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USE OF TITANIUM HYDRIDE FOR THE SYNTHESIS OF TITANIUM ALUMINIDES FROM POWDER MATERIALS

O. M. Ivasishin, A. N. Demidik, and D. G. Savvakin

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Titanium aluminides Ti_3Al and TiAl were synthesized by the use of TiH_2 + Al powder mixtures. Phase transformations occurring upon the decomposition of titanium hydride in vacuum and inert gas and synthesis of titanium aluminides were studied. It was shown that the use of titanium hydride instead of titanium in powder mixtures with aluminum results in a significant activation of diffusion processes, and leads to an accelerated production of single-phase titanium aluminides upon isothermal heating. This is attributable to the small particle size of the charge, high density of defects (including those due to hydrogen-phase hardening) in the titanium and aluminum lattices, and possible reduction of Al_2O_3 films by atomic hydrogen. The type of atmosphere did not noticeably effect the rate of phase formation, however synthesis in vacuum appears to be more practical since hydrogen is completely removed with simultaneous formation of the aluminides. Due to the fact that aluminum reacted completely with titanium in the solid state, final products close to theoretical densities were obtained without the application of high pressure.

The titanium aluminides Ti_3Al (α_2-phase) and TiAl (γ-phase) possess high strength and heat resistance, low density, good oxidation resistance, and are promising structural materials for aero and space technology [1-3]. However, the almost zero ductility of these materials in the range 600-650°C makes it difficult to fabricate parts of complex shape from them, and limits their practical use. Powder metallurgy techniques are a possible solution to this problem, since they can be used to obtain parts of the desired shapes and compositions, in particular from elemental powders, without the need for deformation processes [4-8].

The main shortcomings of using mixtures of pure titanium and aluminum powders to synthesize titanium aluminides are the inhomogeneous phase compositions and substantial porosities of synthesized materials. These necessitate the use of hot (1200-1300°C) isostatic pressing and prolonged thermal annealing operations. Considering the above, the authors of the present work attempted to determine how the synthesis process could be accelerated, find new approaches to the synthesis of titanium aluminides from powder compositions, and chose optimal conditions for the production of single-phase Ti_3Al and TiAl with satisfactory density.

The investigation was carried out on specimens prepared by conventional powder metallurgy methods. The initial titanium (−100 μm, 98.7%) or titanium hydride (−100 μm, 98.2%) powders were mixed with aluminum (−100 μm, 97.4%) in the required proportions and simultaneously ground for 2-10 h in a ball mill with a charge to ball ratio of 1:10. The charges were compacted at room temperature into ingots, which were heated at different rates to 475-1080°C in vacuum or inert gas in order to synthesize the titanium aluminides. The particle size of the initial powders after grinding, and their chemical homogeneity, structure, and phase composition were studied with the aid of the microprobe Superprobe-733 and diffractometer DRON-3M. Phase transformations occurring in the process of heating and synthesis of the titanium aluminides in vacuum and inert gas were investigated by high-temperature x-ray diffractometry in filtered Cu radiation, using diffractometer DRON-3M with a high-temperature attachment URVT-2000, and also by differential thermal analysis (DTA) in an inert gas atmosphere. Chemical homogeneity of the aluminides was studied in the microprobes Superprobe-733 and Cameca-5. A number of specimens were subject to plastic deformation at high temperatures on the equipment PRV-2M.

It is obvious that in order to obtain rapid phase formation by diffusional processes it is necessary to maximally shorten diffusion paths. In powder compacts this is connected with decreasing component particle sizes. However it was

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Fig. 1

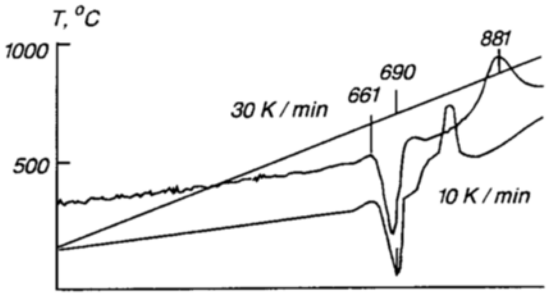

Fig. 2

Fig. 1. Titanium particle covered with an aluminum layer after grinding a Ti + Al powder mixture for 3 h (regime "compo").

