2447-23-P

ENGINEERING RESEARCH INSTITUTE
UNIVERSITY OF MICHIGAN
ANN ARBOR

Project 2447

Preliminary Report on

STUDIES OF THE STRUCTURE OF THE OMEGA PHASE IN Ti-8Cr AND Ti-13Mo ALLOYS

by

(Wilbur C.)
W. C. Bigelow

15 August 1957

METALLURGY RESEARCH BRANCH
AERONAUTICAL RESEARCH LABORATORY (WCRRL)
WRIGHT AIR DEVELOPMENT CENTER
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Contract AF 33(616)-3250
Project 7021, Task 70662

SUMMARY

Studies have been made of Ti-8Cr and Ti-13Mo alloys by electron diffraction, electron microscopic, and single-crystal x-ray diffraction techniques to attempt to determine the structure of the transition omega phase of these alloys. The electron microscopic studies have shown the omega phase to occur in the form of platelets or rods approximately 400Å in thickness. The x-ray diffraction results obtained support those previously reported by Silcock, Davies, and Hardy,[5] and indicate a hexagonal unit cell with $a = 4.60$Å and $C = 2.82$ is preferable to the cubic or orthorhombic cells proposed by other investigators.[1-4]

INTRODUCTION

This report consists of a preliminary description work which was undertaken at the request of the Metallurgy Research Branch of the Aeronautical Research Laboratory of the Wright Air Development Center, to investigate the crystallographic structure of the omega phase of titanium-base alloys. Interest in this work arose from the fact that the structure determined for this phase by Parris, Schwartz, and Frost[1,2,3] differed fundamentally from that determined independently by Spachner and Rostoker.[4] In this connection it is interesting to note that a third structure has also been reported for the phase by Silcock, Davies, and Hardy.[5] The purpose of the present research was to attempt to clarify the situation, and if possible to decide on a correct structure for the omega phase. Before proceeding with a description of the present work, it is desirable to review briefly the three previous investigations.

REVIEW OF PREVIOUS INVESTIGATIONS

The omega phase is a transition phase which forms in alloys of titanium and such elements as vanadium, chromium, iron, molybdenum, manganese, cobalt, and nickel, as an intermediate step in the transformation from the body-centered cubic beta phase to the hexagonal alpha phase. The occurrence of the omega phase tends to suppress the martinsitic beta-to-alpha transition and increases the hardness and strength of the alloys.

The studies of Parris, Schwartz, and Frost were carried out principally on a small single-crystal grain of Ti-8Cr alloy using rotation and Weissenberg single-crystal x-ray diffraction techniques. The grain was examined after solution treatment of 10 minutes at 975-1050°C (1787-1922°F) and after successive aging treatments of 1/2 hr and 1 hr at 371°C (700°F) and 1 hr and

5 hr at 426°C (800°F). The solution and aging treatments were carried out on an electrical resistance heater in a vacuum bell jar at 5×10^{-5} mm Hg pressure. From the data obtained it was concluded that the omega phase has a body centered cubic unit cell with $a_o = 9.80\text{Å}$. The space group chosen was $I\bar{4}3m$ with 54 atoms per unit cell. This structure is similar to that of gamma brass in that its lattice parameter is approximately three times that of the parent matrix. It was also concluded that the (100) planes of the omega phase were parallel to the (100) planes of the parent beta phase in the alloy.

The studies by Spachner and Rostoker were carried out by powder x-ray diffraction techniques using 200-mesh powders of Ti-8Cr, Ti-13Mo, and Ti-15V alloys. These powders were solution-treated for 30 min at 900°C (1652°F), water-quenched, and then aged respectively, 8 hr at 500°C (932°F), 250 min at 400°C (752°F), and 100 hr at 400°C (752°F). These heat treatments were carried out in argon-filled Vycor glass capillaries. The capillaries were water-quenched after the solution and aging treatments to prevent transformations such as might occur during slow cooling. From the analysis of 30 lines in the powder diffraction patterns an orthorhombic unit cell was chosen for the omega phase with the following lattice constants for the three alloys:

	a	b	c
Ti-8Cr	6.203Å	6.489Å	13.63Å
Ti-13Mo	6.231	6.500	13.52
Ti-15V	6.205	6.597	13.63

