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Fig. 1. Phase diagram of the Ti—Cr system

Figure 1: Fig. 1. Phase diagram of the Ti—Cr system

Abstract

Full Text

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ON THE COMPOSITION AND STRUCTURE OF THE COMPOUND OF TITANIUM WITH CHROMIUM

(Presented by Academician I. I. Chernyaev, 27 X 1960)

In connection with the special physicochemical properties of titanium and its alloys, they are finding wide application in many branches of modern technology. A detailed study of the nature of the interaction of titanium with various metals and of the nature of the phases formed in this process is important for the search for new titanium-based alloys (1—4).

The phase diagram of the Ti—Cr system has been studied by a number of authors (5—9). It has been established that the continuous β-solid solutions of titanium with chromium formed in the system decompose below the liquidus line into a number of phases; in this process, at a temperature of about 1350°, a chemical compound is formed (Fig. 1). This compound has a cubic, face-centered lattice of the $MgCu_2$ type with a parameter equal to $a = 6.929$ Å (4). There are discrepancies in the literature concerning the composition of this compound. Some authors give the formula of this compound as $TiCr_2$ (4), others as Ti_2Cr_3 (9).

Fig. 1. Phase diagram of the Ti—Cr system

In the present work we give the results of a study of several compositions of titanium-chromium alloys containing from 1.0 to 80 wt.% chromium and including, as one of the phases, the chemical compound. The compositions of the alloys studied are given below. To establish the composition of the compound, we used a method previously employed by us: directed anodic dissolution of alloys, with separation of the chemical compound as the insoluble part and with its subsequent analytical and X-ray study.

The alloys were obtained by melting the components in an arc furnace* and were subsequently subjected to heat treatment. All alloys were cooled from 600° to room temperature together with the furnace. The heat-treatment schedule, in accordance with the phase diagram, was as follows:

Fig. 2. Diagram of measurement of electrode potentials of an alloy specimen (anode) by the compensation method

Figure 2: Fig. 2. Diagram of measurement of electrode potentials of an alloy specimen (anode) by the compensation method

Alloy composition, wt.% Cr	Annealing time, h at 1200°	Annealing time, h at 1000°	Annealing time, h at 800°	Annealing time, h at 600°
10—45	4	–	100	600
55	4	–	200	–
70	4	24	100	–
80	4	24	100	–

The alloys prepared in this way were subjected to anodic dissolution under the conditions described by us earlier (11—16). For titanium alloys with chromium, we first used the electrolyte proposed by N. I. Bliok (10), consisting of 2 g KCNS and 10 g citric acid in 1200 ml of methanol, with strong cooling.

The recommended anodic current density is 0.013 A/cm^2, with the anode placed in a celluloid bag.

Preliminary experiments carried out by us with the above electrolyte showed that at an anodic current density of 0.013 A/cm^2 no anodic powder separated from the alloys we studied. Subsequent experiments established that a precipitate can separate at a density of 0.03 A/cm^2. In this case we obtained anodic powders in which, according to chemical and X-ray analyses, the compound $TiCr_2$ was detected.

Fig. 2. Diagram of measurement of electrode potentials of an alloy specimen (anode) by the compensation method

As a result of the investigation, we proposed a new electrolyte composition for isolating the compound $TiCr_2$ from titanium-chromium alloys. Composition of the electrolyte: 5 ml HCl (1.19), 3 g succinic acid, 1000 ml methyl alcohol (11). The electrolyte does not require preliminary cooling, nor cooling during electrolysis, which is a major advantage of the proposed method; here calico bags were used, very convenient in the process of anodic dissolution in an acid electrolyte. The electrolyte makes it possible to isolate the metallic compound from alloys with a high chromium content. To select the optimum electrolyte composition, we carried out experiments measuring the anodic potentials of an alloy close in composition to the pure compound $TiCr_2$ and containing 70

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* The alloys were prepared and supplied to us by T. S. Chernova.

Fig. 3. Values of electrode potentials of the Ti—Cr alloy (Cr—70%) in various electrolytes

Figure 3: Fig. 3. Values of electrode potentials of the Ti—Cr alloy (Cr—70%) in various electrolytes

wt.% Cr. The measurement was performed relative to a saturated calomel electrode ($^{11-13}$) by the compensation method (Fig. 2). Measurements were made at the moment of immersion and then at certain time intervals. Before each measurement, the surface of the alloy electrode was ground and washed with alcohol.

