

**PRECIPITATION HARDENING AND EMBRITTLEMENT
OF HIGH-STRENGTH TITANIUM ALLOYS**

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FOREWORD

This report was prepared by the Battelle Memorial Institute under USAF Contract No. AF 33(616)-445. The contract was initiated under Task No. 73510, "Heat Treatment of Titanium Alloys", formerly RDO No. 615-11, "Stress Relief of Titanium", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. E. F. Erbin acting as project engineer.

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Representative alloys of the Ti-Cr, Ti-Fe, and Ti-Mo systems were quenched to retain the beta phase and aged at temperatures in the range 500 to 1000 F for periods up to 1000 hours. The changes which occurred in the alloys were followed by means of X-ray diffraction, hardness, and electrical resistivity. From this data it was concluded that the decomposition of the retained beta phase occurred in three major stages:

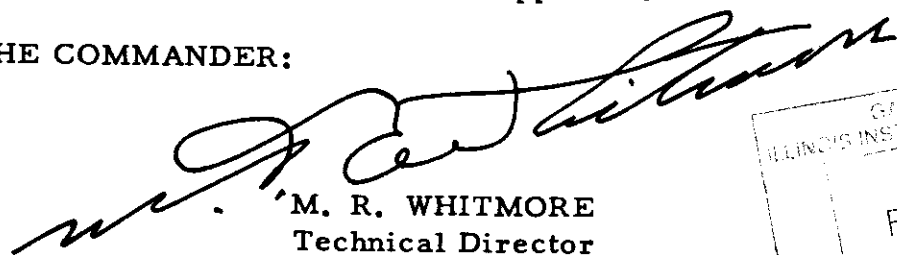
- (1) Precipitation of a metastable transition phase, omega, which apparently causes age hardening. At the same time the beta phase seems to become locally enriched in alloy. Hardness increased to very high values during this stage.
- (2) The omega phase disappears and the alpha phase makes its appearance. The remaining beta phase becomes highly enriched in alloy. Both hardness and resistivity decrease sharply during this stage.
- (3) In the eutectoid systems (Ti-Cr and Ti-Fe), the highly enriched beta decomposes into alpha plus compound. In the Ti-Fe alloys, this stage was accompanied by a further drop in hardness and resistivity. In the Ti-Cr system there is little change in these properties.

The structure of the omega phase has not yet been determined. However, it was shown to be common to at least the majority of beta-stabilized titanium alloy systems, and was apparently not affected by the interstitial impurity content of the alloys.

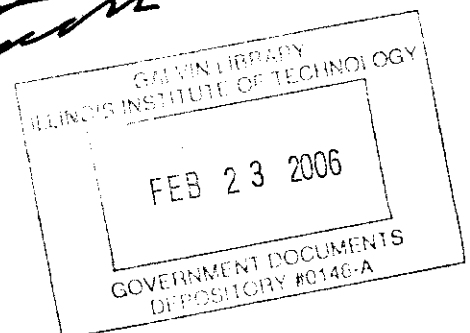
PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



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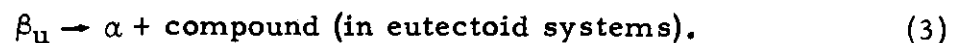
SUMMARY

The work described in this report is a continuation of the study of the age hardening of titanium alloys which was begun under Contract No. AF 33 (038)-3736. The reactions which occur during the decomposition of retained beta to its equilibrium products at temperatures up to 800 F were established. The new phase, omega, which was discovered under the previous contract was shown definitely to be involved in the age hardening of beta-stabilized titanium alloys. Its existence as a metastable transition phase in the transformation of beta to alpha titanium was confirmed. The structure of omega and the mechanism of its formation have not yet been determined.

The following types of binary alloys, which represent both eutectoid and beta-isomorphous systems, were studied:

Ti-Mn
Ti-Fe
Ti-Cr
Ti-Mo

In addition, a complex Ti-3Mn-1Cr-1Fe-1Mo-1V alloy and alloys containing hydrogen and oxygen were investigated. Alloys prepared from both commercial-purity and high-purity titanium were included in the investigation. The reactions that occurred in the alloys during aging at temperatures in the range 500 to 1000 F were ascertained by means of hardness changes, X-ray diffraction examination, and changes in electrical resistivity. The decomposition of the retained-beta phase, as revealed by these experiments, may be expressed by the following equations:



In these equations, β_o represents retained beta of the original alloy content. The β_r is beta somewhat enriched in alloy while β_u represents beta of essentially the highest alloy content attainable at the reaction temperature. The β_r phase was indicated in diffraction photograms by streaking of the original beta spots in the direction of increasing Bragg angle. Generally, Equation (1) represents the reaction that occurred during hardening. Equations (2) and (3) applied during the overaging that occurred upon extended heating at

700 and 800 F. The rates at which these reactions proceeded at a given temperature were much slower in the Ti-10Mo system than in the Ti-Fe or Ti-Cr alloys.

Rates of formation and decay of the omega phase were not affected by the presence of small amounts of interstitial impurities, such as hydrogen and oxygen. Solution treatment in either the beta or alpha-plus-beta-phase regions did affect the initial resistivity and hardness measurement, but the values characteristic of the system after omega formation were about the same for either pretreatment mentioned.

X-ray diffraction work on specimens of Ti-Cr, Ti-V, Ti-Ni alloys and the Ti-Mn complex alloy indicated that an observed deviation from linearity in the thermal-expansion curve of beta-quenched alloys may be due to formation of the omega phase*. Specimens of several alloys quenched after heating to temperatures of 600 and 800 F showed evidence of omega.

Some progress was made on the study of the structure of the omega phase and the crystallographic mechanism by which it forms. For this work, it is necessary to use single crystals, and considerable difficulty was encountered in producing crystals of sufficient perfection. This work is being continued under the extension of the present contract.

INTRODUCTION

Titanium, like many other metals, exists in two allotropic forms. The pure-alpha phase is a hexagonal close-packed structure stable at temperatures up to about 1625 F (885 C). The beta phase is body-centered cubic, and is stable between 1625 F and the melting point of approximately 3150 F (1732 C). The addition of certain alloying elements, e.g., chromium, iron, molybdenum, vanadium, or manganese, tends to stabilize the beta phase to lower temperatures. Alloy composition and heat treatment are the most important factors in strength-ductility relationships which are so important at the present stage of titanium-alloy development. Present use of alloy contents up to 10 per cent produces a high-strength alloy in which considerable quantities of the high-temperature phase are retained at room temperature. The desirable strength and hardness levels possible in these alloys are due, at least in part, to precipitation hardening in the retained-beta phase. The alloys cannot be used in the fully hardened condition because of the severe embrittlement which accompanies the precipitation reaction.

*Adenstedt⁽⁵⁾ first observed this deviation in a Ti-15V alloy.

Contracts

Age hardening in titanium alloys has been studied extensively under Contract No. AF 33(038)-3736(1, 2, 3, 4). This work showed that hardening may occur when alloys are cooled at critical rates from equilibrium beta-phase temperatures or by artificially aging, at 200 to 700 F, alloys previously quenched from the alpha-beta or beta-phase regions. Aging at temperatures above 700 F produced overaging and softening. Alloys aged at 700 F showed high strength although they were low in ductility.

Contrary to the postulate of Adenstedt, et al. (5), that hardening is caused by precipitation of alpha from metastable beta phase, the investigation of Ti-Mn alloys (under Contract No. AF 33(038)-3736) revealed an unidentified group of X-ray diffraction lines^(3, 4) which appeared to be associated with the hardening phenomenon. These were attributed to a new phase which was tentatively assigned the name "omega". The new phase was first found in a Ti-8Mn alloy transformed isothermally at 450 C (842 F) for times up to 1 hour. Longer treatments were effective in precipitating alpha phase and the omega phase disappeared. The omega phase thus appeared to be a metastable transition phase in the transformation from beta to alpha phase. The omega phase has since been detected in aged specimens of Ti-8Cr, Ti-4Fe, Ti-5Fe, and Ti-10Mo alloys.

In the present contract, it was to be established whether the omega phase is an impurity phase or an impurity-sensitive phase dependent upon such impurities as hydrogen and oxygen, and whether it is a transition phase or stable phase in aged alloys. A fundamental study of omega phase was to be made to determine its composition, structure, and mechanism of formation and decay. The ultimate objective was definition of the hardening mechanism and embrittlement caused by it. Definition of the precise mechanism of hardening could contribute to the development of better high-strength alloys or heat treatment for known alloys.

EXPERIMENTAL PROCEDURES

Basic Techniques

The age-hardening studies under Contract No. AF 33 (038)-3736^(1,2,3,4) lead to a research program under the present contract, with the primary objective of studying the formation of omega phase and its relation to the observed aging. Omega-phase formation and age hardening were both accepted as valid, but the relation between the two remained to be established.

A number of methods of attack were considered and pursued to some degree. The most extensive experimental work was in the fields of hardness measurement, electrical resistivity, and X-ray diffraction.

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Initially, hardness changes were used to indicate the various stages of aging. Later, electrical-resistivity measurements were applied in an attempt to determine more closely the kinetics of the aging reactions. The equipment and techniques used in measuring resistivity are fully described in Appendix II. The phases present in the alloys during various stages of aging were determined by means of X-ray diffraction. Details of the procedures used in this work are given in Appendix I.

The results of these test procedures were correlated as much as possible to provide fundamental information on the nature of the omega phase and its role in age hardening.

Melting and Fabrication

The commercial-purity alloys used in this investigation were prepared from titanium sponge of 140 BHN, electrolytic chromium and iron, and pure molybdenum powder. Three-quarter-pound ingots of each composition were arc melted in an inert-electrode cold-mold furnace, fabricated to sheet, and remelted to promote homogeneity. Final fabrication consisted of forging at 1750 F to a slab and rolling to 0.064-inch sheet at 1450 F.

The high-purity alloys were prepared in the form of sheet rolled from arc-melted 100-gram buttons. High-purity iodide titanium was used as a base material. Alloying additions were made with high-purity electrolytic chromium or iron and pure molybdenum powder. Oxygen was added as pure TiO_2 . To insure homogeneity, each 100-gram button was remelted at least four times without removing it from the melting furnace.

All of the high-purity ingots were vacuum annealed to remove the residual hydrogen. This was accomplished by heating in vacuum to 1000 C and holding at this temperature until the pressure in the system was reduced to about 10^{-5} mm of mercury. Previous experience had shown that the residual hydrogen is reduced to a very low value (approximately 0.001 weight per cent) by this treatment.

The 100-gram buttons were rolled at 1450 F to sheets 0.065 to 0.070 inch thick. After pickling to remove surface oxide, 0.02 per cent hydrogen was added to three of the heats in a modified Sievert's apparatus. All heats were then analyzed for the major alloying element.

Heat Treatment

Specimens for metallographic examination, hardness tests, and the majority of the X-ray diffraction work were heat treated as 1/2-inch-square

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sheet sections. Groups of these specimens were sealed in Vycor capsules under a partial pressure of argon prior to heat treatment. The capsules were then heated for 1 hour at desired temperatures in the range 1325 to 1700 F and quenched and broken in iced brine. Specimens to be aged were again sealed in Vycor and quenched after the aging treatment.

AGE HARDENING IN COMMERCIAL-PURITY TITANIUM ALLOYS

Alloys

Preliminary investigations of the mechanism of age hardening were carried out using commercial-purity alloys. Four such binary alloys were available for limited study while high-purity alloys were being prepared. Nominal compositions of the commercial-purity alloys used were as follows:

Ti-8Cr
Ti-4Fe
Ti-5Fe
Ti-10Mo

Heat Treatment

Specimens from each heat were heated in an argon-atmosphere furnace for 1/2 hour at 1700 F and quenched in iced brine. Duplicate quenched specimens were then aged at 700 F for periods of 10 minutes, 40 minutes, 2 hours, 16 hours, and 72 hours, and again quenched.

Hardness Tests and Metallographic Examination

The heat-treated specimens were given a metallographic polish and subjected to Vickers hardness testing. At least three hardness determinations were made on the cross section of each sheet specimen. The average results of these tests are presented in Table 1 and Figures 1 and 2, along with the results of the X-ray diffraction examination which are discussed later in the section.

The two iron alloys had high hardnesses in the as-quenched condition as may be seen in Figure 1. Upon aging at 700 F, their hardnesses increased somewhat to about 570 VHN and remained at this level up to the

TABLE 1. HARDNESS AND X-RAY DIFFRACTION DATA FROM COMMERCIAL-PURITY BINARY TITANIUM ALLOYS SOLUTION TREATED AT 1700 F AND AGED AT 700 F

Nominal Composition, %	Aging Time	Vickers Hardness Number	Intensities of Phase Patterns Observed(a)			
			Untransformed Beta (β_0)	Enriched Beta (β_T)	Omega	TiH (From Etch)
8 Cr	0	330	s	0	0	0
"	10 min	525	s	0	f, vd	mf
"	40 min	539	s	0	mf, d	m
"	2 hr	521	ms	f, vvd	mf, d	0
"	16 hr	536	m	mf, vd	m	0
"	72 hr	550	0	m, vd	m	0
4 Fe	0	534	vs	0	f, d	0
"	10 min	557	s	0	vvf, vd	vf
"	40 min	578	s	0	f, d	f
"	2 hr	574	s	0	mf, d	0
"	16 hr	576	ms	mf, vvd	m	0
"	72 hr	573	mf	mf	ms	0
5 Fe	0	470	vs	0	0	0
"	10 min	546	s	0	Trace	0
"	40 min	566	s	0	f, vd	f, vd
"	2 hr	574	s	0	mf, d	f, vd
"	16 hr	583	ms	f, vvbr	m	mf, vd
"	72 hr	583	0-f	m, vvbr	m	mf, d
10 Mo	0	320	s	0	0	0
"	10 min	435	ms	0	0	(b)
"	40 min	470	s	0	vvf	(b)
"	2 hr	502	s	0	vf, d	mf, vd
"	16 hr	510	s	0	mf	0
"	72 hr	535	s	0	mf	0

(a) Key to abbreviations: s = strong, m = medium, f = faint, v = very, d = diffuse, br = broad.
 (b) An unknown phase, possibly a complex hydride, was present.

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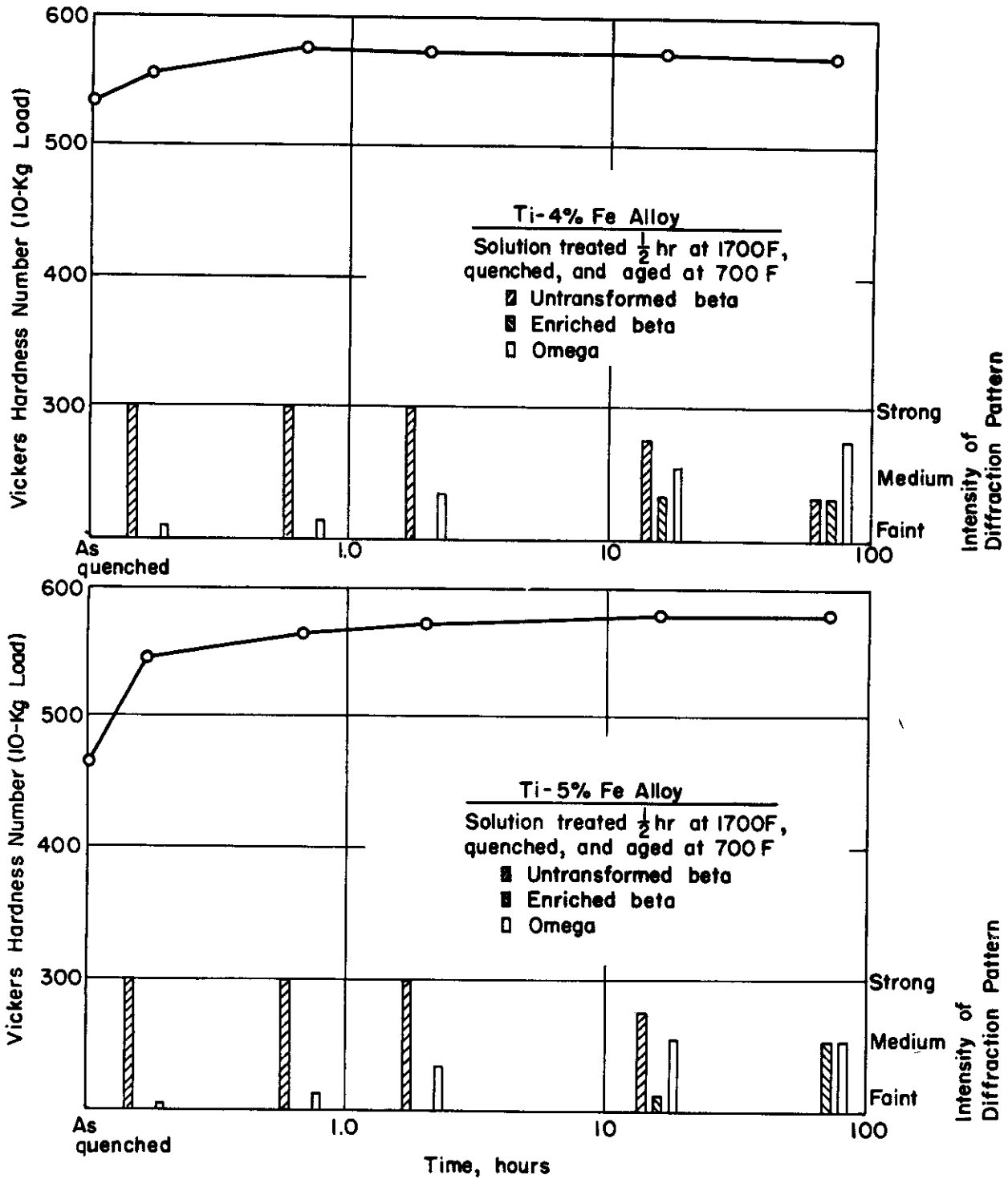


FIGURE 1. EFFECT OF AGING TIME AT 700 F ON THE HARDNESSES AND PHASES OBSERVED IN TWO Ti-Fe ALLOYS MADE FROM PROCESS A SPONGE

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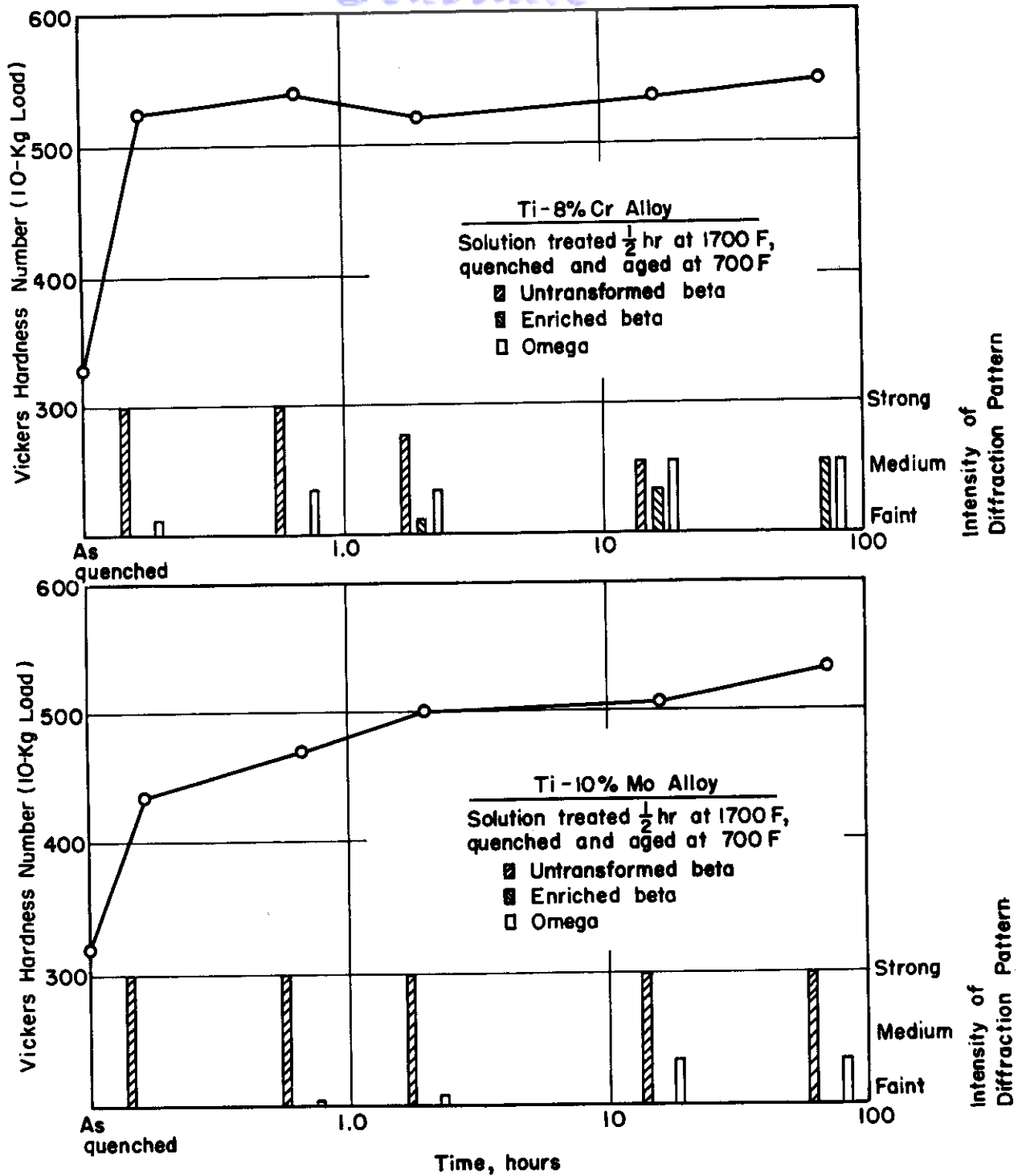


FIGURE 2. EFFECT OF AGING TIME AT 700 F ON THE HARDNESSES AND PHASES OBSERVED IN Ti-Cr AND Ti-Mo ALLOYS MADE FROM PROCESS A SPONGE A-70 29

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maximum aging time of 72 hours. The Ti-8Cr and Ti-10Mo alloys had much lower hardness as quenched (320-330 VHN). Hardnesses of these two alloys increased rapidly to values above 500 VHN upon aging, however. There was no evidence of overaging in any of the alloys at the longest aging time used (72 hours). The X-ray diffraction results confirmed that the new phase, omega, was present in some samples of each of the aged alloys. In fact, a Ti-4Fe alloy contained the omega phase in the as-quenched condition, which probably accounts for its high initial hardness. The Ti-5Fe alloy may also contain omega phase in the as-quenched condition.

Metallographic examination revealed only a single-phase beta structure in all of the alloys after aging treatments up to 16 hours. This was in agreement with earlier work under Contract No. AF 33(038)-3736 on more complex alloys. However, an unresolved precipitate could be detected in the 72-hour specimens of each of the alloys. These specimens were prepared by standard metallographic techniques and etched in a solution consisting of 1 per cent hydrofluoric acid and 3 per cent nitric acid in water.

X-Ray Diffraction

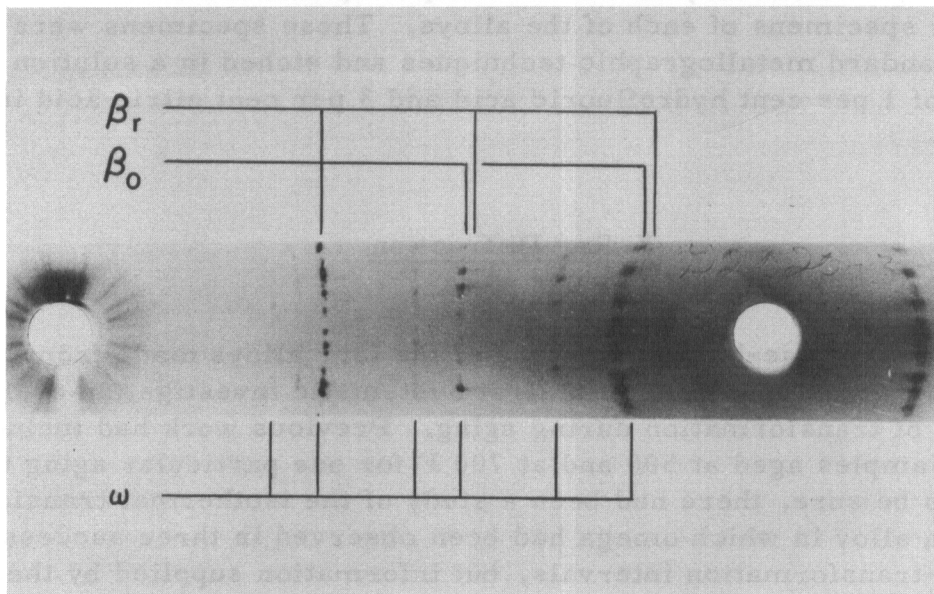
The present age-hardening study of the four alloys made from Process A titanium constituted the first systematic investigation of the mechanism of transformation during aging. Previous work had included studies of samples aged at 500 and at 700 F for one particular aging time only⁽⁴⁾. To be sure, there had been a study of the isothermal transformation of a Ti-8Mn alloy in which omega had been observed in three successive isothermal-transformation intervals, but information supplied by these samples was limited. In the present study, the selected aging treatments of 10 minutes, 40 minutes, 2 hours, 16 hours, and 72 hours at 700 F provided a broad time range.

The phases observed in the photograms of these samples are listed in Table 1, along with the hardnesses of the various specimens. Figures 1 and 2 are graphical representations of the hardnesses of the specimens, and the intensities of the various phases present as determined from the diffraction photograms.