The studies by Silcock, Davies, and Hardy were carried out by single-crystal oscillation x-ray diffraction methods on a single-crystal grain of a Ti-15V alloy which was solution-treated 15 min in purified argon at 900°C (1652°F), water-quenched, and then aged 5 min at 460°C (860°F) in a bath of molten tin. Diffraction patterns obtained in this way showed diffraction spots which could be indexed on the basis of a cubic lattice of the size and orientation proposed by Parris, Schwartz, and Frost; however, it was also found that a simpler hexagonal unit cell with a = 4.60Å and c ≐ 2.82Å would fit the data equally well and provided better agreement between observed and calculated intensities. The space group chosen was P6/mmm with atom positions at, or near, 000, $\frac{1}{3}\frac{2}{3}\frac{1}{2}$, $\frac{2}{3}\frac{1}{3}\frac{1}{2}$. For this hexagonal cell the precipitation orientation would be with (0001) omega planes parallel to the (111) planes of the beta matrix, and it was proposed that coherency occurred on the $(1\bar{2}10)$ omega planes.

It is believed that the different results reported by these different groups of investigators result from experimental difficulties attending the study of the omega phase. Since it is a transition phase, it is intrinsically unstable, and probably cannot be prepared free of the beta phase; therefore pure single crystals of sufficient size for structural analysis by the usual x-ray diffraction methods cannot be obtained. Analysis of the omega structure from studies of a beta single-crystal grain containing the omega phase is also fraught with difficulties. Due to the symmetry of the beta structure, more than one equivalent crystallographic orientation is possible for the omega crystals within a given beta crystal. Patterns obtained will thus be composites of patterns from these several orientations rather than the desired case of patterns from a single orientation. This greatly complicates the analysis of the patterns. In addition the omega reflections are weak compared with the beta reflections in most cases, and in some cases coincide with beta reflections. This further increases the difficulty of accurately analyzing the patterns.

MATERIALS AND METHODS

In the work to be described here, samples of Ti-8Cr and Ti-13Mo alloys were used. These were supplied by the Aeronautical Research Laboratory of the Wright Air Development Center, and it is understood that they were prepared by Prof. Rostoker and his associates at the Armour Research Foundation of the Illinois Institute of Technology. The heat-treatment reported for the Ti-8Cr alloy is: solution treatment at 900°C (1652°F) and water-quenched, then aged 8 hours at 400°C (752°F). The Ti-13Mo alloy was reportedly solution-treated at 900°C, water-quenched, then aged 250 min at 400°C. As received, the samples were in the form of rods 1/4" in diameter and 3-4" long. These were cut to shorter lengths more convenient for use, but were not given additional heat treatments.

The different studies that have been made on these specimens include: (1) electron microscopic studies to determine the size, shape, and distribution of the omega particles in the alloys, (2) electron diffraction studies by reflection techniques from polished and etched surfaces to attempt to obtain diffraction patterns of the omega phase from which information on its structure could be derived, (3) x-ray diffraction studies using a single-crystal grain of the Ti-8Cr alloy and a Buerger precession camera.

The electron microscopic and electron diffraction studies involved examinations of surfaces of the specimens which were polished and etched so as to bring the particles of the omega phase into relief with respect to the beta matrix. For the electron microscopy, these surfaces were examined by means of surface replicas in the form of thin collodion films, prepared by evaporation of a drop of a dilute solution of collodion in amyl acetate on the surface. The films were stripped from the surfaces by standard dry-stripping techniques[6], shadowed with palladium to increase their contrast, and then examined in a Philips Model EM-75 electron microscope. The electron diffraction studies were carried out by directing a collimated beam of electrons across the etched surfaces at a grazing angle so that it would strike the protruding omega particles and produce electron diffraction patterns from them. For this purpose an RCA Model EMD electron diffraction instrument was used.

The x-ray diffraction studies were made on a single-crystal grain of the Ti-8Cr alloy which was separated from the larger bar by careful etching. The grain was mounted in the goniometer head of the Buerger Precession Camera, and its crystallographic orientation relative to the coordinates of the instrument was determined. It was then re-oriented with selected crystallographic axes of the beta phase perpendicular to the x-ray beam and patterns were recorded for various levels of diffraction.

RESULTS

In the electron diffraction and electron microscopic studies, difficulties were encountered in finding procedures which would produce the high quality of polishing and etching required. Because of the high sensitivity of these techniques, the surfaces must be clean and free of all contaminants. Dirt or residues from the polishing or etching treatments may be picked up on the surface replicas and obscure the true structures when the replicas are observed in the electron microscope. Such contamination may also interfere in electron diffraction by producing extra diffraction rings or by preventing the electron beam from striking the true surface of the sample.

