

phys. stat. sol. (a) **65**, 265 (1981)

Subject classification: 1.3; 21.1

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## Thermal Decomposition of the B.C.C. $\beta$ -Solid Solution of Titanium Alloy Containing 6.7 at% Mo, 3 at% Zr, and 1.8 at% Sn

### I. Changes in Crystal and Electron Structure

By

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Changes in the crystal structure of the titanium alloy, containing 6.7 at% Mo, 3 at% Zr, and 1.8 at% Sn, during thermal decomposition are followed by means of X-ray and electron diffraction methods. Parallel to these tests the alteration in the electron structure and chemical bonds of the alloy are investigated with the help of the soft-X-ray emission (SXES) method. Attention is focussed on the at room temperature not equilibrated b.c.c.  $\beta$ -solid solution, on the metastable transition phase  $\omega$ , and on the equilibrium phase  $\alpha$ .

Änderungen in der Kristallstruktur einer Titanlegierung mit 6,7 At% Mo, 3 At% Zr und 1,8 At% Sn werden während des thermischen Zerfalls mittels Röntgen- und Elektronenbeugungsmethoden untersucht. Parallel zu diesen Untersuchungen wird die Änderung der Elektronenstruktur und der chemischen Bindungen der Legierung mit Hilfe der Emission weicher Röntgenstrahlen (SXES) verfolgt. Insbesondere werden die bei Zimmertemperatur nicht im Gleichgewicht befindliche k.r.z.- $\beta$ -Legierung, die metastabile  $\omega$ -Phase und die Gleichgewichtsphase  $\alpha$  untersucht.

### 1. Introduction

In recent years a great number of papers and monographs dealing with the investigation of titanium alloys have been published [1 to 4]. Attention was focussed on the phase composition of the alloys and on the morphology of the components making up the various phases, that is, on the changes in morphology under mechanical stress. The Ti-Mo-Zr-Sn alloys and their metastable phases represent an important group of new structural materials.

The dependence of the properties of the Ti-Mo-Zr-Sn alloys upon the concentration of the alloying components has already been investigated [5].

We shall report in this paper on the structure of single crystals of titanium alloys of composition  $\text{Ti}_{88.5}\text{Mo}_{6.7}\text{Zr}_3\text{Sn}_{1.8}$  by means of X-ray and electron diffraction methods.

Parallel to the investigation of the crystal structure, the electron structure and the chemical bonds in the b.c.c.  $\beta$  solution being not in equilibrium at room temperature, in the metastable transition phase  $\omega$ , and in the equilibrium phase  $\alpha$  of the alloy were studied with the help of the soft-X-ray emission (SXES) method.

### 2. Experimental

The alloy was prepared from high purity metals (Ti 99.9%, Mo 99.9%, Zr 99.9%, Sn 99.9%) in the light arc furnace and remelted six times.

The electropolished single crystals were small cylinders with diameters ranging

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from 0.5 to 0.8 mm and were used in this form for X-ray diffraction and SXES tests. The thin foils for electron diffraction tests were electrolytically produced.

The b.c.c.  $\beta$ -solid solution was decomposed by isothermal treatment at 623, 723, and 823 K under a pressure of  $8 \times 10^{-3}$  Pa.

Since during decomposition of this solid solution the phases  $\alpha$  and  $\omega$  appear in highly dispersed small quantities, we used for their identification not Debye's method, but the far more sensitive X-ray diffraction test in which the [110] and [001] axes of the single crystals were set parallel to the X-ray beam. The diffraction pattern was recorded for both orientations after every ageing phase. The pictures were compared with the theoretically calculated reflections of the phases  $\alpha$  and  $\omega$  for both orientations of the  $\beta$ -crystal. The method of calculation can be found in one of our earlier publications [6]. For the X-ray diffraction tests the  $K_{\alpha}$  radiation of molybdenum was used.

The SXES tests were performed for the  $M_{II}$ - $M_{III}$  transition of titanium, for the  $M_{IV}$ - $M_V$  transition of zirconium, and for the  $N_I$  level of tin. By means of these soft X-ray levels it was possible to study the fine structure and the ageing processes.

