

THE OMEGA TRANSFORMATION IN A Ti-Mn ALLOY

A THESIS

SUBMITTED TO THE FACULTY OF THE UNIVERSITY OF NEVADA
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INTRODUCTION
EXPERIMENTAL PROCEDURE
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Sample Preparation
Agar Test Treatment
Specimen Preparation
X-Ray Diffraction

RESULTS

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X-Ray Diffraction
Metallography
Hardness Tests

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Abstract

Aging studies were made on a Ti-Mn alloy. X-ray diffraction patterns and metallographic specimens were made from the aged samples. Also hardness measurements were made on the aged samples. An extremely brittle structure was noted, and a new phase appeared on the x-ray diffraction patterns.

It is believed that this brittle structure is developed from the alpha-beta region (see Figure 1) and aged at about 1000°F. As structure develops structure is developed. Upon further aging at the same temperature the brittle structure disappears. At first this brittle structure was believed to be a finely divided alpha precipitate formed from the beta phase by quenching. Upon investigation of this structure by x-ray diffraction a series of lines was found. These lines were neither alpha nor beta. It was thus believed that a new phase had been found which was named gamma. This phase was originally found in a Ti-Mn alloy, but has since been found in Ti-Fe, Ti-V, and Ti-Ni alloys.

The discovery of gamma was made in 1952, but the exact structure was not known until 1954. Since that

1. G. K. Murty, Hardness of Titanium, Part I, p. 11-12.
2. State of Material Institute, Development of Titanium base alloys, p. 108.