For polishing, both mechanical and electrolytic methods were tried, including more than 20 polishing electrolytes of compositions given by Tagima[7] and Osadchuk,[8] and various modifications thereof. An even greater number of etching reagents, both immersion and electrolytic, were also tried. Again these included various reagents recommended for titanium and its alloys, and compositional modifications of these reagents. Due to the high resistance of the Ti-8Cr and Ti-13Mo alloys to electrochemical attack, unsatisfactory results were usually obtained with electrolytic polishing mwthods. When mechanical polishing methods were used, however, extreme difficulty was encountered in removing the abrasive polishing powders to obtain surfaces clean enough for electron diffraction. The most satisfactory overall results were obtained by mechanically polishing with 3/0 emery, and then with Linde "A" alumina on a wax lap, and following this with a light electrolytic polish in one of the reagents listed in Table I to remove worked metal and the polishing powders from the surfaces.

Table I. Solutions used for
Polishing Titanium Alloys

(1) 77 ml glacial acetic acid
15 ml chromic acid (43%)
8 ml hydrofluoric acid (48%)

Should be used fresh for best results at a temperature of about 10°C with currents of 3-5 amp/cm^2.

(2) 100 ml solution (1)
6 ml perchloric acid (70%)

use as above

(3) 37 ml nitric acid (tech. conc.)
37 ml lactic acid (85%)
18.5 ml hydrochloric acid (37%)
7.5 ml hydrofluoric

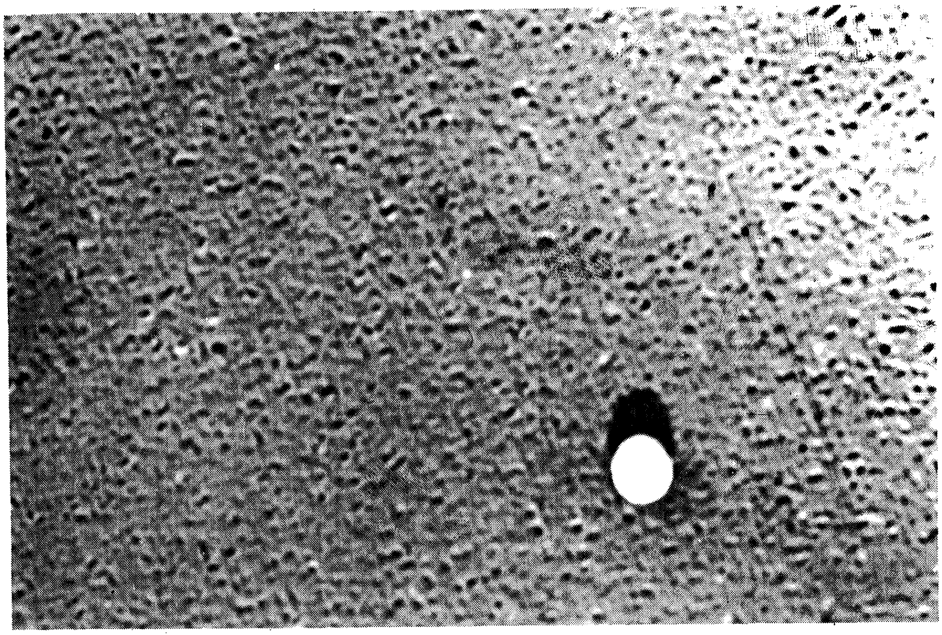
Immersion, use at 60-80°C

Most of the etching reagents tried produced pitting and staining of the surfaces; however, it was possible to obtain reasonably good results, particularly with the Ti-8Cr alloy, by etching electrolytically at low currents in polishing solution 1 of Table I.