The method and apparatus were described in one of the earlier communications [7].

### 3. Results

The diffraction patterns recorded immediately after hardening at 1373 K contain only the  $\beta$ -matrix reflections of the b.c.c.  $\beta$ -solid solution.

The electron diffraction pictures show in addition to the  $\beta$ -matrix reflections certain diffuse effects in the form of quasi-circular arcs.

The deviations of the electron configurations on the SXES curves recorded in this state ( $\beta$ ) indicate quite clearly the presence of the alloying components. (For the sake of comparison the curve of pure titanium was also recorded, see Fig. 1.) The characteristic peaks of the alloying components (A, Zr; B, Sn) changed in a manner which is typical of the chemical bonds in the alloy (Fig. 2).

After heat treatment at 623 K for 30 min beside the reflections of the b.c.c.  $\beta$ -matrix the reflections characteristic of the  $\omega$ -phase also appear in the X-ray and electron diffraction pictures (Fig. 3 and Table 1). When the period of heat treatment at 623 K is prolonged to 2, 6, 15 and 40 h, respectively, the intensity of the reflections of the  $\omega$ -phase in the X-ray diffraction pictures will increase, and in the electron diffraction pictures an f.c.c. phase with a lattice constant of 0.44 nm will appear beside the reflections of the b.c.c.  $\beta$ -matrix.

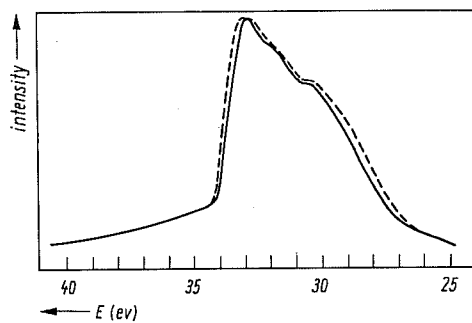


Fig. 1

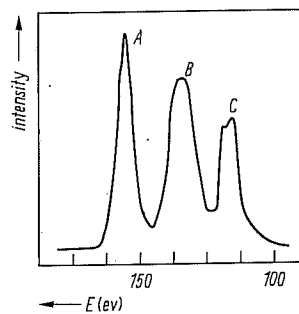


Fig. 2

Fig. 1. The SXES curve of the  $\beta$ -phase of Ti-Mo-Zr-Sn alloy (---) compared to the Ti  $M_{II-III}$  level. As reference we also plotted the pure Ti curve (—)

Fig. 2. The SXES peaks of alloying element in the  $\beta$ -phase of the alloy. (The reference Ti curve as base line is subtracted!)

Table 1  
Summary of the measured phase compositions during different heat treatments of the Ti-Mo-Zr-Sn alloy

ageing time (h)	0	0.5	2	6	15	40	method
623	$\beta + \omega$	$\beta + \omega$	$\beta + \omega$	$\beta + \omega$	$\beta + \omega$	$\beta + \omega$	X.D.
623	$\beta + \omega$	$\beta + \omega$	$\beta + \omega$	$\beta + \omega$	$\beta + \omega$	$\beta + \omega$	E.M.
723	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha$	X.D.
723	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha_1 + \alpha_2$	$\beta + \alpha_2$	$\beta + \alpha_2$	$\beta + \alpha_2$	E.M.
823	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha$	X.D.
823	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha$	$\beta + \alpha$	E.M.

X.D. X-ray diffraction, E.M. electron microscopy, D.E. diffuse effects

Heat treatment at 623 K for 40 h will result beside the reflections of the  $\beta$ - and  $\omega$ -phases in the appearance of reflections characteristic of the  $\alpha$ -phase.

The SXES records of the  $\beta + \omega$  phases show a fundamental change, namely a definite increase of the interval containing the characteristic peaks of the alloying components (Table 2).

