ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 6, pp. 1118–1122. © Pleiades Publishing, Ltd., 2008.
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Chemical Transformations of TiAl and Ti_3Al Intermetallides in Amonium Medium

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Received January 29, 2008

Abstract—Hydrogenation, hydronitriding, disproportionation, and dispersing in the TiAl–NH_3 and Ti_3Al–NH_3 systems in the temperature range 100–500°C under a pressure of 1.5 MPa in the presence of an NH4Cl activator have been studied . Phase transitions have been studied and conditions for formation of fine intermetallide powders with a medium particle size of 0.15–0.30 μm have been determined.

DOI: 10.1134/S1070363208060029

Alloys of Ti–Al systems containing about 50 at % titanium, in particular, the intermetallides TiAl and Ti_3Al can be used as construction materials in aerospace and nuclear technics [1, 2]. Therewith, one of the key operations is grinding of cast alloy, since the structure and properties of powders predetermine the quality of final products. Mechanical grinding of cast alloys, which is most commonly used in industry, is not always feasible for producing metal powders because of the plasticity of metals and their alloys, inhomogeneity of the resulting fine particles and their tendency for oxidation on contact with traces of water vapors and oxygen, dustiness, and, as a result, losses of the starting material. Therefore, for grinding alloys it is sometimes more expedient to make use of internal strains produced in such materials on their reaction with hydrogen (hydride dispersing) [3]. However, the latter technique is, in many respects, inferior to ammonia dispersing which involves reaction of alloys with gaseous ammonia under heating. Ammonia dispersing provides finer powders, sometimes with a nanometer particle size [4].

The Ti–Al system was shown to comprise a number of intermetallic compounds, two of which, Ti_3Al and TiAl, are in the titanium-enriched region [5]. The intermetallide Ti_3Al crystallizes in the hexagonal syngony and has a Ni_3Sn structure with the following lattice parameters, Å: *a* 5.793, *c* 4.655. The TiAl intermetallide is tetragonal (*a* 3.988, *c* 4.076 Å).

Both the intermetallic compounds react with hydrogen at 7000 MPa and 300°C. After 24-h hydrogenation, a single-phase Ti_3AlH_6 (3.4 wt % hydrogen, edge-centered cubic lattice, *a* 4.413 Å) and a hydride corresponding to the formula $TiAlH_2$ are formed. According to X-ray diffraction data, during hydrogenation TiAl disproportionates to form titanium dihydride and $TiAl_3$. The same reaction is observed when TiAl is hydrogenated at lower pressures (150–180 MPa) at 400–600°C: After depressurization, the product contained 0.7 wt % hydrogen, which corresponds to titanium dihydride (H/Ti 0.5) [6, 7].

Treatment of Ti_3Al with hydrogen under lower pressures (below 5 MPa) and temperatures below 500°C gives rise to three hydride phases: α-$Ti_3AlH_{0.6}$ (*a* 2.89, *c* 4.66 A), β-$Ti_3AlH_{1.5}$ (*a* 3.28 Å), and γ-$Ti_3AlH_{5.2}$ (*a* 4.36 Å) [6, 8]. The hydride reachest in hydrogen decomposes by the following scheme.

$$Ti_3AlH_{5.2} \xrightarrow{165\text{–}300^{\circ}C} Ti_3AlH_{3.0} \xrightarrow{320\text{–}360^{\circ}C} Ti_3AlH_{2.0} \xrightarrow{380\text{–}640^{\circ}C} Ti_3AlH_{0.2}.$$

Over the last decade several research teams have studied hydrogen absorption by the intermetallide Ti_3Al under a pressure of 10 MPa at various temperatures [7, 9–12], as well as the equilibrium pressure [9] and structure of the hydride phases formed [9, 10, 12].

Table 1. Conditions and results of treatment of the intermetallide TiAl with ammonia

