 1/2 hour before the conclusion of the exposure time, the specimen was removed from the desiccator and allowed to come into equilibrium with the darkroom atmosphere.

(4) The emulsions were developed 6 minutes in an Acrol developer held at 68 F. A wash in water of 3 to 5 seconds followed development and the emulsions were fixed for 2 minutes in Kodak F-5 hypo. A final wash of 5 minutes in water completed photographic processing.

(5) The dried emulsions were examined in place by conventional metallographic techniques.

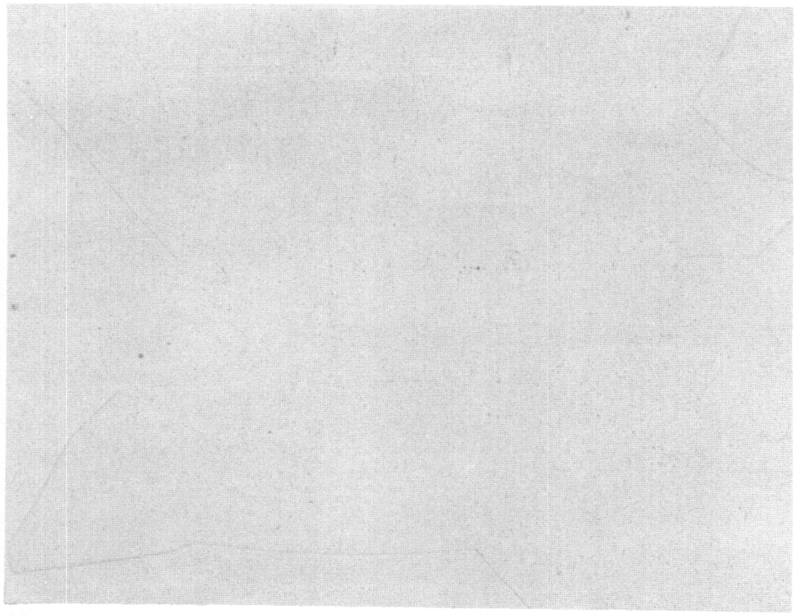
Examples of photomicrographs of the autoradiographs appear in Figures 36, 37, and 38. In most cases, it is possible to obtain the exposed silver distribution and the associated metallographic structure in a single exposure. In cases where the etched metallographic structure texture interfered, an autoradiograph was made on a polished but unetched surface.

The as-quenched solution-treated specimens may be compared in Figures 36a and 36b. In Figure 36a, the control sample shows the etched structure with only a few artifacts in the photographic emulsion. This type autoradiograph resulted from the control samples in all cases. The exposed silver grain distribution is quite apparent in Figure 36b, which has been neutron irradiated. The developed silver grains show a rather even distribution, indicating a uniform distribution of the iron atoms in solid solution.

The effect of an 8-hour aging treatment is shown in Figures 37a and 37b. In this case, a polished and etched surface is shown in Figure 37a, while Figure 37b has not been etched. The microstructure revealed in the area shown seems to indicate a second phase at the grain boundaries, which is not revealed by the autoradiograph of the unetched specimen. Again, the distribution of the exposed and developed silver grains does not show a pattern of concentrations, even though omega is known to be present in this specimen in considerable amounts.

