CHEMISTRY

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1961

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

CHEMISTRY

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INVESTIGATION OF THE NATURE OF A CHEMICAL COMPOUND IN THE Ti–Si SYSTEM

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

In connection with the investigation of the nature of alloys containing titanium silicides, it became necessary to study the metallic compound formed in alloys of the binary Ti–Si system in the composition range 0.25-7.5 wt. % Si. The most extensive study of the phase diagram of the titanium–silicon system was carried out by Hansen and co-workers (^{1}), who, by the method of X-ray analysis, demonstrated the existence of metallic compounds discovered in this system by metallographic means (^{2}). According to these authors, the phase they found has a composition of 37.5-40 at. % silicon. Pietrokowsky and Duwez (^{3}) believe that the crystal structure of this phase corresponds to the formula derived on the basis of chemical composition. This compound, of hexagonal structure, is isomorphous with the compounds Mn_5Si_3, Fe_5Si_3, Ti_5Sn_3, Ti_5Ge_3 (^{2}).

The present work is an investigation of the nature of the metallic compound in titanium alloys with a low silicon content (0.25%-7.5% Si (wt. %))* by means of electrolytic isolation of the compound in an insoluble state on the anode. In the literature there is no description of electrolytes suitable for anodic dissolution and isolation of titanium silicides from titanium-base alloys.

Fig. 1

For the experiments, alloys were used which, after melting, were annealed at 1000° for 24 hours, quenched in water, and at 500° for 500 hours, quenched in water, in accordance with the phase diagram.

* The alloys for the investigation were prepared and supplied to us by E. N. Pylaeva.

The new electrolyte we proposed for the anodic separation of the $TiCr_2$ phase from titanium-chromium alloys (^{4}) of the following composition: 3 ml of H_2SO_4 (1.84), 3 g of succinic acid, 1000 ml of methanol, also made it possible to isolate the intermetallic phase from Ti–Si alloys containing 7.5 wt.% Si.

In all experiments carried out with the indicated alloy, the presence of the phase is confirmed by chemical and X-ray analysis. This phase is titanium silicide Ti_5Si_3 of strictly stoichiometric composition corresponding to the chemical formula. However, for other investigated alloys of the Ti—Si system containing small amounts of silicon—0.25; 0.50; 0.75; 1.0; 2.0%—it was not possible to isolate titanium silicide by anodic dissolution in the indicated electrolyte.

In this connection, we proposed a new electrolyte of the following composition: 15 ml of H_2SO_4 (1.84), 3 g of ascorbic acid, 1000 ml of methyl alcohol ([5]). In this electrolyte it is possible to carry out anodic dissolution of titanium-base alloys of the Ti—Si system containing small amounts of silicon, with separation of titanium silicide Ti_5Si_3 of exact chemical composition, with the weight ratio Ti : Si = 2.85% or 1.68 at.%.

Table 1

Results of microchemical analysis of anodic powders.
Electrolyte: 15 ml of H_2SO_4 (1.84), 3 g of ascorbic acid, 1000 ml of methyl alcohol.
(Duration of experiment 1.5 hours. Current density 0.05 A/cm^2)

Si content in the charge, wt.%	Found in anodic powder, wt.% Ti	Found in anodic powder, wt.% Si	Ti+Si, wt.%	Ti : Si, wt.%	Found, at.% Ti	Found, at.% Si	Ti+Si, at.%	Ti : Si, at.%	Composition of compound	Results of X-ray analysis
0.25	powder is not separated	powder is not separated	powder is not separated	powder is not separated	powder is not separated	powder is not separated	powder is not separated	powder is not separated	powder is not separated	powder is not separated
0.50*	72.66	27.18	99.84	2.70	61.05	39.35	100.40	1.60	Ti_3Si_3	Ti_5Si_3
0.50*	74.99	24.78	99.77	2.82	62.32	37.67	99.99	1.66	Same	—
0.75*	74.02	26.30	100.32	2.81	62.25	37.75	100.00	1.65	Same	Ti_5Si_3
75*	75.00	25.16	100.16	2.97	63.90	36.10	100.00	1.77	Same	
1.00	75.95	23.71	99.66	2.74	65.25	34.73	99.98	1.67	Same	
2.00*	74.85	25.00	99.85	2.99	63.50	36.93	100.40	1.71	Same	
2.00*	74.95	25.04	99.99	2.99	63.68	36.32	100.00	1.75	Same	
7.50*	74.00	26.32	100.32	2.87	63.12	36.86	99.98	1.71	Same	Ti_5Si_3
7.50*	75.00	25.00	100.00	3.00	64.48	35.50	99.98	1.80	Same	

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* The electrolyte contained 3 ml of H_2SO_4 (1.84), 3 g of ascorbic acid, and 1000

ml of methanol.