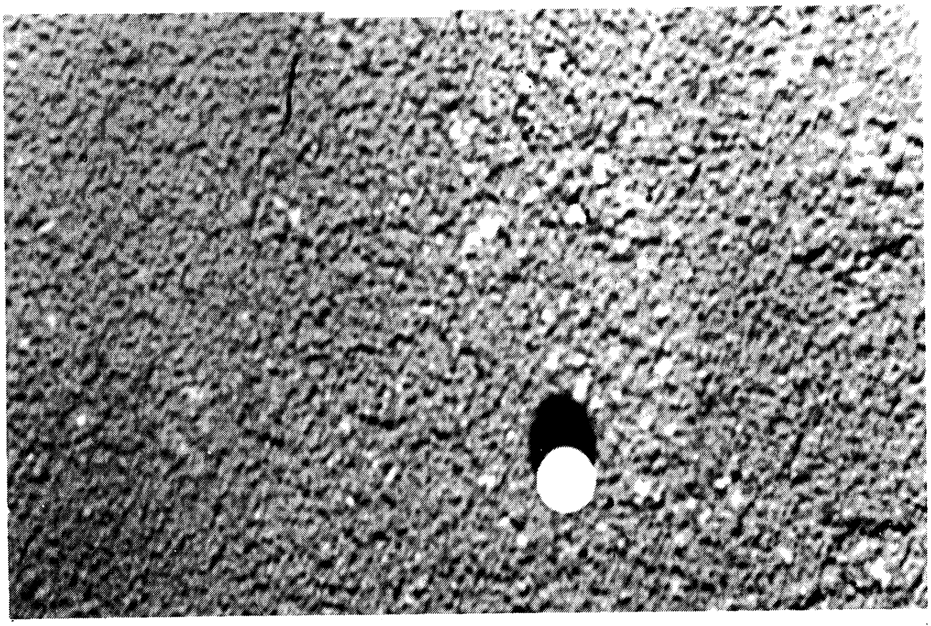
Electron micrographs have been obtained from both of the alloys which show a fine dispersion of very small precipitate particles. Typical micrographs are reproduced in Figure 1. The particles generally appear to be in the form of rods or platelets, and their "diameter" or "thickness", as the case may be, appears to be of the order of 400Å. It is believed that these particles are the omega particles, for their size and distribution as indicated by the electron micrographs is in general agreement with the conclusions previously reached from the characteristics of their x-ray diffraction lines.[1,2,3] They are also of the proper size and dispersion to produce marked age-hardening of the alloys.

The electron diffraction results were in general less satisfactory in that it was not possible to obtain patterns which could be definitely identified as arising from the omega phase. The principal difficulty apparently involved surface contamination during the polishing and etching operations, for in most cases diffuse halos or powder patterns of continuous rings were obtained rather than the spotty patterns expected from large-grained sample of the type being examined. Because of the small size of the omega particles and the general difficulties encountered in etching them into relief these results are not unexpected, for the slightest trace of surface contamination would be sufficient to prevent good electron diffraction patterns from being obtained.

In the x-ray diffraction studies of the Ti-8Cr single-crystal grain, patterns were obtained which showed the weak omega reflections among the stronger reflections from the beta phase. Unfortunately Dr. C. E. Nordman, who carried out most of these x-ray studies, is traveling abroad at the present time so that it is not possible to present the data in detail; however, the results will be summarized now, and a full report will be submitted upon his return in September. In general, the analyses of patterns from the



a. Ti-8Cr alloy.



b. Ti-13Mo alloy.

Fig. 1. Electron micrographs from the titanium-base alloys (X30,000).

hk1, hk2, hk3, and hk4 levels of the reciprocal lattice of the beta phase, plus patterns along 111, and 100 axes, showed very good agreement with the hexagonal structure proposed by Silcock, Davies, and Hardy.[5] Indices matching the triple-body-centered cubic cell proposed by Parris, Schwartz, and Frost,[1] could be assigned (as has been pointed out by Silcock, et al.); however, the patterns of the individual reciprocal lattice levels provided by the precession technique, showed too many reflections missing to make this structure plausible. It was not possible to show any reasonable agreement between the observed reflections and the orthorhombic structure proposed by Rostoker, et al.[4]

As a further check, a comparison was made of the "d" values reported by the various investigators. As shown in Table II, the "d" values and intensities reported by Parris, Frost and associates, agree very well with those reported by Silcock, Davies, and Hardy. It is also interesting to note that almost the same set of "d" values appear in the data of Rostoker, et al. but that there are several extra lines. Since intensity data are not given, it is difficult to make a good comparison, but it is possible that these extra lines arise from some material other than the omega phase. For example, many of them agree very closely with values reported for the alpha phase of the titanium alloys. They could also result from oxides or other surface contaminants, which would be more likely to contribute to powder patterns than to single-crystal patterns.