Sample no.	TiAl particle size, µm	Treatment conditions		Brutto formula of product under a pressure of 1.5 MPa	Specific surface area, $m^2 g^{-1}$
		T, °C	time, h		
1	100	100	25	$TiAlH_{0.7}$	0.5
2	100	150	30	$TiAlH_{1.5}$	0.4
3	100	200	30	$TiAlH_{1.9}N_{<0.1}$	0.4
4	100	250	30	$TiAlH_{0.9}N_{<0.1}$	0.5
5	100	300	30	$TiAlH_{0.6}N_{0.2}$	5.7
6	100	350	30	$TiAlH_{2.2}N_{0.2}$	3.1
7	100	400	30	$TiAlH_{0.5}N_{0.1}$	2.8
8	100	450	30	$TiAlH_{0.2}N_{0.1}$	3.7
9	100	500	30	$TiAlH_{0.1}N_{0.1}$	1.5
10	50	150	28	$TiAlH_{1.3}N_{<0.1}$	1.7
11	50	200	32	$TiAlH_{1.4}N_{<0.1}$	2.0
12	50	250	28	$TiAlH_{3.4}N_{0.2}$	2.5
13	50	300	28	$TiAlH_{0.6}N_{0.1}$	3.6
14	50	350	30	$TiAlH_{2.7}N_{0.1}$	2.0
15	50	400	30	$TiAlH_{0.6}N_{0.2}$	2.1

In the present work we have performed an experimental study of the possibility of preparing fine powders of Ti_3Al and TiAl containing in their crystal lattices some hydrogen and nitrogen, by treatment of the intermetallic compounds with ammonia in the temperature range 100–500°C.

It was found that up to 200°C the intermetallide TiAl with the particle size 200 µm is fairly stable in the ammonium medium: The metal matrix is preserved, but it gradually accumulates some nitrogen and hydrogen, which gives rise to new insertion phases with increased specific surface area. Thus, the sample that is present in the autoclave at 250°C and ~1.5 MPa contains the greatest amount of hydrogen (for the series) and traces of nitrogen, which corresponds to the composition $TiAlH_{1.4}N_{<0.1}$. The specific surface area of this sample is larger than the initial specific surface area by an order of magnitude (0.3 against 0.04 $m^2 g^{-1}$), average particle size 5.0 µm. Therewith, the crystal lattice parameters of the sample are virtually unchanged. As the reaction temperature is increased to 400°C, the specific surface area increases further, but the intermetallide metal matrix is still preserved. These findings point to increasing dispersity of the material (particle size 0.9–1.6 µm). Therewith, the metal matrix accumulates nitrogen and simultaneously loses hydrogen. As a result, the product of hydronitriding at 400°C has the composition $TiAlH_{0.4}N_{0.1}$ which is preserved after depressurization. Ammonium treatment of powdered alloys at 450°C and higher temperatures results, by X-ray diffraction data, in decomposition of the hydridonitride phase to form a cubic titanium nitride (*a* 4.241 Å) and appearance to a new phase $TiAl_2$, implying that nitriding under these conditions is accompanied by disproportionation.

Data on ammonium treatment of TiAl (particle size 100 and 50 µm) are presented in Table 1.

Reaction of TiAl with the particle size 100 µm with NH_3 begins already at 100°C (Table 1, sample no. 1) and, too, involves formation of hydride phases with crystal lattice parameters slightly different from those in the starting intermetallide (*a* 3.992, *c* 4.066 Å). It should be noted that the products of ammonia treatment at 100–150°C contain no hydrogen after depressurization. As the ammonia treatment temperature is raised to 200°C, the intermetallide continues to accumulate hydrogen (Table 1, sample nos. 2 and 3), and, under pressure, the phase composition of the product (Table 1, sample no. 3) corresponds to $TiAlH_{1.9}N_{<0.1}$, i.e. the sample contains traces of nitrogen. Therewith, the specific surface area of the hydride phases changes only slightly (0.4 $m^2 g^{-1}$), and their particle size is 3.0–3.5 µm. Upon depressurization gas evolution occurs, and the product of hydronitriding at 250°C (Table 1, sample no. 4) has the composition $TiAlH_{0.1}N_{<0.1}$.

At the hydronitriding temperatures 300–350°C, ammonia as a source of hydrogen and nitrogen favors joint insertion of these elements into the crystal lattice of the intermetallide, and the product formed at 300°C (Table 1, sample no. 5) has, after depressurization, the largest specific surface area (5.7 $m^2\ g^{-1}$) and, correspondingly, the smallest particle size (0.3 μm) at the formula composition $TiAlH_{0.4}N_{0.2}$. At the same temperatures, the hydridonitride phase starts to decompose, and further hydronitriding at 400–500°C (Table 1, sample nos. 7–9) occurs similarly to the reaction of ammonia with TiAl with the particle size 200 μm. The specific surface area of the products of nitriding at 450°C is 3.7 $m^2\ g^{-1}$ (Table 1, sample no. 8), and at 500°C it decreases to 1.5 $m^2\ g^{-1}$ (Table 1, sample no. 9), particle size 0.4 and 1.0 μm, respectively.

