A.V. Dobromyslov

Institute of Metal Physics, Ural Branch of Russian Academy of Sciences, Ekaterinburg, Russia

THE REGULARITIES OF PHASE AND STRUCTURAL TRANSFORMATION IN BINARY TITANIUM ALLOYS WITH METALS OF IV–VIII GROUPS OF THE PERIODIC TABLE

ABSTRACT

Martensitic $\beta \rightarrow \alpha'(\alpha'')$ and $\beta \rightarrow \omega$ transformation in a series of Ti-base alloys with transition metals of groups IV–VIII have been investigated using the techniques of X-ray diffraction, optical and transmission electron microscopy. Phase and structural information is given on the non-equilibrium and metastable modifications occurring in these alloys during quenching from high-temperature β -field and aging. The conditions of the orthorhombic α'' -phase, ω -phase and metastable β -phase formation in binary titanium-base alloys with d -metals of V–VIII groups were investigated. It was established that the position of the alloying metal in the Periodic Table defines the presence or absence of the α'' -phase in the alloy after quenching and the minimum concentration of the alloying metal necessary for formation of the α'' -phase, ω -phase and metastable β -phase.

Key words: titanium alloys; phase transformation; α'' -phase; ω -phase; metastable β -phase

INTRODUCTION

The determination of the general regularities of the phase and structural formation in the titanium-base alloys in depending on position of the alloying metal in the Periodic Table is one of the important task of the phase transformation theory. Binary titanium alloys with d -metals of 4–6 periods are excellent model objects for establishing general regularities regarding the formation of non-equilibrium and metastable phases. In binary titanium-base alloys rapidly quenched from the β -phase, martensite transformation can occur independently of the type of the equilibrium phase diagram. Two martensitic phases, α' or α'' , are formed in quenched titanium-base alloys. The type of martensite crystal structure is determined by the composition of the alloy. At a certain concentration of the alloying element the β -phase is retained in quenched titanium alloys as a metastable phase. Up to now the effect of the alloying element type on the compositional boundaries of the non-equilibrium and metastable phases formation has been studied insufficient. However, the determination of the concentration fields of the α'' -, ω - and metastable β -phases is very important for the establishment of the general regularities regarding the formation of non-equilibrium and metastable phases. The purpose of the present research was to study the phase constitution of binary titanium-

base alloys with *d*-metals of 4-6 periods (IV-VIII groups) and to establish the relation between features of phase formation of these alloys and the position of the alloying element in the Periodic Table.

EXPERIMENTAL PROCEDURE

We studied binary titanium-base alloys containing different amount of V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, Ru, Rh, Pd, Ta, W, Re, Os, Ir, Pt and Zr. The alloys were prepared from iodide Ti (99,96 wt.%), V (99,7 wt.%), Cr (99,95 wt.%), Mn (98,53 wt.%), Fe (99,84 wt.%), Co (99,98 wt.%), Ni (99,99 wt.%), Cu (99,99 wt.%), Nb (99,6 wt.%), Mo (99,9 wt.%), Ru (99,9 wt.%), Rh (99,9 wt.%), Pd (99,91 wt.%), Ta (99,5 wt.%), W (99,95 wt.%), Re (99,9 wt.%), Os (99,99 wt.%), Ir (99,9 wt.%), Pt (99,9 wt.%). All alloys were melted in a tungsten-arc furnace under a helium atmosphere. The specimens were homogenised in the β -phase region (1000 or 1100°C) and quenched from these temperatures in iced or brine water.

RESULTS AND DISCUSSION

Formation of the α'' -phase

The optical and transmission electron microscope studies show that quenched binary titanium-base alloys with low content of the alloying element have a martensite structure. Two martensite phases, α' and α'' , are formed. The transition from hexagonal α' -phase to orthorhombic α'' -phase occurs under a certain concentration of alloying metal. The compositional limit of the α'' -phase formation depends on the type of the alloying metal. Figure 1 shows the X-ray diffraction patterns of titanium-base alloys with minimum or close to minimum concentration of alloying metal, at which the orthorhombic α'' -phase is formed in the alloys after quenching. In accordance with the data obtained in previous works [1-4] we were revealed the α'' -phase in quenched Ti-V, Ti-Nb, Ti-Ta, Ti-Mo, Ti-W, Ti-Re, and Ti-Ru alloys. Besides, we were established that the α'' -phase is formed also in quenched binary titanium-base alloys with iridium and osmium. The formation of the orthorhombic α'' -phase in the titanium-base alloys with other alloying metals of V-VIII groups was not observed. Table 1 summarised results obtained in the course of this study.