Fig. 2. DTA heating curves for a Ti + Al mixture.

found that because of their high ductility it was not possible to decrease the particle sizes of the initial titanium and aluminum powders by ball milling. During the milling process aluminum smeared over the titanium particles, covering them with a 15-20 μm thick layer (Fig. 1); the size of the titanium particles was not less than 50 μm. When such charges were used to synthesize the titanium aluminides the following thermokinetic effects were observed.

According to the DTA data there were no noticeable exothermic effects upon heating up to the melting point of aluminum which might indicate the initiation of titanium aluminide formation (Fig. 2). Strong reaction of titanium compounds with aluminum began only after the aluminum was completely melted. The temperature range of this process depended upon the heating rate. High-temperature x-ray diffractometry confirmed that only an insignificant amount of the phase $TiAl_3$ was formed in the Ti + Al charge up to the melting point of aluminum, but all of the aluminum reacted quickly to form this phase when the melting temperature was exceeded. The reaction with molten aluminum led to the formation of material with a large number of pores; the volume of the ingot increased by 2-3 times during the synthesis process.

Single-phase material was not obtained by annealing Ti + Al charges at high temperatures. At 475°C, the temperature at which the first traces of aluminide were detected by high-temperature x-ray diffractometry, only an insignificant amount of $TiAl_3$ was found after 24 h. The intensity of the Al x-ray diffraction lines did not noticeably decrease (Fig. 3a). At 900°C all of the aluminum entered into the reaction, however 24 h of annealing was clearly insufficient to obtain single-phase aluminides (Fig. 3b). Even raising the isothermal annealing temperature to 1080°C did not yield single-phase material.

The enumerated deficiencies are a result of the large particle size of the charge, and weak activation of solid-phase diffusion processes. The authors attempted to correct these by substituting titanium hydride for the original pure titanium powder. It is known that the particle size of brittle titanium hydride is rapidly decreased by grinding, and that hard splinters of hydride can penetrate into the soft aluminum particles in an actively milled TiH_2 + Al mixture, producing a large number of lattice defects. The decomposition of titanium hydride upon heating is accompanied by the effect of hydrogen-phase hardening [9] because of the different specific volumes attributable to titanium atoms in the titanium hydride and α- or β-titanium lattices, resulting in the formation of supplemental lattice defects. Furthermore, it is assumed that the atomic hydrogen evolved in the decomposition of titanium hydride is able to reduce the oxide film on the surface of aluminum particles:

$$6H + Al_2O_3 = 2Al + 3H_2O. \tag{1}$$

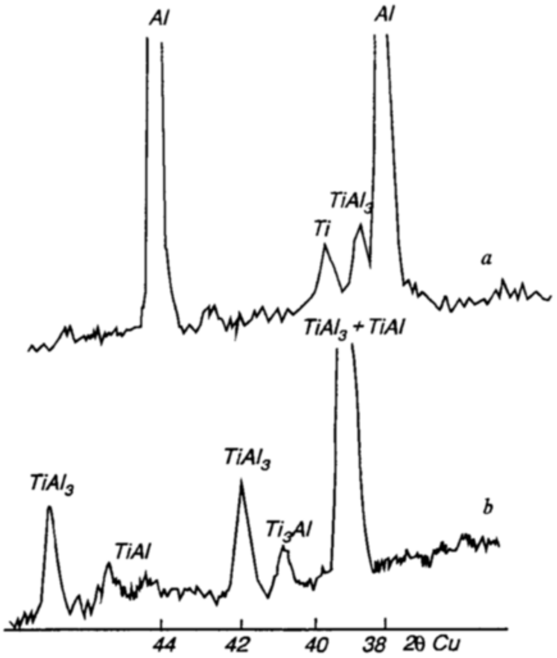

Fig. 3

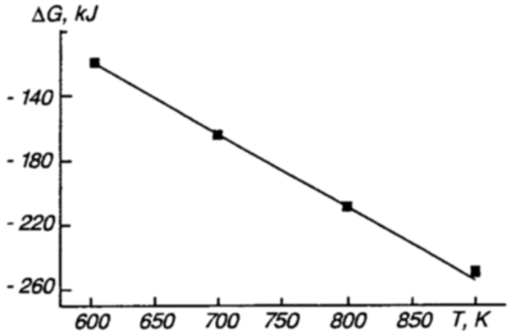

Fig. 4

Fig. 3. X-ray diffraction patterns for Ti + Al specimens after annealing for 24 h at (a) 475 and (b) 900°C.