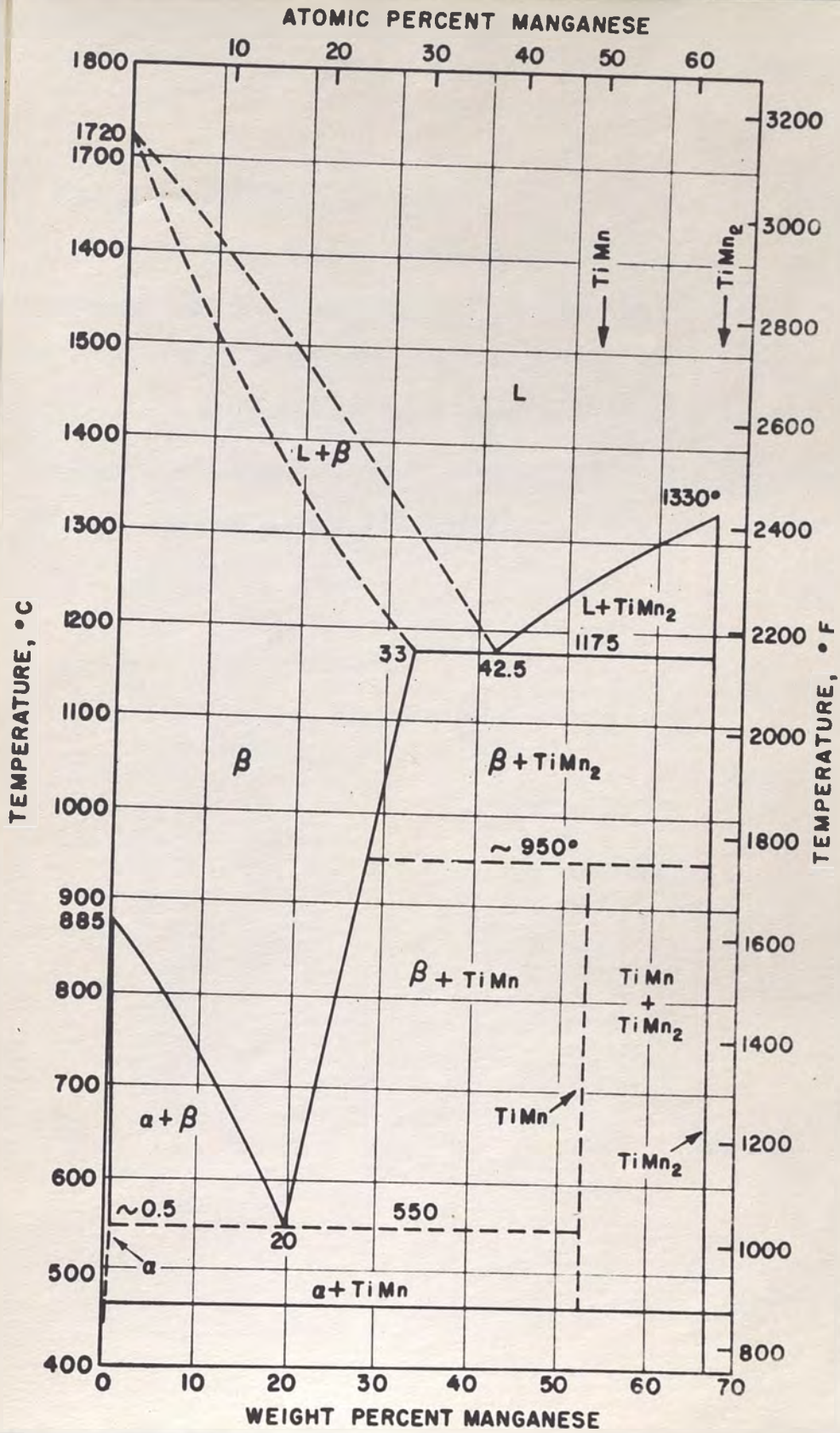
Introduction

Titanium exists in two allotropic forms. It is in the close-packed hexagonal alpha form from room temperature to 1625°F where it transforms to the body centered cubic beta form. This form is stable between 1625°F and the melting point, 3150°F. The beta form can be stabilized at lower temperatures by the addition of certain alloying elements, such as Cr, Fe, Mo, V, or Mn.

If certain beta stabilized alloys are quenched from the alpha-beta region (see Figure 1) and aged at about 800°F, an extremely brittle structure is developed. Upon further aging at the same temperature the brittle structure disappears. At first this brittle structure was believed to be a finely divided alpha precipitate formed from the metastable beta produced on quenching. Upon investigation of this structure by x-ray diffraction means a series of lines was found. These lines were neither alpha nor beta. It was thus believed that a new phase had been found which was named omega. This phase was originally found in a TiMn alloy, and has since been found in TiCr, TiFe, and TiMo alloys.

The discovery of omega was made in 1952², but its crystal structure was not known until 1955. Since then

1. W. K. Adenstedt, Handbook on Titanium, Part 1, p. II-1-3.
2. Battelle Memorial Institute, Development of Titanium Base Alloys, p. 102.



* Max Hansen, Donald J. McPherson, and William Rostoker, Constitution of Titanium Alloy Systems, p. 71.

it has been indexed as cubic, orthorhombic, and hexagonal³.

The most extensive studies which have been made on the omega phase are by Parris, Schwartz, and Frost⁴. Their results, based on single-crystal Weissenberg x-ray diffraction techniques on a Ti-8Cr alloy, show the structure of omega to be a complex body centered cubic crystal with 54 atoms per unit cell (see Figure 2).

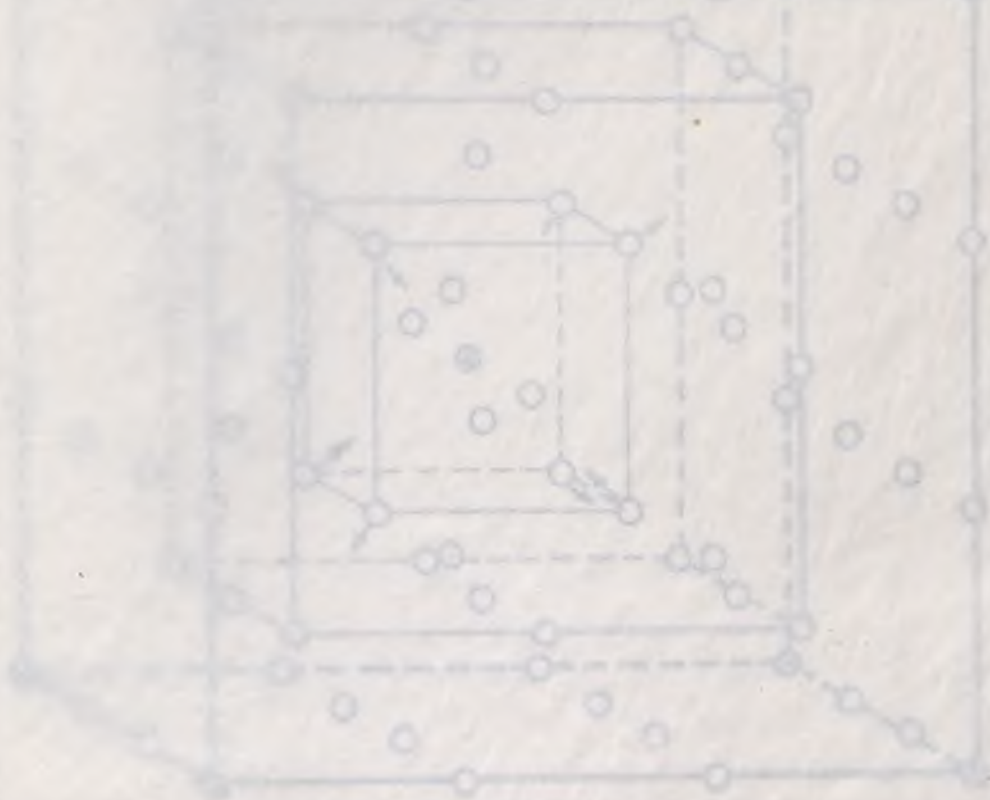


Figure 2. Schematic diagram of the omega phase structure in a body-centered cubic unit cell of omega phase in a Ti-8Cr alloy.