The analysis of data presented in the table 1 allows finding out a number of general rules, characterising the formation of the α'' -phase in binary titanium-base alloys. The formation of the α'' -phase in quenched alloys depends on the position of alloying metal in the Periodic Table. Both the group number and the periodic number influence on the conditions of the α'' -phase existence in the alloys. In the alloys with alloying metals of 4-th period, the α'' -phase is formed only in the Ti-V alloy. In the alloys with metals of the 5-period the presence of the α'' -phase was established in the Ti-Nb, Ti-Mo, and Ti-Ru alloys. With metals of the 6-period the α'' -phase is formed in the all alloys from

tantalum to iridium. Thus, the orthorhombic α'' -phase is formed in all binary titanium alloys the alloying metals of which are located in the Periodic Table below line drawn from chromium to platinum.

Fig.1. X-ray diffraction patterns of different binary titanium-base alloys, showing the α'' -phase peaks

Table 1. Minimum concentration of the alloying metal necessary for the formation of the orthorhombic α'' -phase in binary titanium alloys, at. %

IVA	VA	VIA	VIIA	VIII A			IB
Ti	V α'' 9	Cr —	Mn —	Fe —	Co —	Ni —	Cu —
Zr —	Nb α'' 11	Mo α'' 4-5	Tc α'' ?	Ru α'' 2	Rh —	Pd —	Ag ?
Hf —	Ta α'' 15	W α'' 5	Re α'' 3	Os α'' 2	Ir α'' 2	Pt —	Au ?

Formation of metastable β -phase

The X-ray diffraction study shows that the β -phase is retained in rapidly quenched titanium alloys at a certain concentration of the alloying metal. Table 2 summarised results obtained in the course of this study on compositional limit for the complete stabilisation of metastable β -phase in quenched titanium-base alloys. The titanium

alloys are arranged in the table 2 according to the position of the alloying metal in the Periodic Table.

Table 2. Minimum concentration of the alloying element necessary for the complete stabilization of the β -phase in binary titanium alloys with d-metals of 4-6 periods, at. %

Ti-V	Ti-Cr	Ti-Mn	Ti-Fe	Ti-Co	Ti-Ni	Ti-Cu
15	7	6	5	7	9	11
Ti-Nb	Ti-Mo	Ti-Tc	Ti-Ru	Ti-Rh	Ti-Pd	Ti-Ag
23	5	?	3	4	11	?
Ti-Ta	Ti-W	Ti-Re	Ti-Os	Ti-Ir	Ti-Pt	Ti-Au
35 (30)	10	5	3	3	7	?

The analysis of data presented in the table 2 allows finding out a number of general regularities, characterising the forming of metastable β -phase in binary titanium-base alloys. Both the group number and the period number influence on the minimum concentration of the alloying metal necessary for the complete stabilisation of the β -phase in quenched alloy. In 4-th period, β -stabilising effect of the alloying metal increases with increasing the group number from vanadium up to iron, and then it decreases from cobalt up to copper. In the Ti-Fe alloys the complete stabilisation of the β -phase occurs at the lesser concentration of the alloying metal. Similar change of the minimum concentration of the alloying metal necessary for the complete stabilisation of metastable β -phase is observed in binary titanium-base alloys with the alloying metals of 5-th and 6-th periods. The largest concentration of the alloying metal necessary for the complete stabilisation of the β -phase during quenching is observed in the Ti-Ta alloys and it is 35 at.%. The lesser concentration of the alloying metal necessary for the complete stabilisation of the β -phase is observed in the Ti-Ru, Ti-Os, and Ti-Ir alloys, and it is 3 at. %.