DISCUSSION AND CONCLUSIONS

From the results which have been obtained, and from an analysis of those previously reported, it appears that the hexagonal structure proposed by Silcock, Davies, and Hardy[5] is to be preferred to the cubic structure proposed by Parris and Frost, and associates[1,2,3] and the orthorhombic structure proposed by Spachner, Domagala, Goldenstein, and Rostoker.[4] Some uncertainties still exist

TABLE II. COMPARISON OF DIFFRACTION DATA FOR OMEGA PHASE

Ti-8Cr	Ti-7.7V			Ti-16V		
Rostoker[4]	Parris[1,3]			Silcock[5]		
d	d	I	hkl	d	I	hkil
				3.98	vvw	$10\bar{1}0$
2.806	2.79	w	222	2.82	mw	0001
2.5608						
2.2720	2.28	vvs	330	2.30	vs	$10\bar{1}1$
1.8178				1.99	vvw	$20\bar{2}0$
1.7803	1.77	vvw	125	1.78	m	$11\bar{2}1$
1.7269	1.71	vvw				
1.6244	1.62	vs	600	1.62	s	$20\bar{2}1$
1.5933	1.547	vvw				
1.4741				1.50	vvw	$12\bar{3}0$
1.4088	1.402	m	444	1.41	vs	0002
1.3613						
1.3253	1.322	vvs	336	1.33	vvw	$12\bar{3}1$
1.3041						
1.2494						
1.2299						
1.2013	1.200	m	118	1.20	vs	$11\bar{2}2$
1.1507	1.15	vs	660	1.15	(?)	$22\bar{4}0$
1.1300						
1.0976				1.10	vvw	$13\bar{4}0$
1.0843						
1.0692				1.06	w	$22\bar{4}1$
1.0290	1.026	vw	390	1.03	s	$12\bar{3}2$
1.0089						
0.9923	1.000	vw	448	0.99	vvw	$40\bar{4}0$
0.9676	0.965	vw	277	0.97	s	$30\bar{3}2$
0.9426	0.949	vs	666	0.94	m	$40\bar{4}1$
0.9338	0.927	vvw	1,3,10			
0.9151	0.913	m	774	0.91	ms	$10\bar{1}3$
0.8908	0.888	mw	2,4,10	0.89	ms	$22\bar{4}2$

as to the type of unit cell and the exact space group, however, in spite of the fact that the hexagonal cell proposed gives reasonably good agreement with observed data. These uncertainties arise from difficulties in interpreting the patterns as a result of the fact that it has not been possible to separate the omega phase from the parent beta phase. The multiplicity of orientations of the omega particles in the beta matrix, and the fact that in some cases beta and omega reflections coincide makes unequivocal interpretation impossible.

There is a possibility that some of these ambiguities could be resolved by electron diffraction studies, if the omega particles can be separated from the beta matrix by extraction replica techniques. Because of success which has been achieved with these methods in studies of the phase of nickel-base alloys, it is proposed to attempt applying them to the omega phase before the final report on this work is submitted.

REFERENCES

1. W. M. Parris, C. M. Schwartz, and P. D. Frost: " Precipitation Hardening and Embrettement of High-Strength Titanium Alloys." WADC Technical Report 54-355, Wright Air Development Center, Ohio, 1956.

2. A. E. Austin and J. R. Doig: "Structure of the Transition Phase Omega in Ti-Cr Alloys." Transactions AIME, Journal of Metals, January 1957, p. 27.

3. P. D. Frost, W. M. Parris, L. L. Hirsch, J. R. Doig, and C. M. Schwartz: "Isothermal Transformation of Titanium-Chromium Alloys." Transactions ASM, 46, 231 (1954)

4. S. A. Spachner, R. F. Domagala; A. W. Goldenstein, and W. Rostoker: "Structural Changes in Commercial Titanium and Titanium-Base Alloys on Heat Treatment." WADC Technical Report 55-352, Wright Air Development Center, Ohio, 1956.

5. J. M. Silcock, M. H. Davies, H. K. Hardy: "The Structure of the Omega Precipitate in Ti-16V Alloy." Institute of Metals Monograph and Report Series No. 18., The Institute of Metals, London, 1955, p. 93.

6. L. O. Brockway and W. C. Bigelow: "The Investigation of Minor Phases of Heat-Resistant Alloys by Electron Diffraction and Electron Microscopy" WADC Technical Report 54-589, Wright Air Development Center, Ohio, 1956.

7. S. Tajima and T. Mori: "Electropolishing Titanium." Products Finishing, 19, 26 (1954)

8. R. Osadchuk, W. P. Koster, and S. F. Kahles: "Recommended Techniques for Polishing Titanium for Metallographic Examination." Metal Progress, Oct. 1953, p. 129; "Metallographic Structures in Commercial Titanium," ibid., Nov. 1953, p. 93.