Ammonium chloride is readily removed by evacuation of samples at 300°C. Such operations decrease the content of nitrogen several times (the nitrogen content of sample no. 5, Table 1, decreases from 4.2 to 1.0 wt %) and remove chlorine almost completely (to <0.1 wt %). Ammonium chloride is also readily removed by washing with alcohol. Such treatment decreases the nitrogen content of sample no. 6 from 3.6 to 2.2 wt % (chlorine content <0.1 wt %). Evidence for efficient removal of NH_4Cl is also provided by X-ray phase analysis.

The example of a 100-μm sample was used to show that in the absence of NH_4Cl almost no hydronitriding takes place: The product formed after 30-h treatment has the composition $TiAlH_{0.1}N_{<0.1}$ and scarcely developed specific surface (<0.1 $m^2\ g^{-1}$).

As seen from Table 1, ammonia treatment of TiAl with the particle size 50 μm results in a deeper hydrogenation of the metal matrix compared to TiAl with a larger particle size, i.e. in the first case reaction products obtained at the same temperature generally contain more hydrogen. The highest hydrogen content was observed in the sample obtained at 250°C (sample no. 12, Table 1, brutto formula $TiAlH_{3.4}N_{0.2}$ under pressure). Products formed from the starting 50-μm alloy under ammonium treatment were found to tend for caking at increased treatment temperatures, which unfavors all processes.

In whole, the 50- and 100-μm samples of the starting intermetallide TiAl show similar hydrogenation patterns: The quantity of hydrogen in the samples first gradually increases to reach a maximum at 200–250°C and then decreases. The trends in the specific surface areas of the products obtained from TiAl with different particle sizes, too, are similar to each other: As the temperature increases, the specific surface area increases to reach a maximum about 300°C and then sharply decreases. Moreover, at 250–300°C the crystal lattice of the intermetallide features the highest nitrogen content, which, too, favors decomposition. Noteworthy is the fact that both series of samples treated with ammonia at 350°C contain much hydrogen (Table 1, sample nos. 6 and 14), but, therewith, have a sharply decreased specific surface area. Probably, this temperature is the most favorable for decomposition of the hydridonitride phase formed at lower temperatures.

Thus, the reaction of TiAl with ammonia in the presence of NH_4Cl can be described by schemes (1)–(3).

$$TiAl + NH_3 \xrightarrow[NH_4Cl]{100–150°C} TiAlH_x, \tag{1}$$

$$TiAl + NH_3 \xrightarrow[NH_4Cl]{200–350°C} TiAlH_xN_y, \tag{2}$$

$$TiAl + NH_3 \xrightarrow[NH_4Cl]{400–500°C} TiAl_2 + TiN_x. \tag{3}$$

These schemes allow one to trace stage-by-stage the process of phase transition from the starting intermetallide TiAl to its complete decomposition products (TiN, $TiAl_2$) and note that ammonium plays a special role in these processes, decomposing the TiAl metal matrix.

Naturally, the above schemes do not embrace all processes that occur upon treatment of the intermetallide with ammonia in the presence of a promoter. Thus, it is well known that the formation of titanium nitride is favored, or, to be exact, preceded by the formation of titanium hydride. The X-ray patterns of the reaction products show overlapping peaks, which does not allow to draw unambiguous conclusions regarding the presence of the hydride phase.

Ammonia treatment of the intermetallic compound Ti_3Al (particle size 100 μm, specific surface area 0.05 $m^2\ g^{-1}$) in the presence of a promoter (NH_4Cl) was performed in the same temperature range (100–500°C). The hydronitriding results (Table 2), too, point to gradual accumulation in the intermetallide of hydrogen and nitrogen with preservation of the metal matrix.

The reaction of ammonia with Ti_3Al begins at 100°C (Table 2, sample no. 1) and proceeds as the temperature is raised to 150°C (Table 2, sample no. 2) to form hydride phases containing no nitrogen. Therewith, like with TiAl, crystal lattice parameters change only slightly (sample no. 2: *a* 5.793, *c* 4.681 Å), and, upon depressurization, reaction products evolve hydrogen and convert into the starting intermetallide.

With further increase of the temperature of ammonia treatment the intermetallide starts to accumulate nitrogen, and, under pressure, the hydroniriding products obtained at 200 and 250°C (Table 2, sample nos. 3 and 4) already contain detectable quantities of nitrogen: the phase compositions $Ti_3AlH_{3.0}N_{<0.1}$ and $Ti_3AlH_{2.0}N_{<0.1}$, respectively. Therewith, the specific surface are of the resulting phases increases by an order of magnitude (0.2 and 0.5 m^2 g^{-1}), particle size 7.1 and 2.8 μm.