Table 2

Effect of current density on the composition and yield of the phase.
Electrolyte: 1000 ml of methanol, 15 ml of H_2SO_4 (1.84), 3 g of ascorbic acid.
(The alloy studied contained 7.5% Si; duration of experiment 1.5 hours)

Current density, A/cm^2	Phase yield, wt.%	Found, wt.% Ti	Found, wt.% Si	Found, wt.% Ti+Si	Found, wt.% Ti : Si	Found, at.% Ti	Found, at.% Si	Found, at.% Ti+Si	Found, at.% Ti : Si
0.03	12.09	75.20	24.54	99.74	3.05	64.23	35.76	99.99	1.79
0.05	11.36	75.06	24.64	99.70	3.04	64.11	35.88	99.99	1.78

Table 1 gives the results of microchemical analysis of anodic powders of Ti—Si alloys. After anodic dissolution, the powder brushed from the specimen was washed during centrifugation with water, then with alcohol, and dried in a stream of hydrogen in a quartz test tube on an oil bath. The dried precipitate was subjected to microchemical and X-ray analysis*.

We investigated the effect of current density on the composition and yield of the phase and established that the optimum current density lies within the range 0.03 A/cm^2—0.05 A/cm^2 (Table 2).

* The X-ray structural analysis was carried out by M. A. Volkova.

At a current density of 0.1 A/cm^2, very strong heating of the sample occurs. Replacing ascorbic acid in the electrolyte as complexing agent with sulfosalicylic acid also makes it possible to carry out experiments on the separation of the titanium silicide phase of strictly stoichiometric composition (Table 3).

Table 3

Results of microchemical analysis of anodic powders.
Electrolyte: methanol 1000 ml, 15 ml H_2SO_4 (1.84), 3 g sulfosalicylic acid.
(Current density 0.05 A/cm^2, duration of the experiment 1.5 hours)

Si content in alloy, wt. %	Phase yield, wt. %	Found, wt. %	Found, wt. %	Found, wt. %	Found, wt. %	Found, at. %	Found, at. %	Found, at. %	Found, at. %
		Ti	Si	Ti+Si	Ti : Si	Ti	Si	Ti+Si	Ti : Si

Si content in alloy, wt. %	Phase yield, wt. %	Found, wt. %	Found, wt. %	Found, wt. %	Found, wt. %	Found, at. %	Found, at. %	Found, at. %	Found, at. %
0.50	12.90	74.83	25.04	99.87	2.98	63.62	36.36	99.98	1.74
0.75	12.14	74.70	24.94	99.64	2.99	63.68	36.32	100.00	1.75
2.00	13.32	74.67	25.08	99.76	2.88	63.59	36.41	99.99	1.74

The material-chemical balance of the electrolysis products, carried out relative to the loss in weight of the anode, showed good results, as follows (in grams): weight of dry anodic powder 0.0742; found in the powder: Ti 0.0363, Si 0.0043; found in the electrolyte after separation of the Ti phase: 0.04840, Si 0.0105; total 0.6093; loss in anode weight 0.6144.

Procedure for microchemical analysis

A 0.01 g portion of dried anodic powder, weighed on a microbalance, is placed in a platinum crucible and fused with 5 g of accurately weighed potassium persulfate, which is added in two portions. After fusion of the first portion of the salt, the crucible is cooled, the second portion is added, and it is again heated in a muffle furnace. The fused mass is leached in water containing 10 ml H_2SO_4 (1.84), and the solution is evaporated twice to dense white fumes.

The precipitated silicic acid is filtered off and washed with 5% (by volume) warm HCl until a negative reaction for iron salts is obtained (test with a crystal of yellow prussiate of potash). The filtrate is retained for determination of titanium. The washed precipitate, placed in a platinum crucible, is dried and ignited in a muffle at 1000°, and weighed.

The precipitate is moistened with 1-3 drops of H_2SO_4 (1 : 1) and 2 ml HF, carefully evaporated to dryness, ignited, the crucible is cooled, and it is weighed again. The difference between the first and second weighings corresponds to the amount of silicic acid.

A blank experiment is carried out through all stages of the analysis. Titanium was determined in the filtrate after silicon by the colorimetric method with hydrogen peroxide.

In all investigated alloy samples of the Ti—Si system, the compound Ti_5Si_3 was found by microchemical and X-ray structural analysis methods.

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Received
18 V 1960

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