Fig. 3. Values of electrode potentials of the Ti—Cr alloy (Cr—70%) in various electrolytes:
I —methanol 1000 ml, 5 ml HCl, 3 g succinic acid; **II** —electrolyte IV; **III** —electrolyte I; **IV** —electrolyte III

As can be seen from the values obtained (Fig. 3), the anodic potential in all the electrolytes tested is established at once and remains stable, which is confirmed by the character of the anodic polarization curve recorded during the anodic dissolution of the alloy. We carried out experiments to study the solubility of anodic powder containing the pure $TiCr_2$ phase (alloy with 20% Cr) in the proposed electrolyte. Microchemical analysis of the electrolyte was performed 30 min, 60 min, 1.5 h, and 24 h after the start of dissolution of the anodic powder at $t = 21°$. Ti and Cr were not detected in the solutions studied. Similar experiments were carried out with an anode made of a crushed alloy (Cr 65%), close in ⋯

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Fig. 4. X-ray diffraction pattern of the alloy

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Fig. 1. Debyegram of calcirthite (Fe $k\alpha\beta$; $2R = 57.3$ mm)

Table 1

Results of microchemical analysis of anodic powders obtained in various electrolytes (experiment duration 1.5 h; current density 0.1 A/cm^2; the titanium alloy studied contains 20% Cr)

Electrolyte	Found in anodic powder, wt. %: Cr	Found in anodic powder, wt. %: Ti	Sum of Cr and Ti, wt. %	Cr : Ti, wt. %	Found in anodic powder, at. %: Cr	Found in anodic powder, at. %: Ti	Sum of Cr and Ti, at. %	Cr : Ti, at. %	Composition of compounds
I	68.63	31.37	100.00	2.18	66.83	33.17	100.00	2.01	$TiCr_2$
II	68.37	31.61	99.98	2.16	66.65	33.35	100.00	1.99	$TiCr_2$
III	68.34	31.59	99.93	2.16	66.58	33.42	100.00	1.99	$TiCr_2$

Note. Electrolyte I: 3 ml H_2SO_4 (conc.), 1000 ml methyl alcohol, 3 g ascorbic acid. Electrolyte II: 3 ml H_2SO_4 (conc.), 1000 ml methyl alcohol, 3 g succinic acid. Electrolyte III: 5 ml HCl (1.19), 1000 ml methyl alcohol, 3 g salicylic acid.

Table 2

Effect of current density on the anodic isolation of the $TiCr_2$ phase (experiment duration 1.5 h; alloy contains 20 wt. % Cr)

Current density, A/cm^2	Weight of collected powder, g	Found, wt. %: Cr	Found, wt. %: Ti	Found, wt. %: sum	Found, at. %: Cr	Found, at. %: Ti	Found, at. %: sum	Cr : Ti
0.03	0.0102	68.29	31.55	99.84	66.59	33.40	99.99	1.99
0.05	0.0098	68.64	31.49	100.13	66.75	33.25	100.00	2.00
0.10*	0.0118	68.27	31.65	99.92	66.51	33.48	99.96	1.99

* The yield of the phase is 16.18 wt. %.

in composition to the compound $TiCr_2$. The alloy did not dissolve anodically in this electrolyte, which indicates the high selectivity of the electrolyte.

Experiments carried out in other electrolytes also showed satisfactory and readily reproducible results (Table 1).

In all experiments the ratio of the chromium content to titanium corresponds to the theoretical value, equal to 2.0 (at. %) or 2.17 (wt. %).

Special experiments set up to study the effect of anodic current density (Table 2) on the dissolution of the $TiCr_2$ phase showed that an anodic current density in the range 0.03-0.1 A/cm^2 is optimal. In all experiments, the compound $TiCr_2$ of stoichiometric composition is formed at the anode as the insoluble fraction.

Composition of the electrolyte: 5 ml HCl (1.19), 3 g succinic acid, 1000 ml methanol.

Anodic dissolution was carried out on titanium alloys with a chromium content of 1.0–80%. In our experiments the total volume of electrolyte was 1000 ml. The experiment duration was 1.5 h. After dissolution was complete, the anodic precipitate was washed off, centrifuged, then washed during centrifugation three times with distilled water and twice with alcohol during decantation. After centrifugation, the centrifuge tube with the anodic precipitate was dried in a stream of hydrogen, in a wide quartz tube placed in an oil bath, at 160°. Upon reaching this temperature, heating was stopped, but the passage of hydrogen was continued for 3 h. The dried powder was analyzed by microchemical and X-ray diffraction methods. Composition of the electrolyte: 5 ml HCl (1.19), 3 g succinic acid, 1000 ml methyl alcohol (Table 3).

For microchemical analysis of the anodic powder for chromium and titanium content, a 0.005 g sample was weighed on a microbalance and dissolved in H_2SO_4 (1 : 2), oxidized with HNO_3 (1.40), and twice evaporated to fumes of sulfuric acid—

Table 3

Results of microchemical analysis of anodic powders
(duration of experiment 1.5 hours; current density 0.1 A/cm^2)