³ F. C. Holden, G. W. Calverley, P. D. Frost, *Journal of Applied Physics*, **36**, 12 (1965).

3. F. C. Holden and R. I. Jaffee, *Beta Transformation in Titanium Alloys*, p. 31.
4. W. M. Parris, C. M. Schwartz, and P. D. Frost, *Precipitation Hardening and Embrittlement of High-Strength Titanium Alloys*.

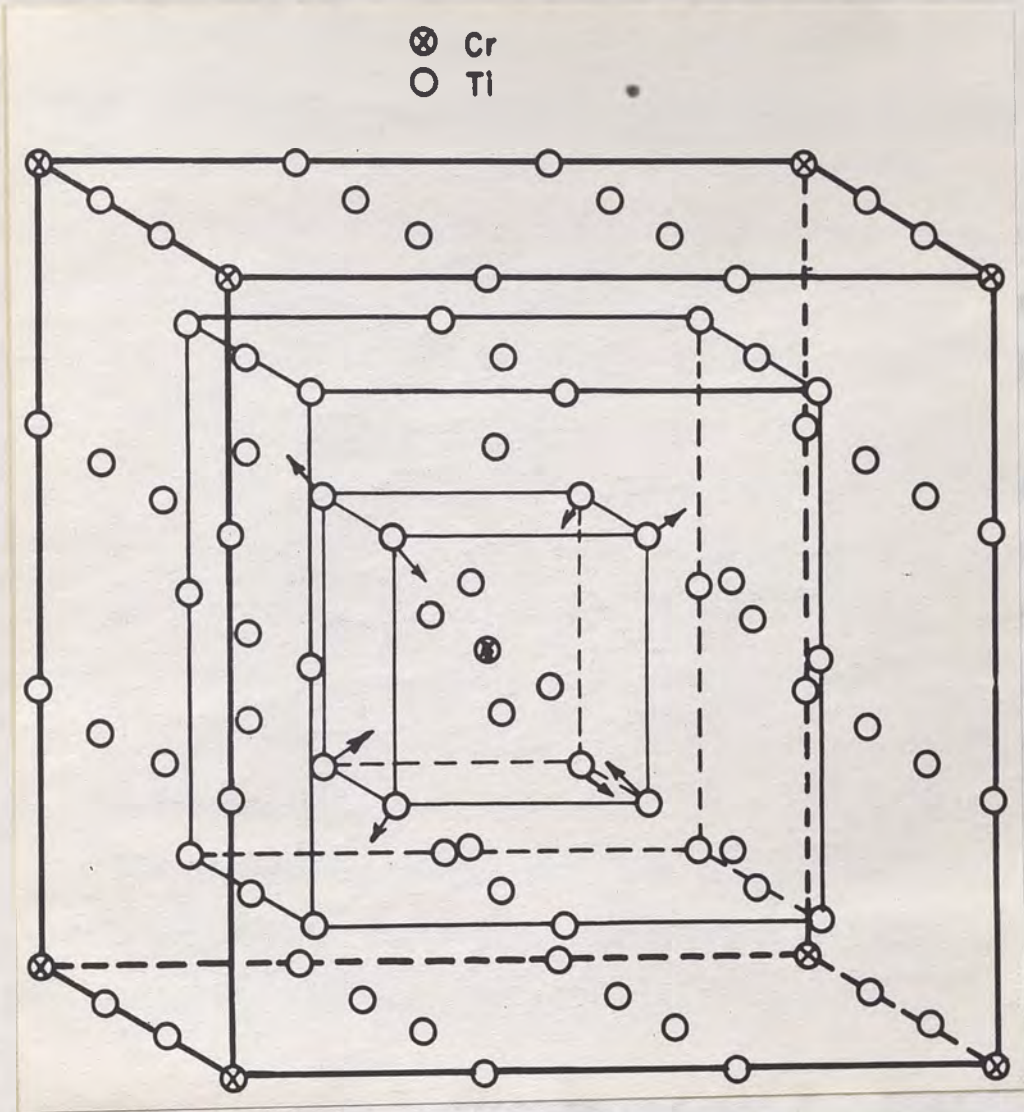


Figure 2. Schematic diagram of the atomic positions in triple-body-centered unit cell of omega phase in a Ti-Cr alloy.*

* W. M. Parris, C. M. Schwartz, P. D. Frost, Precipitation Hardening and Embrittlement of High-Strength Titanium Alloys, p. 14.