Isothermal treatment of the alloy at 723 K showed that this temperature rise had greatly accelerated the decomposition of the b.c.c.  $\beta$ -solid solution. At this temperature the  $\alpha$ -phase appeared within 30 min. Prolonged heat treatment up to 40 h caused no essential change in the  $\beta + \omega$  phase composition (Table 1), only the quantity of the  $\alpha$ -phase increased parallel with the prolongation of heat treatment, as indicated by the higher intensities of the characteristic reflections.

On the electron diffraction pictures the situation after 30 min heat treatment corresponds to the Burger orientation of the  $\alpha$ -phase (Fig. 4). After heat treatment for 2 h the  $\beta$ -matrix, Burger's  $\alpha$ -phase, and all reflection lines characteristic of the  $\{10\bar{1}2\} \langle 10\bar{1}1 \rangle$  double ( $\alpha_2$ ) phase appear together in the electron microscopic picture. When thermal treatment is continued, only the characteristic reflections of the  $\beta$ - and  $\alpha$ -phases will be visible on the electron microscopic picture (Fig. 5).

On the foils the  $\alpha$ -phase is doubled only by electrolytic polishing [8], no similar effect can be observed on single crystals.

Heat treatment at 823 K also results in the  $\alpha$ -phase. Experiments on foils showed the repeated doubling of the  $\alpha$ -phase.

After the appearance of the  $\alpha$ -phase (at 823 K, after 5 h) the changes in the electron structure and chemical bonds continued in the direction started at the development of the  $\omega$ -phase. The equilibrium conditions stabilized and corresponding to the equilibrium the new bonds produced a higher intensity. The C peak with characteristic fine structure appearing in the equilibrated  $\beta + \alpha$  phase is shown in Fig. 6.

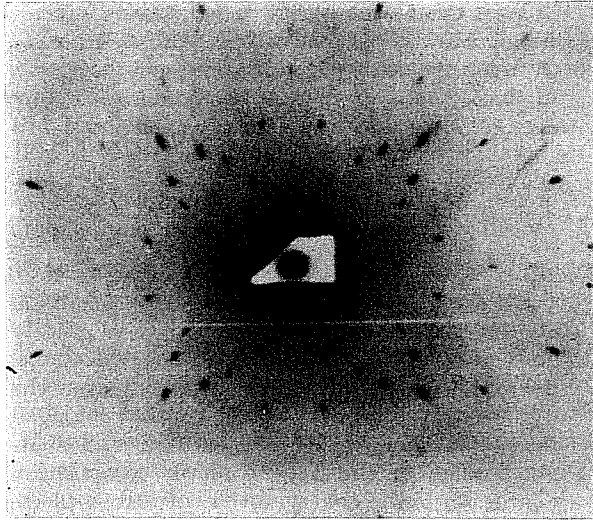


Fig. 3. The X-ray diffraction pattern of a Ti-Mo-Zr-Sn alloy monocrystal after 6 h heat treatment at 623 K. The reflections of  $\beta$ - and  $\omega$ -phases are well seen

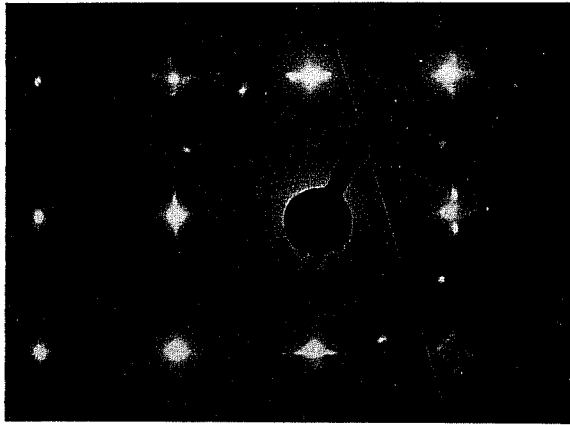


Fig. 4. Electron diffraction pattern of Ti-Mo-Zr-Sn alloy after 30 min heat treatment at 723 K. The reflections of  $\beta$ - and  $\alpha_1$ -phases are well seen

