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The synthesis of hydrides of intermetallic Ti_2Co under an accelerated electron beam

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Abstract

The hydrogen absorption properties of the intermetallic compound Ti_2Co under an accelerated electron beam were studied. It was found that under irradiation at dose rates of 0.05–0.7 Mrad/s and beam current 150 μA, Ti_2Co interacted with hydrogen. The optimal parameters for the thermal-radiation synthesis of the hydride Ti_2CoH_{3-x} in hydrogen atmosphere were determined. The process of hydrogenation after irradiation, the so-called 'cold synthesis', was investigated and is discussed here. The results of irradiation hydrogenation were related to the absorption properties of the products of combustion of IMC in hydrogen in self-propagating high-temperature synthesis (SHS) mode.

Keywords: Intermetallic compound–hydrogen systems; Hydrides; Absorption; Irradiation; Electron beam

1. Introduction

The hydrides of intermetallic compounds (IMC) are interesting because of their active and readily liberated hydrogen content. The existing traditional methods of hydride production require a preliminary activation of alloys (usually a bakeout in vacuum at temperatures of 300–900°C, a rather laborious, difficult process) before their saturation with hydrogen. Some of the IMCs able to absorb hydrogen at room temperature require a high hydrogen pressure (≥30 atm). The other IMCs require long-time exposure to hydrogen at a rather high temperature (300–400°C). The intermetallides on the basis of titanium and zirconium, on the one hand, and of nickel, cobalt and iron, on the other, belong to the second group.

In earlier work, in order to solve the problem of IMC saturation by hydrogen, we used the self-propagating high-temperature synthesis (SHS) method [1]. Using this technique, the initial alloys were also synthesized and a number of IMC hydrides were obtained [2,3]. The alloy Ti_2Co synthesized by the SHS mode had a face-centered cubic (f.c.c.) lattice structure with parameter $a = 11.31$ Å [4]. The combustion product of this alloy in hydrogen, the hydride Ti_2CoH_3, also had the f.c.c. structure with parameter $a = 11.89$ Å; the hydrogen content of the hydride reached 1.6–1.7 wt% [5].

Investigation of radiation chemical processes in inorganic materials shows that, under electron beam radiation, their physical and chemical properties are improved. The intensive stream of ionizing radiation leads to the excitation of the electronic and nuclear sublattices of a solid inorganic material. Besides being independent of the beam dose, a portion of the primary radiation energy is transformed into thermal energy leading to sample heating (thermoradiation processes) [6]. The results of numerous investigations devoted to the study of the imperfections of real crystalline structures as well as of solid bodies has produced the suggestion that all kinds of defects essentially influence diffusion, synthesis, backing and other processes in the solid state [7].

The aim of the present work was to investigate the influence of an electron beam on the formation of intermetallic hydrides in the Ti_2Co–H_2 system.

2. Experimental

A method was developed for carrying out experiments with a focused electron beam using a hermetic camera installed in front of the high-current electron accelerator LAE-5. The volume of the specially designed and prepared

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stainless steel camera is approximately 2 l. It is provided with a device for evacuation as well as for regulation of the gas inlet and outlet. The suggested optimal vacuum is 10^{-3}–10^{-6} Torr. The maximal pressure is 2–3 atm. Optimal conditions for the experiments were: energy of accelerated electrons 4 MeV, average current 150 μA. A collimated beam ensures even irradiation over the sample surface. A system was developed for temperature measurement during irradiation. An 'S'-type Pt/Pt–Rh thermocouple was used. The hydrogenation products were analyzed using chemical, X-ray and DTA analyses. Differential-thermal analysis of hydrogenation products was carried out on a Derivatograph Q-1500 (Hungary) in argon atmosphere at 20°/min.

For the investigations, Ti_2Co alloy was synthesized using the SHS method. The sample sizes were selected according to the requirement of uniform irradiation by the accelerated electron beam: diameter no more than 20 mm, width no more than 5 mm.

3. Results and discussion

3.1. Thermal-radiation synthesis in the system Ti_2Co–H_2

Previous experiments have shown that, under irradiation at a dose rate in the range 0.05–0.7 Mrad/s, IMC interact with hydrogen, i.e. thermal-radiation synthesis (TRS) is realized. It should be noted that the interaction temperature appeared to be much lower than in the systems studied earlier, Ti–H_2, Ti–C–H_2 and Ti–N–H_2, and the reaction time was longer by an order of magnitude.