Experimental Procedures

Alloy Preparation

All the alloys used were made from 120 BHN Ti sponge⁵ produced at the United States Bureau of Mines Station in Boulder City, Nevada, and electrolytic Mn from the Electro-Manganese Corp., having a purity of 99.9%. The Mn was first heated to 1470°F (5°) for one hour in a vacuum at .03 microns pressure to remove any hydrogen which causes embrittlement of the beta phase in Ti alloys. Four 70 gram portions were weighed, each having a composition Ti-8Mn. These portions were next pressed into compacts at 120,000 pounds pressure. The compacts were melted into buttons (see Figure 3) in an inert atmosphere arc furnace, on a chilled copper mold, by a thoriated tungsten electrode.

Two of these buttons were then hot rolled into .060 inch thick sheets for x-ray diffraction specimens.

Table 1 gives the analyses of all four buttons.

Table 1

Button Number	Type Sample	Per Cent Mn
1	Metallographic	6.5
2	Metallographic	6.3
3	X-Ray	6.3
4	X-Ray	6.2

5. It is common practice to express the purity of Ti sponge by giving the Erinell Hardness Number of the metal produced from the sponge instead of an analysis. For example, 100 BHN is quite pure sponge, while 150 BHN is commercial grade.



Figure 3. Bottom. (Left) Titanium sponge and (Right) electrolytic manganese used in making alloys. Top. (Left) Titanium alloy button after melting and (Right) titanium alloy compact before melting.

Specialized Investigation

Specimens for metallographic examination were prepared by the standard procedure which involves

Heat Treatment

The two buttons and sheets were given a one-hour solution treatment at 1450°F ($\pm 5^\circ$) in an inert atmosphere tube furnace. The alloys were then quenched to room temperature in iced brine to retain the beta phase.

Sample Preparation

The two buttons were cut into sections about 3/8"x3/8"x1/2" for metallographic samples. The two sheets were cut into sections about 1/2"x1" for x-ray diffraction samples. All cutting was done on a water-cooled, cut off wheel to avoid heating the samples.

Aging Heat Treatment

The aging heat treatments were made by placing the samples to be studied in a lead bath which was held at a constant temperature near 775°F. A preliminary test was made to determine the maximum aging time which would produce a brittle structure. It was found that after 40 minutes aging time the samples began to regain their ductility. Aging times were decided to be from 10 to 50 minutes in ten-minute intervals. Later, in x-ray diffraction studies the interval was cut to five minutes. After a sample had been in the lead bath the proper length of time, it was removed and quenched in water.

Specimen Preparation

Specimens for metallographic examination were prepared by the standard procedure which includes:

mounting in bakelite; hand grinding through four grades of emery paper (#1 through #3/0); and three stage lapping (first stage on slipper satin with a water suspension of #600 grit silicon carbide, second stage on slipper satin with a water suspension of 1 micron levigated alumina, and third stage on miracloth with a water suspension of .3 micron levigated alumina).

Two types of x-ray specimens were prepared. The first were the original sheet samples with the oxide layer and any possible lead contamination ground off, and the disturbed metal layer removed by a light etch. The second type of x-ray specimens were prepared by shearing small fragments off the sheet specimens for use in a powder camera. After shearing they were dissolved in a 50% HF- 50% Ethylene Glycol solution (volume/volume) until they were between .025" and .050" in diameter and at least 3/8" long.

X-Ray Diffraction

Two methods of obtaining x-ray data were used. The first was using the sheet specimens in a goniometer with a recording counter indicating the position and relative intensities of the diffracted lines. It was found that the fluorescence of Ti was too great, and the counter would indicate only the very intense lines; the rest of them were lost in the background.

Sliver samples were then used in a powder camera

in an attempt to get better resolution of the weaker lines. The resulting patterns were difficult to read because of the spottiness of some of the lines caused by the large grain size of the specimens.

The individual spots of some of the lines did give definite proof of a phase transformation by their broadening and being resolved into two or three distinct lines (see Figure 4).

Hardness Measurements

The attempts to measure the hardness of the omega phase were failures. Both the Rockwell Superficial Hardness Tester and the Vickers Hardness Tester were used, but all of the impressions made by their indenters had cracks radiating from them (see Figure 5) except those in specimens aged 50 minutes or more. A thirty-kilogram load was used on the Rockwell machine, while only a two and one half kilogram load was used on the Vickers machine; This cracking indicated the presence of an extremely brittle structure, but would not give a true hardness reading.



3.5X Alpha Lines



3.5X Beta Lines



3.5X Aged Beta Lines

Figure 4. Enlargements of the front reflection regions of x-ray photographs illustrating line broadening and doublets in the photograph of the aged specimen. (Aged fifteen minutes at 783°F ($\pm 2^{\circ}$).