Fig. 4. Temperature variation of the Gibbs thermodynamic potential for reaction (1) in the decomposition range of titanium hydride.

The Gibbs thermodynamic potential $G(T)$ of this reaction varies according to:

$$\Delta G(T) = -399700 + 200.11T + 3RT\ln\frac{P_0}{4\cdot 10^{-9500/T+15.62}}\ (\mathrm{J}),$$

where T is temperature; P_0 is normal atmospheric pressure; R is universal gas constant. Calculations showed that this reaction is energetically favored over the entire decomposition range of titanium hydride (Fig. 4). At the same time reduction by molecular hydrogen is energetically unfavorable, and for the process to run it is necessary that at least 0.0001 part of hydrogen remains in the atomic state.

It was assumed that all of the enumerated factors, namely a highly dispersed charge, high concentration of lattice defects (including those attributable to hydrogen-phase hardening), and reduction of the oxide film on aluminum must substantially activate diffusion and accelerate phase formation during synthesis. Considering that hydrogen is easily removed from titanium alloys by heating in vacuum, the use of titanium hydride should have no negative consequences.

The use of TiH_2 + Al mixtures substantially increases the dispersion of milled charges compared to that of mixtures based on pure titanium, and produces a hydride particle size of 1.5-2 μm (Fig. 5). Aluminum particles are deformed into ~2 μm thickness platelets (Fig. 5), which substantially shortens the mutual diffusion path and is a good prerequisite for accelerated phase formation.

The DTA specimens revealed significant differences between the processes occurring in TiH_2 + Al and Ti + Al mixtures when heated. Under the given heating conditions (inert gas, rate 10-30 deg/min) titanium hydride decomposed, accompanied by the appearance of three endothermic peaks (Fig. 6a). When mixtures of titanium hydride and aluminum were heated the exothermic effect of aluminide phase formation was superimposed on the endothermic effect of hydride decomposition (Fig. 6b). Obviously, the synthesis process was displaced to temperatures below the melting point of aluminum.

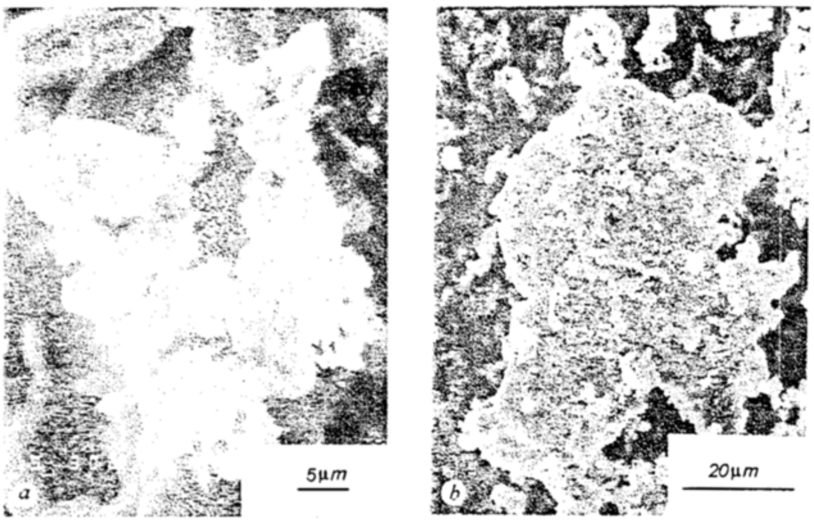

Fig. 5. Microphotographs of powders after grinding for 2 h. (a) Titanium hydride; (b) TiH_2 + Al mixture. Regime "compo".