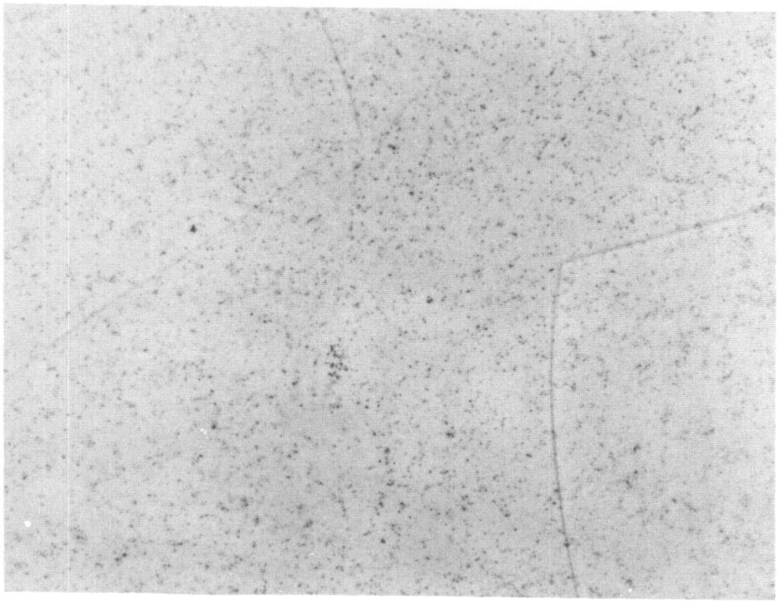
Autoradiographs of specimens after 72 hours of aging at 800 F are shown in Figures 38a and 38b; again, a comparison of etched and unetched surfaces. On the unetched sample, there was a tendency for the developed grains to appear in clouds, leaving other adjacent areas lower in iron concentration. This segregation of the iron would be expected since there is both metallographic evidence in Figure 38a and X-ray diffraction evidence from earlier work that considerable amounts of alpha and enriched beta were present in this specimen. The alpha appears in Figure 38a as a fine Widmanstätten structure.

Thus, the autoradiographic work showed no clear evidence of omega formation and the concurrent alloy enrichment of the parent beta phase. The crystallographic structure proposed earlier in the report for the omega phase evidently develops on a scale that is not shown within the limits of the autoradiographic technique. The alpha precipitation at 800 F, however, is on a large enough scale to be shown by these techniques.