The thermogram of the irradiation process using a dose rate 0.1 Mrad/s is presented in Fig. 1. The temperature profile (curve 1) reflects the complex character of the process: in the beginning, along with an increase in the radiation dose, radiation heating of the IMC sample occurs (up to 80°C), then a sharp temperature jump up to 250°C appears because of the exothermal interaction of IMC with hydrogen. On reaching the maximum temperature, a smooth lowering of the sample temperature occurs, although irradiation of the sample was continued for several minutes. In the figure, the temperature profile of the radiation heating of Ti_2CoH_3 hydride in hydrogen at the same dose rate of 0.1 Mrad/s is demonstrated (curve 2) as a 'blank experiment'. Comparison of the curves clearly shows that the proportion of radiation heat in the total heat release is small. The main heat release is due to the exothermal interaction of IMC with hydrogen. The data for the chemical and X-ray analyses of the product testify that a hydrogen-containing phase with a hydrogen concentration of about 1.0–1.54 wt% is generated.

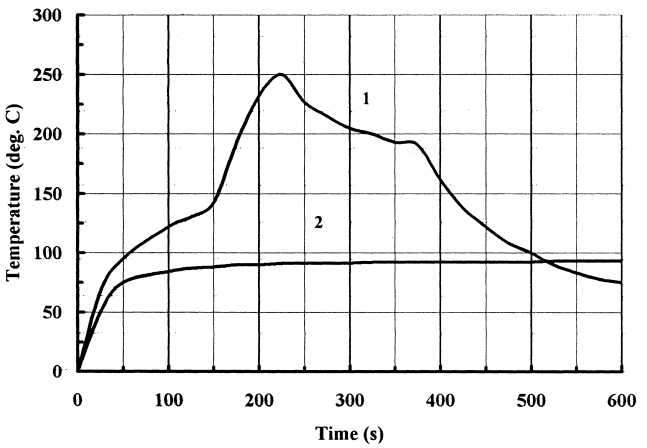

Fig. 1. TRS thermograms (1) and temperature profile of the radiation heating of Ti_2CoH_3 (2) at a dose rate of 0.1 Mrad/s.

Table 1 shows the effect of irradiation on the phase composition and hydrogen content of the synthesized product. From the table it can be seen that, with increasing dose rate, the reaction temperature increases; however, the hydrogen concentration in the product remains low. Contrary to the systems investigated previously in our laboratory, Me–H and Me–nonMe–H, in this case TRS takes place, but does not produce the hydrogen-saturated phase Ti_2CoH_3.

Fig. 2 shows diffractograms of IMC Ti_2Co and its hydrogen-containing phases obtained under SHS and TRS conditions. According to the phase composition, the hydrides formed by TRS can be referred to as solid solutions of hydrogen in IMC, however it is necessary to note that the lattice is disordered and the diffraction peaks have wide bases, indicating the probability of the formation of nano-dimension particles.

Thus, the effect of the beam on the metal matrix of IMC in hydrogen aggravates its absorption properties, probably because of radiation damage. We note for comparison that, if the IMC Ti_2Co, not subjected to any external physical action (mechanical, thermal, radiation etc.), is used in the SHS combustion, a normal hydrogen-rich hydride Ti_2CoH_3 is obtained (Fig. 2b).

3.2. Irradiation of the IMC Ti_2Co and its hydride

In order to explain the thermal-radiation process, to estimate the contribution of the radiation to the observed

Table 1
Summary of the experimental conditions and results for TRS in the Ti_2Co–H_2 system

Dose rate (Mrad/s)	Dose (Mrad)	T_{begin} (°C)	T_{max} (°C)	H_2 content (wt%)	Phase composition
0.05	35	82	160	1.54	Solid sol. + Ti_2CoH_3
0.10	37	85	250	1.05	Solid sol.
0.20	20		360	1.08	Solid sol.
0.30	66	195	375	1.12	Solid sol.
0.40	72		523	1.08	Solid sol.
0.50	100	215	483	1.00.	Solid sol.
0.70	86	200	622	1.10	Solid sol.