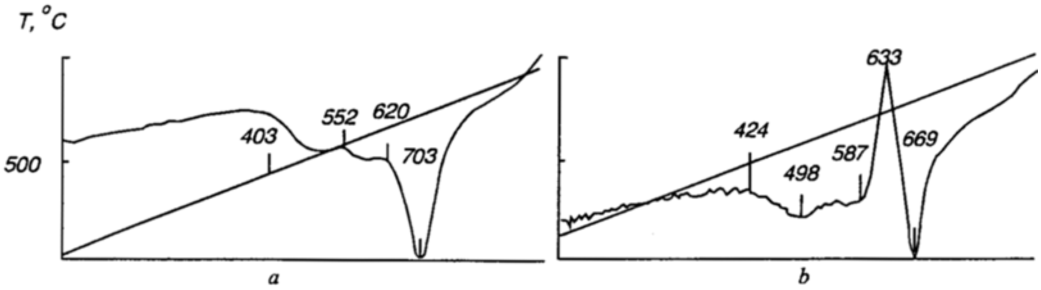

Fig. 6. DTA heating curves for (a) titanium hydride and (b) TiH_2 + Al powders.

High-temperature x-ray diffraction analysis supplemented and confirmed the above results. The role of the atmosphere in which heating took place was clearly revealed. When TiH_2 + Al mixtures were slowly (10 deg/min) heated in vacuum, in which case an external pressure did not hinder the evolution of hydrogen, decomposition of the hydride was detected at 300-320°C (Fig. 7). The diffraction lines of titanium hydride disappeared completely at 380-400°C, and were replaced by the lines of α-titanium (although evolution of hydrogen from the specimen continued up to substantially higher temperatures — approximately 600-650°C). Formation of the first aluminide phase, $TiAl_3$, began immediately after titanium hydride decomposition was completed, and at about 600°C the formation of this phase proceeded rapidly; the aluminum lines disappeared. Thus when titanium hydride was used, aluminum reacted completely even in the solid state with the formation of a mixture of $TiAl_3$ and unreacted titanium. Rapid diffusion at higher temperatures led to the formation of TiAl and Ti_3Al.

When TiH_2 + Al charges were heated in a helium atmosphere the gas pressure hindered the evolution of hydrogen, and, therefore, decomposition of the titanium hydride was displaced to higher temperatures (640°C was the highest temperature at which hydride existed). The temperature range of decomposition also depended on the heating rate. Increase to 20-30 deg/min in a helium atmosphere led to the formation of β-Ti, which stabilized the hydrogen which had not yet evolved. Thus, by varying the atmosphere (vacuum or inert gas) and the heating rate it was possible to change the sequence of phase transformations in the decomposition of titanium hydride, and obtain either α- or β-titanium. It should be noted that in a vacuum, synthesis takes place after the hydride is completely decomposed, but in an inert gas the two processes occur simultaneously. A noticeable difference in the rates of phase formation in the two cases was not observed, but it was established that synthesis in vacuum reduces the hydrogen concentration to 0.01-0.02 mass %. The mechanical properties of the end product should not be affected by this concentration of hydrogen.

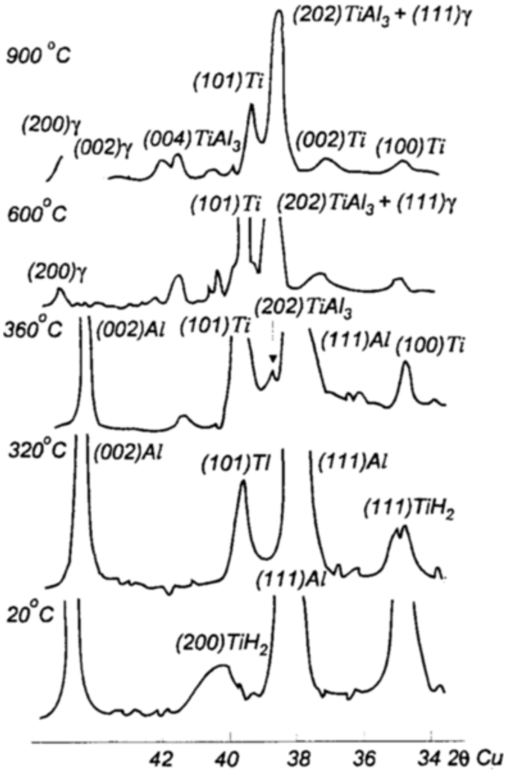

Fig. 7. X-ray diffraction patterns for heated TiH_2 + Al powder mixtures.