The concentration limit of the alloying metal, at which the complete stabilisation of metastable β -phase occurs, can be expressed through number of electrons per atom. These values are changed in sufficiently broad range from 4,1-4,12 e/a (Ti-V, Ti-Mo, Ti-Os and Ti-Ir alloys) up to 4,76 e/a (Ti-Cu alloy). According to [2-4] the electron-to-atom ratio necessary for the complete stabilisation of the β -phase at room temperature is $\sim 4,2$. However, the data obtained in this study indicate that the electron-to-atom ratio, at which the complete stabilization of the β -phase occurs in binary titanium-base alloys with transition metals, has not a constant value.

Up to now the correlation between the M_s temperatures of binary titanium-base alloys and the position of alloying elements in the Periodic Table are not established. The minimum concentration of the alloying metal, at which the complete stabilization of the β -phase take place, allows to determine the M_s curve position of every alloy at room temperature. So we can use such data to arrange the M_s curves, obtained for different alloys [5, 6], depending on the group number of the alloying metal. Figure 2 shows the M_s curves for titanium-base alloys with the alloying metals of 4, 5, and 6 periods. We can see that the identical change of the M_s curves with the increase of the group number is observed for titanium-base alloys with the alloying metals of all three periods. The increase of the group number of the alloying metal primary leads to decreasing the M_s temperatures. However, when crystal structure of the alloying metal becomes FCC, the increase of the M_s curves occurs with increasing the group number of the alloying metal. Similar behavior of the M_s curves of titanium-base alloys of all three periods

testifies that the position of the alloying metal in the Periodic Table is essential factor, which determines the process of martensitic $\beta \rightarrow \alpha'(\alpha'')$ transformations. For alloying metals with BCC structure, the M_s temperatures decrease the stronger the greater the group number, and opposite, for alloying metals with FCC structure, the M_s temperatures decrease the stronger the lesser the group number.

Thus, for binary titanium-base alloys the position of the alloying metal in the Periodic Table defines the minimum concentration of the alloying metal necessary for complete stabilization of the β -phase during quenching, and the shape of the M_s curves.

Fig.2. The M_s point of titanium as a function of alloying additions for: a – 4 period; b – 5 period; c – 6 period (square for M_s point at high temperature [5]; circle for M_s point at high temperature [6]; M_s point at temperature 0°C according to our data)

Formation of ω -phase

As mentioned above, the β -phase is retained in titanium-base alloys in a metastable state after rapid cooling. No evidence for the occurrence of the athermal ω -phase is found by X-ray diffraction in this case. Formation of the ω -phase depends on quenching rate. It is formed in many titanium-base alloys with transition metals of 4-6 periods in slowly quenched specimens. In Ti–Nb, Ti–Ta, Ti–W and Ti–Re systems, the ω -phase is observed only after ageing in the temperature range 300 to 500°C. Figure 3 illustrates morphology of the ω -phase in some titanium-base alloys. The particles of the ω -phase in the Ti–V, Ti–Cr, Ti–Mn, Ti–Fe, Ti–Co, Ti–Ni, Ti–Rh alloys have ellipsoidal morphology. The particles of the ω -phase in the Ti–Nb, Ti–Mo and Ti–Re alloys have cubical morphology. Electron diffractions studies show that it is observed a continuous change in diffraction patterns with increasing content of alloying metal in the alloy. The

ω -phase has sharp reflections in low solute content alloys and diffuse reflections in high solute content alloys.

Fig.3. Dark-field images of ω -particles in titanium-base alloys after ageing: a - Ti-5 at.% Fe, 400°C -1000'; b- Ti-7 at.% Co, 400°C-178'; c- Ti-35 at.% Ta, 400°C -562'; d - Ti-7 at.% Re, 400°C -562'

CONCLUSIONS

The structure of titanium-base alloys with *d*-metals of V-VIII, I groups of the Periodic Table, quenched from β -phase region, was studied. It was established the effect of the position of the alloying metal in the Periodic Table on the formation conditions of the orthorhombic α'' -phase and metastable β -phase. It is established that in quenched alloys the ω phase is formed in all titanium-base alloys with *d*-metals of V-VIII groups of the Periodic Table.

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