The omega phase in the Ti-8Cr and Ti-4Fe alloys was very diffuse after 10 minutes at 700 F, and gradually became sharper after 16- and 72-hour aging periods. The untransformed beta (β_0) was distinguished by comparison with the beta in the as-quenched samples. It was very sharp, exhibiting K-alpha resolution of the 211 reflection even with vanadium radiation. However, after rather long aging times (such as 16 hours in the Ti-8Cr alloy), the 211 reflections of β_0 were not detected. In such cases, certain very sharp reflections in the 110 region were taken as the last

remaining evidences of β_0 , since neither omega nor enriched beta (β_r) gave very sharp reflections.

The enriched beta (β_r) reflections occurred as doublets with the β_0 reflections; i. e., they were always side by side when both were observed. This is shown clearly in the typical photogram in Figure 3. The β_r reflections appeared as broad streaks, and covered a range of 1 degree θ or more when present with sharp β_0 lines. These streaks indicated that within each beta grain, a wide variation in lattice constant existed. After a very long aging time, the β_r streaks became shorter because the intensity of each streak at low values of θ had decreased to the vanishing point. This effect was probably due to the near elimination of the β_0 regions.



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FIGURE 3. DEBYE-SCHERRER PHOTOGRAM OF THE Ti-4Fe ALLOY QUENCHED FROM 1700 F AND AGED 16 HOURS AT 700 F

Reflections of the various phases are designated

There was an omega reflection beside every 200 and 211 β_0 reflection, but at slightly smaller θ angle, which gave the observer the impression that the beta-phase reflection had doubled (see Figure 3). While the omega reflections paired the 211 β_0 reflections, there were many more omega reflections than 200 β_0 reflections.

An interpretation of a typical photogram of a sample which has undergone partial decomposition of β_0 is given in Table 2. This table supplants Table 20 of last year's report (WADC Technical Report 52-334), in which

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TABLE 2. ANALYSIS OF AN X-RAY DIFFRACTION PHOTOGRAM OF A COMMERCIAL-PURITY Ti-4Fe ALLOY SOLUTION TREATED AT 1700 F AND AGED AT 700 F

Exposure: Vanadium radiation, self-filtered by the sample; 57.3-mm Debye camera

Relative Intensity ^(a)	Interplanar Spacing ^(b) , d, A	Phase ^(c)	Miller Indices of Beta Phase, hkl
vf, d	2.80	ω	-
m, d	2.30	ω	-
vs	2.29	β_o	110
f, br	~2.29-2.26	β_r	110
mf, d	1.78	ω	-
mf, d	1.63	ω	-
m	1.623	β_o	200
vf, vbr	~1.623-1.59	β_r	200
f, d	1.412	ω	-
ms, d	1.334	ω	-
s	1.328	β_o	211
vf, vbr	~1.328-1.308	β_r	211

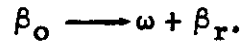
(a) Abbreviations: s = strong, m = medium, f = faint, v = very, d = diffuse, br = broad.

(b) Interplanar spacings not corrected for absorption.

(c) ω = omega, β_o = intransformed beta, β_r = beta of reduced lattice constant (enriched in alloy).

some omega reflections were misinterpreted as β_0 . The transformations in the Ti-5Fe were essentially the same as those in the Ti-4Fe, but there was no evidence of omega in the as-quenched condition. The Ti-10Mo alloy showed no enriched-beta constituent distinct from untransformed beta, although enriched beta would have lower lattice constants than β_0 in Ti-Mo solid solution. The intensity of the omega phase in Ti-Mo alloys was difficult to estimate because the strong omega reflections were not resolved from the beta.

The examination of the present alloys aged at 700 F from 10 minutes to 72 hours indicated that the reaction occurring was



This particular set of samples did not cover a long enough aging time to show the decomposition of omega phase.

Isothermal Transformation of Commercial-Purity Ti-12.3 Mn Alloy

A portion of the preliminary work, using commercial-purity materials, was done on a Ti-12.3Mn alloy. In a previous complete study of the isothermal transformation of a Ti-8Mn alloy⁽⁶⁾, the omega phase had been detected after 10, 30, and 60 minutes at 450 C.

The X-ray diffraction analyses showing the constituents observed during transformation in eight Ti-12.3Mn samples quenched from 950 C are given in Table 3. The data show that untransformed beta, β_0 , decomposed into enriched beta, β_u , plus alpha. No omega was identified in these samples. The basis used for identifying omega was detection of interplanar spacings of 2.83, 1.79, or 1.41 A. Other observations, however, led to the suspicion that a transition phase resembling omega was present in each sample transformed 60 minutes. In the photograms of these 60-minute samples, the reflections which occurred at the positions of the beta reflections were diffuse. They also occurred at slightly higher interplanar spacings, and showed a type of streaking often seen in photograms of omega-plus-enriched-beta samples. These facts are evidence of some type of partial transformation. In fact, it seems likely that omega could have been present, but with its structure imperfectly developed in such a way that the reflections at 2.83, 1.79, and 1.41 A were not sharp enough to be detected. A similar indeterminacy in identifying omega was also encountered in a Ti-15Cr sample described later in the section on Correlation of Dilatometer Traces and Phase Composition. In each of these instances, the alloy content was 4 to 7 per cent above the minimum needed for complete retention of the beta phase upon quenching.

TABLE 3. RESULTS OF X-RAY DIFFRACTION EXAMINATION OF A Ti-12.3Mn ALLOY
ISOTHERMALLY TRANSFORMED AFTER QUENCHING FROM 950 C

Isothermal Transformation Temperature, C	Time, hr	Estimated Intensity(a) of Phase Patterns				Lattice Constant of Beta, A
		β_0 (b)	β_u (c)	Alpha	Omega	
450	1/2	s	0	0	0	3.242
"	1	s, d	0	0	0?	3.252
"	8	0	vs, d	m, d	0	3.206
"	168	0	st, d	m	0	3.189
500	1/2	vs	0	0	0	-
"	1	vs, d	0	0	0?	3.284
"	24	0	vs, d	m, d	0	3.206
"	144	0	vs, d	m	0	3.206
As quenched and etched(d)		vs	0	0	0	3.265
As quenched and etched (d), degassed at 800 C and fast cooled		vs	0	0	0	3.224

(a) Abbreviations: vs = very strong, s = strong, m = medium, d = diffuse.
 (b) β_0 = untransformed beta phase.
 (c) β_u = ultimate beta (relatively high alloy content).
 (d) Quenched and etched approximately 4 months before examination.

Contrails

The lattice constants of the untransformed beta, β_0 , in the Ti-12.3Mn samples were high by varying amounts even where the patterns were very sharp. The lattice constant of β_0 in one etched sliver of an as-quenched Ti-12.3Mn sample was reduced 0.04 Å by degassing for 20 minutes at 800 C, indicating that the increase was due to hydrogen penetration.

AGE HARDENING IN HIGH-PURITY TITANIUM ALLOYS

Alloys

The preliminary work using commercial-purity binary alloys did not eliminate the possibility that hardening and/or the omega phase might be affected by the impurities present. However, the results obtained in the sponge alloys served as a guide for planning a research program using high-purity binary alloys. This investigation formed the major part of the research work done under the current contract. The compositions of the high-purity alloys selected for the investigation were as follows:

Ti-8Cr
Ti-8Cr-0.1O
Ti-8Cr-0.02H

Ti-4Fe
Ti-4Fe-0.1O
Ti-4Fe-0.02H

Ti-11Mo
Ti-11Mo-0.1O
Ti-11Mo-0.02H

Ti-12Cr
Ti-16Cr
Ti-3Mn-1Cr-1Fe-1Mo-1V

Intermetallic compounds are formed in both the titanium-iron and the titanium-chromium system. On the other hand, the titanium-molybdenum system has no compound. With this selection of alloys, it was believed possible to determine what effects, if any, the formation of titanium compounds might have either in the age-hardening mechanism or in the embrittlement of beta-stabilized alloys. The Ti-8Cr, Ti-4Fe, and Ti-11Mo compositions were selected to provide retained-beta structures of the lowest alloy content attainable in each system. Compositions of lower alloy content transform to a supersaturated-alpha structure upon quenching. The additions of oxygen and hydrogen were made to these alloys to study

Continued

the effects of an alpha-stabilizing interstitial element and a beta-stabilizing interstitial element on the age-hardening reaction and embrittling mechanism. Analyses of specific melts appear in Table 4.

Phase Changes During Aging

Initial studies of the age hardening of high-purity alloys consisted largely of:

- (1) Determination of the hardness changes which occurred during aging of the Ti-8Cr, Ti-4Fe, and Ti-11Mo alloys
- (2) Determination of the phases present after various stages of aging as indicated by X-ray diffraction examination.

Hardness tests were also made on aged specimens of the three alloys containing oxygen and hydrogen. No X-ray diffraction work was done on the latter compositions, however, because of the close similarity of their hardness curves to those of the base alloys. Chemical analyses of these alloys were not made for the same reason.

Hardness Versus Aging Time

Specimens of the Ti-8Cr, Ti-4Fe, and Ti-11Mo alloys, including the heats with oxygen and hydrogen additions, were quenched from 1700 F to retain a 100 per cent beta structure and aged for various times up to 1000 hours at temperatures of 500, 700, and 800 F.

The average Vickers hardnesses of the aged specimens of Ti-4.13Fe,* Ti-8.10Cr,* and Ti-10.2Mo* alloys are plotted as a function of aging time in Figures 4, 5, and 6, respectively. These charts are representative of the three heats of each alloy system. Hydrogen and oxygen were found to have only small effects on the hardness after aging. The nature of these minor effects is illustrated in Figure 7, in which the hardnesses of the Ti-8.10Cr, Ti-8.01Cr-0.10, and Ti-8.04Cr-0.02H alloys aged at 800 F are plotted. Aging curves for additional heats are given in Appendix III.

The curves, in general, are typical of age hardening. Except for the iron alloys, there was a sharp increase in hardness initially at all temperatures. Upon aging at 700 and 800 F for relatively long times, the

*Several heats having nominal compositions Ti-4Fe, Ti-8Cr, and Ti-11Mo were made. When specific heats are referred to, the actual composition is used, e.g., Ti-4.13Fe.

TABLE 4. COMPOSITION OF HIGH-PURITY TITANIUM ALLOYS
USED FOR AGE-HARDENING STUDIES^(a)

Heat	Intended Composition, %	Actual Composition, %
X	Unalloyed Ti	-
X-498	8Cr	8.10Cr
X-2	8Cr	7.70Cr
X-499	8Cr-0.10 ^(b)	8.01Cr
X-500	8Cr-0.02H ^(b)	8.04Cr
X-501	11Mo	10.2Mo
X-3	11Mo	11.5Mo
X-502	11Mo-0.02H ^(b)	10.0Mo
X-503	11Mo-0.10 ^(b)	10.8Mo
X-504	4Fe,	4.13Fe
X-1	4Fe	4.06Fe
X-505	4Fe-0.10 ^(b)	4.11Fe
X-507	4Fe-0.02H ^(b)	4.11Fe
X-540	12Cr	12.8Cr
X-541	16Cr	16.1Cr

(a) High-purity iodide titanium, electrolytic chromium and iron, and pure molybdenum powder were used in these heats.

(b) Analyses for oxygen and hydrogen were not made. Previous experience indicates that the actual contents of these elements should be very close to the nominal.

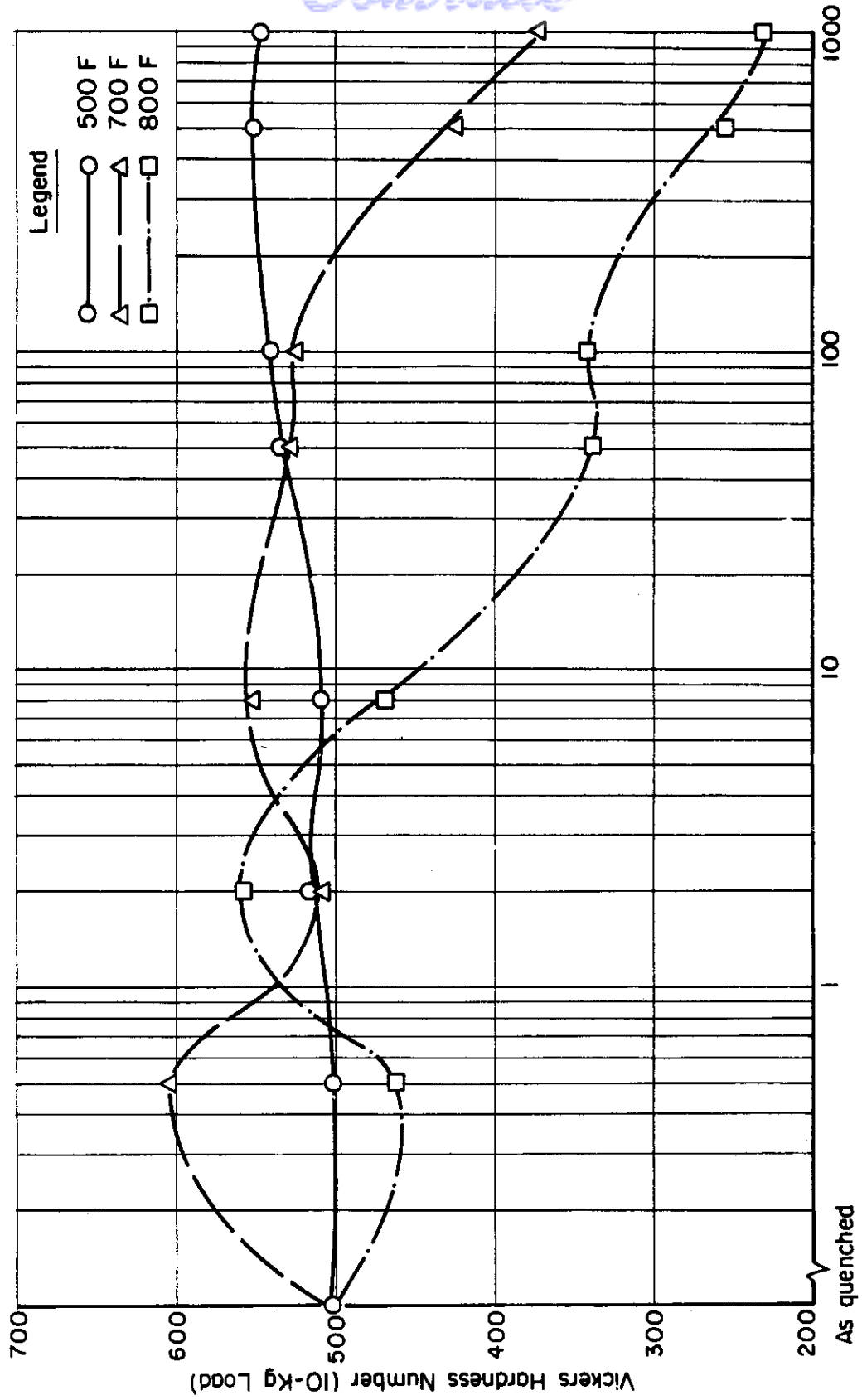
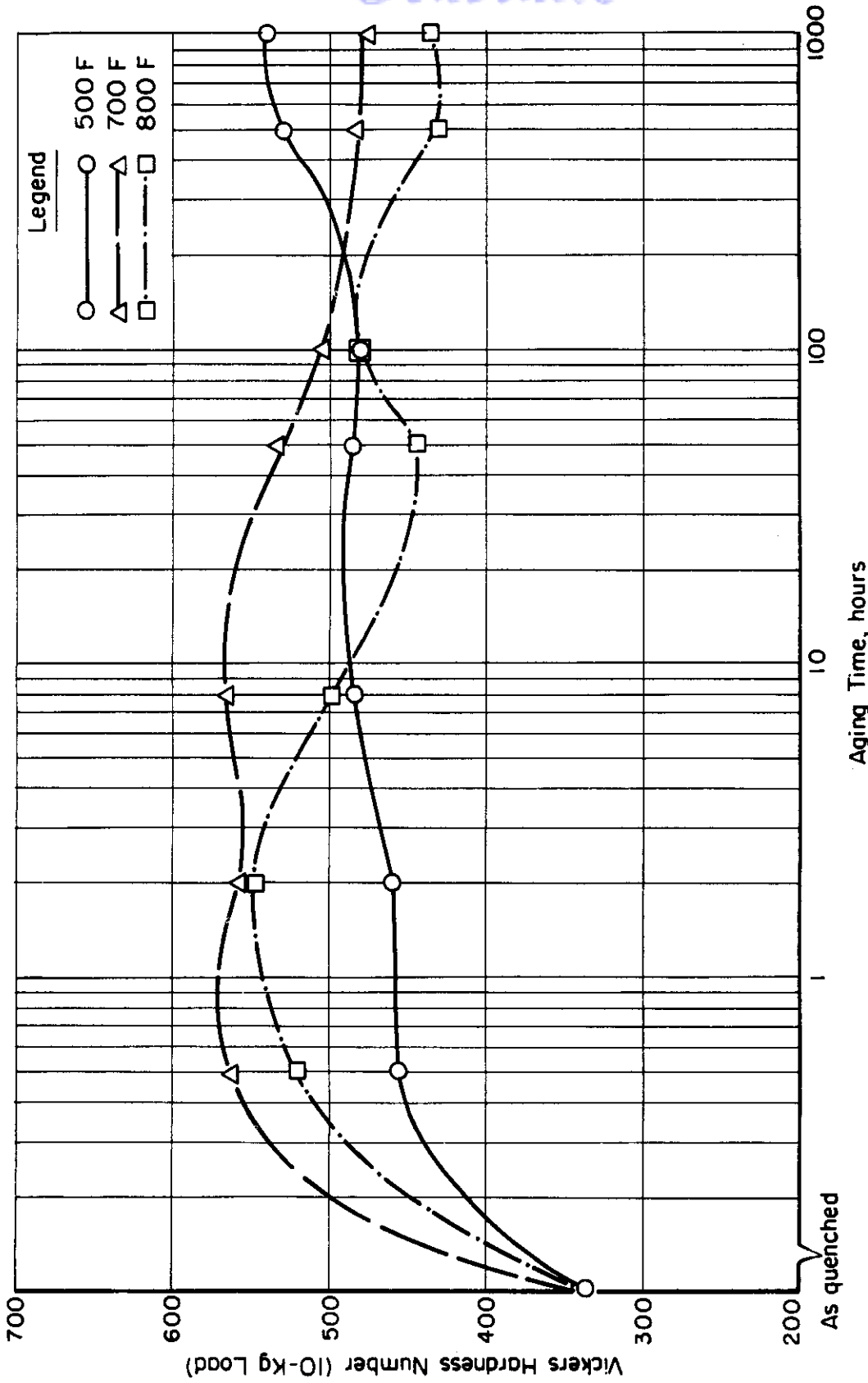


FIGURE 4. EFFECT OF TIME AND TEMPERATURE ON VICKERS HARDNESS OF AN IODIDE Ti-4.13 Fe ALLOY QUENCHED FROM 1700F AND AGED AT THE TEMPERATURES SHOWN

A-8824



Aging Time, hours

FIGURE 5. EFFECT OF TIME AND TEMPERATURE ON VICKERS HARDNESS OF AN IODIDE Ti-8.1 Cr ALLOY QUENCHED FROM 1700F AND AGED AT THE TEMPERATURES SHOWN

A-8825

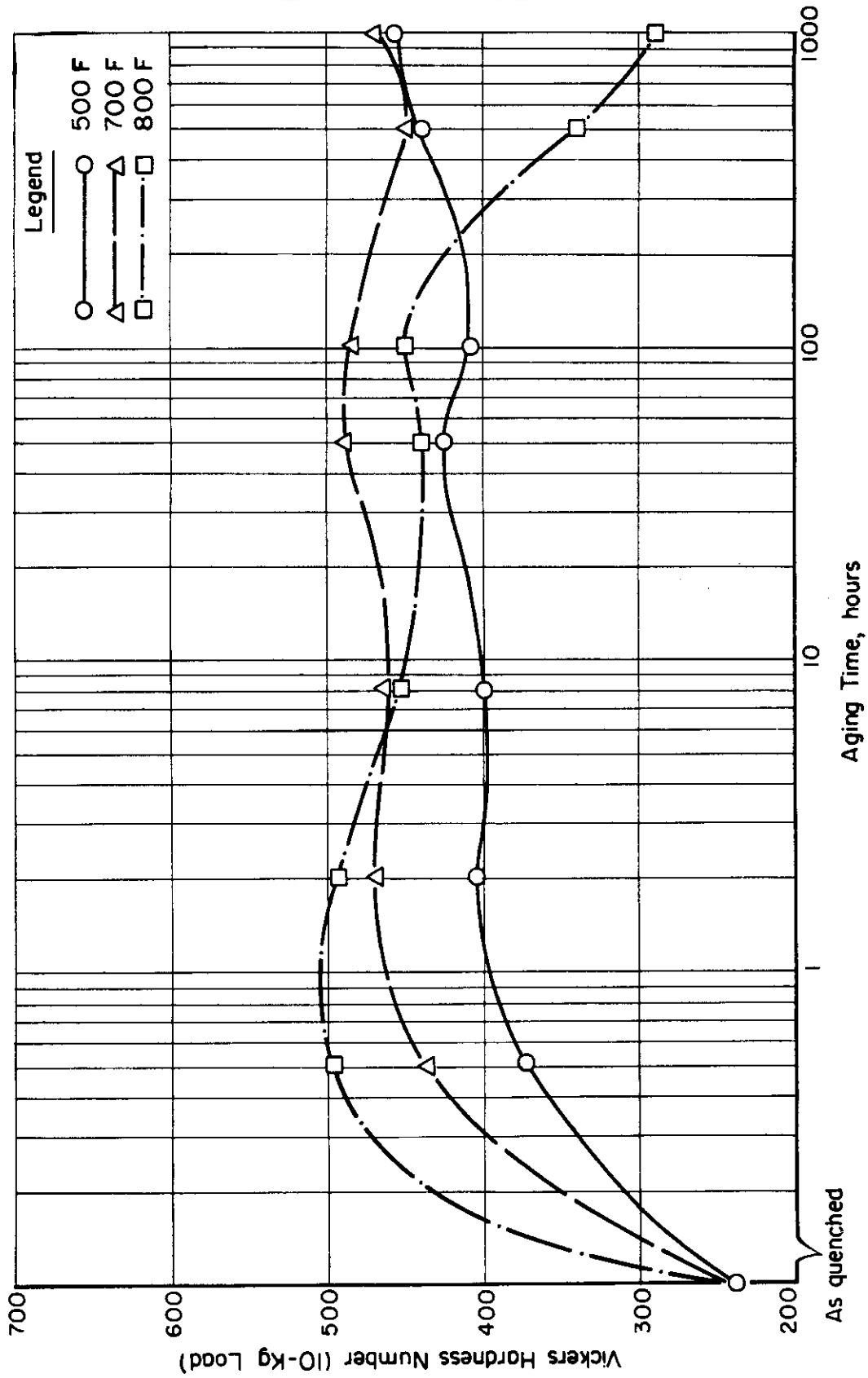


FIGURE 6. EFFECT OF TIME AND TEMPERATURE ON VICKERS HARDNESS OF AN IODIDE Ti-10.2 Mo ALLOY QUENCHED FROM 1700F AND AGED AT THE TEMPERATURES SHOWN

A-8826

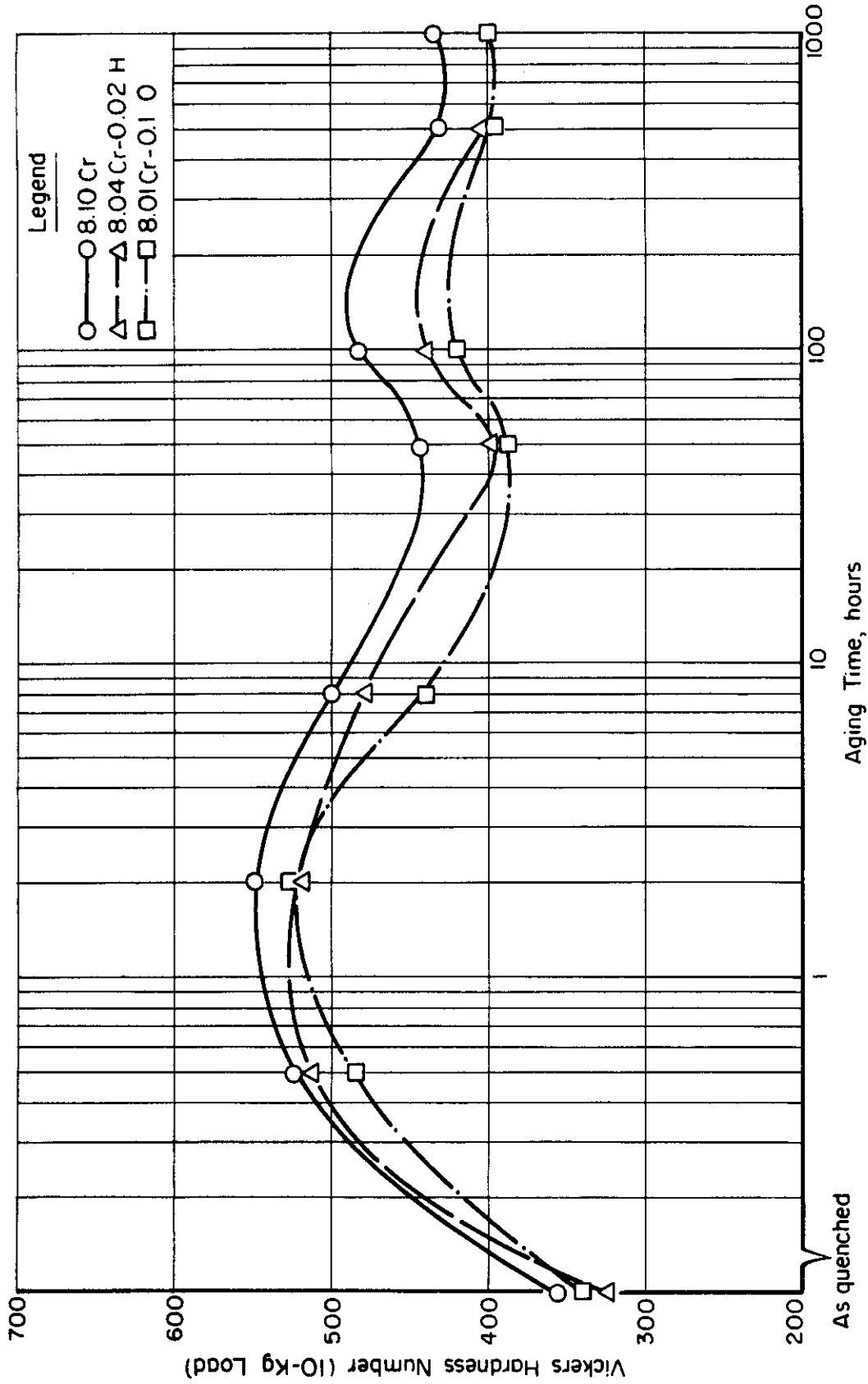


FIGURE 7. EFFECT OF INTERSTITIAL IMPURITIES ON HARDNESSES OF Ti-Cr ALLOYS QUENCHED FROM 1700 F AND AGED AT 800 F

A-8827

hardnesses decreased, indicating overaging. At 500 F, a peak hardness was not reached during the test time of 1000 hours.