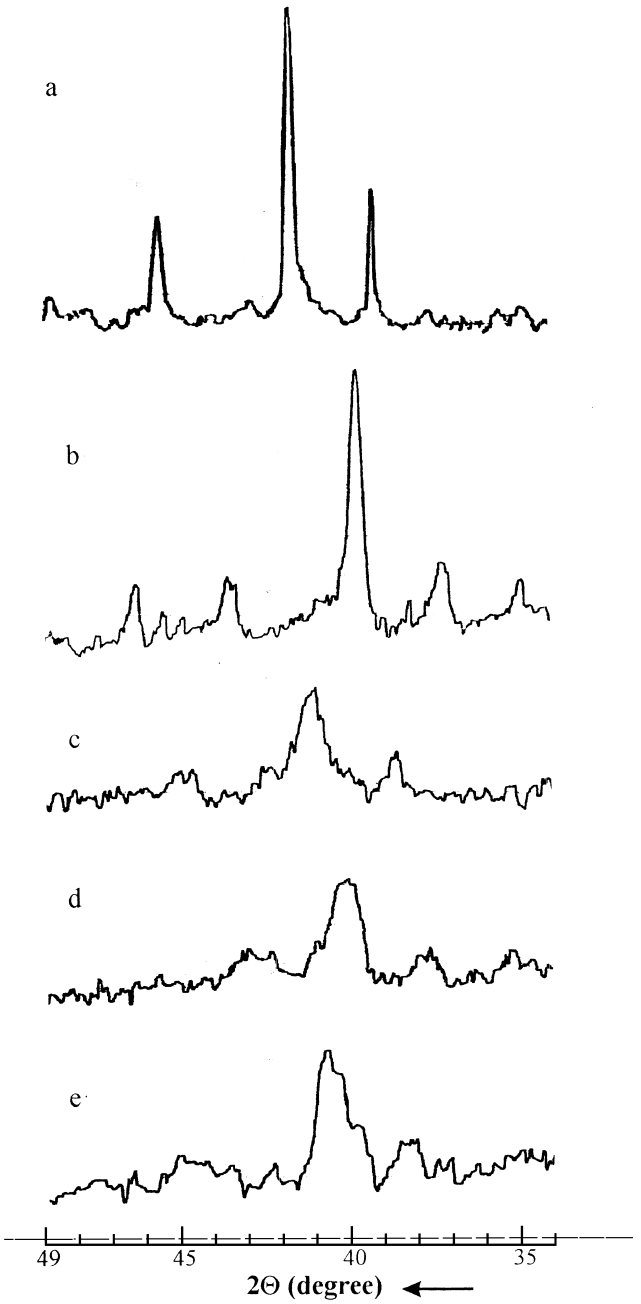

Fig. 2. XRD patterns of IMC Ti_2Co (a) and hydrides obtained in the $Ti_2Co–H_2$ system by (b) SHS, (c) TRS, (d) irradiated SHS hydride, and (e) 'cold synthesis' hydride.

heat effects and to observe the behavior of the solid phase upon irradiation in the absence of chemical reaction, 'blank experiments' were carried out.

First, the dependencies of the maximum temperatures of radiation warming on the radiation dose rate (Fig. 3) were measured for the initial IMC in vacuum (curve 1), and for the previously synthesized hydride Ti_2CoH_3 (hydrogen content 1.9 wt%) in hydrogen (curve 2). In the latter case, irradiation of the sample up to a temperature not exceeding the temperature of hydride dissociation (300°C) was

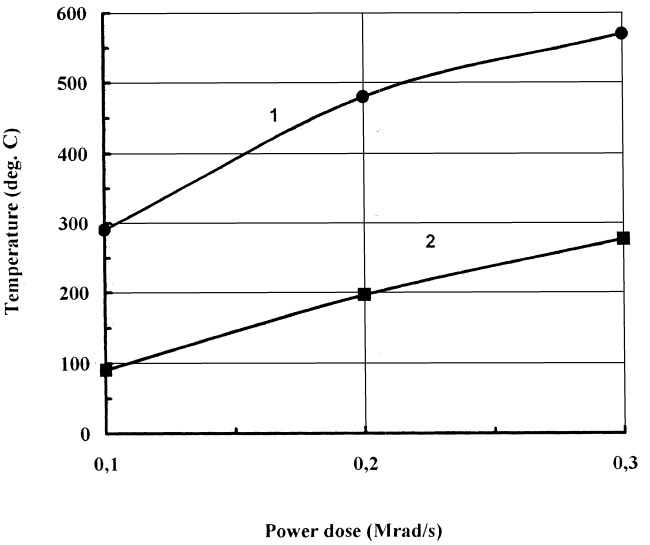

Fig. 3. Dependence of the temperature on dose rate for Ti_2Co in vacuum (1) and Ti_2CoH_3 in hydrogen (2).

performed. In this case, the total radiation dose was 180 Mrad, and the hydrogen concentration decreased from 1.9 wt% in the initial hydride to 1.5 wt% in the final product. At the same time, ordering of the crystalline structure of the sample took place — the initial two-phase material (along with IMC hydride, the solid solution of hydrogen in IMC was also present) was transformed into a single-phase hydride of composition Ti_2CoH_{3-x}. The reflections in the diffractograms of the final hydride are widened (Fig. 2d).