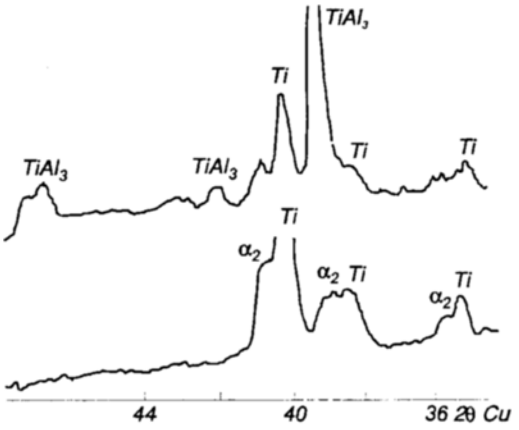

Fig. 8

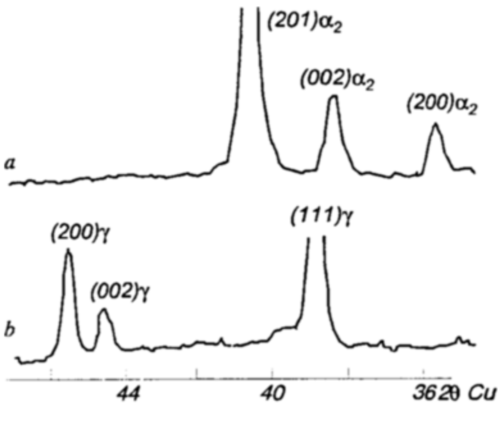

Fig. 9

Fig. 8. X-ray diffraction patterns for TiH_2 + Al specimens (compositions TiAl and Ti_3Al) after annealing for 24 h at 475°C.

Fig. 9. X-ray diffraction patterns for TiH_2 + Al specimens after annealing at 900°C. (a) Ti_3Al; (b) TiAl.

In spite of substantial acceleration of the synthesis process, single-phase titanium aluminides were not formed when TiH_2 + Al charges were continuously heated. Therefore, in order to complete the process the specimens were isothermally annealed at 475, 620, 900, and 1080°C for 2-24 h in vacuum. Investigation of the phase composition of the specimens after annealing showed a clear advantage for the TiH_2 + Al mixture over the Ti + Al at all temperatures. For example, upon annealing at 475°C for 24 h the aluminum in TiH_2 + Al mixtures reacted completely to form aluminides (Fig. 8), while after similar treatment of Ti + Al mixtures only traces of $TiAl_3$ were detected (Fig. 3a).

Single-phase Ti_3Al and TiAl (depending on the charge composition) were synthesized from TiH_2 + Al mixtures by annealing at 900°C for 5-6 h (Fig. 9a, b), clearly demonstrating the advantage of using hydride.

One of the main problems in fabricating components from titanium aluminides by powder metallurgy methods is to lower the porosity which forms in the end product during the reaction with molten aluminum [10]. Hot isostatic pressing [5-8], and high (200:1) degrees of deformation after preliminary extrusion and degassing of the initial powder materials [4] are used to eliminate this. These operations substantially complicate and increase the expense of the manufacturing process. Using titanium hydride instead of titanium makes it possible to obtain a highly dense end product, differing from the theoretical by no more than 5% (thanks to the complete reaction of aluminum with titanium in the solid state), without the use of hot pressing.

It was also determined that plastic deformation in vacuum at 700-900°C substantially accelerates the formation of titanium aluminides from TiH_2 + Al charges, and practically completely eliminates porosity. By optimizing parameters such as temperature, rate and degree of deformation, degree of vacuum, single phase Ti_3Al and TiAl could be produced in 20-30 min, while only $TiAl_3$ was formed in control specimens annealed in the same way but not subject to deformation. It was established that a substantial increase in the rate of phase formation occurs in the deformation rate range $(1\text{-}4)\cdot 10^{-4}$ sec^{-1}. Electron microscopic examination of materials obtained in this way did not reveal any porosity, and deviations of their densities from theoretical were within the error of the measurements.

The investigations carried out show that it is possible to produce single-phase Ti_3Al and TiAl from charges of titanium hydride and aluminum powders. The use of titanium hydride instead of pure titanium has a number of advantages, namely: substantially less time required to form single-phase material, lower synthesis temperature, ability to produce high density aluminides without the application of high pressures. These advantages are obtained as a result of the substantial activation of diffusion in the solid state which is produced by the small particle size of titanium hydride after mechanical treatment, hydrogen-phase hardening during heating, and possible reduction of the oxide film on aluminum particles by atomic hydrogen.

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