The iron alloys had a relatively high as-quenched hardness of 500 VHN. X-ray diffraction examination of the Ti-4.13Fe alloy revealed some omega phase, indicating these alloys aged during the quench. No omega was detected in the as-quenched chromium or molybdenum alloys. The higher as-quenched hardness in the chromium alloys (335 VHN) compared to that of the molybdenum alloys (240 VHN) may have been a result of a difference in solid-solution hardening effect, or of an undetected aging reaction in the Ti-Cr alloy. The increase in hardness of about 250 points to the maximum is about the same in both the chromium and molybdenum alloys.

The 700 and 800 F aging curves had two maxima, indicating that more than one hardening mechanism was operating. In some cases, the rise in hardness to the second peak was small and could be within the limits of experimental error. However, the peaks occurred in the alloys containing hydrogen and oxygen as well as in the degassed alloys of each system, and probably indicate a true structural change during aging.

The relative rates of reaction, as deduced from the hardness changes, vary for the three alloys. On the basis of time to reach maximum hardness, the iron alloys aged most rapidly, followed by the chromium and molybdenum alloys in the order named. If overaging or softening is considered, the iron was most rapid, and the molybdenum alloy softened more readily than the chromium alloy. The chromium alloy may have an extended hardening region because of the precipitation of considerable quantities of an intermetallic compound, $TiCr_2$, in later stages of aging.

Phase Identification by X-ray Diffraction, Hardness, and Resistivity Measurements

The X-ray diffraction examination was applied to iodide alloys which had been given aging treatments to precipitate alpha and intermetallic compounds. This work showed that omega phase disappeared on sufficient aging, and, therefore, should be classed as an unstable or transition phase.

Visually estimated diffraction-pattern intensities of various phases present in the aged iodide alloys described in the preceding section are shown in Table 5, along with the hardnesses of duplicate specimens. The effects of aging at 800 F on hardness, resistivity, and X-ray data are given in Figures 8 to 10. For reference, similar resistivity data on pure iodide titanium appear in Figure 11.

TABLE 5. HARDNESS AND X-RAY DIFFRACTION DATA FOR DEGASSED IODIDE TITANIUM ALLOYS SOLUTION TREATED 1/2 HOUR AT 1700 F AND AGED

Composition, %	Aging		VHN (10-Kg Load)	Intensities of Phase Patterns Observed(a)					Compound	TiH (From Etch)	
	Temp. F	Time, hr		Untransformed Beta, β_0	Enriched Beta, β_I or β_{II}	Omega, ω	Alpha, α				
4.13 Fe	None	-	502	s	0	vvf, vd	0	0	0	0	
	500	50	536	s	0	vf, vd	0	0	0	0	
	500	500	552	s	0	mf, vd	0	0	0	0	
	700	1/2	606	s	0	vf, vd	0	0	0	0	
	700	50	530	0?	mf, vvv br	s	0	0	0	0	
	700	100	527	0	mf, vvv br	s	0	0	0	vvf	
	700	500	425	0	0-m, vvd	vs	vf - mf	0	0	0	
	800	1.2	464	s	mf, vvv br	m	0	0	0	0	
	800	2	560	ms	mf, vvv br	m	0	0	0	f, vd	
	800	8	471	0	m, vvv br	s	0	0	0	0	
	800	50	341	0	m, d (β_{II})	0?	s	0	0	vvf	
	800	100	372	0	m, (β_{II})	0	s	0	0	0	
	800	500	255	0	0	0	s	0	ms	0	
	8.10 Cr	None	-	338	s	0	0	0	0	0	0
		500	2	459	s	0	Trace	0	0	0	vvf, vd
		500	50	485	s	0	vvf, vvd	0	0	0	mf, vvd
500		500	531	s	0	mf, vd	0	0	0	0	
700		50	532	0	m, vd	ms	f	0	0	mf, vd?	
700		500	483	0	m, vvvd, (β_{II})	mf	ms	0	0	0	
800		1/2	519	0	m, vv br	ms	0	0	0	f, vd	
800		2	548	0?	m, vvd	ms	0	0	0	f, vd	
800		8	498	0	ms, vd	s	vf, d	0	0	0	
800		50	443	0	0?	0	s	0	0	0	
800		100	483	0	0?	0	s	0	0	0	
800		500	430	0	0?	0	s	0	0	0	
800		1000	435	0	0?	0	s	0	0	0	
10.2 Mo		None	-	238	s(b)	0	0	0	0	0	0
		500	500	441	s(b)	0	0	0	0	0	mf, (c)?

TABLE 5. (Continued)

Composition, %	Aging		VHN (10-Kg Load)	Intensities of Phase Patterns Observed(a)					TiH (From Etch)
	Temp, F	Time, hr		Untransformed Beta, β_o	Enriched Beta, β_r or β_u	Omega, ω	Alpha, α	Compound	
10.2 Mo	500	1000	455	s(b)	0	0	0	0	f, (c)?
	700	50	488	ms(b)	0	0	0	0	m, vd
	700	500	477	s	0	0	0	0	m, vd
	700	1000	470	s	0	0	0	0	mf
	800	1/2	498	s	0	0	0	0	f, vd
	800	50	439	s	0	0	0	0	mf
	800	100	450	s	0	0	0	0	0
	800	500	339	0 or m	0?	0	0	0	vf, d
	800	1000	289	0 or mf	ms, vd (β_u)	0?	ms	0	0-mf, d
	1000	8	310	0	s, d (β_u)	0?	ms	0	0
	1000	100	286	0	s, d (β_u)	0?	ms	0	0

(a) s = strong, m = medium, f = faint, v = very, br = broad (in angle theta), d = diffuse (perpendicular to theta as well as parallel), sh = sharp.
 (b) The untransformed-beta pattern had one or more distortions which are believed to be caused by hydrogen absorbed from the etchant.
 (c) There may be a hydride present which does not have the usual TiH structure.

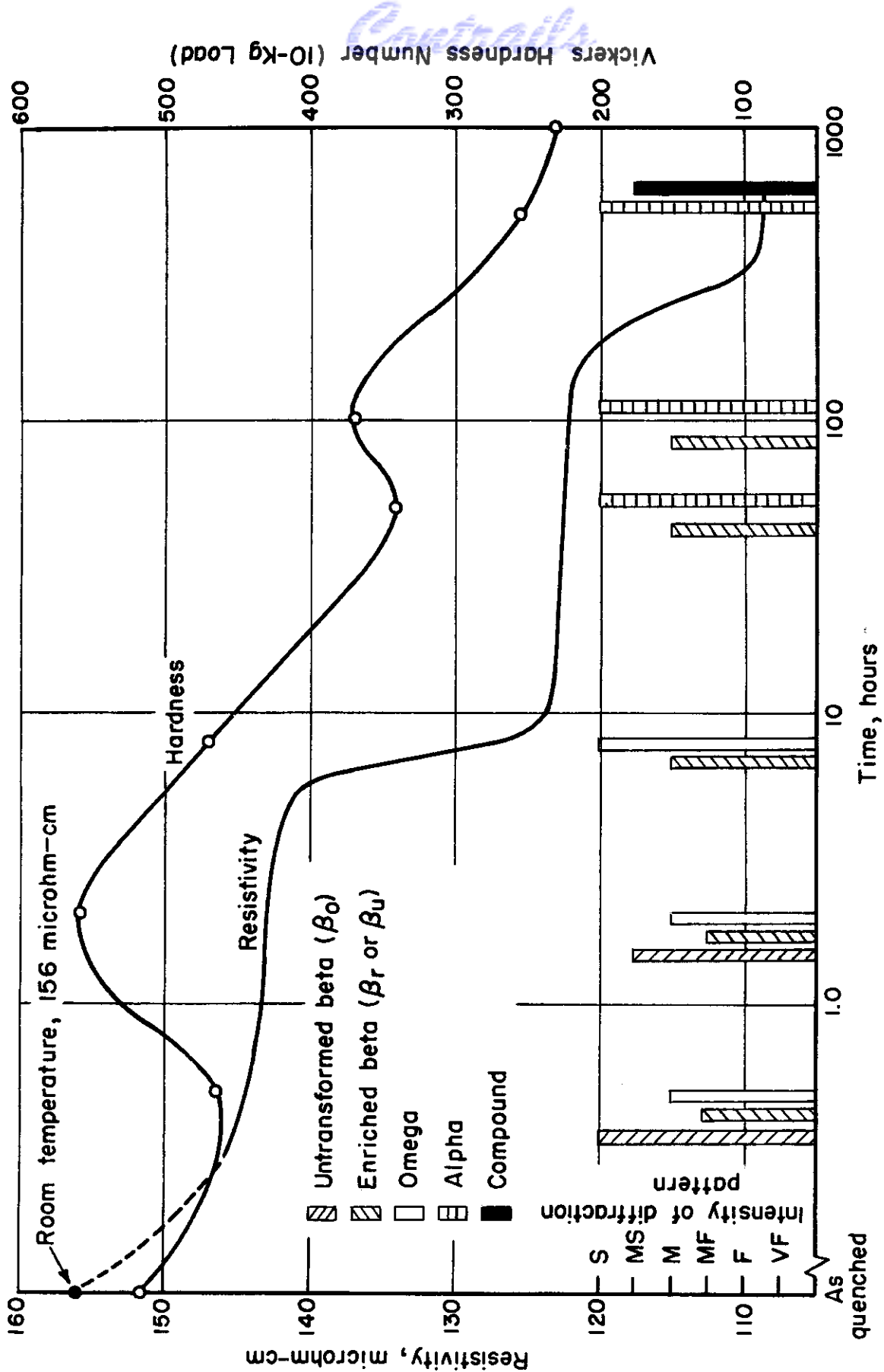


FIGURE 8. EFFECT OF AGING AT 800F ON THE RESISTIVITY, HARDNESS, AND X-RAY DIFFRACTION-PATTERN INTENSITIES OF THE Ti-4.13 Fe ALLOY QUENCHED FROM 1700 F

A-9566

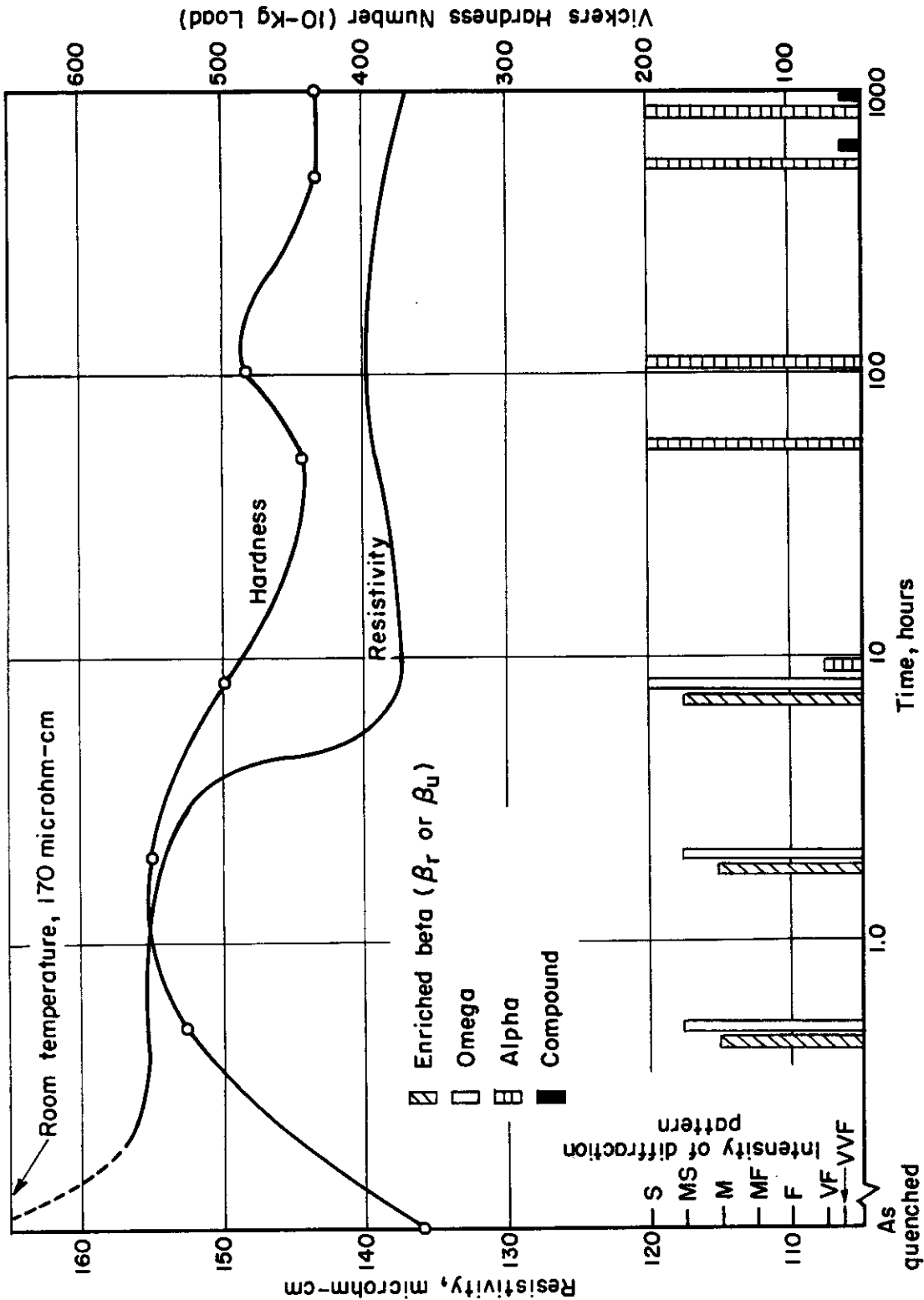


FIGURE 9. EFFECT OF AGING AT 800F ON THE RESISTIVITY, HARDNESS, AND X-RAY DIFFRACTION-PATTERN INTENSITIES OF THE Ti-8.1 Cr ALLOY QUENCHED FROM 1700 F

A-9564

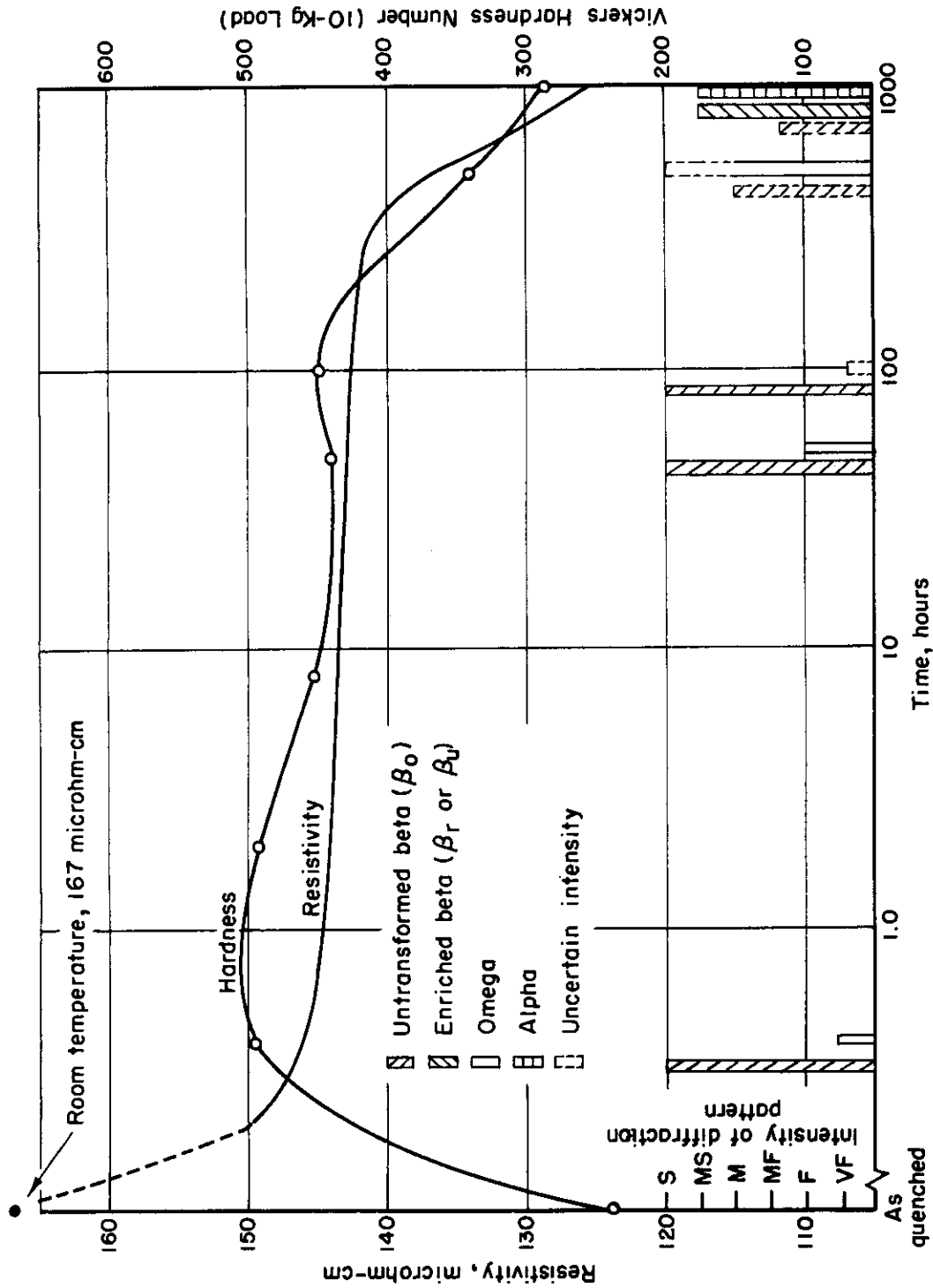


FIGURE 10. EFFECT OF AGING AT 800F ON THE RESISTIVITY, HARDNESS, AND X-RAY DIFFRACTION-PATTERN INTENSITIES OF THE Ti-10.2 Mo ALLOY QUENCHED FROM 1700F

A-9565

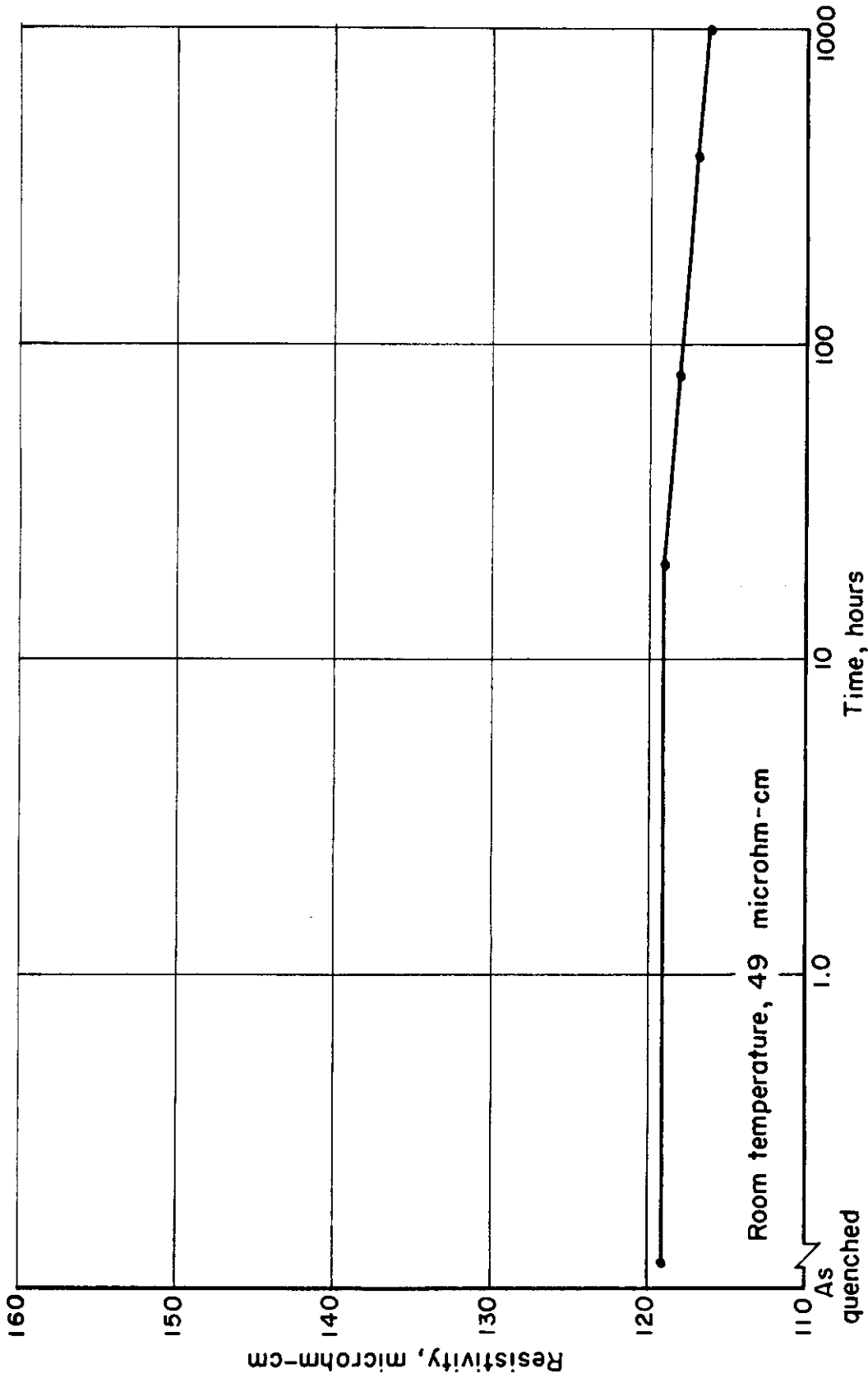


FIGURE II. EFFECT OF AGING AT 800 F ON THE RESISTIVITY OF IODIDE TITANIUM QUENCHED FROM 1700 F

A-11945

Contrails

The results obtained from the aging of iodide alloys at 700 and 800 F agree with those discussed for the commercial-purity alloys in the preceding section. The study of the iodide alloys, however, being conducted at three different temperature levels showed the strong effect of the temperature factor. The transformation at 800 F appeared to be faster than at 700 F. At 500 F, the transformation was much slower than at 700 F, being barely perceptible in 500 hours.

The omega phase was found to have disappeared completely in the Ti-4.13Fe alloy after 500 hours at 800 F; in the Ti-8.10Cr alloy after 50 hours at 800 F; and in the Ti-10.2Mo alloy after 1000 hours at 800 F. Moreover, it disappeared from the Ti-8.10Cr alloy almost completely after 500 hours at 700 F.

According to the systematic aging study of commercial-purity alloys and the comprehensive study of iodide alloys, the state of transformation of the aged Ti-4.13Fe or Ti-8.10Cr specimens can be classified by their X-ray diffraction photograms into one of the following seven consecutive stages:

- (1) β_o^*
- (2) $\beta_o + \text{diffuse pattern of } \omega$
- (3) $\beta_o + \beta_r + \omega$, where the β_r reflections are seen as streaks extending from ω or β_o reflections in the direction of increasing Bragg angle θ , and the ω pattern is usually only slightly diffuse
- (4) $\beta_r + \omega$, where the β_r streaks are resolved from the ω reflections, and in some cases are actually spot reflections
- (5) $\beta_r + \omega + \alpha$
- (6) $\beta_u + \alpha$, where the lattice constant of β_u is smaller than the lattice constant of the β_r in Stage (4)
- (7) $\alpha + \text{intermetallic compound}$ (in systems where a compound can occur).

The last stage did not occur in the Ti-4.13Fe and Ti-8.10Cr alloys at 800 F until aging times considerably longer than those at which Stage (6) ($\alpha + \beta_u$) appeared. This indicates that compound nucleation is very slow.

* β_o is beta phase of original alloy composition.

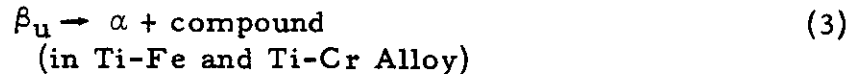
β_r is beta phase of somewhat higher alloy content.