250X N19287

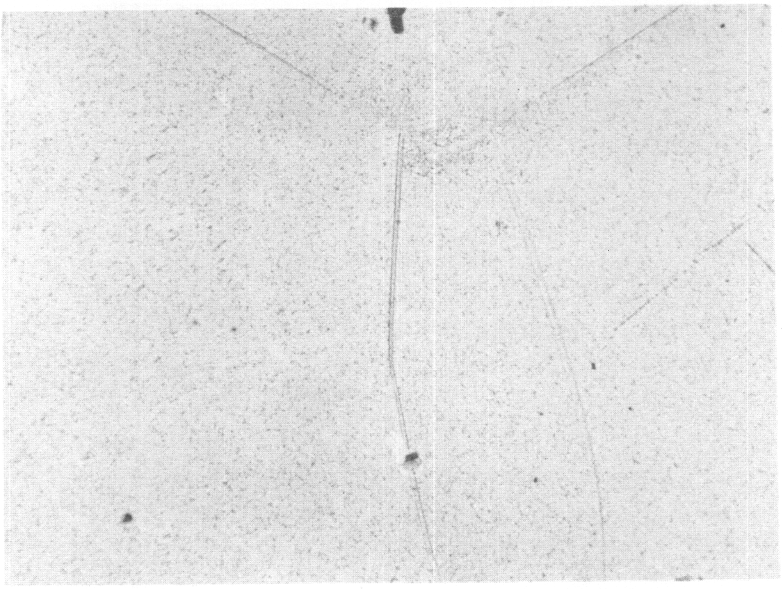
Control Specimen - Not Irradiated



500X N19293

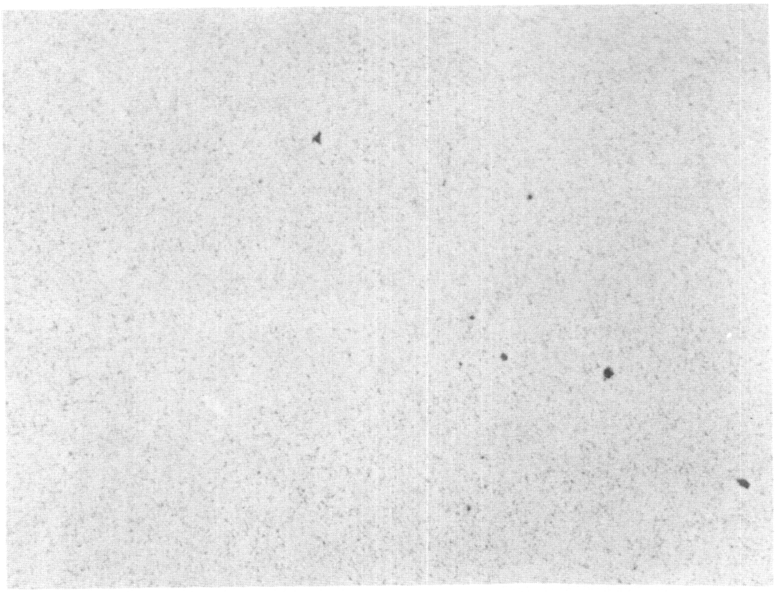
Radioactive Specimen

FIGURE 36. AUTORADIOGRAPHS OF CONTROL SPECIMEN 1 AND RADIOACTIVE SPECIMEN OF Ti-4Fe ALLOY QUENCHED AFTER 1 HOUR AT 1700 F



250X N19289

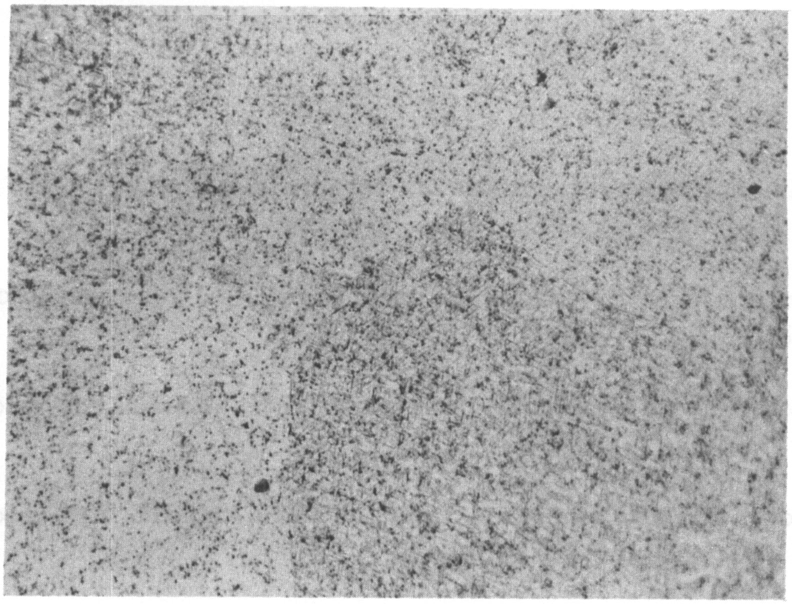
Polished Surface Etched in 1.5 per cent HF-3.5 per cent HNO_3