Results

X-Ray Diffraction

To aid in interpreting the diffraction patterns, ideal patterns were calculated using the relationship $d = a_0 / \sqrt{h^2 + k^2 + l^2}$ and the fact that $\sqrt{h^2 + k^2 + l^2}$ is an even integer for a body centered cubic lattice⁶. a_0 for the beta phase was taken from the graph plotted by Hansen, McPherson, and Rostoker⁷ to be 3.26 angstroms. As this is the same size unit cell Parris, Schwartz, and Frost measured in the beta phase of their Ti-8Cr alloy⁸, the omega unit cell was taken to be the same size as theirs, 9.80 angstroms. The alpha interplanar spacings were taken from the standard card published by the American Society for Testing Materials. Tables 2, 3, and 4 list the calculated and standard interplanar spacings and the observed interplanar spacings from the x-ray photographs. Table 5 compares the interplanar spacings of the aged specimens with the standard and calculated interplanar spacings. The patterns were also compared with the TiH pattern to make sure that the brittleness observed was not due to the presence of hydrogen.

6. H. P. Klug and L. E. Alexander, X-Ray Diffraction Procedures, pp. 343-347.
7. M. Hansen, D. J. McPherson, and W. Rostoker, Constitution of Titanium Alloy Systems, p. 239.
8. W. M. Parris, O. M. Schwartz, and P. D. Frost, Precipitation Hardening and Embrittlement of High-Strength Titanium Alloys, p. 8.

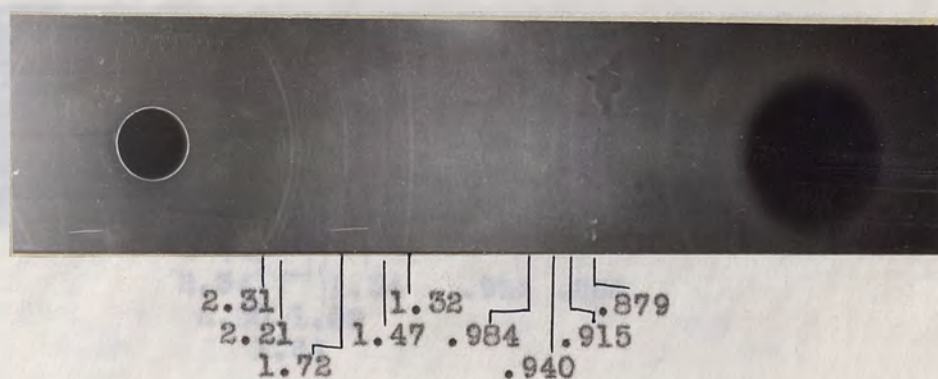


Figure 6. X-Ray photograph of alpha Ti.

Table 2. Standard and observed interplanar spacings of alpha Ti x-ray pattern.

Standard	Observed
2.56	
2.34	2.31
2.24	2.21
1.73	1.72
1.48	1.47
1.33	1.32
1.27	
1.25	
1.23	
1.17	
1.12	
1.07	
.99	.98
.95	.94
.92	.92
.89	
.88	.88

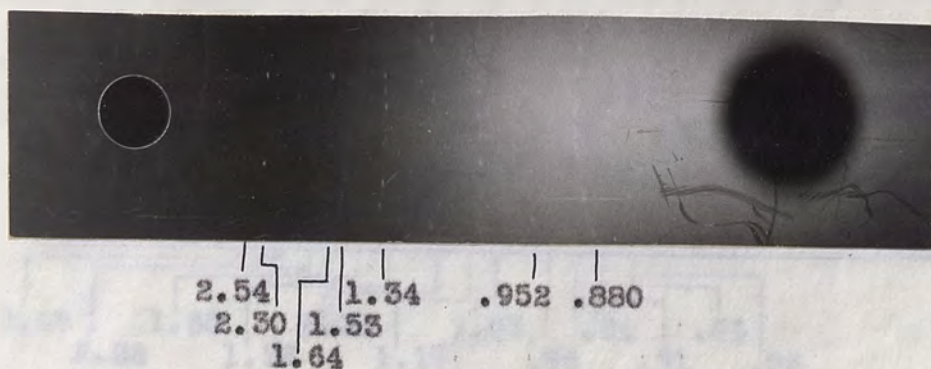


Figure 7. X-Ray photograph of retained beta Ti.

Table 3. Calculated interplanar spacings of beta Ti and observed interplanar spacings of retained beta Ti.

Calculated	Observed
2.48	2.54
	2.30
1.62	1.64
	1.53*
1.33	1.34
1.15	
1.03	
.94	.95
.87	.88

* Very faint and diffuse line.