β_u is beta phase whose composition approaches the transus at the aging temperature (e.g., Ti-Mo, Ti-V alloys) or the extrapolation of the beta transus (e.g., Ti-Fe, Ti-Cr alloys).

Conclusions

The Ti-10.2Mo alloy was believed to follow the same sequence of reactions, but the enriched beta β_r was never detected in the presence of omega.

From the data in Table 5, considering especially the consecutive stages of the transformation, one may write the transformation process in the three following reactions:



At certain stages of aging, Reactions (2) and (3) may proceed concurrently. Since alpha appears to supplant omega without great change in beta, it seems most likely that omega is low in alloy content, though perhaps not so low as alpha.

Enriched beta in the Ti-10.2Mo alloy was observed only in the three samples aged sufficiently to transform the alloy to the alpha-plus-beta state. The β_r type, which was identified from streaked or doubled reflections in Ti-Cr and Ti-Fe alloys, was not observed in Ti-Mo alloys. However, it is doubtful that β_r could be detected even if it were present, for the line positions move only slightly even in transforming to β_u . It was difficult to distinguish between β_o , β_r , and omega in the Ti-Mo alloys, and the apparent absence of the enriched beta may have been a result of experimental limitations.

The enrichment of beta in Ti-Mo, Ti-Cr, and Ti-Fe alloys probably depends upon the ability of the alloys to achieve thermodynamic equilibrium between alpha and beta. In the Ti-Mo system, where the $\beta/\alpha + \beta$ boundary slopes toward higher molybdenum concentrations with decrease in temperature, an all-beta sample held at constant temperature below the $\alpha/\alpha + \beta$ boundary has to decompose eventually into alpha and enriched beta having the composition denoted by the intersection of the $\alpha/\alpha + \beta$ boundary and the temperature ordinate. Alloys in eutectoid-type systems such as Ti-Fe and Ti-Cr should behave in the same way at temperatures above the eutectoid. Below this temperature, the composition of the enriched beta should approach the extrapolation or continuation of the $\beta/\alpha + \beta$ boundary (or transus) to the aging temperature as long as no compound is nucleated^(7, 8, 9, 10). If the compound formation is sluggish, the equilibrium between beta and compound or alpha and compound are naturally nonexistent until compound is formed.

The actual compositions of enriched beta, as deduced from lattice-parameter measurements of the Ti-4.13Fe and Ti-8.10Cr alloys, agreed

Contrails

fairly well with extrapolated values. For example, the theoretical chromium content of the beta phase in equilibrium with alpha in Ti-Cr alloys at 800 F (427 C) should be about 35 per cent⁽¹¹⁾, as illustrated in Figure 9. The actual concentration range deduced from X-ray photograms was 23 to 44 per cent. The theoretical value for the titanium-iron alloy transformed at 800 F should be between 17 and 23 per cent iron⁽¹¹⁾, depending upon which constitution diagram is accepted. The actual concentration determined from X-ray results was 17 to 19 per cent.

In one Ti-10.2Mo sample showing enriched beta, the measured lattice constant corresponded to an average value of about 27 weight per cent molybdenum, with a maximum of 33 per cent. In this alloy, the composition of the enriched beta must approach the true equilibrium value if given sufficient time. However, extrapolation of the curve established by Hansen and co-workers⁽¹¹⁾ gives a value of about 45 per cent. Failure to reach this value was due to lack of sufficient time or to inaccuracy of extrapolating the curve to 800 F.

After 500 hours at 800 F, the beta pattern in the Ti-4.13Fe alloy was absent, and sharp medium-to-strong reflections of the compound TiFe appeared.

TiCr₂ reflections appeared along with those of alpha in the photograms of the Ti-8.10Cr alloy aged for 500 or 1000 hours at 800 F. No beta reflections were observed in these samples nor those after 50 and 100 hours of aging. While the absence of a beta pattern normally would indicate the absence or practical absence of beta, the hardness and resistivity curves indicate that some precipitation occurred between 20 and 500 hours, and this could have been TiCr₂ precipitating from beta. The photograms of the samples at 50 and 100 hours do not reveal the presence of the chromium in the alloy, and those for the 500- and 1000-hour samples show very weak TiCr₂ patterns. A failure of the diffraction films to account for all of the chromium also occurred in the study of the isothermal transformation of a Ti-8Cr alloy⁽⁷⁾ at 450 C (842 F), where, again, age hardening at long-time transformation occurred. In these cases, the beta pattern and/or TiCr₂ pattern may have been present but too diffuse to be detected. X-ray diffraction patterns taken with monochromatized X-rays or electron microscopical examination might reveal a finely dispersed minor phase.

Effect of Aging on Resistivity

The general sequence of reactions during aging has been established by hardness and X-ray diffraction examination. However, the exact mechanisms of the reactions are not known. Also, the times for initiation of the various reactions were not accurately determined because considerable

Contrails

quantities of a phase must be present for detection either by hardness changes or X-ray diffraction.

Electrical resistivity is known to be sensitive to many structural changes which occur in metals. Therefore, it was believed that resistivity measurements made during aging might help to establish the kinetics of aging more accurately and assist in determining the active mechanisms.

The apparatus used is described in Appendix II. Initial work was carried out on specimens of the Ti-8.10Cr, Ti-4.13Fe, and Ti-10.2Mo alloys. A sample of unalloyed iodide titanium was included as a control specimen. Each alloy was quenched from 1700 F in the beta field, and aged at 800 F. This aging temperature was chosen because the X-ray data have indicated that all of the major reactions involved in the transformation of titanium alloys occur within a 1000-hour period at this temperature. The resistivity versus aging-time curves for the three alloys and the unalloyed titanium are shown in Figures 8 through 11. For convenience in interpreting the resistivity changes, the hardnesses of the alloys and the phases present are plotted on the same charts.

The specimens reached temperature about 12 minutes after insertion into the furnace. At this point, the resistivities of the alloys were considerably lower than the room-temperature values. This initial drop is shown as the dotted portion of the curves in Figures 8 to 10, inclusive. Upon reaching the aging temperature, the curves for the alloys leveled off and continued to drop gradually up to a time of about 3 hours for the Ti-8.10Cr alloy, 5 hours for the Ti-4.13Fe alloy, and 250 hours for the Ti-10.2Mo. At these points, there was a second sharp drop in resistivity, followed by a second plateau in the case of the iron and chromium alloys. The second plateau was not reached in the Ti-10.2Mo alloy at the maximum time of 1000 hours. A third sharp decrease in resistivity occurred in the Ti-4.13Fe alloy between about 100 and 300 hours. The resistivity of the unalloyed specimen remained essentially constant for about 20 hours. Between 20 and 1000 hours, its resistivity decreased gradually from 119 to 116 microhm-cm. This slight decrease may have been due to relief of quenching stresses.

The initial sharp decrease in resistivity of the alloys from the room-temperature values is evidently associated with formation of the omega phase. This phase was detected by X-ray diffraction after 30 minutes of aging in all alloys, indicating that it was present in considerable amounts. According to X-ray results, the omega phase continued to increase in amount along the first plateau in the resistivity curve, reaching a maximum during or just after the second drop in resistivity.

Originally, it was believed that the second resistivity drop was due to loss of coherency between the omega and the beta phases. However, the magnitude of the decrease was rather large to be explained solely on this

Continued

basis. It seems more likely that the formation of alpha nuclei at this stage of aging could account for a large part of the decrease. Alpha was not shown by X-ray diffraction in specimens taken from hardness samples aged for times corresponding to the beginning of the second resistivity plateau. However, it is well known that considerable quantities of a phase of very small particle size may be present without being detected by ordinary diffraction methods.

The third sharp change in resistivity of the Ti-4.13Fe alloy was believed to be connected with the formation of a titanium-iron compound. Oddly enough, the formation of $TiCr_2$ in the Ti-8.10Cr alloy was not accompanied by a resistivity decrease. The reasons for the difference in behavior of the two alloys during the compound-precipitation stage are not well understood at present. It may be connected with the specific resistivities of the different compounds or with a coherency phenomenon.

The progress of aging as indicated by hardness in Figures 8 to 10 correlated reasonably well with the phase changes indicated by the resistivity curves and X-ray diffraction results. Hardness increased sharply with the initial formation of the omega phase. At about the time that the second resistivity drop indicated either loss of coherency or alpha formation, hardness also decreased rather sharply. During compound formation in the iron and chromium alloys, the resistivities and hardnesses showed the same trend, decreasing in the iron alloy and remaining essentially constant in the chromium alloy. This trend in the latter alloy suggested that the $TiCr_2$ precipitate may be coherent with the beta matrix. The resulting lattice strain could account for the retention of high hardness and resistivity.

Since electrical resistivity was apparently highly sensitive to phase changes in titanium alloys, it was decided to base subsequent age-hardening and phase-identification work on resistivity curves. It was hoped also to define further the age-hardening mechanism by studying resistivity changes during aging. Therefore, a second series of resistivity versus aging-time curves was made at temperatures of 700 and 800 F with the following objectives:

- (1) Confirmation of the relationship between age-hardening reactions and resistivity changes.
- (2) Determination of the effect of primary alpha* on the age-hardening reactions. This is of particular importance since the recommended heat treatments for high-strength alloys involve solution treatments in the alpha-beta phase regions.

*Primary alpha is defined as the equilibrium alpha present in the structures of specimens quenched from temperatures in the alpha-beta-phase regions of the alloy.

- Continued*
- (3) Study of the age-hardening mechanism in alloys having higher percentages of beta-stabilizing elements. The Ti-12.8Cr and Ti-16.1Cr alloys were used for this investigation. A composition which is becoming of commercial significance, Ti-3Mn-1Cr-1Fe-1Mo-1V, was also included.

In cases where hardness and X-ray data were not already available for the particular alloy or aging conditions used, additional specimens were heat treated for these purposes. The aging times were selected to correspond to significant points on the resistivity curves. The alloys used, and the solution and aging temperatures for each, are listed in Table 6. In the case of the Ti-4.06Fe, Ti-7.70Cr, and Ti-11.5Mo alloys, the alpha-beta solution temperature was selected to give approximately 50 per cent primary alpha in the resulting microstructure.

The resistivity curves and hardness data obtained in these tests are plotted in Figures 12 through 20. The present contract expired before phase-identification work could be started on these specimens. However, some interesting general observations can be made based on the available data.

Considering Figures 12 through 14, the relative changes in resistivity with time at 700 F were much slower than those occurring at 800 F (Figures 15 through 18). However, the same trend applies at the lower temperature, i. e., a continual decrease in resistivity coincident with the appearance of omega in the X-ray patterns. A puzzling anomaly occurred in the Ti-4.13Fe alloy aged at 700 F (Figure 12). Alpha appeared in the photograms of this alloy aged for 500 hours. According to the resistivity data, the sharp decrease which was thought to accompany alpha formation had not occurred at this aging time. It is hoped to resolve this anomaly in future work.

According to the resistivity data for the Ti-4.06Fe and Ti-11.5Mo alloys quenched from the alpha-beta-phase region and aged at 800 F (Figures 15 and 16), the primary alpha had only slight effects on the advanced aging reactions. The resistivity curves of both alloys had essentially the same shape as those obtained on similar alloys quenched from the beta field and aged at the same temperature. The sharp decreases began at about the same aging times, but were extended over a somewhat longer time period in the alpha-beta solution-treated material. The initial decrease in resistivity from room-temperature values was markedly affected by the alpha-beta treatment, however. This decrease was very slight in the case of the iron alloy and resistivity actually increased in the Ti-11.5Mo alloy. The latter case indicated that the normally expected increase in resistance due to thermal effects actually overshadowed the effects due to omega formation..

TABLE 6. TITANIUM AND TITANIUM-ALLOY SPECIMENS
MEASURED FOR ELECTRICAL RESISTIVITY
DURING AGING (IODIDE TITANIUM)

Specimen	Alloy Composition, weight per cent	Solution Temperature, F	Aging Temperature, F
A1	4.13Fe	1700	800
A2	8.10Cr	"	"
A3	10.2Mo	"	"
A4	0	"	"
B1	4.13Fe	"	700
B2	8.0Cr	"	"
B3	10.2Mo	"	"
B4	12.3Cr	"	"
B5	16.2Cr	"	"
B6	4.0Fe	1425	800
B7	8.0Cr	1325	"
B8	11.0Mo	1325	"
B9	3Mn, 1Fe, 1Cr, 1Mo, 1V	1700	"
B10	3Mn, 1Fe, 1Cr, 1Mo, 1V	1400	"

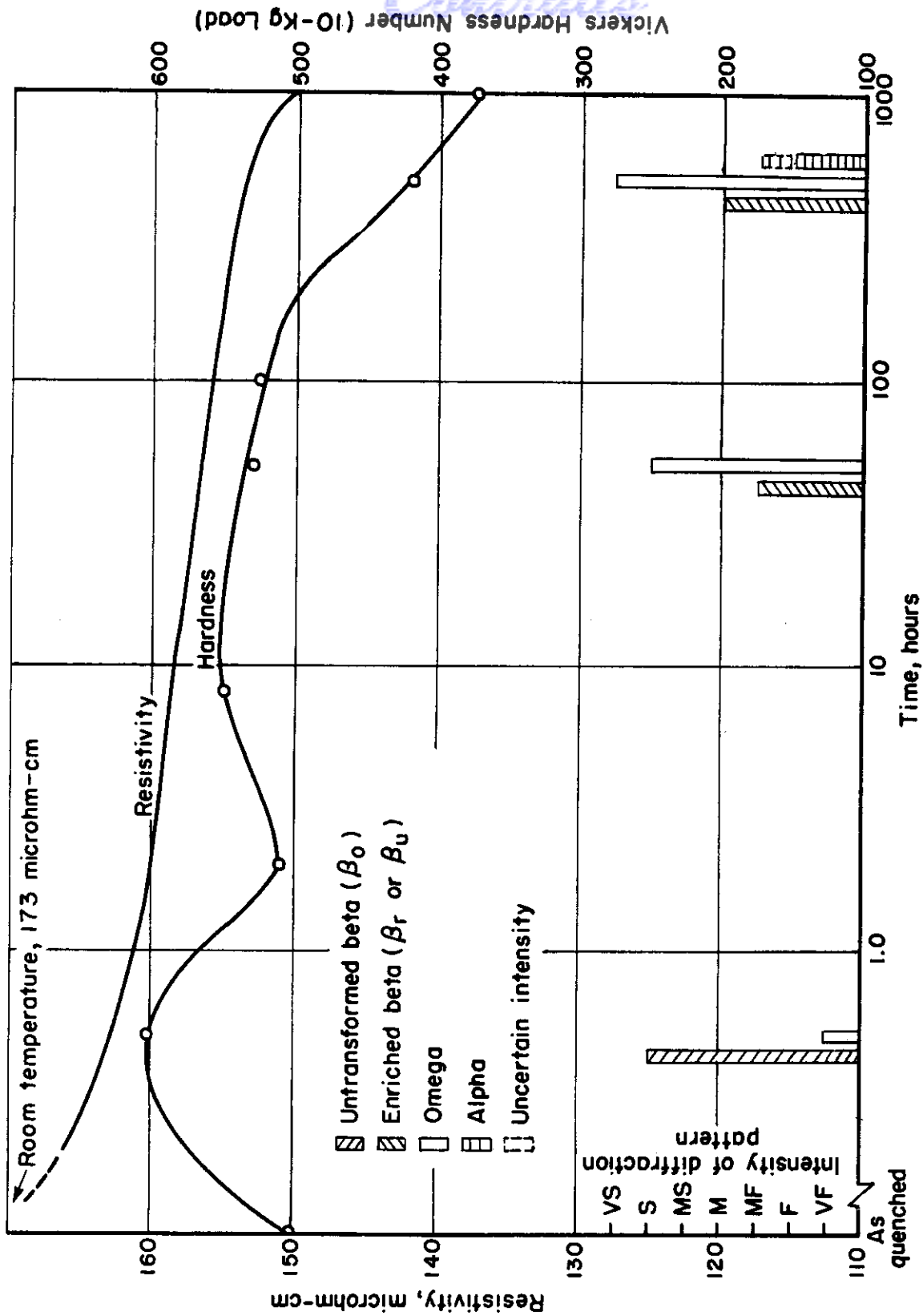


FIGURE 12. EFFECT OF AGING AT 700 F ON THE RESISTIVITY, HARDNESS, AND X-RAY DIFFRACTION-PATTERN INTENSITIES OF A Ti-4.13 Fe ALLOY QUENCHED FROM 1700 F

A-11946

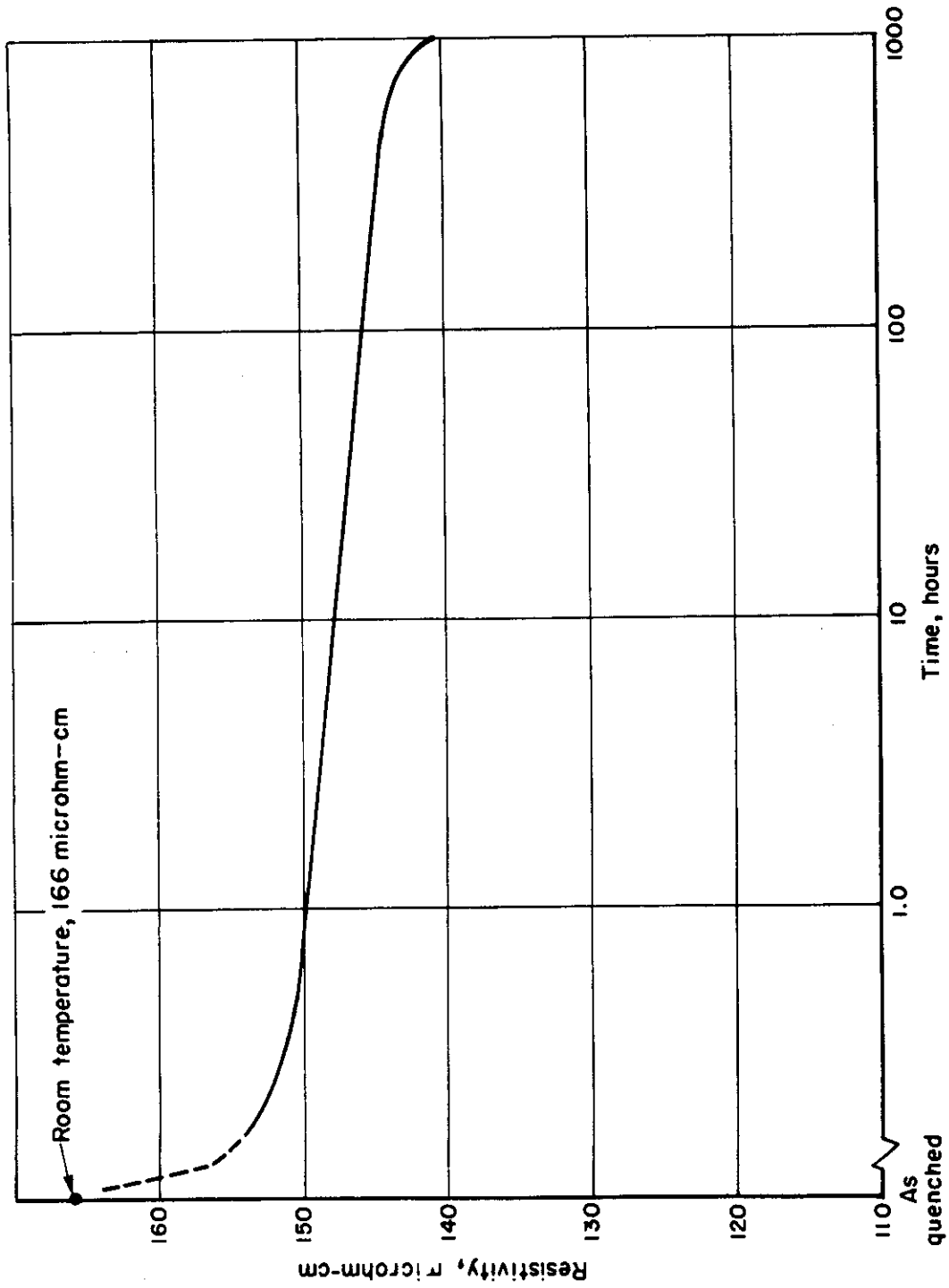


FIGURE 13. EFFECT OF AGING AT 700F ON THE RESISTIVITY OF A Ti-7.70 Cr ALLOY QUENCHED FROM 1700F

A-11947

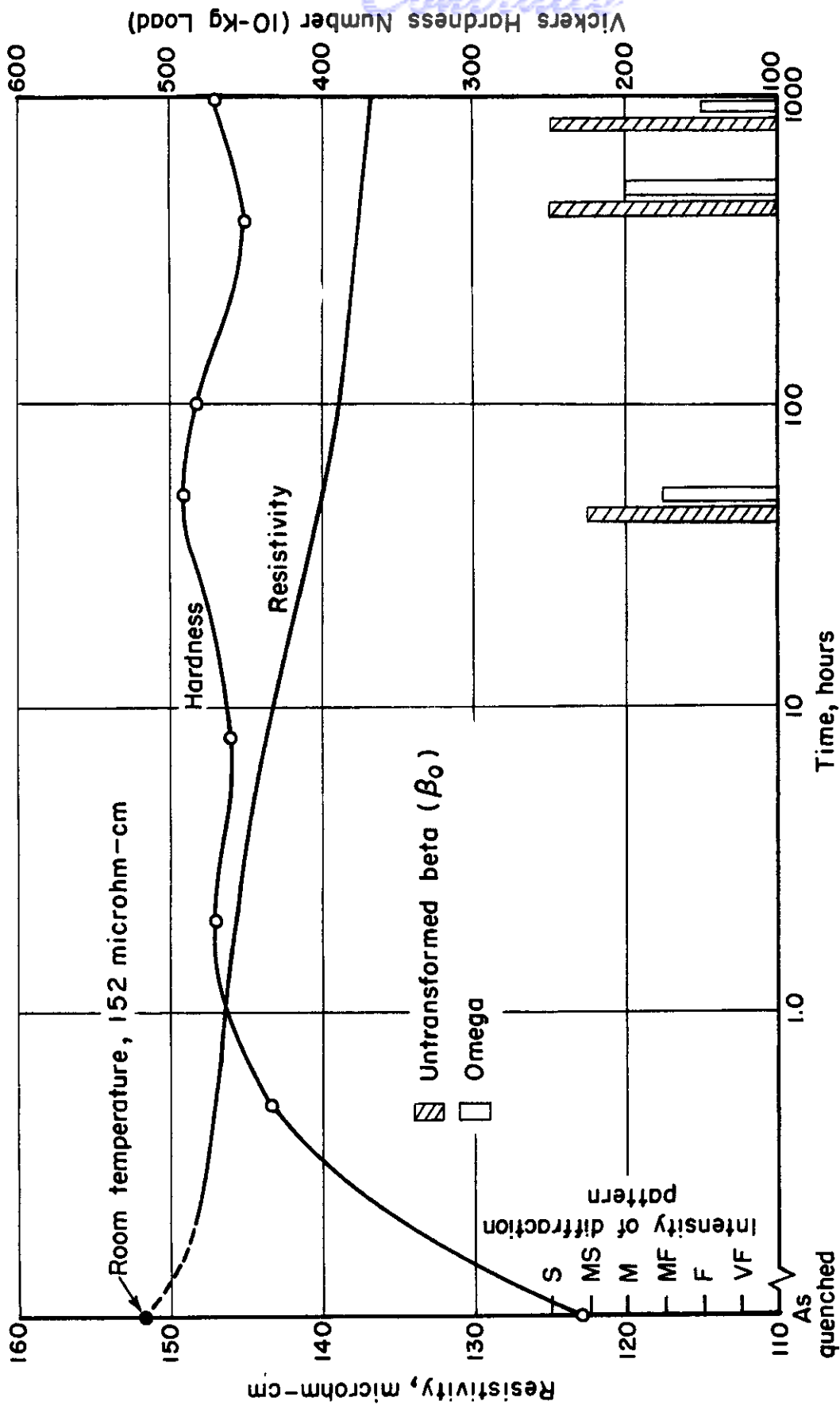


FIGURE 14. EFFECT OF AGING AT 700F ON THE RESISTIVITY, HARDNESS, AND X-RAY DIFFRACTION-PATTERN INTENSITIES OF A Ti-10.2 Mo ALLOY QUENCHED FROM 1700F