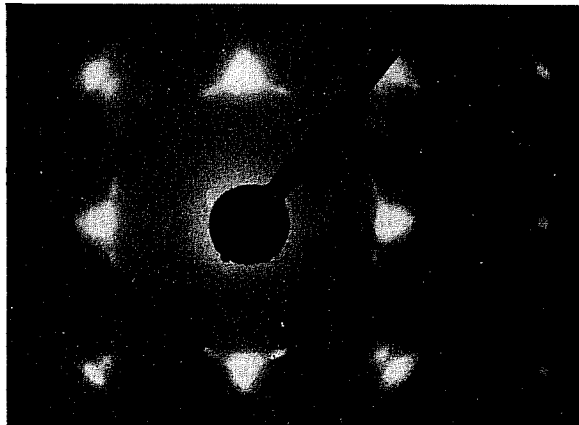


Fig. 5. Electron diffraction pattern of Ti-Mo-Zr-Sn alloy after 40 h heat treatment at 723 K, with the reflections characteristic of  $\beta$ - and  $\alpha_2$ -phases

ffraction pattern  
alloy monocrystal  
ment at 623 K.  
- and  $\omega$ -phases

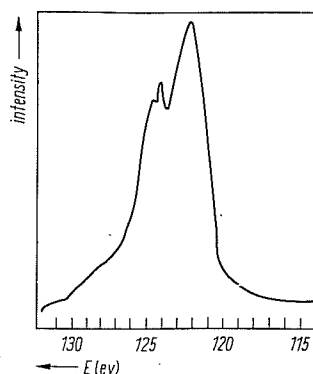


Fig. 6. The peak C in the SXES record of the  $\alpha$ -phase of the alloy

ffraction pattern  
alloy after 30 min  
723 K. The red  
 $\alpha_1$ -phases are

Table 2

Summary of the measured Ti  $M_{II-III}$  peaks of different phases of the Ti-Mo-Sn alloy

phase	peak energy (eV) ( $\pm 0.2$ eV)	asymmetry at half intensity	half-width (eV)
Ti reference	32.9	0.2	11.0
Ti-Mo-Zr-Sn $\beta$	33.1	0.2	11.7
Ti-Mo-Zr-Sn $\beta + \omega$	33.0	0.2	12.4
Ti-Mo-Zr-Sn $\beta + \alpha$	33.0	0.3	12.1

Table 3

Relative intensity of the C peak of SXES records in different phases of the Ti-Mo-Zr-Sn alloy

phase	C (%)
Ti	—
$\beta$	20
$\beta + \omega$	25
$\beta + \alpha$	100

#### 4. Discussion

The diffuse effects appearing beside the reflections of the b.c.c.  $\beta$ -matrix are the results of not-correlated linear crystal defects parallel to the direction of the crystal axis [9]. Increase in the half-width of the SXES curve plotted under the same conditions and the rather more markedly blurred fine structure indicate a dissolved state within the alloy [10] (Fig. 1). The half-width of the typical peaks of the alloying components which were plotted at the same time also increased and a new peak (peak C, Fig. 2) due probably to mixed bonds developed. (The properties of this mixed bond will be

ffraction pattern  
alloy after 40 h  
723 K, with the  
characteristic of  $\beta$ - and

studied later, and we intend to report on an acceptable explanation in the next part of our series of communications. The work is now in progress.)

Effects typical of a new phase appear in all three methods by which the decomposition process is followed, though in electron configuration only quantitative changes were observed (increase of peak C). The appearance of an f.c.c. phase with a lattice constant of 0.44 nm on the electron diffraction pictures is due to the re-arrangement of the elastic stresses arising during heat treatment, during polishing [11]. The metastable transition phase which is formed during of heat treatment is responsible for the appearance of elastic stresses. The re-arrangement of stresses by way of a martensitic mechanism gives rise to a f.c.c. phase in certain places of the foil.

Appearance of the stable  $\alpha$ -phase leads to a further considerable increase (see Table 3) of peak C, as testified by the study of the electron structure, which suggests that the development of the  $\alpha$ -phase is accompanied by significant complex bond formation.

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(Received February 5, 1981)