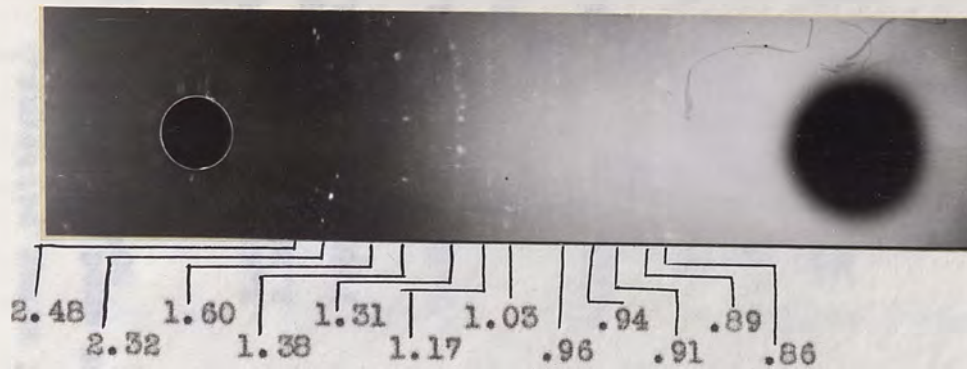


Figure 8. X-Ray photograph of Ti-6.3Mn alloy solution treated at 1450°F and quenched, then aged fifteen minutes at 783°F ($\pm 2^{\circ}$).

Table 4. Calculated interplanar spacings of omega Ti and observed interplanar spacings of Ti-6.3Mn alloy solution treated at 1450°F and quenched, then aged fifteen minutes at 783°F ($\pm 2^{\circ}$).

Calculated	Observed
2.83	
	2.48
2.32	2.32
1.59	1.60
1.42	1.38
1.33	1.31
1.21	1.17
1.14	
1.04	1.03
.97	
.96	.96
.94	.94
.82	.91
.89	.89
.86	.86

Table 5. Standard, calculated, and observed interplanar spacings of x-ray patterns.

Standard Alpha Lines	Calculated Beta Lines	Calculated Omega Lines	Lines observed on patterns of aged specimens							
			10*	15*	20*	25*	30*	40*	50*	
		2.83								
2.56										
	2.48			2.48	2.49			2.46		2.50
2.34		2.32	2.32	2.32	2.32			2.28		
2.24									2.26	2.24
	1.62	1.59	1.59	1.59	1.58	1.60	1.60	1.60	1.61	1.62
1.48									1.43	
		1.42	1.38	1.38	1.38					
1.33	1.33	1.33	1.30	1.31	1.31	1.30	1.31	1.32	1.32	1.32
1.23										
		1.21	1.19	1.17	1.19	1.19			1.20	1.19
1.17	1.15	1.14								
		1.04								
	1.03		1.02	1.03	1.02	1.02	1.02	1.02		1.02
.99										
		.97								
		.96	.96	.96	.96	.96	.96	.96	.96	.96
.95										
	.94	.94	.94	.94		.94	.93			
.92		.92	.91	.91		.91				
.89		.89	.89	.89	.89	.88	.89	.89	.89	.89
	.86	.86	.86	.87	.87	.87	.87	.87	.87	.87

* Aging time in minutes.

As can be seen from Figures 6, 7, and 8, it would be very difficult to attempt to index these patterns without having some idea of the structures. In the alpha pattern (see Figure 6) only the most intense lines registered, so the beta and aged beta samples undoubtedly had a number of planes whose diffracted lines did not register. The 2.30 line in the retained beta pattern (see Figure 7) should not be there, indicating that perhaps the quench was not severe enough to depress completely the omega transformation. This has been observed in other alloy systems when the alloy content was low⁹. The aged beta pattern (see Figure 8) shows a doubling of the 2.32 line and a diffuse broadening of the 1.60 and 1.31 lines to cover the ranges from 1.59 to 1.62 and 1.31 to 1.33.

The most positive proof of a new phase being present is the appearance of the 1.38 lines and the 1.19 lines and the 0.96 lines, which do not fit either the alpha or the beta pattern.

Metallography

There is no positive proof of the existence of the omega phase by metallographic means. A dark etching structure can be shown in photomicrographs (see Figures 10 and 11) of Ti alloys which have been shown by x-ray

9. H. A. Robinson et al. Precipitation Hardening and Embrittlement of High-Strength Titanium Alloys, p. 4.

means to contain omega¹⁰. By using a shadow-casting, replica technique on electron microscope samples, this dark etching phase has been shown to be a series of etching pits¹¹.