A-11948

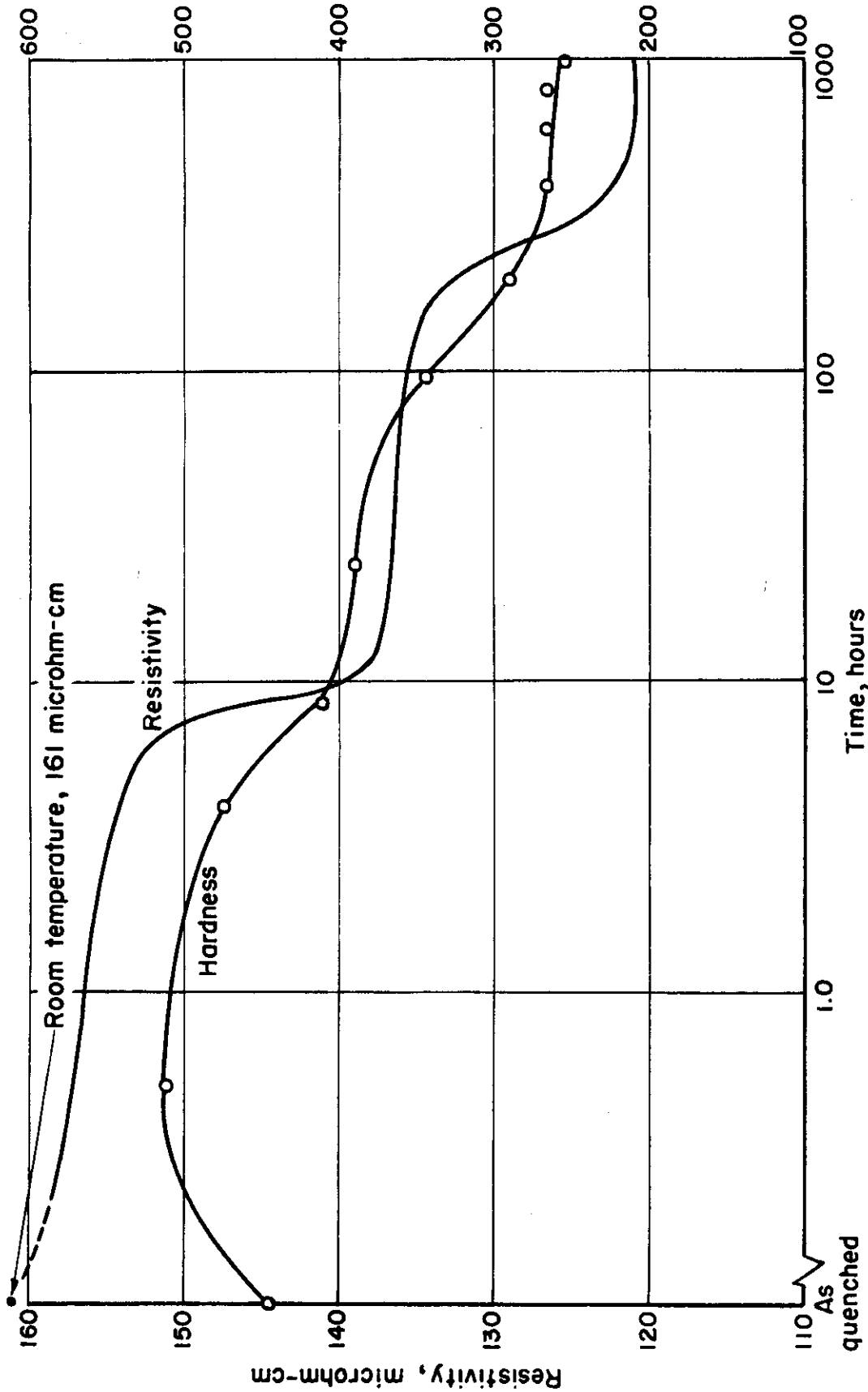


FIGURE 15. EFFECT OF AGING AT 800F ON THE RESISTIVITY AND HARDNESS OF A
Ti - 4.06 Fe ALLOY QUENCHED FROM 1425F

A-11949

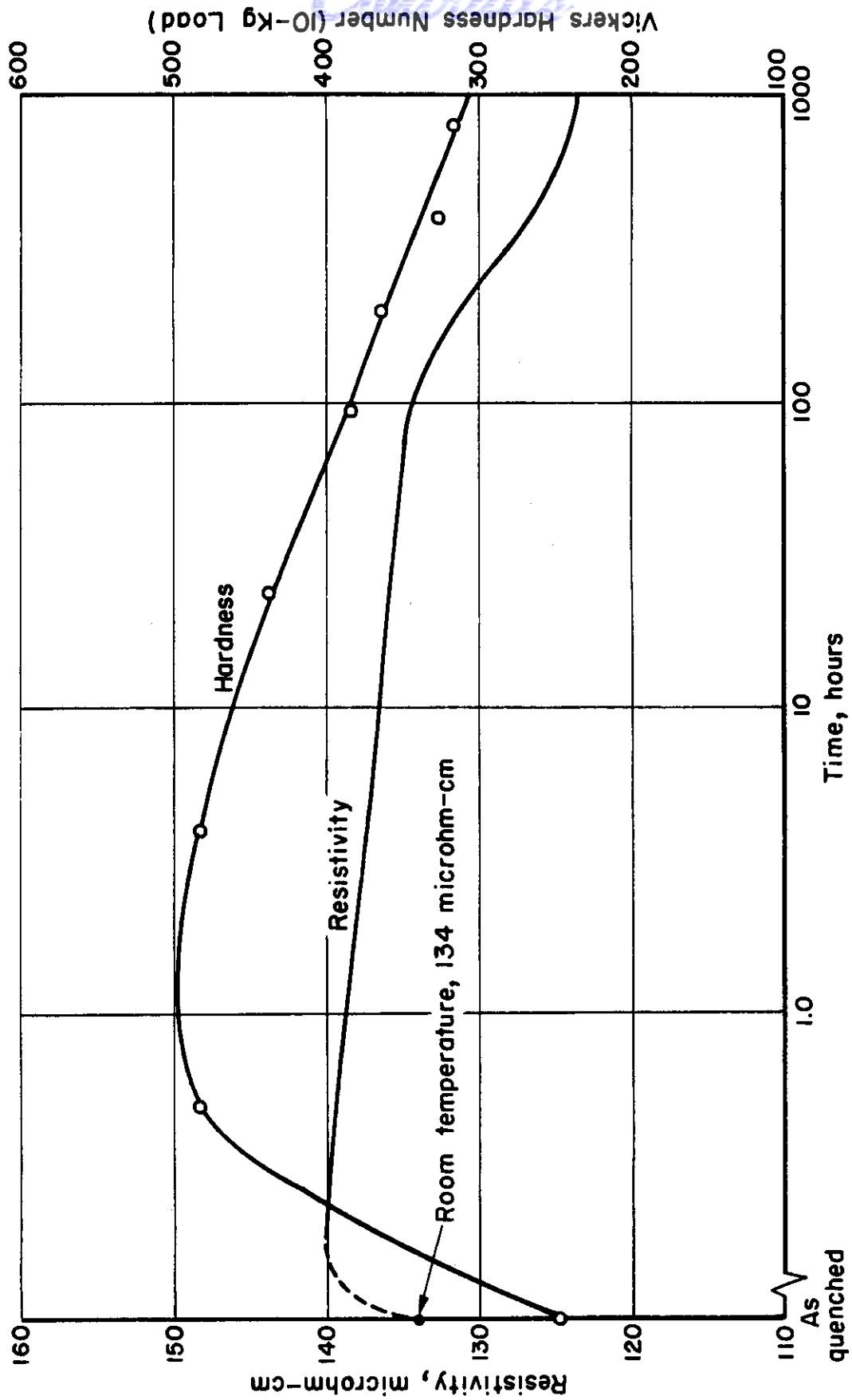


FIGURE 16. EFFECT OF AGING AT 800F ON THE RESISTIVITY AND HARDNESS OF A Ti-11.5 Mo ALLOY QUENCHED FROM 1325F

A-11951

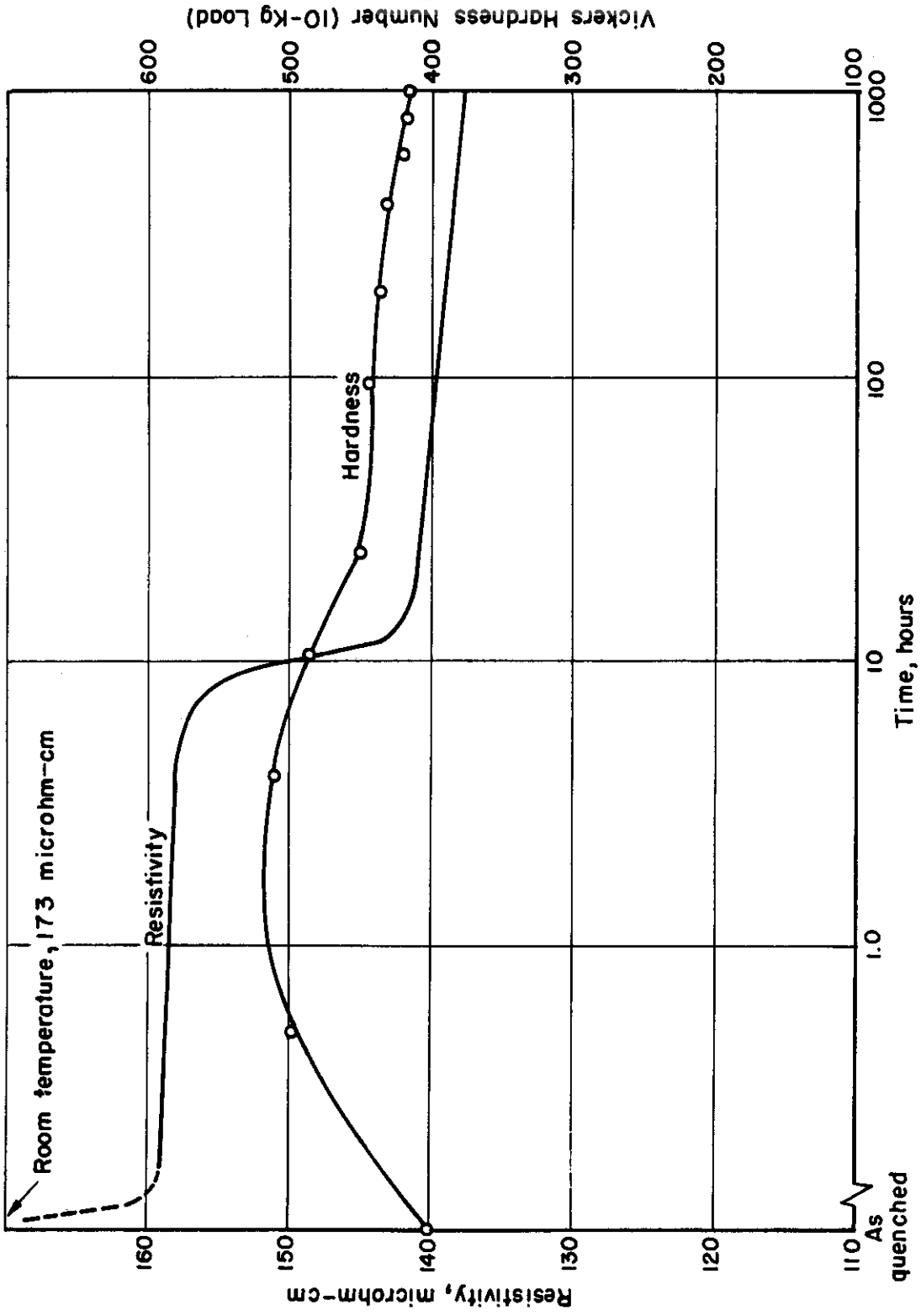


FIGURE 17. EFFECT OF AGING AT 800F ON THE RESISTIVITY AND HARDNESS OF A Ti-3 Mn-1 Cr-1 Fe-Mo-IV ALLOY QUENCHED FROM 1700F

A-11951

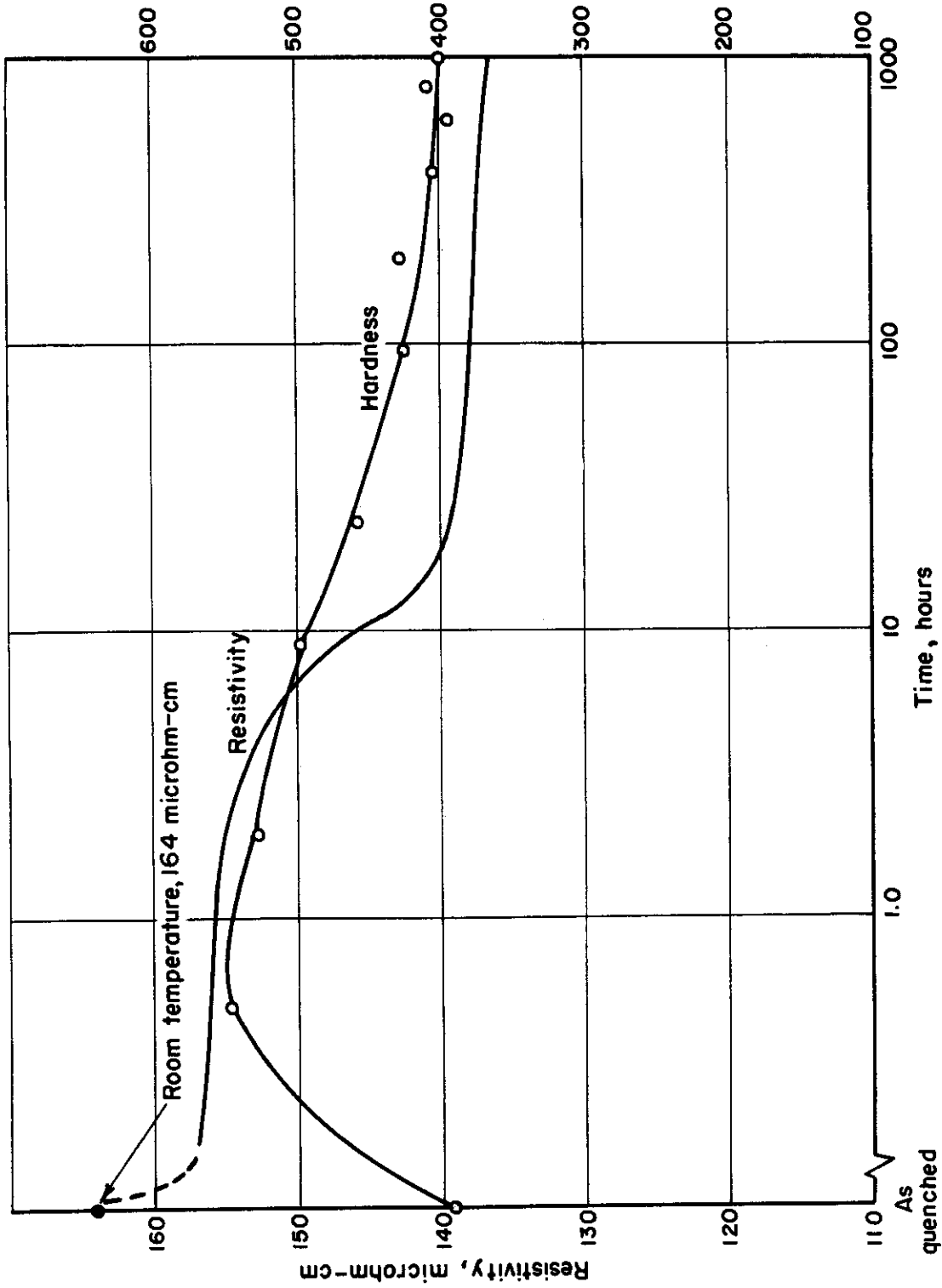


FIGURE 18. EFFECT OF AGING AT 800F ON THE RESISTIVITY AND HARDNESS OF A Ti-3Mn-1Cr-1Fe-1Mo-1V ALLOY QUENCHED FROM 1400F

A-11952

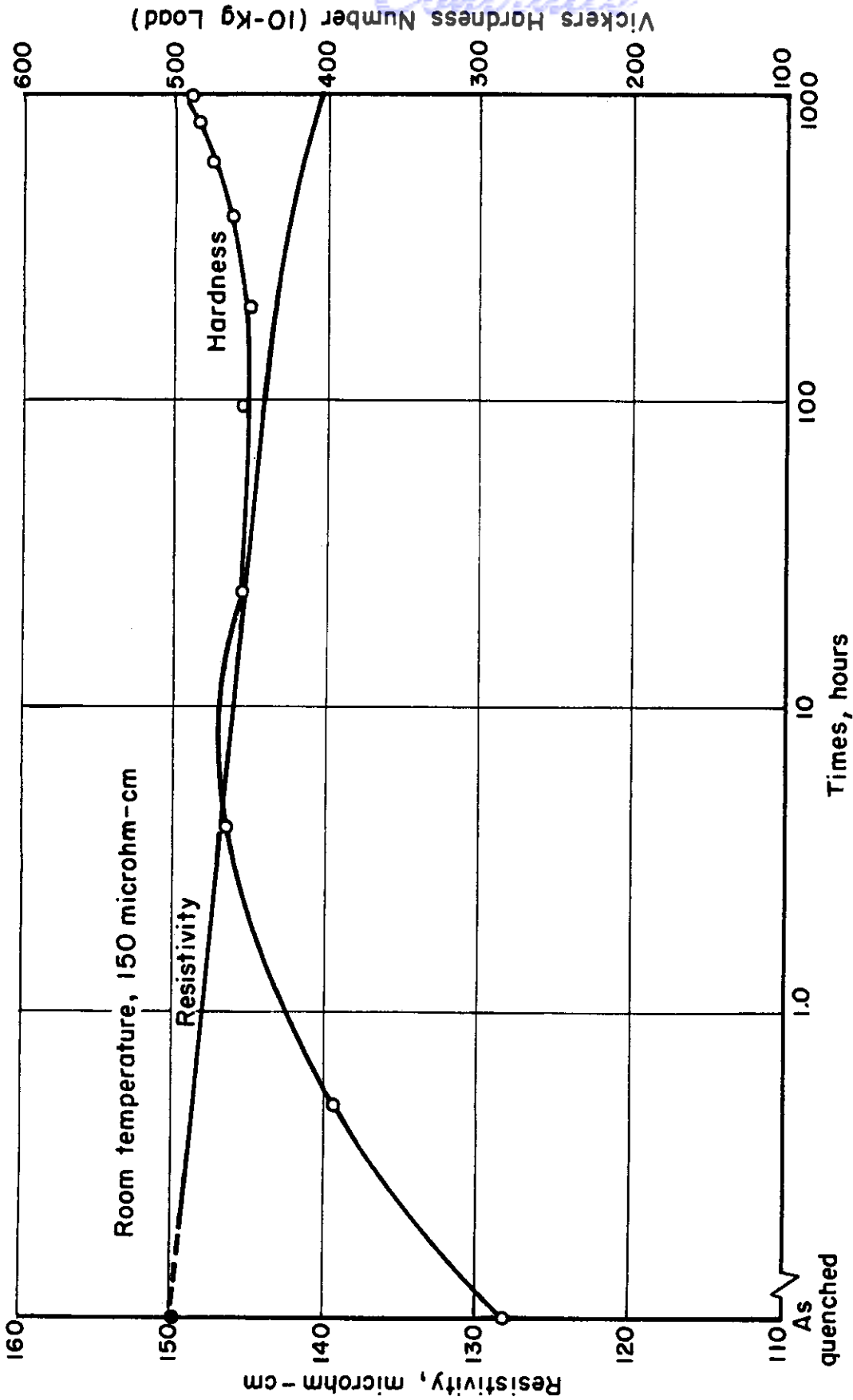


FIGURE 19. EFFECT OF AGING AT 700F ON THE RESISTIVITY AND HARDNESS OF A Ti-12.8 Cr ALLOY QUENCHED FROM 1700F

A-11953

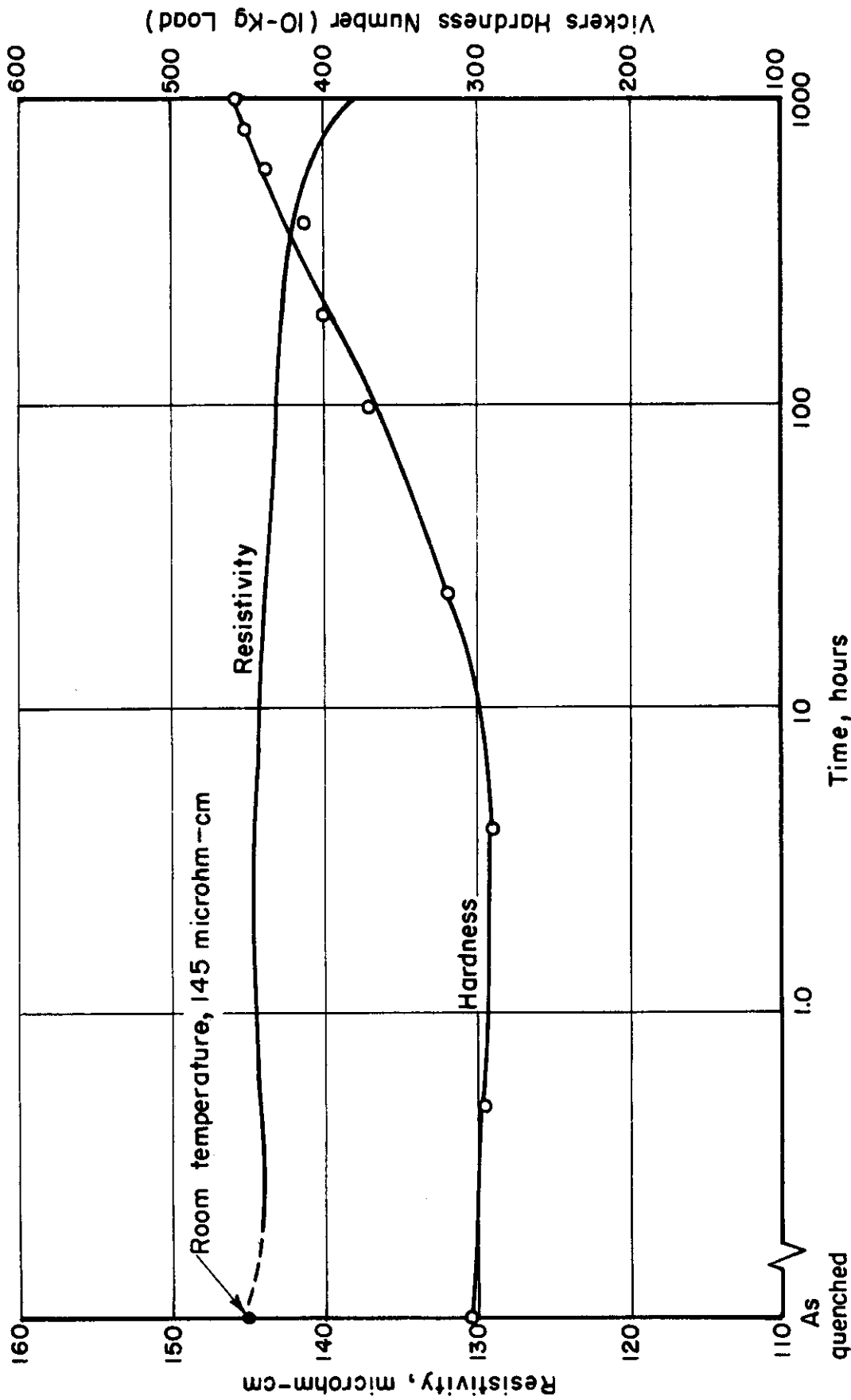


FIGURE 20. EFFECT OF AGING AT 700F ON THE RESISTIVITY AND HARDNESS OF A Ti-16.1 Cr ALLOY QUENCHED FROM 1700F

A-11954

Continued

The data shown in Figures 17 and 18 indicate that the Ti-3Mn-1Cr-1Fe-1Mo-1V alloy undergoes essentially the same sequence of aging reactions as a Ti-8Cr alloy (Figure 9). The hardness and resistivity curves for the Ti-12.8 and Ti-16.1Cr alloys (Figures 19 and 20) suggest that these richer alloys also undergo aging reactions similar to those of a Ti-8Cr alloy. However, the rate of the initial hardening reaction decreased with increasing alloy content.

Effect of Short-Time Aging on Room-Temperature Resistivity

The absolute changes in resistivity caused by the early aging reactions could not be determined from the preceding experiments because the resistivity value at zero time at the aging temperature was not known. To obtain some idea of the magnitude of this change, a few specimens of the Ti-7.70Cr alloy previously quenched from 1700 F were aged in a lead bath at 700 F for times ranging from 0 to 20 minutes and quenched. Resistivity was then determined on these specimens at room temperature. The results of these tests are given in Table 7.

TABLE 7. ROOM-TEMPERATURE RESISTIVITY OF Ti-7.70Cr ALLOY AFTER SHORT AGING TIMES

Aging Time at 700 F, minutes	Electrical Resistivity, 10^{-6} ohm-centimeters
0	166
5	131
10	125
20	121

Apparently, resistivity decreases very rapidly during the early stages of aging. In fact, the decrease is of such speed and magnitude as to suggest a possible ordering phenomenon rather than a precipitation reaction. This possibility will be investigated further.

Two etchants of the following compositions were used on the specimens subjected to microscopic examination:

- (1) 1.5% HF, 3.5% HNO₃, balance water
- (2) 50% HF, 50% ethylene glycol.

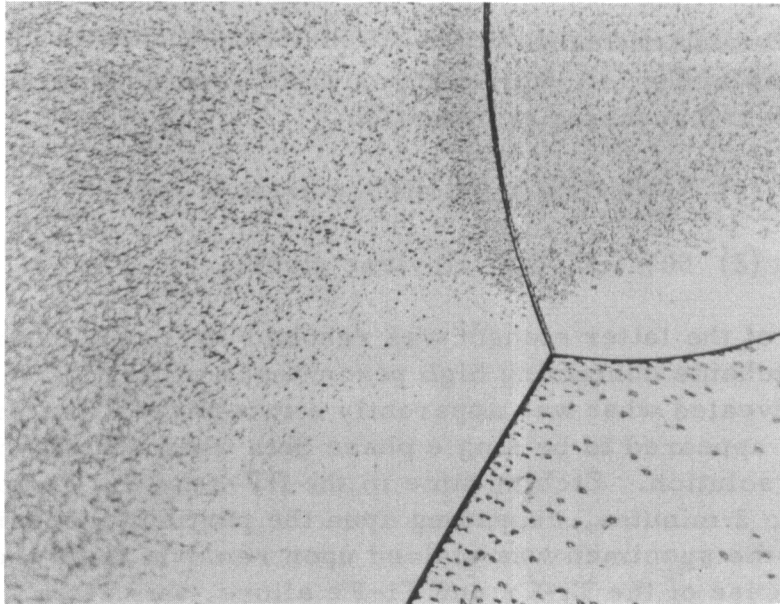
The composition of the latter etchant was reached after considerable experimentation with etchants containing high percentages of HF. In many cases, these etchants revealed what was apparently a two-phase structure in specimens which appeared to be single phase beta when etched with the HF-HNO₃-water solution. Etching time in the HF-ethylene glycol solution was 30 seconds to 2 minutes, depending upon the particular specimen. In some instances, the specimen was stained upon removal from the etching solution. In the case of the Ti-Cr and Ti-Fe alloys, this stain was readily removed by a brief swab with the HF-HNO₃-water solution. Ti-Mo specimens in advanced stages of aging stained heavily with either etchant and no structure could be observed.