The task of the second experimental series was to research the possibility of post-hydrogenation phenomena, i.e. of additional insertion of hydrogen into the crystal lattice of the hydride phase, and/or of homogenization of the already obtained product as a result of radiation processing in hydrogen. Two hydride samples were irradiated in hydrogen up to an identical total dose with beams of different dose rates. The experimental conditions and results are listed in Table 2.

In both cases, a loss of part of the hydrogen by the matrix is observed, but in the case of low-dose irradiation

Table 2
Experimental conditions and results

	Sample I	Sample II
Radiation dose rate (Mrad/s)	0.2	0.6
Dose (Mrad)	100	100
Temperature of radiation heating (°C)	185	475
Hydrogen concentration (wt%)		
Before irradiation	1.50	1.80
After irradiation	1.27	1.12
Phase composition		
Before irradiation	Ti_2CoH_3 + solid solution	Ti_2CoH_3
After irradiation	Ti_2CoH_3	Solid solution

Table 3
Summary of the experimental conditions and results of 'cold synthesis'

Dose rate (Mrad/s)	Dose (Mrad)	Radiation heating temp., T_{rad} (°C)	Cooling temp., T_{cool} (°C)	CS temp., T_{cs} (°C)	H_2 content (wt%)	Phase composition
0.1	25	265	60	283	0.9	Sol. solut.
0.15	21	385	60	100	0.47	Sol. solut.
0.2	50	440	60	115	1.44	Ti_2CoH_3
0.25	38	500	60	77	1.47	Ti_2CoH_3
0.3	48	535	70	235	1.48	Ti_2CoH_3
0.4	80	800	70	250	1.72	Ti_2CoH_3
0.45	142	760	40	160	1.87	Ti_2CoH_3
0.5	200	790	40	152	1.65	Ti_2CoH_3
0.55	66	823	40	92	1.90	Ti_2CoH_3
0.6	90	825	40	207	1.90	Ti_2CoH_3
0.8	80	810	60	135	1.79	Ti_2CoH_3
1.0	80	780	60	132	1.79	Ti_2CoH_3
Furnace	–	800	60	100	1.23	Sol. solut + Ti_2CoH_3

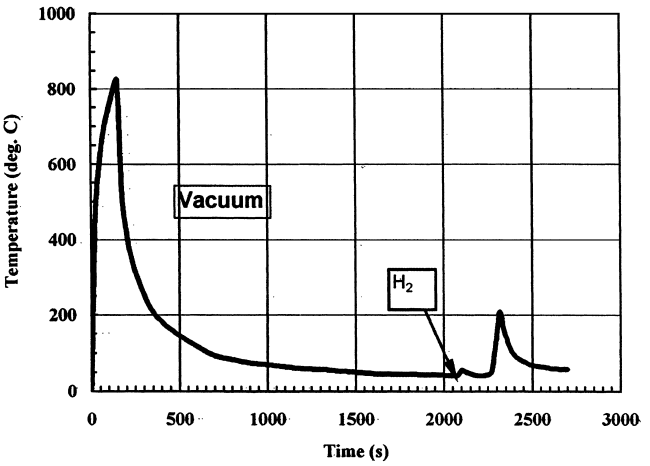

Fig. 4. Thermogram of 'cold synthesis' in the $Ti_2Co–H_2$ system (dose rate 0.6 Mrad/s).

(sample I) the lattice was ordered and the f.c.c. lattice of the IMC hydride was formed. Radiation warming of the second sample exceeded the limit of the thermal stability of the hydride (300°C). This resulted in exclusion of hydrogen by the initial hydride with f.c.c. structure; more exactly, in its disruption and the creation of a hydrogen solid solution in IMC in the sample cooling stage. This once again confirms the above reasoning that the defects created with high-dose (temperature) radiation apparently aggravate the adsorptive ability of the metal matrix.

3.3. 'Cold synthesis' of hydride in the system $Ti_2Co–H_2$

Upon investigation of the thermal-radiation processes in Me–H and Me–nonMe–H systems, the phenomenon of 'cold synthesis' (CS) was observed. A series of experiments was carried out under CS conditions. The initial IMC Ti_2Co was exposed to irradiation in vacuum, then the beam was switched off, the sample cooled in vacuum and the camera filled with hydrogen. In several seconds the thermocouple detected an exothermal effect similar to the SHS process. The experiments were carried out over a wide range of doses (20–100 Mrad) and dose rates (0.1–1.0 Mrad/s). A typical thermogram of the CS process is presented in Fig. 4.