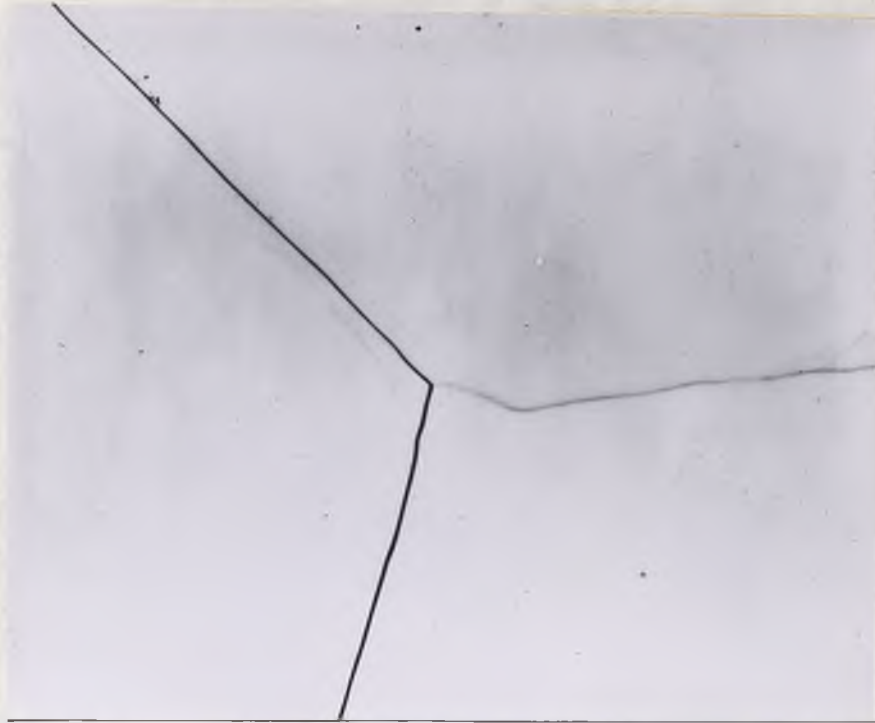
Figure 9 shows the large clear grains of retained beta, Figures 10 and 11 show, within the grains, the dark etching structure which is believed to be associated with the omega phase, and Figure 12 shows the alpha platelets which have been formed from the retained beta upon a longer aging treatment. Alpha Ti in a beta matrix is very easy to detect as alpha is strongly birefringent, while beta is not.

Hardness Tests

While the hardness tests were a failure in that no accurate readings could be obtained from the specimens suspected to contain the omega phase, they did indicate that there was an extremely brittle phase present in these specimens and that this phase disappeared upon further aging.

10. W. M. Parris, C. M. Schwartz, and P. D. Frost, Precipitation Hardening and Embrittlement of High-Strength Titanium Alloys, p. 52.

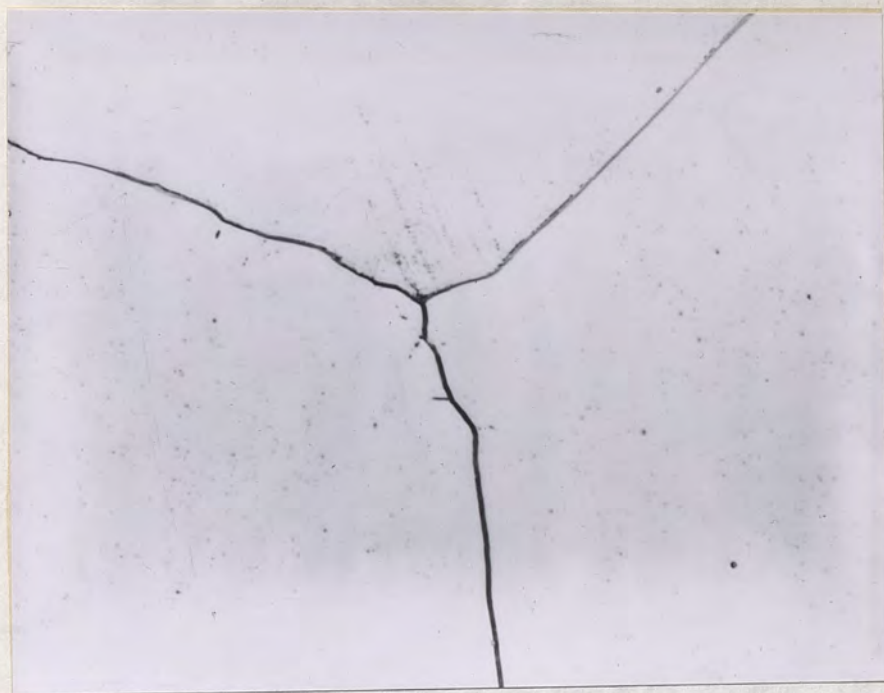
11. Ibid., p. 58.