The HF-glycol etchant revealed a fine precipitate in the Ti-4.13Fe and Ti-8.10Cr alloys aged at 500 F. This precipitate was unresolved using conventional etching techniques. Figures 21 through 24 show several examples of an increase of the precipitate phase with increase in aging time at 500 F. The dark-etching areas in these photomicrographs may indicate omega phase, since diffraction lines of this phase appear in all specimens responding to the etch.

The HF-glycol etch is an improvement over etchants formerly used, but it is not entirely satisfactory. It does not reveal a second phase in some alloys aged at 700 and 800 F where considerable amounts of omega are known to be present. Staining is serious in some cases, particularly the Ti-10.2Mo alloy.

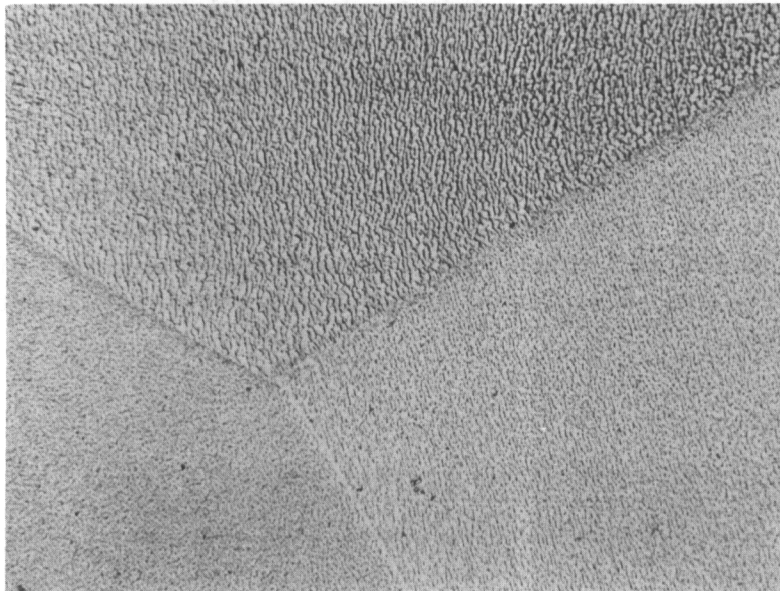
INDEPENDENCE OF OMEGA PHASE FROM INTERSTITIAL IMPURITY ELEMENTS

At the beginning of the present contract period, the newly discovered omega phase had been observed only in alloys made from commercial-purity titanium and its existence had not been generally verified. Therefore, it was necessary to determine whether omega is a transition phase common to pure binary substitutional alloys, as the early work appeared to indicate, or, alternatively, whether it is an impurity phase dependent on the presence



500X 50% HF-50% Ethylene Glycol Etch N5771

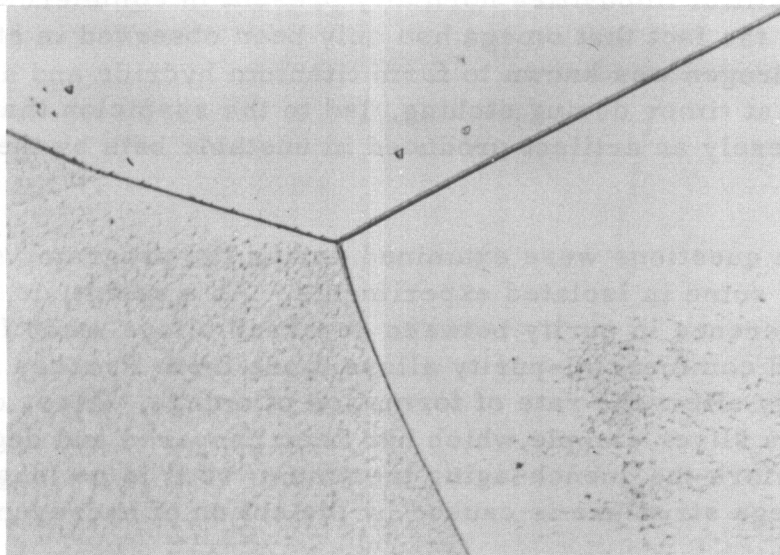
FIGURE 21. Ti-4Fe ALLOY, ICED BRINE QUENCHED FROM 1700 F AND AGED 1/2 HOUR AT 500 F



500X 50% HF-50% Ethylene Glycol Etch N5774

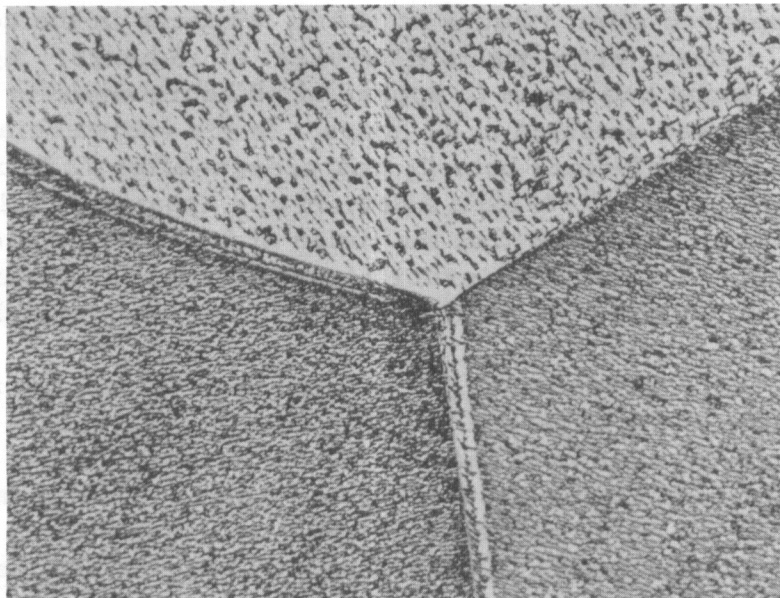
FIGURE 22. Ti-4Fe ALLOY, ICED BRINE QUENCHED FROM 1700 F AND AGED 500 HOURS AT 500 F

Dark etching areas are believed to indicate the omega phase.



500X 50% HF-50% Ethylene Glycol Etch N5770

FIGURE 23. Ti-8Cr ALLOY, ICED BRINE QUENCHED FROM 1700 F AND AGED 1/2 HOUR AT 500 F



500X 50% HF-50% Ethylene Glycol Etch N5772

FIGURE 24. Ti-8Cr ALLOY, ICED BRINE QUENCHED FROM 1700 F AND AGED 8 HOURS AT 500 F

Dark etching areas are believed to indicate the omega phase.

of the interstitial impurities normally present in commercial-purity alloys. In addition, the fact that omega had only been observed in etched samples, and that hydrogen was known to form titanium hydride and dissolve in the beta lattice at times during etching, led to the suspicion that omega itself might be merely an artifact produced in unstable beta by the entrance of hydrogen.

These questions were examined during the program, some systematically and some in isolated experiments. As a result, it can be stated that the difference in purity between degassed alloys made from iodide titanium and commercial-purity alloys made from Process A titanium does not seriously affect the rate of formation of omega. Also, omega has been detected in a sliver sample which had been prepared and degassed of hydrogen before the quench-aging treatment; so it is no longer suspected that the omega structure is caused by the action of hydrogen during the etch.

The general effect of interstitial impurities on omega formation was seen in the comparison of the X-ray diffraction examination of commercial-purity alloys (Table 1) and vacuum degassed iodide alloys (Table 5). The effect on hardness has been presented in Figure 7.

In the iodide Ti-8.10Cr alloy in 700 F aging, the untransformed beta β_0 had disappeared after 8 hours at 700 F, whereas in the commercial-purity Ti-8Cr alloy, some was still present at 16 hours. Again, in the iodide alloy, alpha had begun to appear at 50 hours while in the commercial alloy, no alpha was detected at 72 hours. In the commercial-purity Ti-4Fe alloy, some untransformed beta β_0 was present after 72 hours of aging, whereas in the iodide Ti-4.13Fe alloy, it was apparently all transformed in 50 hours. These data show that the times of formation and decay of omega are definitely within the same order of magnitude and appear to be slightly shorter in the degassed iodide alloys than in the commercial-purity alloys.

For reasons of economy, the iodide alloys were examined by X-ray diffraction only in the degassed form. Those having 0.02H and 0.10 additions were not examined because all the hardness-aging time curves entered the various stages about the same times. This behavior was taken to indicate that the rates of transformation were essentially the same. The degassed Ti-8.10Cr and Ti-4.13Fe alloys had higher hardnesses in the as-quenched condition than the corresponding alloys having hydrogen and oxygen additions. In view of the fact that oxygen hardens titanium alloys, the higher hardness for the purer alloy in the as-quenched condition indicated that it aged more rapidly during the quench, which may be further evidence that interstitial impurities retard the formation of omega.

In addition to the above-mentioned studies of aging of sheet made from degassed buttons, a hardness and X-ray diffraction study was made of a commercial-purity Ti-8Mn alloy degassed in sheet form for the purpose

of removing hydrogen. The treatment consisted of heating for 4 hours at 900 C at a pressure of 10^{-5} mm of mercury or lower. This treatment should have removed all but a few parts per million of hydrogen. It was then sealed in an evacuated quartz capsule and quenched by breaking the capsule under water after a 10-minute solution treatment at 950 C. The hardnesses and the phases observed by X-ray diffraction are listed in Table 8. The as-quenched hardness was no different from the nondegassed samples, and rather intense patterns of omega were observed after long aging times.

While the above evidence showed that omega could be formed in samples having very low hydrogen content, a suspicion remained that the new phase might be an artifact produced by the entry of hydrogen into the unstable beta lattice during etching of the samples. The basis for this suspicion was the ease with which the hydrogen was observed to enter the beta lattice, forming a phase identified by X-ray diffraction as TiH.

Therefore, it was necessary to find omega in sample surfaces that had not been etched. It was decided to try filings. A sample of iodide Ti-8Cr alloy was chosen which showed a good intensity of omega pattern in sliver form in a Debye camera and in flat sample form on the spectrometer. In the as-filed condition, alpha and beta were identified although no alpha had been observed before filing. Aging of the filings in an evacuated capsule for 15 minutes at 700 F only increased the intensity of the alpha pattern. Apparently the cold work of filing had caused the omega to transform to alpha.

After the failure of this experiment, it was decided to degas a sliver specimen to remove any hydrogen from the etch, and quench and age without active acid or atmosphere contact. With the Vycor-tube vacuum furnace available, it was found necessary to study a Ti-8Mn sliver in order to have some untransformed beta β_0 left after the sample cooled down in the tube. The combination degassing and beta-izing treatment was performed at 800 C (1470 F) for 20 minutes. After the fast cool, some alpha was present in the sample, either from having the sample in the alpha-beta solution-treating field or from transformation during cooling. However, untransformed beta, enriched beta, and a trace of omega were also present. After 30 minutes of aging in high vacuum at 700 F, the relative intensity of the omega pattern had increased to very faint. Thus it was proved that omega is not an artifact produced by etching.

TABLE 8. HARDNESS AND CONSTITUTION OF Ti-8Mn ALLOY AFTER VACUUM ANNEALING TO REMOVE HYDROGEN, SOLUTION TREATING, AND AGING

Aging Treatment	Hardness, VHN	Intensities of Phase Patterns Observed(a)		
		Untransformed Beta (β_0)	Enriched Beta (β_r)	Omega
As quenched	395	--	--	--
4 hr 500 F in oil	428	--	--	--
24 hr 500 F in oil	441	vs	0	0
16 hr 700 F in air	--	ms	m, br	m
4 hr 500 F in oil + 120 hr 700 F in air	--	0	m, vbr	ms

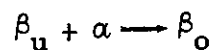
(a) Key to abbreviations: s = strong, m = medium, v = very, br = broad.

Contrails
CORRELATION OF DILATOMETER TRACES
AND PHASE COMPOSITION

Adenstedt and coworkers⁽⁵⁾ found a negative deviation from linearity in the thermal expansion curve of a beta-quenched Ti-V alloy on heating, although the curve was linear on cooling. They reported that the deviation occurred in the range 600 to 900 F and suggested that it was due to alpha precipitation. In view of the discovery of the omega phase, this deviation was investigated by X-ray diffraction methods to establish whether or not it has any relation to the omega and alpha precipitation.

Dilatometer curves were made at the Materials Laboratory, Wright Air Development Center, of Ti-10Cr, Ti-15Cr (two sets of samples), Ti-7.5Ni, Ti-15V, and Ti-3Mn-1Fe-1Cr-1Mo-1V alloys. For the purpose of comparing transformations and structural changes with the dilation curves, samples which had been beta-quenched were heated in the dilatometer at 1 F/min and quenched from various temperatures. Each of the five compositions was quenched from 400, 600, 800, 1000, 1220, and 1500 F. One set of Ti-15Cr samples was quenched only at 600, 650, 800, and 1000 F. The samples were all of 1/16-inch-square cross section. They were etched into sliver shapes and examined in the Debye camera. The various phases observed in each sample are listed in Tables 9 and 10. Unfortunately the dilation curves are not available for comparison, but it is understood that, in general, the deviation from linearity started around 600 F and ended around 900 F, and that the deviation for the 3Mn complex alloy was considerably smaller than for the other alloys. The detection of considerable amounts of omega at 800 F in the 10Cr, 7.5Ni, and 15V titanium alloys, and of alpha at 1000 F, suggested that omega was responsible for the deviation from linearity in these three alloys.

In the Ti-10Cr alloy, for example, little if any omega was detected after quenching from 400 and 600 F. After quenching from 800 F, the untransformed beta had disappeared, having become converted to enriched beta, and omega was observed in medium intensity. At 1000 F, the omega was gone, but alpha was present in quantity. At 1220 F, a lesser intensity of alpha was detected; also, the enriched beta had disappeared and "untransformed" beta was observed, presumably because of the partial completion of the reverse reaction



occurring on reaching the beta/alpha-plus-beta transus. The sample quenched on reaching 1500 F showed a very faint, very diffuse pattern of omega which was undoubtedly formed during the quench, while the sample was passing through the temperature range where the maximum rate of transformation occurs.

TABLE 9. X-RAY DIFFRACTION ANALYSES OF Ti-Cr ALLOYS
QUENCHED FROM DILATOMETER FURNACE

Composition, per cent	Temperature Before Quench, F	Phase Patterns Observed(a)				
		β_0	β_r or β_u	ω	α	Other
10Cr	400	s	0	0	0	0
"	600	s	0	vvf?	0	TiH vvf, d
"	800	0	m, br	m	0	0
"	1000	0	ms	0	ms	0
"	1200	s	0	0	mf	0
15Cr	400	s (mf)(b)	0	0	0	TiCr ₂ mf
"	600	s (mf)(b)	0	0	0	TiCr ₂ vf
"	800	vs (mf)(b)	0	0	0	TiCr ₂ f
"	1000	s	vf	0	f	TiCr ₂ vf
"	1220	mf	s, br(c)	0	vf	TiCr ₂ mf
"	1500	ms (mf)(b)	0	0	vvf	TiCr ₂ mf
15Cr	As quenched	s	0	0	0	0
"	600	s	0	0	0	0
"	650	s	0	0(d)	0	0
"	800	s(e)	0	0	0	0
"	1000	0	s	0	f	0

(a) Abbreviations: s = strong, m = medium, f = faint, v = very, d = diffuse, br = broad, β_0 = untransformed beta, β_r or β_u = beta with reduced lattice constant, ω = omega, α = alpha.

(b) Specimen segregated. Intensity in parentheses applies to segregated region.

(c) Lattice constant expanded compared to sample above it in table.

(d) No omega was definitely detected, but an unexplained diffuse line was observed at 1.202 Å, which is an omega line position.

(e) Beta lattice is slightly expanded with small lattice constant spread.

Contrails

TABLE 10. X-RAY DIFFRACTION ANALYSES OF Ti-Ni, Ti-V, AND
Ti-3Mn COMPLEX ALLOYS QUENCHED FROM
DILATOMETER FURNACE

Composition, per cent	Temperature Before Quench, F	Phase Patterns Observed(a)				
		β_0	β_r or β_u	ω	α	Other
7.5Ni	400	s	0	vvf, vd	0	0
"	600	0	s	m, d	0	0
"	800	0	0?	mf	ms	Ti ₂ Ni vvf
"	1000	0	0	0	ms	Ti ₂ Ni m
"	1220	0	0	0	s	Ti ₂ Ni ms
"	1500	0	0	0	ms	Ti ₂ Ni m
15V	400	s	0	vf, vd	0	TiH mf(b), d
"	600	s	0	vf, d	0	TiH vf(b), d
"	800	0	ms, br	s	0	0
"	1000	0	ms, d	0	m	0
"	1220	s	0	vvf, d	vvf	0
"	1500	s	0	vvf, d	0	TiH vvf(b), d
3Mn Complex	400	ms	0	0?	ms	0
"	600	ms(c)	0	0	ms	0
"	800	0?	mf, vd(d)	0	ms	0
"	1000	0	m, vd(d)	0	ms	0
"	1220	0	ms, d(c)	0	ms	0
"	1500	0	m, d(c)	0?	m, d	0

(a) Abbreviations: s = strong, m = medium, f = faint, v = very, d = diffuse, br = broad, β_0 = untransformed beta, β_r or β_u = beta with reduced lattice constant, ω = omega, α = alpha.

(b) A hydride may be present which does not have the usual TiH structure.

(c) Lattice constant expanded compared to sample above it in table.

(d) Lattice constant contracted compared to sample above it in table.

In the Ti-7.5Ni alloy, the omega was developed as low as 600 F, and was still present along with alpha and some Ti₂Ni at 800 F. From 1000 to 1500 F only alpha and Ti₂Ni were detected.

The Ti-15V alloy developed a strong intensity of omega in the sample quenched from 800 F. At 1000 F, only transformed beta and alpha were detected, but at 1220, where the reverse reaction ($\beta_u + \alpha \rightarrow \beta_o$) should be almost complete according to the constitution diagrams(5, 14), only untransformed beta, a very, very faint pattern of alpha, and a very, very faint diffuse pattern of omega were observed.

The two Ti-15Cr alloys include one which was strongly segregated and another which was homogeneous in the as-quenched state. The non-homogeneous alloy quenched from 400 and 600 F where little or no transformation had taken place, showed a few reflections from grains of relatively low chromium concentration and Debye rings from TiCr₂ in addition to a uniform solid solution, which made up the bulk of the material. At 1000 F, the untransformed beta of lower chromium concentration was apparently replaced by enriched beta; the alpha observed here probably came from the lower chromium containing grains also, as in the Ti-10Cr alloy at this temperature. The untransformed beta which made up the bulk of the sample appeared unchanged. At 1200 F, only a medium faint pattern of untransformed beta (that showing K-alpha resolution) remained. The rest of the beta pattern showed a heterogeneous chromium concentration within each grain. The concentration was somewhat reduced from the original. At 1500 F, the X-ray photogram was similar to that of the 400 F quench, except for the trace of alpha which probably formed in the low-chromium portions of the sample during cooling.

The homogeneous Ti-15Cr alloy showed evidence of beta decomposition at 800 F in that the individual spot reflections showed a small but definite range in Bragg angle, so that K-alpha resolution of each spot was lost. A minor lattice expansion was also noted, but this expansion may not be real, for frequent observations have been noted of lattice expansion caused by hydrogen. Decomposition of the homogeneous alloy at 1000 F is more characteristic of a Ti-15Cr composition than the extreme stability of the beta in an inhomogeneous alloy where the lattice constant for the untransformed beta indicated a composition of about 18 per cent chromium. Failure to identify omega in the Ti-15Cr alloys in spite of evidence for a transformation was paralleled by observation in the Ti-12.3Mn alloy (see Isothermal Transformation of Commercial-Purity Ti-12.3Mn Alloy).

The Ti-3Mn complex alloy differed from the others in three respects:

- (1) It was very fine grained, giving continuous Debye rings rather than spots

- (3) The alpha phase showed a rather strong preferred orientation.

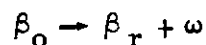
No omega phase was detected positively in any of the samples of the Ti-3Mn complex alloy. However, the samples of this alloy did not seem to be comparable with the other alloys because it appeared that this alloy was quenched from the alpha-plus-beta state rather than the all-beta state. Hence, alpha-beta interfaces might have prevented formation of omega by providing growing edges for alpha. The beta-phase pattern in the sample quenched from 400 F was sharp and undoubtedly represented the beta existing at the solution-treating temperature. In the sample quenched from 600 F, however, the beta appeared to have undergone an expansion in lattice constant. There would seem to be no logical explanation for an expansion of beta (signifying alloy enrichment) at this point. However, these apparent-beta lines fit closely the positions of the strongest lines of omega, and no evidences of the unequivocal omega lines were detected. Therefore, the following tentative explanation is suggested: The beta in the alpha-beta structure as-quenched was moderately enriched above the nominal alloy content, because it was in equilibrium with alpha. Somewhere below 600 F, some omega transformation occurred. The unequivocal omega reflections were undetected, either because of fine grain size, or for the same unknown reason that they were not seen in the Ti-12.3Mn and Ti-15Cr alloys.

At 800 and 1000 F, there occurred a diffusing and successive contraction of the beta lattice. This change is undoubtedly the evidence of decomposition of the as-quenched beta into enriched beta plus alpha. At 1220 F, expansion of the beta lattice was observed, which was probably the result of the beta composition losing alloy content while following the beta/alpha-plus-beta boundary above the eutectoid and perhaps also the extrapolation of it, below the eutectoid temperature.

The sample taken to 1500 F before quenching appeared to have undergone further expansion in the beta lattice.

Further experience with this alloy, permitting the observation of omega patterns from fine-grained and coarse-grained samples, and knowledge of the transformation behavior of the alloy would be required before one could distinguish between beta and omega.

The evidence from the Ti-10Cr, Ti-7.5Ni, and Ti-15V alloys showed that omega formed at the time when the deviation from linearity in the dilatometer trace occurred. Therefore, it was quite probable that the transformation



was responsible for the deviation.

CRYSTALLOGRAPHIC MECHANISM OF TRANSFORMATION

Investigation of the hardening phenomenon in beta titanium requires the application of effective methods and tools of fundamental research. This portion of the investigation, as originally proposed, was to include:

- (1) Verification or rejection of the precipitation-hardening concept by the study of lattice coherency
- (2) Determination of the mechanism of precipitation and the crystallographic orientation of the precipitate lattice with the matrix lattice during the stage when coherency exists
- (3) Identification of the precipitate phase, or phases, in several alloys.

One of the objectives of this program was to examine the possibility of preventing embrittlement in high-strength alloys.

The study of polycrystalline samples has contributed considerable knowledge of the hardening reaction. However, the information obtainable from powder data was incomplete, and it was necessary to obtain more basic information on the hardening by the use of single crystals or single grains.

When this research program was initiated, it was not expected that the precipitate phase would be easily detectable in polycrystalline X-ray samples. However, the omega phase which was discovered and which appeared to be responsible for the hardening, did give strong diffraction patterns, stronger than is usually obtained in precipitation-hardening systems at the time of maximum hardness. Although the composition and structure of omega phase were unknown, it was first presumed to be low in alloy content, since it appeared to be replaced by alpha on further aging. Although the formation of omega appeared to be the cause of hardening, the mechanism did not appear to be that of lattice coherency. In the early stages of precipitation, as is illustrated by the Ti-4Fe and Ti-8Cr alloys aged a few minutes at 700 F (or not at all), there appeared to be no directionality to the diffusing of omega spots. The beta spots also showed no streaking. It, therefore, was tentatively concluded that the polycrystalline samples showed no evidence of coherency between the matrix and the precipitate in the early stages of aging. With single crystals viewed with long exposure times, however, it might be possible to detect evidence of coherency in these early stages of aging.

The streaking of the beta in the theta direction after moderate aging has been taken to indicate enrichment of the beta in local regions. However,

Conclusions

a part of the streaking may be due to coherency. Also, it may be postulated that finite concentration gradients within the beta would constitute lattice coherency and would harden the beta. The mechanism might be as follows: Local regions of β_T coherent with β_0 could be strained, owing to lattice constant differences, in a manner analogous to coherency hardening. The continuity of the streaks, however, does not necessarily indicate that the concentration gradients were finite.

At 800 F in the later stages of aging, the precipitation of the TiFe compound probably involved coherency, since the compound was crystallographically oriented with the matrix and a slight bump in the hardness curve was observed. Of course, by the time the sharp pattern of the compound was observed, the coherency had certainly disappeared.

In the later stages of aging of the Ti-8.10Cr alloy at 800 F, there is indirect evidence from the powder data that coherency exists during the precipitation of $TiCr_2$. At 50 and 100 hours of aging, enriched beta ceased to be detected and only alpha was observed; thus, the chromium in the alloy was unaccounted for. At 500 and 1000 hours, $TiCr_2$ was observed, but the intensity was insufficient to account for all the chromium.

The purpose of the work using single crystals of beta was to determine (1) the orientation relations of the transformation, (2) the crystal structure of omega, and (3) the extent of coherency between omega and beta. The plan was to obtain the data necessary for these objectives with single-crystal oscillation methods of the type used by Preston⁽¹³⁾. For this work, a Weissenberg camera that embodies more powerful techniques in addition to the oscillating-crystal techniques used by Preston is available. This type of work is preferred over the stationary crystal, or so-called Laue, methods using characteristic radiation^(13 through 19), partly because the latter methods would not be so useful in determining the crystal structure of omega. The data obtained in the orientation study were to be used in working out the structure of omega. In fact, any proposed structure would need to be verified by the single-crystal oscillation methods.