The conditions of the experiments, the radiation heating, cooling, and 'cold synthesis' temperatures and the characteristics of the products obtained are shown in Table 3.

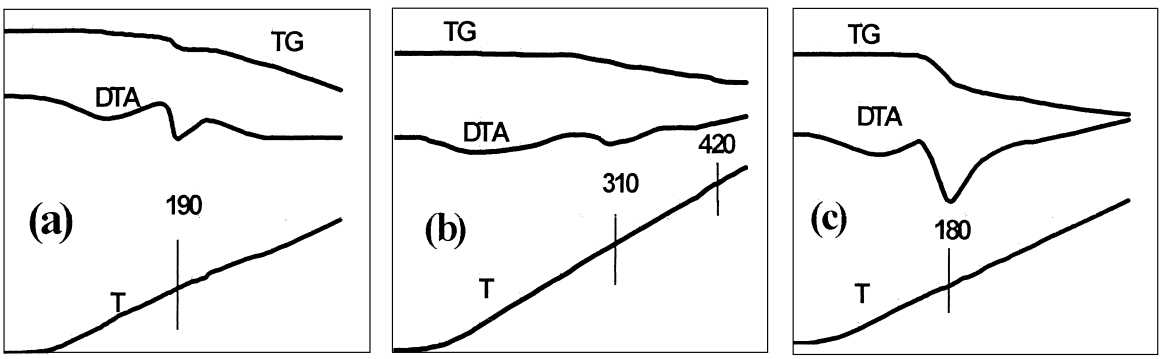

Fig. 5. Typical TG and DTA curves for hydrides in the $Ti_2Co–H_2$ system: (a) SHS; (b) TRS; (c) 'cold synthesis'.

The temperature range of radiation heating of IMC is 265–825°C. It can be seen that CS starts in the sample cooled to a temperature not lower than 40–60°C.

The data in the table demonstrate that, at a low dose rate (0.1–0.15 Mrad/s), the hydrogenation process proceeds exothermally; however, the hydrogen concentration in the products is low. At a radiation dose rate of $\geq$0.2 Mrad/s, 'cold synthesis' is observed in the system. The temperature jump of 'cold synthesis' is up to 70–300°C lower than in the Me–H system [8]. Temperature measurements are difficult because the compact IMC sample quickly becomes fragile and disintegrates during hydrogenation. It is impossible to determine the precise synthesis temperature using a thermocouple. However, the registered maximum temperatures are comparable to the temperatures developed in SHS processes (120–300°C).

With respect to the formation of the products, we note that a high preliminary irradiation dose rate promotes the formation of phases with a high hydrogen concentration during subsequent CS.

The nature of CS is not clear at present, but it would not be correct to explain this phenomenon only in terms of heating of the metal matrix. Radiation damage created in the crystal lattice and promoting the hydrogenation reaction plays a considerable role. To confirm this, thermal activation of the metal matrix of IMC was carried out: after heating the sample in the camera up to the temperature developed upon irradiation in the above experiment (800°C), the sample was cooled to 60°C and the system was then filled with hydrogen (1 atm). The thermocouple did not detect any temperature change. Hydrogenation took place only with an increase of hydrogen pressure up to 10 atm; the thermocouple detected 100°C. The obtained product contained 1.23 wt% hydrogen. The diffractogram of the hydride obtained in the 'cold synthesis' mode is shown in Fig. 2e.

Fig. 5 shows TG and DTA curves of TRS, CS, and SHS product decomposition. Note the hydride decomposition processes in the SHS and CS modes, suggesting identical behavior for the metal matrix during hydride synthesis. The absence of endothermal effects for the decomposition of the TRS product demonstrates the imperfection of the lattice of the TRS product.

Thus, it appeares that the irradiation of a metal matrix in vacuum at different dose rates promotes the formation of a hydride in CS mode. Irradiation of IMC in hydrogen, i.e. TRS, or irradiation of the initial hydride in hydrogen aggravates the adsorptive properties of IMC. It is possible that, under irradiation in hydrogen, 'poisoning' of the initial metal matrix by contamination with electrolytic hydrogen (oxygen, water vapor, etc.) occurs. If the adsorption of hydrogen by the matrix was reduced because of radiation damage or defects, it would also be observed under irradiation in vacuum with subsequent CS.

Besides, it is possible that, with TRS, when sluggish heating of the sample in a hydrogen atmosphere occurs, a partial dissolution of hydrogen in the initial IMC takes place, which weakens the exothermal effect of their interaction.

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