At 300–500°C, too, hydronitriding preserves the metal matrix. The product of ammonia treatment at 500°C (Table 2, sample no. 9) has the formula $Ti_3AlH_{2.8}N_{0.35}$ under pressure and $Ti_3AlH_{0.45}N_{0.35}$ upon depressurization. The latter sample has the largest specific surface area (8.8 m^2 g^{-1}) and, correspondingly, the smallest particle size (~0.2 μm). According to its X-ray phase analysis (*a* 5.831, *c* 4.593 Å), it contains traces of titanium dihydride, which provides evidence for initiation of decomposition of the starting intermetallide Ti_3Al and a higher stability of the latter compared to TiAl.

Thermal analysis showed that the samples obtained at 100–250°C lose all hydrogen with an exothermic effect at 270–280°C.

Thus, our research on the reaction of the intermetallides TiAl (particle size 200, 100, and 50 μm) and Ti_3Al (particle size 100 μm) with ammonia in the presence of NH_4Cl as a promoter established that: (1) depending on temperature, the TiAl–NH_3 and Ti_3Al–NH_3 systems undergo hydrogenation/hydronitriding to form the hydride/hydridonitride phase of the starting intermetallic compounds, whereas the TiAl–NH_3 system undergoes disproportionation to form a new intermetallide phase; (2) chemical dispersing is better performed with a 100-μm intermetallide powder; (3) ammonia treatment of TiAl at 300°C results in formation of titanium aluminum hydridonitride; upon depressurization the latter gives a fine powder the starting intermetallide containing a little hydrogen and nitrogen and having the particle size of 0.3 μm; and 4) the particle size of titanium aluminum hydridonitride obtained at 450–500°C from Ti_3Al is 0.25–0.15 μm.

EXPERIMENTAL

Starting reagents. The intermetallic compounds Ti_3Al and TiAl were obtained by sintering the metals (purity: Ti 99.98%, Al 99.99%) in an oven with an unconsumable tungsten electrode under high-purity argon, followed by annealing of Ti_3Al at 1000°C for 1 week and of TiAl at 800°C for 2 weeks. The alloys were washed with alcohol and ether to remove traces of oil, after which the oxide film was removed mechanically. Experiments were performed with intermetallide powders prepared by mechanically grinding metal shot in a metal mortar and subsequently sieving 200, 100, and 50-μm fractions for TiAl and a 100-μm fraction for Ti_3Al. The specific surface area of these powders was 0.04–0.06 m^2 g^{-1}. The composition of the starting alloy was esatb;ished by X-ray phase analysis. The unit cell periods of the smelted intermetallides Ti_3Al (*a* 5.792, *c* 4.660 Å) and TiAl (*a* 3.976, *c* 4.100 Å) are nicely consistent with published data [5]. Unlike the single-phase Ti_3Al, the intermetallide TiAl contains trace admixtures of Ti_3Al, and, according to the chemical analysis, the composition of the alloy is $Ti_{1.02}Al$.

Chemical grade ammonium chloride was dried in a vacuum for 9 h at 150°C. Sodium-dried ammonia was 99.99% pure.

Table 2. Conditions and results of treatment of the intermetallide Ti_3Al with ammonia

Sample no.	Treatment conditions		Brutto formula of product under a pressure of 1.5 MPa	Specific surface area, m^2 g^{-1}
	T, °C	time, h		
1	100	30	$Ti_3AlH_{2.8}$	0.1
2	150	32	$Ti_3AlH_{3.0}$	0.1
3	200	30	$Ti_3AlH_{3.0}N_{<0.1}$	0.2
4	250	30	$Ti_3AlH_{2.0}N_{<0.1}$	0.5
5	300	28	$Ti_3AlH_{0.3}N_{0.10}$	0.8
6	350	28	$Ti_3AlH_{0.5}N_{0.15}$	1.8
7	400	30	$Ti_3AlH_{0.6}N_{0.25}$	3.6
8	450	30	$Ti_3AlH_{0.7}N_{0.25}$	5.7
9	500	30	$Ti_3AlH_{2.8}N_{0.35}$	8.8

Experimental procedure. The reaction of the intermetallides with ammonia (so-called hydronitriding) was studied in the presence of NH_4Cl (10 wt % of the starting intermetallide) at the initial ammonia pressure 0.5–0.8 MPa.