The studies were started using single beta-matrix crystals of Ti-4.13Fe and Ti-8.10 Cr alloys in the as-quenched and lightly aged condition. Good single-grain samples were selected and oriented by back-reflection Laue photographs. It was observed that the number of Laue spots registered from the beta-plus-omega grains was multiplied over those obtained from body-centered-cubic metals, although the cubic symmetry was apparently retained. The samples were adjusted on the goniometer sample holder so as to have the desired crystallographic direction parallel to the rotation axis.

Oscillating-crystal photograms were taken of several crystals and it was found that the Weissenberg camera showed crystal splitting which the back-reflection Laue camera did not show in the orientation of the stationary

Contrails

crystal. Several of these grains proved to be strained or split into two or more single crystals. However, one grain was obtained which was apparently a single crystal. Study was just started with this crystal at the close of the current project. The initial orientation-rotation patterns were obtained. These patterns showed that the omega structure is more complex than the beta and indicated that it is oriented relative to the beta phase. This sample was one of the Ti-4.13Fe alloy which had been aged 2 hours at 800 F before being etched out of the 1/8-inch sheet material.

All of the material used for the single-crystal work had been prepared with coarse retained-beta grains by heating 4 hours at 2400 F in vacuum, sealing when cool in quartz capsules, solution treating at 1700 F, and quenching. The grains were isolated by inserting through holes in polyethylene sheets and then etching to 0.5-mm diameter in the slow-acting solution described previously. All of the as-quenched samples examined were too imperfect to use. Distortion from hydriding or damage during quenching contributed to the imperfection. It was concluded that after isolation by etching, the samples should be degassed and fast cooled in single-crystal form so as to avoid damage to the beta lattice.

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X-RAY DIFFRACTION METHODS AND
SAMPLE PREPARATION

It had been found possible, in previous X-ray diffraction work at Battelle, to study the process of transformation in titanium alloys through the use of small wedges⁽⁷⁾ or slivers⁽⁶⁾ etched out of 1/16-inch-thick sheet samples. These samples, which were examined in small Debye cameras, presented a surface area less than 1 square millimeter to the X-ray beam. How well they represented the total sample depended only on the uniformity of the alloy.

In previous studies under Contract No. AF 33(038)-3736, the isothermal transformation of Ti-Cr alloys was studied with oscillated wedge samples, while the isothermal transformation of Ti-Mn and the age hardening of Ti-Cr, Ti-Fe, and Ti-Mo alloys were studied with sliver samples which were rotated during exposure.

Wedge or sliver specimens of a coarse-grained alloy are superior to filings. Minor phase sensitivity is improved and lines of phases which might be confused are more readily resolved. If the parent beta phase gives a spotty pattern, the omega and alpha phases transformed from it also yield spotty patterns. A weak pattern is registered darker if it is spotty, because the X-ray exposure of the spotty Debye rings is distributed over shorter lengths of arc. In addition, the reflection spots from wedge and sliver samples are not broadened by large sample-size effects.

In the present studies, sliver samples were used. Exposures were made in 57.3-mm Debye cameras using vanadium radiation, which was self-filtered by the titanium-base alloy samples. Additional examination of some samples was also made with filtered copper radiation.

The use of sliver X-ray diffraction samples has one particular disadvantage for beta-stabilized alloys in that hydrogen sometimes enters the sample during etching, forming titanium hydride and expanding the beta lattice⁽⁴⁾. The hydrogen did not seem to alter the diffraction photographs of samples consisting of alpha-plus-enriched beta; ordinarily it produced hydride and expanded the beta only when untransformed beta was present.

Some experiments were done early in the contract period on preventing hydrogen entry, or minimizing its effects. For this work, the Ti-5Fe alloy in the as-brine-quenched condition was chosen for experimentation. It was

found that with nitric-lactic-hydrofluoric acid mixtures (which had been used previously) the hydrogen effect was most serious when the reaction was most violent, producing distorted, expanded beta as well as a strong hydride pattern. The lactic acid was of no value in excluding hydrogen. Substitution of common nitric acid by white or red fuming nitric did not solve the problem. Hydrogen pickup was minimized by using a low hydrofluoric-nitric acid ratio of 1:25, with no added water. This acid ratio produced a very slow reaction evolving no gas at first, later emitting a line of fine bubbles from the specimen tip. The bubbling could be reduced or stopped by adding more nitric acid. This appeared to prevent the distortion and expansion of the beta lattice, but usually produced some hydride. The addition of a moderate amount of acetic acid to make a solution of 50-ml nitric acid, 15-ml acetic acid, and 2-ml HF did not produce more hydride and gave a smoother surface.

In a few instances, the distortion and expansion of the beta was observed to disappear on standing. K-alpha resolution in the (211) line with vanadium radiation was then usually obtained. In the study of isothermal transformation of a Ti-12.3Mn alloy, a different situation was encountered. Good patterns of untransformed beta showing K-alpha resolution were obtained, either immediately after etching, or after standing, but the lattice constants of the untransformed beta were too large. When one of these Ti-12.3Mn sliver samples was degassed in a good vacuum for 20 minutes at 800 F, and cooled rapidly to prevent transformation of the beta, the lattice constant was found to have been reduced 0.04 A. Presumably, the only cause of this reduction could have been removal of hydrogen, since other gases would not have been removed by this vacuum treatment, while volatilization of manganese would have caused the lattice constant to change in a direction opposite from that observed. This showed that hydrogen dissolved in the beta of the Ti-12.3Mn alloy at room temperature to form a uniform solid solution.

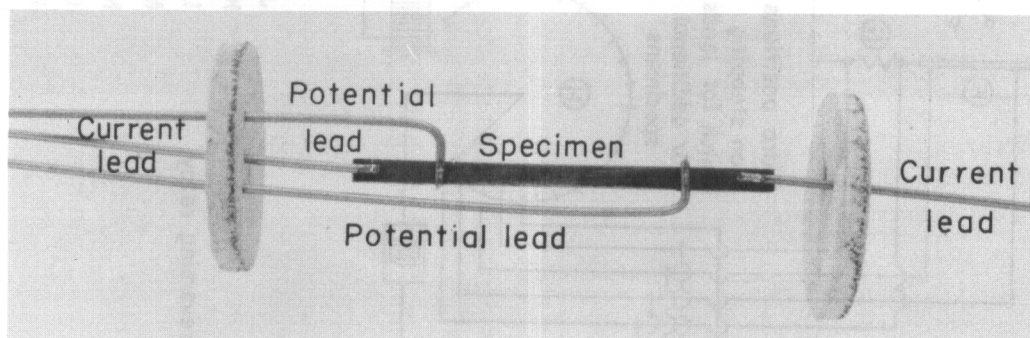
In the study of the aging of iodide alloys, little trouble with hydriding of the Ti-4Fe was encountered (see Table 1 of text), but in the Ti-8.10Cr series, five samples showed TiH, while in the Ti-10.2Mo series, five samples which contained the omega phase showed TiH, and two others in a less advanced state of transformation showed another structure which was not face-centered cubic like TiH. It is possible that this was a complex hydride. This same situation was also observed in untransformed Ti-15V samples.

In summary, the problem of hydrogen absorption in X-ray samples during etching appears practically solved for the Ti-4Fe and Ti-8Cr alloys, but one may still detect some TiH in them. The Ti-10Mo alloy showed a very strong tendency toward hydriding, and it was often necessary to reprepare a sample of this alloy. The etches used, however, were those found satisfactory for the Ti-Fe alloy, and some development work on etchants for Ti-Mo alloys might yield a more suitable etchant. In any

event, since the hydride pattern is known, it can be eliminated from consideration of any specific photogram.

ELECTRICAL-RESISTIVITY APPARATUS

The electrical-resistivity measurements were made by the voltage-drop method at temperatures of 700 and 800 F, with tests up to 1000 hours in duration. The specimens were small bars with a rectangular cross section. A typical size was 0.04 by 0.09 by 3 inches long. The specimens varied only slightly in cross section in order to minimize the spread of resistivity values. Figure II-1 shows a typical specimen, full size, with current leads spot welded to the ends and potential leads welded to the mid-portion of the bar. Alundum disks supported the specimen assembly.



N12214

FIGURE II-1. SPECIMEN FOR ELECTRICAL-RESISTIVITY MEASUREMENTS SHOWING CURRENT AND POTENTIAL LEADS

Figure II-2 shows the electrical circuit diagram for the entire resistivity-measuring apparatus. For simplicity, the circuit of only one specimen is shown, whereas a number of specimens were measured in sequence during the resistivity work. The number of specimens is limited by the number of positions on a stepping switch which selects the measuring circuit.

Photographs of the resistivity apparatus appear in Figures II-3a and II-3b. The numbers used in the following description of the apparatus and its operation are the reference numbers used in Figure II-3.

The test specimens are located in Vycor tubes (1) in temperature-controlled furnaces (2). A dummy specimen, in close proximity to the test pieces, supports a thermocouple to measure specimen temperatures. All

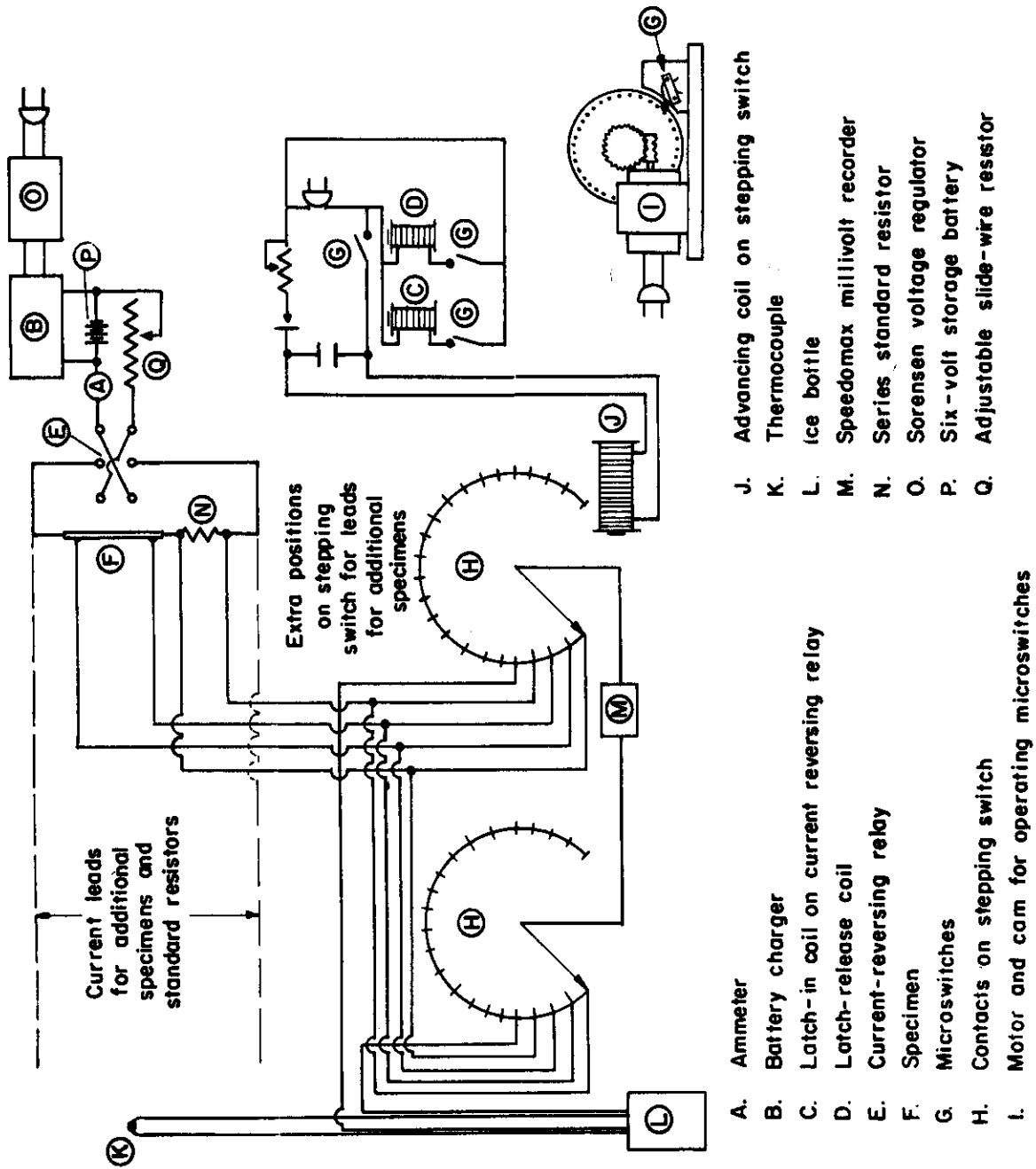


FIGURE II-2. WIRING DIAGRAM FOR ELECTRICAL-RESISTIVITY MEASURING APPARATUS

0-22072

thermocouple-lead junctions are in a common oil bath (3) to maintain constant temperature.

Each test specimen is in series with a manganin standard resistor (4). Calculations from the potential drop across the standard resistor provide a measure of the current flowing in each specimen. The direct current for the specimens comes from a storage battery (5) with a dry-stack battery charger (6) in parallel. A Sorenson voltage regulator (7) prevents fluctuations in the direct current flow. The voltage output from the regulated source is adjusted to maintain the specific gravity of the battery electrolyte at a constant level throughout the testing period.

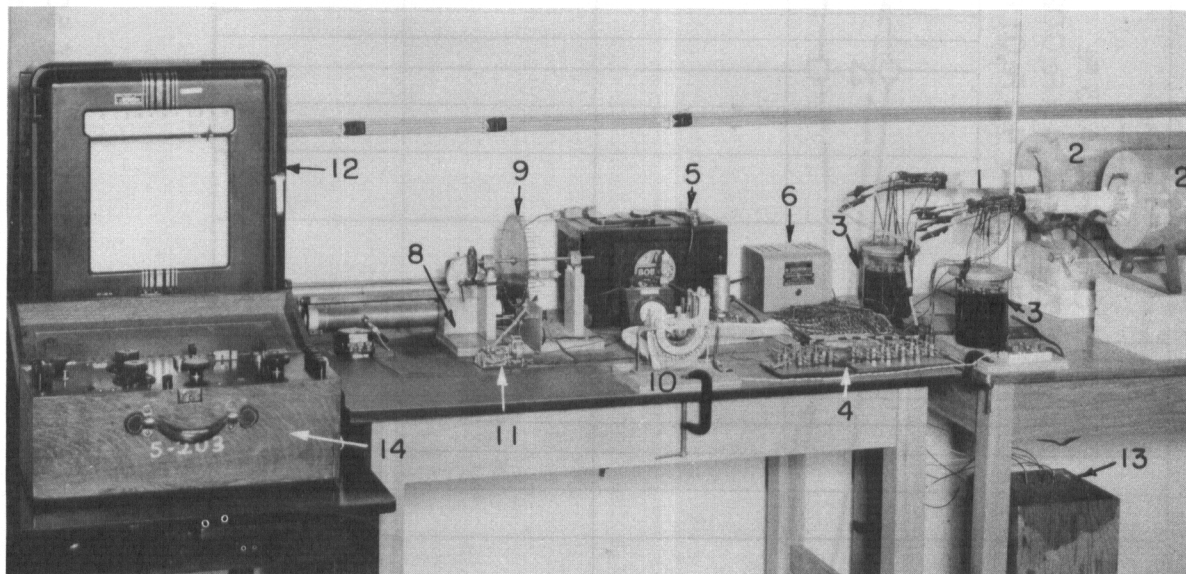
A small back-gear motor (8) drives a 50-point cam (9) at a rate of 6 revolutions per hour. The cam contact points actuate microswitches which operate a 50-position stepping switch (10) and a direct-current reversing relay (11). Five positions on the stepping switch (10) are necessary for each test specimen. The sequence utilized for a specimen measurement is: (a) millivolt drop over the standard resistor with current flow in normal direction, (b) millivolt drop in specimen with normal current flow, (c) millivolt drop in specimen with current direction reversed, (d) millivolt drop over the standard resistor with current flow reversed, and (e) millivolt output of temperature-measuring thermocouple. Thermal and induced-current effects in the circuit are reduced by averaging (a) and (d) in calculating the current flow, and by averaging (b) and (c) in calculating specimen resistances.

The output from the positions on stepping switch (10) go to a millivolt strip-chart recorder (12) having a 2-second full-scale movement. The 50 positions on this switch make it possible to test 10 samples at a time. A semiprecision potentiometer (14) is used to calibrate the recorder, although it is equipped with automatic standardization and maintains calibration quite well.

The gas train used to protect the test specimens from oxidation appears in Figure II-3b. Argon, from a tank (15), is purified in a drying tower (16) and a furnace (17) containing titanium chips at 850 C. The argon atmosphere surrounding the samples is very close to static with a slight positive pressure maintained by the head of oil in a pressure-release bottle. Controllers (18) maintain all furnace temperatures.

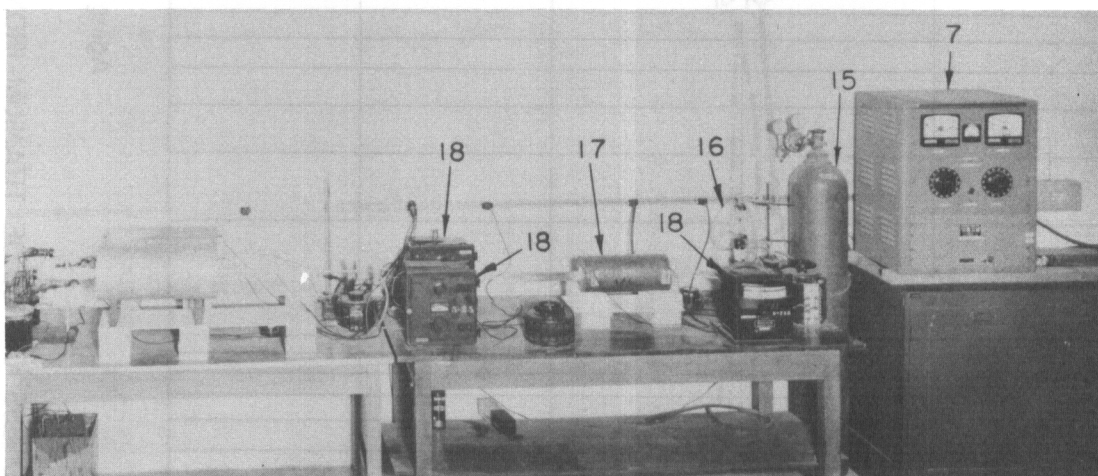
Reference Numbers on Figure II-3.

<u>Number</u>	<u>Figure</u>	<u>Description</u>
1	II-3a	Vycor tubes containing specimens
2	II-3a	Specimen furnaces
3	II-3a	Oil baths to maintain junction temperatures
4	II-3a	Standard series resistors
5	II-3a	6-volt storage battery
6	II-3a	Battery charger
7	II-3b	Sorenson voltage regulator
8	II-3a	Back-gearred motor
9	II-3a	Cam, 50 positions, 6 rph
10	II-3a	Stepping switch, 50 positions
11	II-3a	Current-reversing relay
12	II-3a	Millivolt recorder
13	II-3a	Ice thermocouple junction bottle
14	II-3a	Semiprecision potentiometer
15	II-3b	Argon cylinder
16	II-3b	Constant-pressure bottle and fillers
17	II-3b	Purifying furnace
18	II-3b	Furnace-temperature controllers



(a)

N12213



(b)

N12212

FIGURE II-3. APPARATUS FOR MEASURING ELECTRICAL RESISTIVITY

See facing page for list of numbered items.