Cr content in the alloy by charge, wt. %	Cr content in the alloy by chemical analysis, wt. %	Found in anodic powder, wt. % Cr	Found in anodic powder, wt. % Ti	Sum Cr and Ti, wt. %	Ratio Cr : Ti, wt. %	Found in anodic powder, at. % Cr	Found in anodic powder, at. % Ti	Sum Cr and Ti, at. %	Ratio Cr : Ti, at. %	Results of X-ray analysis ***
1.0	0.95	68.35	31.81	100.17	2.15	66.15	33.85	100.00	1.95	$TiCr_2$
2.0	2.12	68.57	31.22	99.99	2.19	66.96	33.05	100.01	2.01	$TiCr_2$
10.00 *	10.12	68.53	31.38	99.94	2.17	66.86	33.14	100.00	2.010	$TiCr_2$
15.50	15.65	68.45	31.60	100.05	2.16	66.61	33.39	100.00	1.994	$TiCr_2$
17.50	17.37	68.42	31.55	99.97	2.16	66.63	33.36	99.99	1.997	$TiCr_2$
20.00 **	19.89	68.61	31.43	100.04	2.18	66.78	33.21	99.99	2.010	$TiCr_2$ $TiCr_2$
30.0	30.22	68.45	31.48	99.93	2.17	66.70	33.30	100.00	2.000	$TiCr_2$

Cr content in the alloy by charge, wt. %	Cr content in the alloy by chemical analysis, wt. %	Found in anodic powder, wt. % Cr	Found in anodic powder, wt. % Ti	Sum Cr and Ti, wt. %	Ratio Cr : Ti, wt. %	Found in anodic powder, at. % Cr	Found in anodic powder, at. % Ti	Sum Cr and Ti, at. %	Ratio Cr : Ti, at. %	Results of X-ray analysis ***
45.0	45.05	68.38	31.56	99.94	2.16	66.62	33.37	99.99	2.000	$TiCr_2$
65.0	64.80	68.80	31.33	100.13	2.19	66.59	33.41	100.00	1.99	$TiCr_2$
70.0	69.52	68.34	31.52	99.86	2.16	66.60	33.40	100.00	1.96	$TiCr_2$
80.00	79.68	68.45	31.64	100.09	2.16	66.48	33.41	99.89	1.990	$TiCr_2$

* Phase yield 16.72%.
** Phase yield 16.88%.
*** X-ray analysis carried out at TsNIITMASH.

To determine titanium, the latter was precipitated with a 6% cupferron solution, followed by colorimetric completion of the analysis with hydrogen peroxide. Chromium was determined from a separate 0.01 g sample, without separating titanium, by dissolution in H_2SO_4 (1 : 6) according to the described method (^{14}).

From the data of Table 3 it is evident that, in alloys containing from 1.0 to 80% Cr, anodic dissolution releases the metallic compound $TiCr_2$ of stoichiometric composition.

The results of X-ray analysis * (Fig. 4) confirm the presence of the $TiCr_2$ phase (the alloy contains 20% Cr). Material-chemical balance of the products of electrolysis relative to the loss in weight of the anode: current density 0.1 A/cm^2, electrolyte 5 ml HCl (1.19), 3 g succinic acid, 1000 ml methyl alcohol. Weight of dry anodic powder 0.0406 g. Found in the electrolyte after separation of the phase: Ti 0.1750 g, Cr 0.0167 g, total 0.2323. Loss in anode weight 0.2399 g.

The investigation carried out on a series of compositions of titanium-chromium alloys with a chromium content of 1.00-80% showed the presence in the alloys of the metallic compound $TiCr_2$.

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CITED LITERATURE

[1] S. G. Glazunov, E. K. Molchanova, *Phase Diagram of Titanium Alloys*, Moscow, 1954.
[2] I. I. Kornilov, *Izv. AN SSSR, OKhN*, 1954, No. 3, 392.
[3] I. I. Kornilov, N. G. Borisova, *DAN*, 108, No. 6 (1956).
[4] I. I. Kornilov, P. B. Budberg, *Usp. khim.*, 25, No. 12 (1956).
[5] M. McQuillan, *J. Inst. Metals*, 79, 379 (1950).
[6] R. van Thyn et al., *Trans. Am. Soc. Metals*, 44, 974 (1952).
[7] P. Duwez, J. Taylor, *Trans. Am. Soc. Metals*, 44, 494 (1952).
[8] C. Cuff et al., *J. Metals*, 4, 848 (1952).
[9] I. I. Kornilov, V. S. Mikheev, T. S. Chernova, *Tr. Inst. Metallurgii*, 2, 126 (1957).
[10] N. I. Blok, A. I. Glazova, N. F. Lashko, *Zav. lab.*, 22, No. 1, 35 (1956).
[11] R. B. Golubtsova, Author' s certificate No. 120925 of 28 IV 1959.
[12] R. B. Golubtsova, L. A. Mashkovich, *DAN*, 106, No. 6, 1011 (1956).
[13] R. B. Golubtsova, L. A. Mashkovich, *DAN*, 111, No. 4, 824 (1956).
[14] R. B. Golubtsova, *DAN*, 118, No. 1 (1958).
[15] R. B. Golubtsova, *DAN*, 124, No. 1 (1959).
[16] R. B. Golubtsova, L. A. Nude, *DAN*, 130, No. 2, 318 (1960).
[17] G. Nortwitz, M. Codell, *Anal. chim. acta*, 9, No. 6, 555 (1953).

* X-ray analysis was carried out at TsNIITMASH.

Note: Figure translations are in progress. See original paper for figures.

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