500X

Etchant 20 HF 20 HNO₃ 60 H₂O

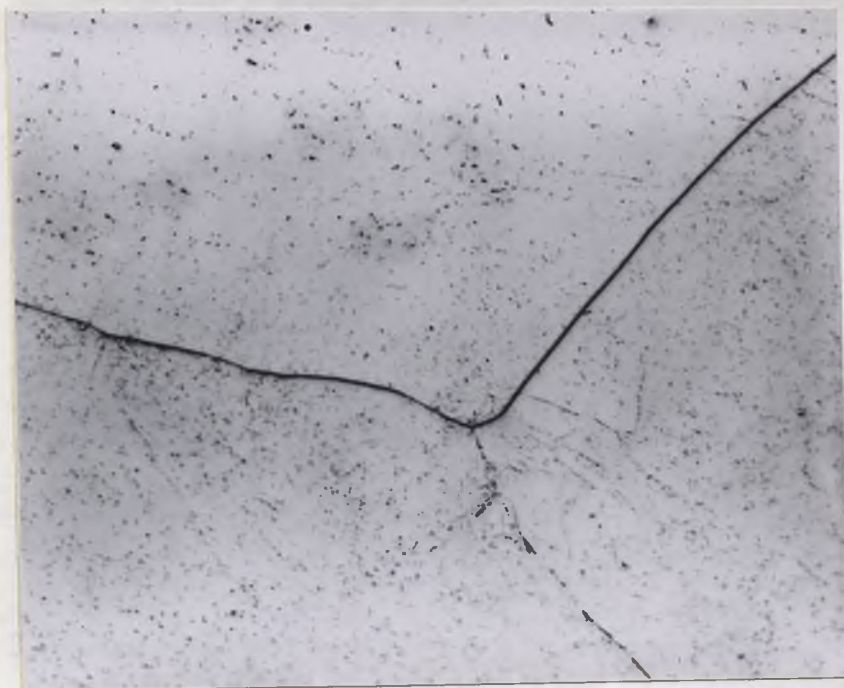
Figure 9. Microstructure of Ti-6.5 Mn alloy solution treated at 1450°F and quenched. Retained beta.



500X

Etchant 20 HF 20 HNO₃ 60 H₂O

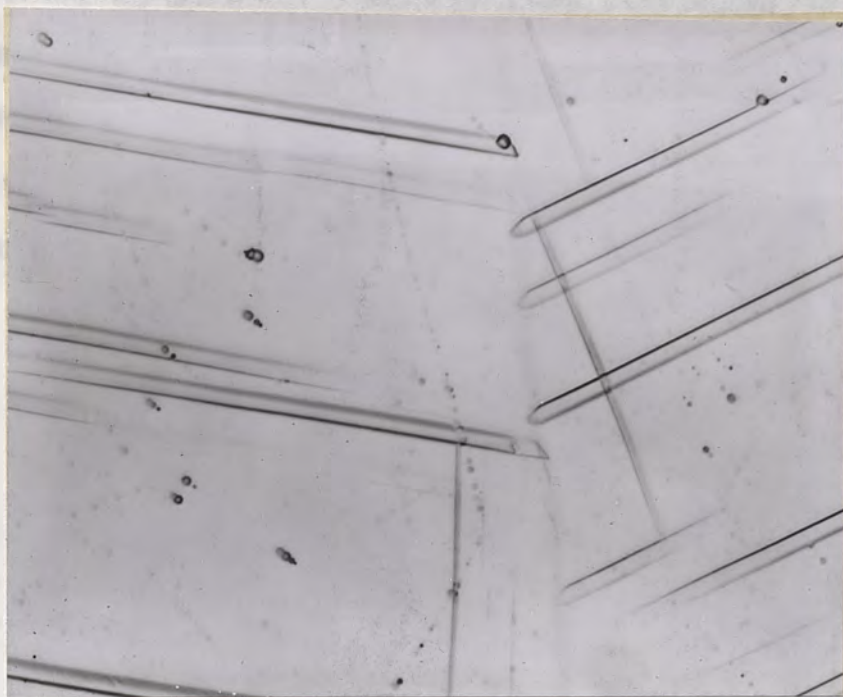
Figure 10. Microstructure of Ti-6.5 Mn alloy solution treated at 1450°F and quenched, then aged ten minutes at 775°F (±2°). Retained beta. The dark etching structure within the grains is believed to be associated with the omega phase.



500X

Etchant 20 HF 20 HNO₃ 60 H₂O

Figure 11. Microstructure of Ti-6.5 Mn alloy solution treated at 1450°F and quenched, then aged twenty minutes at 775°F ($\pm 2^\circ$). Retained beta. The dark etching structure within the grains is believed to be associated with the omega phase.



500X

Etchant 20 HF 20 HNO₃ 60 H₂O

Figure 12. Microstructure of Ti-6.5Mn alloy solution treated at 1450°F and quenched, then aged forty minutes at 775°F (±2°). Alpha platelets in a beta matrix.

Conclusion

The omega phase does exist as a separate phase having a distinct crystal system, which can be indexed as a body-centered cubic system. Hardness tests indicate that it is extremely brittle and could be responsible for the low temperature embrittlement encountered in some Ti alloys.

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Metals, April 27, 1958, p. 741.

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8. Silcock, J. M., et al. Structure of the Omega-Precipitate in Titanium-16 per cent Vanadium Alloy. Nature. April 23, 1955. p. 731