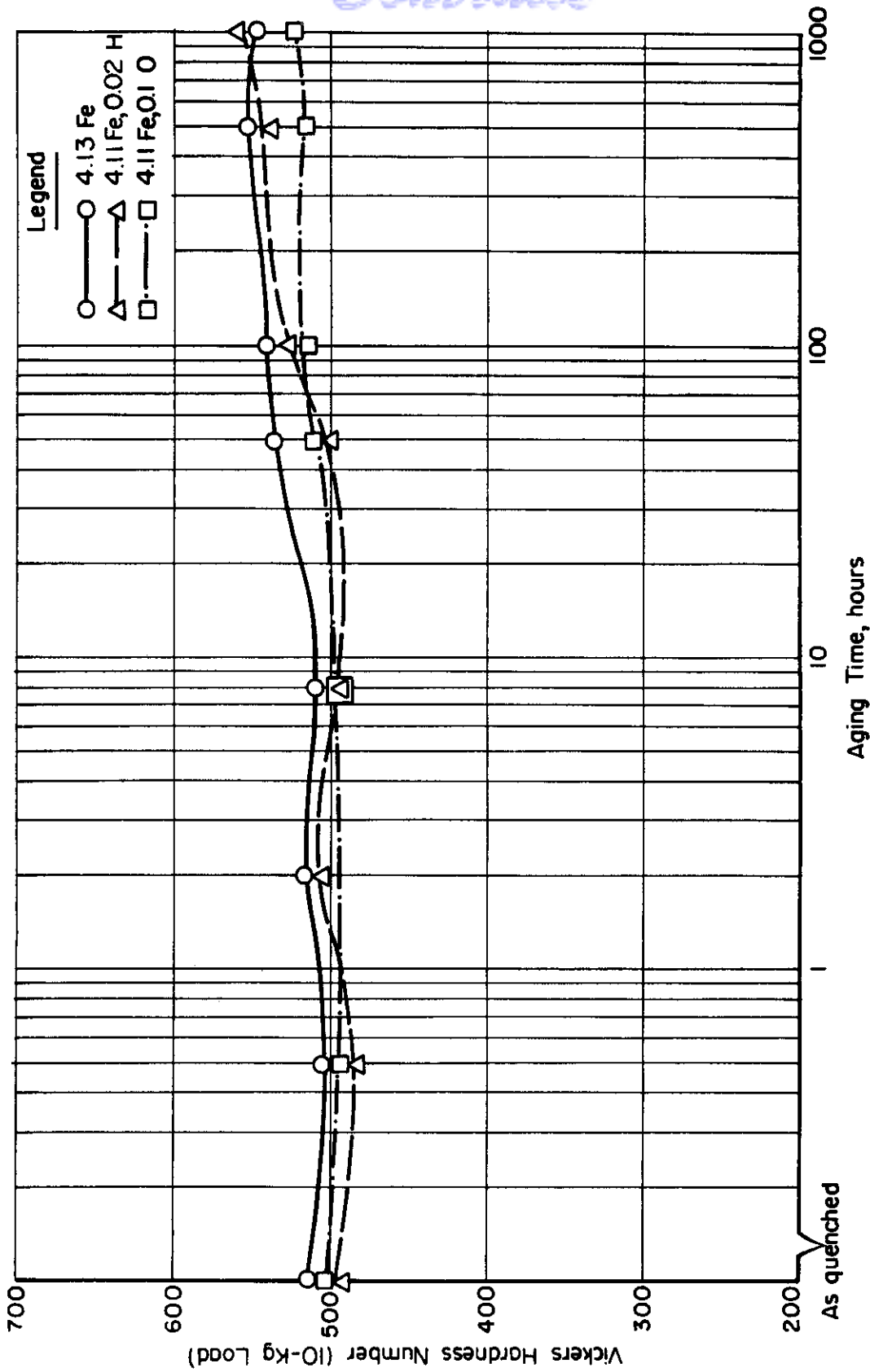


FIGURE III - I. HARDNESS OF 100IDE TITANIUM-IRON ALLOYS QUENCHED FROM 1700F AND AGED AT 500F

A-8629

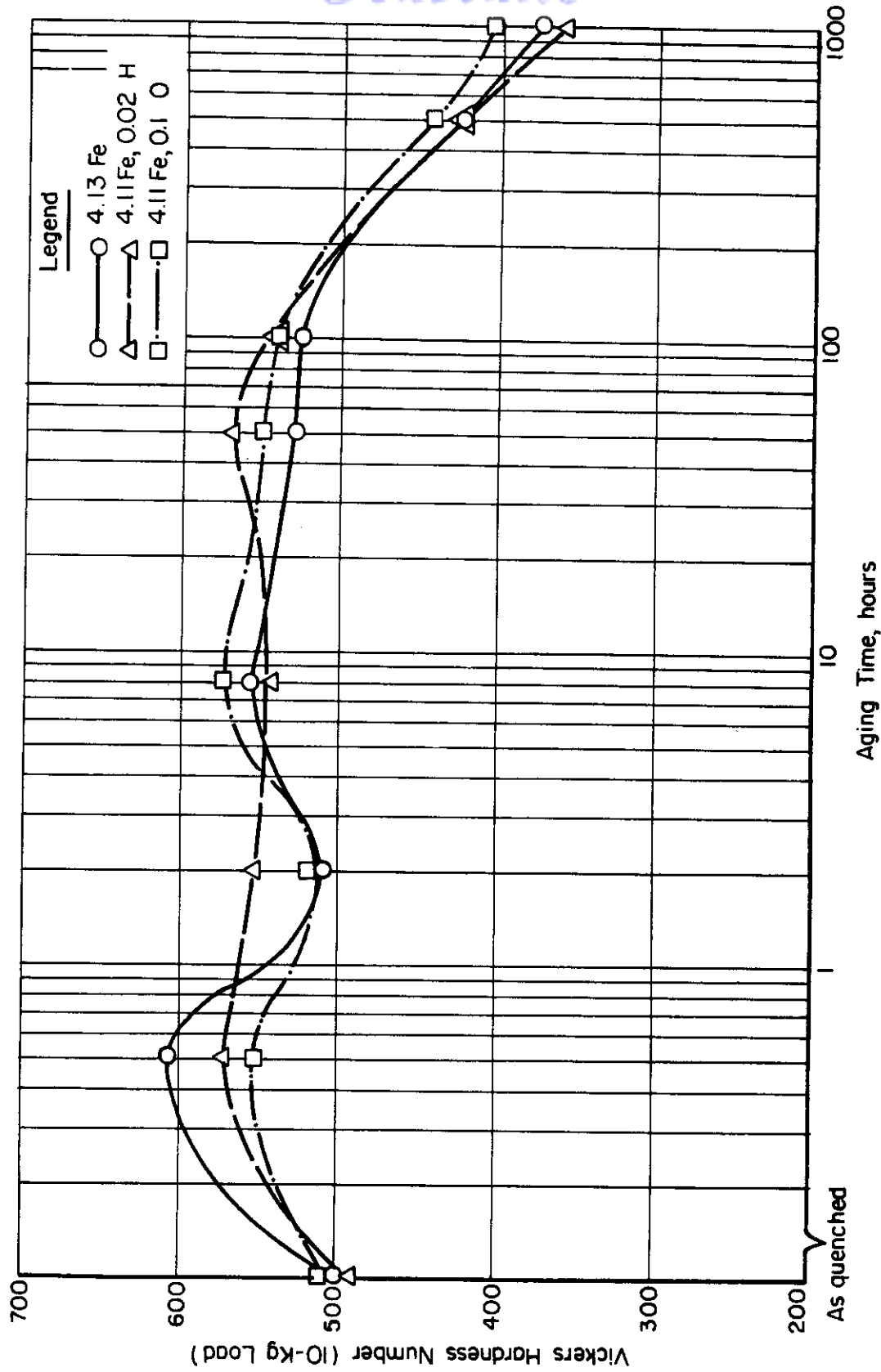


FIGURE III-2. HARDNESS OF IODIDE TITANIUM-IRON ALLOYS QUENCHED FROM 1700F AND AGED AT 700F

A-6830

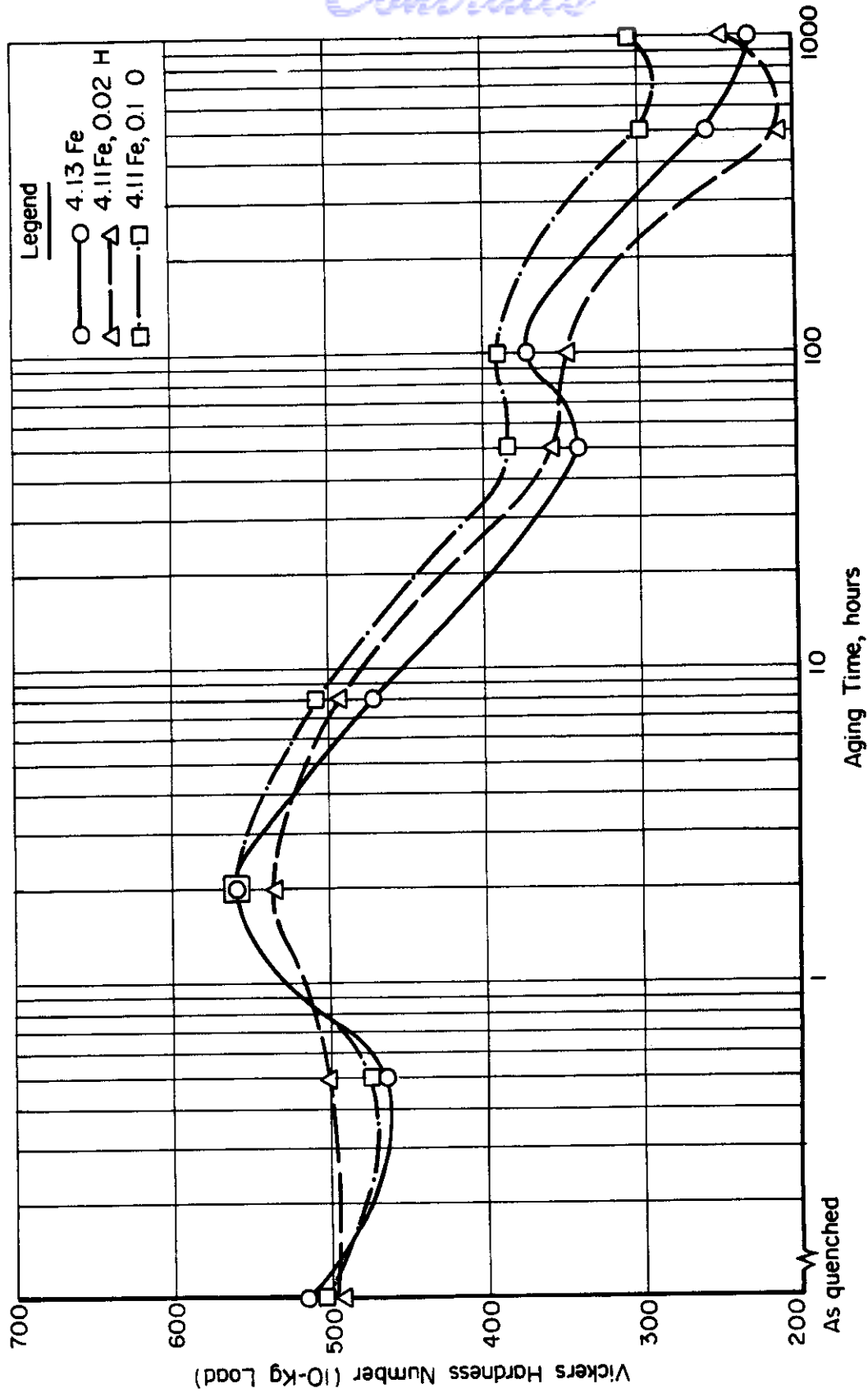


FIGURE III -3. HARDNESS OF IODIDE TITANIUM-IRON ALLOYS QUENCHED FROM 1700F AND AGED AT 800F
A-8831

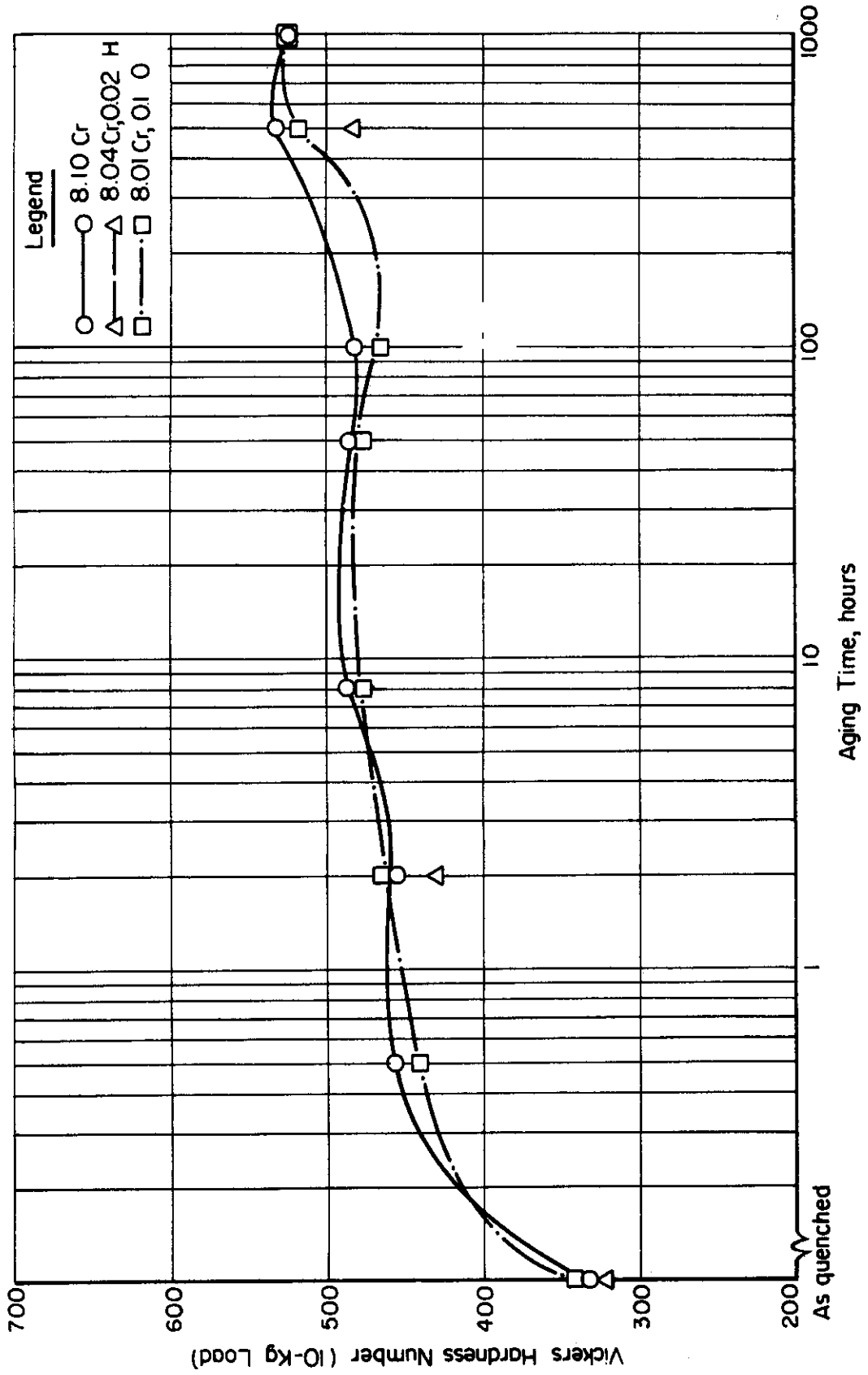


FIGURE III - 4. HARDNESS OF IODIDE TITANIUM-CHROMIUM ALLOYS QUENCHED FROM 1700F AND AGED AT 500F

A-8832

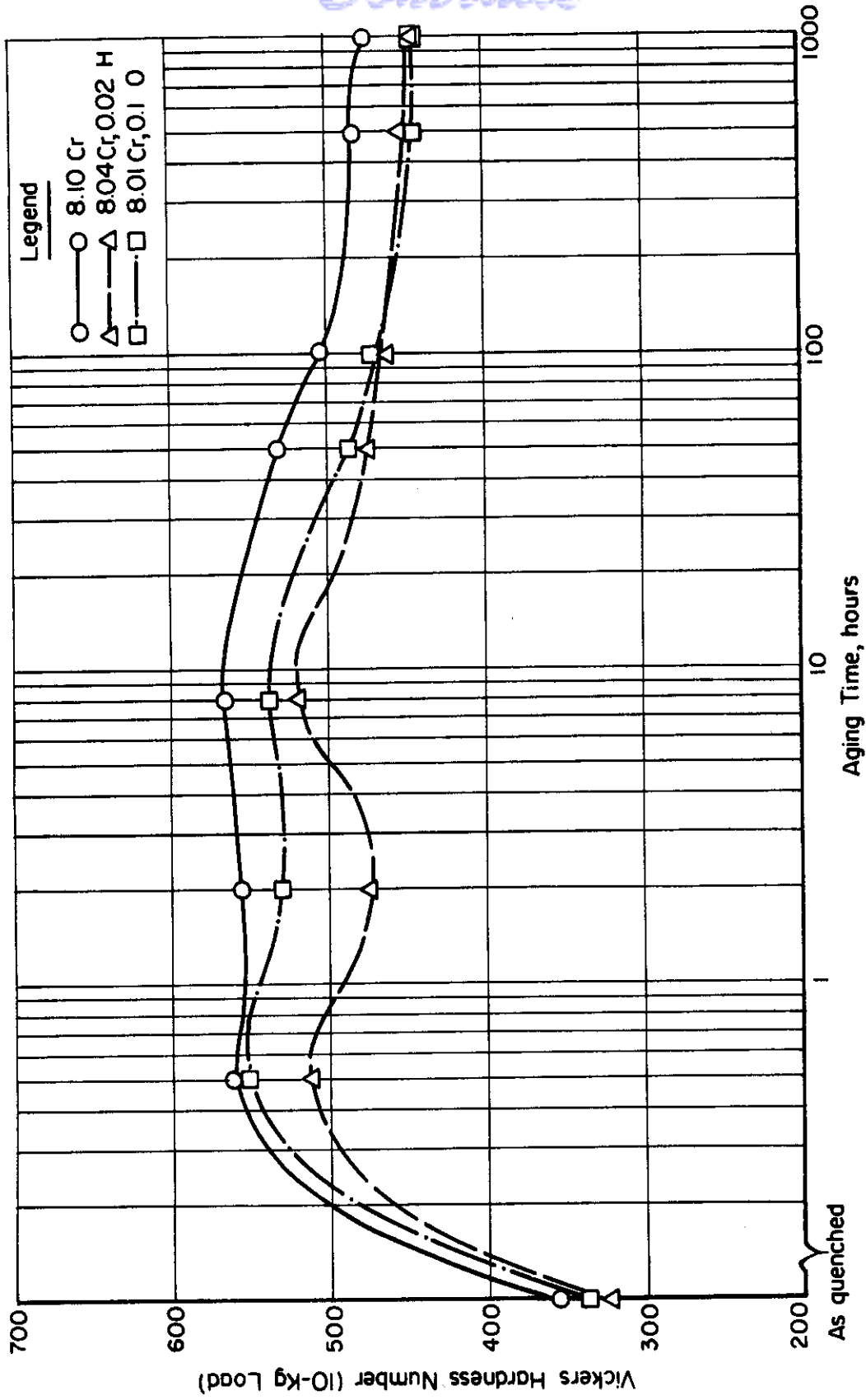


FIGURE III-5. HARDNESS OF IODIDE TITANIUM-CHROMIUM ALLOYS QUENCHED FROM 1700F AND AGED AT 700F

A-6633

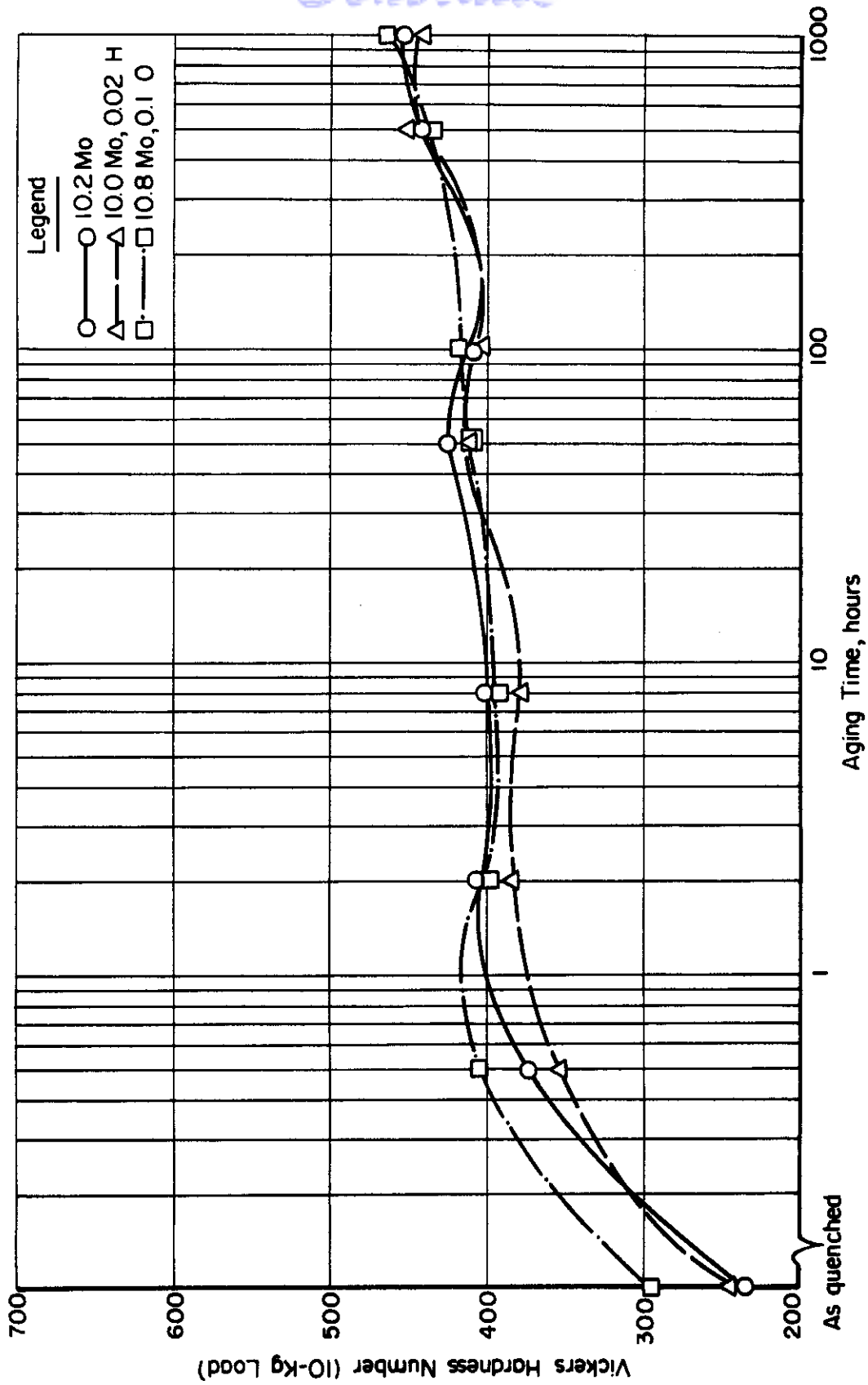


FIGURE III-6. HARDNESS OF IODIDE TITANIUM-MOLYBDENUM ALLOYS QUENCHED FROM 1700F AND AGED AT 500F

A-8834

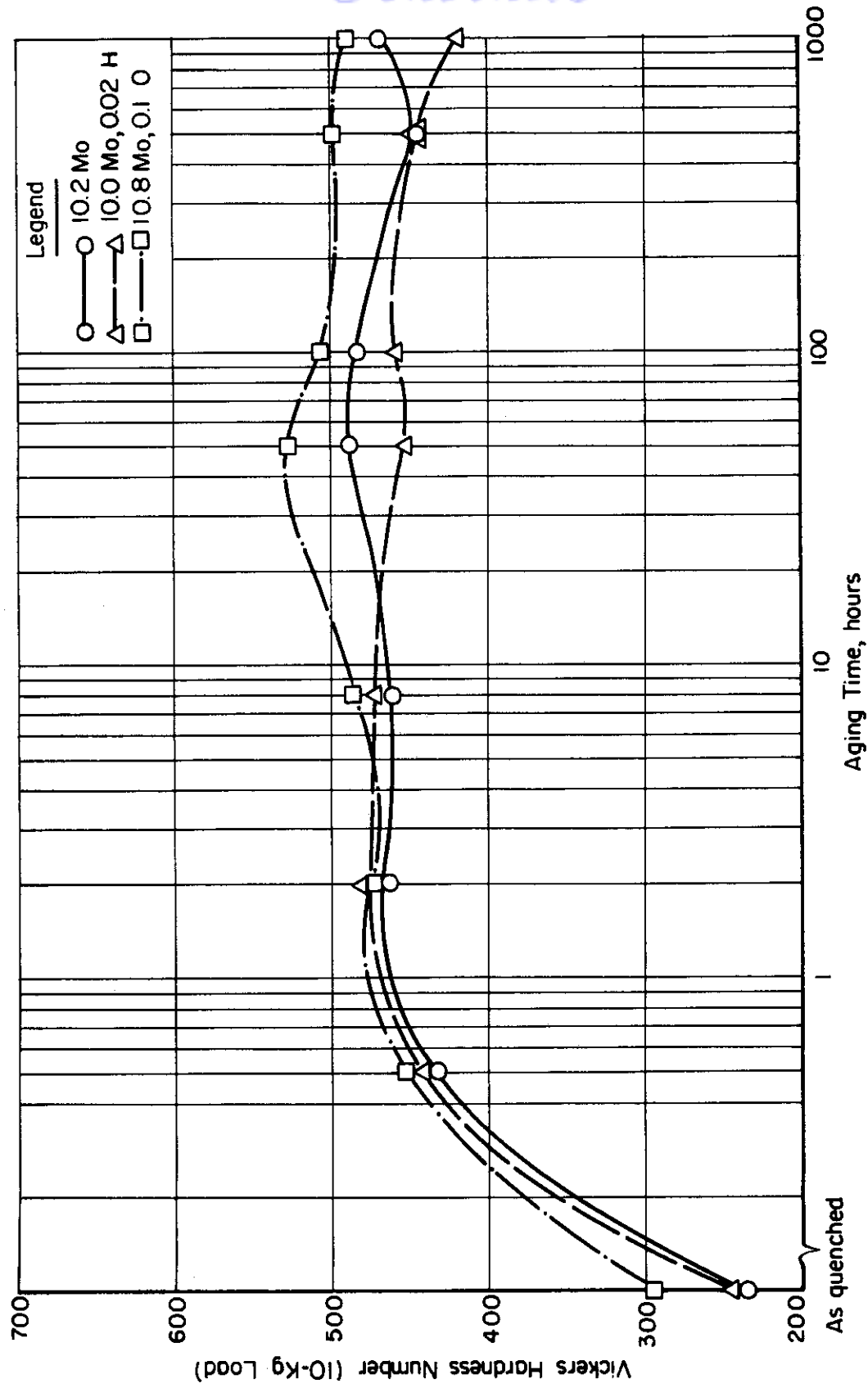


FIGURE III-7. HARDNESS OF IODIDE TITANIUM-MOLYBDENUM ALLOYS QUENCHED FROM 1700F AND AGED AT 700F
A-6835

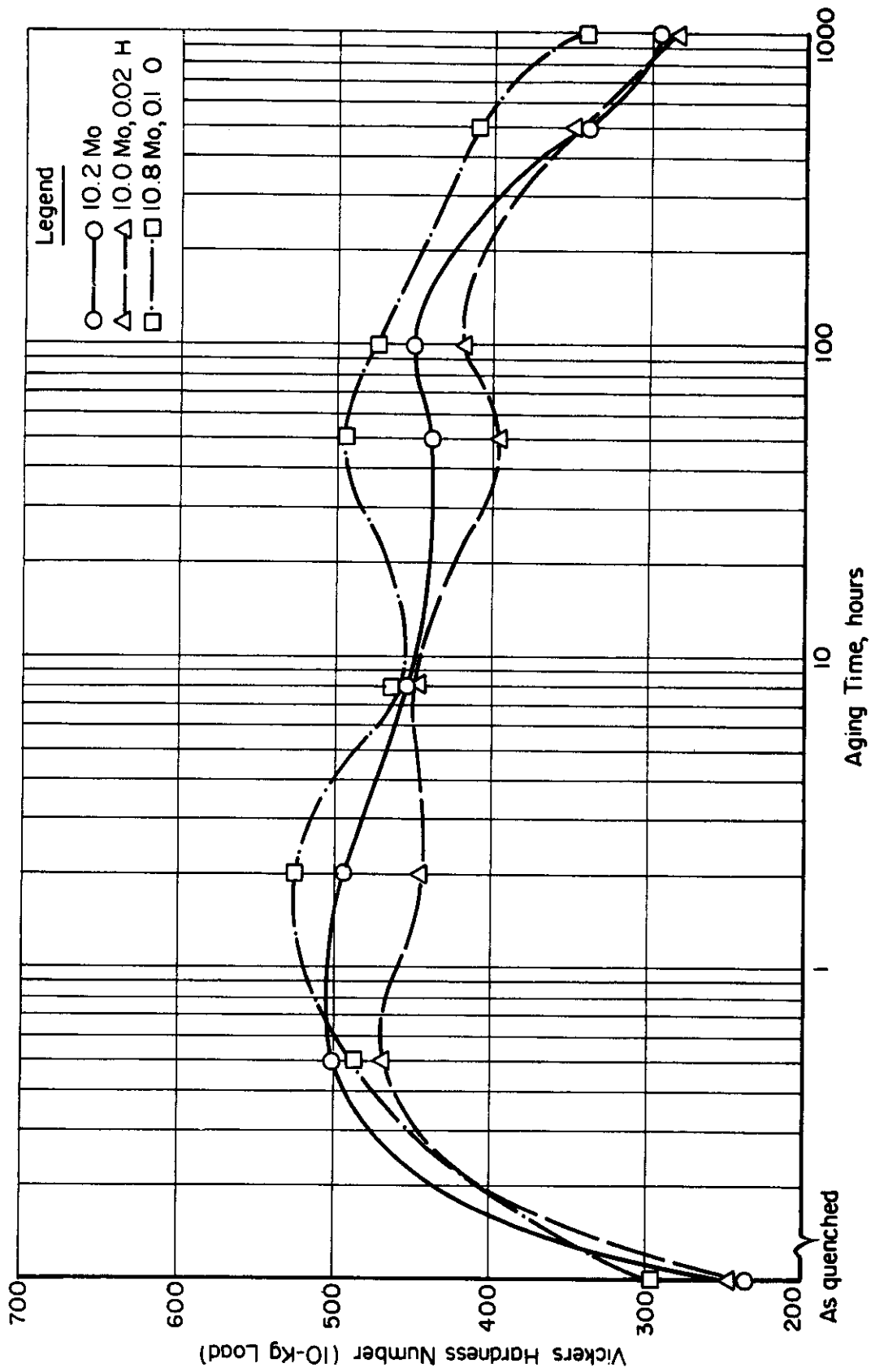


FIGURE III-8. HARDNESS OF IODIDE TITANIUM-MOLYBDENUM ALLOYS QUENCHED FROM 1700F AND AGED AT 800F

A-6636

Contrails