A mixture (0.8–1.0 g) of powders was grinded in an agate mortar at room temperature and placed into the high-pressure autoclave reactor 60 ml in volume. The reactor was evacuated for 0.5 h at room temperature to a residual pressure of about 1 Pa, after which it was filled with ammonia to a pressure of 0.5–0.8 MPa, kept at room temperature for 0.5 h, and then heated at various temperatures for 3 h, cooled to room temperature, and then heated again. As a rule, the pressure in the system was no higher than 1.5 MPa. When the required number of hydrogenation–dehydrogenation cycles had been completed, the reactor was cooled under ammonia to room temperature, excess ammonia was discharged into a buffer vessel, and solid reaction products were unloaded in an inert atmosphere and analyzed.

Ammonium chloride was removed from the reaction products in two ways. The first involved mechanical stirring of a mixture of a sample (~0.1 g) and 10 ml of absolute ethanol for 1 h at room temperature (the procedure was repeated in twice). The second procedure involved evacuation to ~1 Pa at 300° C for 3 h.

Methods of analysis. X-ray diffraction studies were performed on a DRON ADP-1 diffractometer (CuKα radiation). The error in interplanar spacings was within 0.005 Å.

The specific surface areas were measured by the low-temperature adsorption of crypton after volatile reaction products has been removed from the solid phase in a vacuum of 1.3×10^{-3} Pa at 300°C for 15 h, and calculated by the BET method [13]. The error is specific surface areas was within 10%.

Thermal analysis was performed on a Netzsch STA 409 Luxx simultaneous thermal analyzer under argon (temperature ramp rate 10 deg min^{-1}).

The hydrogen pressure was measures by a standard gauge (accuracy rating 0.4). The compositions of the resulting phases were found volumetrically and chemically. Analysis of the reaction products for hydrogen was performed by a standard procedure by burning in oxygen. Nitrogen was determined by Kjeldahl, and chlorine was determined by turbidimetry.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 07-03-00237).

REFERENCES

1. *Metal Hydrides*, Müller, W.M., Blackledge, J.P., and Libowitz, G.G., Eds., New York: Academic, 1968.
2. Sokolova, E.I., Padurets, L.N., Shilov, A.L., and Kuznetsov, N.T., *Koord. Khim.*, 1992, vol. 18, no. 5, p. 515.
3. Fokin, V.N., Tarasov, B.P., Korobov, I.I., and Shilkin, S.P., *Koord. Khim.*, 1992, vol. 18, no. 5, p. 526.
4. Fokin, V.N., Shilkin, S.P., Fokina, E.E., Tarasov, B.P., and Mozgina, N.G., *Zh. Neorg. Khim.*, 1998, vol. 43, no. 1, p. 13.
5. *Diagrammy sostoyaniya dvoinyh metallicheskih sistem: Spravochnik* (State Diagrams of Binary Metal Systems. Handbook), Moscow: Mashinostroenie, 1996, vol. 1.
6. Semenenko, K.N., Verbetskii, V.N., Zontov, V.S., Ioffe, M.I., and Tsutsuran, S.V., *Zh. Neorg. Khim.*, 1982, vol. 27, no. 6, p. 1359.
7. Hashi, K., Ishikawa, K., Suzuki, K., and Aoki, K., *J. Alloys Comp.*, 2002, vol. 330–332, p. 547.
8. Rudman, P.S., Reilly, J.J., and Wiswall, R.H., *J. Less-Common Met.*, 1979, vol. 58, p. 231.
9. Ito, K., Okabe, Y., Zhang, L.T., and Yamaguchi, M., *Acta Mater.*, 2002, vol. 50, p. 4901.
10. Kojima, Y., Watanabe, M., Yamada, M., and Tanaka, K., *J. Alloys Comp.*, 2003, vol. 359, p. 272.
11. Hashi, K., Ishikawa, K., Suzuki, K., and Aoki, K., *Scripta Mater.*, 2001, vol. 44, p. 2591.
12. Maeland, A.I., Hauback, B., Fjellvag, H., and Sorby, M., *Int. J. Hydrogen Energy*, 1999, vol. 24, p. 163.
13. *Eksperimental'nye metody v adsorbtsii i molekulyarnoi khromatografii* (Experimental Methods in Adsorption and Molecular Chromatography), Kiselev, A.V. and Dreving, V.P., Moscow: Mosk. Gos. Univ., 1973, p. 198.