250X N19288

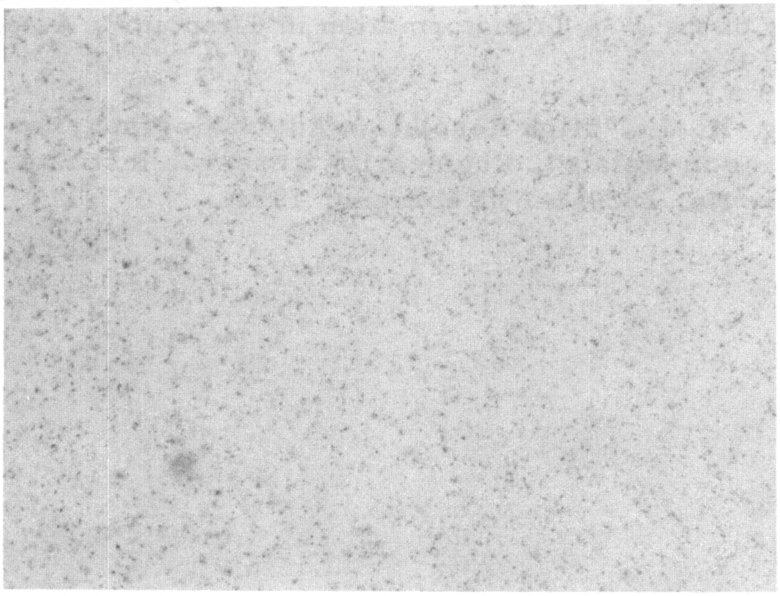
Polished Surface, Unetched

FIGURE 37. AUTORADIOGRAPHS OF RADIOACTIVE Ti-4Fe ALLOY AFTER 1 HOUR AT 1700 F, QUENCHED, AND AGED AT 800 F FOR 8 HOURS



500X N19290

Etched in 1.5 Per Cent HF-3.5 Per Cent HNO_3



500X N19312

Unetched

FIGURE 38. AUTORADIOGRAPHS OF RADIOACTIVE Ti-4Fe ALLOY AFTER 1 HOUR AT 1700 F, QUENCHED, AND AGED AT 800 F FOR 72 HOURS

REFERENCES

(1) "Research and Development on Titanium Alloys", Air Force Technical Report No. 6218, Part 2 (June, 1950).

(2) "Development of Titanium-Base Alloys", Air Force Technical Report No. 6623 (June, 1951).

(3) "Development of Titanium-Base Alloys", WADC Technical Report 52-249 (June 18, 1952).

(4) "Development of Titanium-Base Alloys", WADC Technical Report 52-334 (December 31, 1952).

(5) "Precipitation Hardening and Embrittlement of High-Strength Titanium Alloys", WADC Technical Report 54-355 (June, 1954).

(6) Barrett, C. S., Structure of Metals, Second Edition, McGraw-Hill Book Company, Inc. (1952).

(7) Williams, A. J., Cahn, R. W., and Barrett, C. S., "The Crystallography of the β-α Transformation in Titanium", Acta. Metallurgica, 2, 117 (1954).

(8) Gomberg, H. J., "High Resolution Autoradiography for Study of Grain Boundaries in Metals", Engineering Research Institute, University of Michigan, No. 2029-1-F (February, 1954).

APPENDIX

The equation for calculating the density of a beta-omega-phase mixture was derived as follows.

The lattice-constant data on beta show a linear change up to 20 atomic per cent chromium. The calculated density of beta would, therefore, also be linear and is given by

$$\rho \text{ beta} = 4.49 + 2 \times \text{atomic fraction Cr in beta.}$$

Assuming constant composition of omega with a chromium concentration of 3.7 atomic per cent, the density of omega was calculated to be 4.62. If in the partially transformed specimen the fraction of omega is denoted as x, the fraction of beta is then 1 - x. The total atomic per cent chromium may be denoted as K. Then the portion of the chromium of the specimen in omega is 0.037x, and that in beta is K -0.037x. The concentration of chromium in beta is $\frac{K - 0.037x}{1 - x}$. For the 8 weight per cent chromium alloy K = 0.075. Then density of enriched beta is given by

$$\rho \text{ beta} = 4.49 + 2 \times \frac{0.075 - 0.037x}{1 - x} .$$

Assuming that the mean density is linear, then

$$\rho \text{ specimen} = x \ \rho \text{ omega} + (1 - x) \ \rho \text{ beta},$$

or

$$\rho = 4.62x + (1 - x)\left(4.49 + 2 \times \frac{0.075 - 0.037x}{1 - x}\right)$$

$$= 4.64 + 0.066x.$$

Similarly, for the assumption of a defect structure of a 52-atom cell, the same as gamma brass, the density of omega is 4.41. Then the mean density is given by

$$\rho = 4.41x + (1 - x)\left(4.49 + 2 \times \frac{0.075 - 0.037x}{1 - x}\right)$$

$$= 4.64 - 0.13x.$$