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Thermal-radiation synthesis of zirconium hydridonitrides and carbohydrides

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Abstract

The interaction of $ZrN_{0.17}$ (HCP structure) and $ZrC_{0.4}$ (FCC structure) with hydrogen under the action of an accelerated electron beam was investigated. The experiments were carried out on the linear accelerator LAE-5 in the range of irradiation dose power 0.1–1 MRad/s up to a dose of 100 MRad. Upon irradiation of nitrogen solid solutions in zirconium and non-stoichiometric zirconium carbides in a hydrogen atmosphere, thermal-radiation synthesis of zirconium hydridonitrides and carbohydrides takes place. The main dependencies of the temperature of the process and of both the final chemical and phase compositions on the irradiation dose and dose power are studied. The mechanism of hydridonitride and carbohydride formation under irradiation is determined. The phenomenon of cold synthesis of hydridonitrides and carbohydrides was observed: if the sample is previously electron-irradiated in vacuum, its reaction with hydrogen takes place at room temperature. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Thermal-radiation synthesis; Hydridonitride; Carbohydride

1. Introduction

The combustion processes in the Zr–N–H and Zr–C–H systems have been investigated in detail by the method of self-propagating high-temperature synthesis (SHS) [1–3]. It was shown that the hydridonitrides and carbohydrides of zirconium are formed in one technological stage, at combustion of solid solution of nitrogen in zirconium ($ZrN_{0.17}$) and of the mixture Zr+0.4C in a hydrogen atmosphere. The main regularities of creation of hydridonitrides and carbohydrides of zirconium with HCP structure and with high contents of hydrogen were found.

The purpose of the present work is to investigate the thermal-radiation processes in the Zr–N–H and Zr–C–H systems, and to implement the thermal-radiation synthesis of zirconium hydridonitrides and carbohydrides. The principal interest of the present study is the detection of the influence of accelerated electrons on the processes of synthesis and on the chemical composition of the indicated compounds.

It is known that under the influence of sufficiently energetic ionizing irradiation in the solid state, distortion of the crystal lattice structure and defect formation essentially affecting the synthesis are usually observed [4,5]. An increase in the number of the 'radiation defects' is observed on irradiation of some interstitial phases (for example, carbides, borides, etc.) which is usually related with the non-metallic sublattice. There is an opinion that the metalloid atoms can be moved to a nonequivalent position. It is also known that the 'radiation defects' in carbides and nitrides of transition metals are observed more often than in metals.

For that reason, the study of carbon and nitrogen influence on the thermal-radiation processes in the system Zr–H was important.

2. Experimental

To perform the present investigations, a hard solution of nitrogen in zirconium, $ZrN_{0.17}$, (HCP structure, nitrogen content 2.53 wt.%) and a non-stoichiometric zirconium carbide $ZrC_{0.4}$ (FCC structure, carbon content 5.0 wt.%) were synthesized by SHS method.

The synthesized compounds had grain sizes of <100 μm and were cold pressed to form cylindrical tablets of $d = 20$ mm$\times h = 5$ mm.

The irradiation was carried out on a high-current linear accelerator of electrons LAE-5 in a focused electronic beam. The working parameters of the accelerator were: power 4 MeV, average current 150 μA. The collimated

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electron beam provided even irradiation of all the sample volume.

Samples were placed in the special chamber and evacuated down to 10^{-3} mm. The temperature of the sample was measured in the course of irradiation by Pt/Pt–Rh thermocouples. The irradiation was performed with different doses and dose powers (0.025–1 MRad/s), both in vacuum and hydrogen, at $P_{\mathrm{H}} = 1$–2 atm.

In these experiments, zirconium powder of PCRK-1 grade, hydrogen of electrolytic purity, lamp black and nitrogen of 99.51% purity were used.

The products of synthesis were studied by methods of chemical, X-ray (diffractometer Dron-2) and differential-thermal (Derivatograph Q-1500) analyses.

3. Results and discussion

3.1. Synthesis of zirconium hydridonitrides

It was shown that on reaction of $ZrN_{0.17}$ with hydrogen under irradiation by dose powers 0.2–1 MRad/s, thermal-radiation synthesis (TRS) of zirconium hydridonitrides ($ZrN_{0.17}H_{1.37-1.65}$) takes place, like TRS of binary hydrides of group IV metals (Table 1).

In Fig. 1, the temperature profile of the thermal-radiation process (curve 1) at a dose power of 0.4 MRad/s is presented. On increasing the radiation dose up to 16 MRad ($t = 40$ s), the temperature of sample smoothly increases up to 280°C, then a sharp jump of temperature up to 612°C is observed with further irradiation up to 60 s. Afterwards, a smooth lowering of temperature begins, even irradiation is continued up to a dose 100 MRad ($t = 250$ s). If we stop the irradiation immediately after the temperature jump ($t = 60$ s), a faster lowering of sample temperature happens (Fig. 1, dashed lines).

In Fig. 1, the temperature profiles registered upon irradiation of $ZrN_{0.17}$ in vacuum (curve 3) and of $ZrN_{0.17}H_{1.6}$ in hydrogen (curve 4) with a dose power of 0.4 MRad/s are also presented. These experiments were carried out as 'blank experiments' to explain the temperature profile at TRS. As seen in curve 3, with increasing of irradiation dose in vacuum, the temperature of sample smoothly increases up to 650°C; after that it changes insignificantly. To obtain the temperature profile at irradiation of sample in hydrogen, zirconium hydride $ZrN_{0.17}H_{1.6}$, inert in hydrogen, was used instead of $ZrN_{0.17.}$ It enables us to register the temperature developed solely as a result of irradiation. With the increase of radiation dose in hydrogen, a smooth rise of temperature up to 400°C is observed (curve 4). On reaching the dose 68–70 MRad ($t = 120$ s), the temperature of the sample practically stops increasing. Note that the temperature developed in sample at irradiation in hydrogen is lower than in vacuum at the same level of dose.

The temperature profiles in Fig. 1 (curves 1, 2 and 4) clearly demonstrate that the rise of temperature on the curve 1 is due to conversion of the accelerated electrons' energy to thermal energy. The further sharp jump of temperature from 280 to 612°C indicates the exothermic reaction $ZrN_{0.17} + H_2$ in all of the sample volume. The temperature profile of the 'blank experiment' actually confirms the suggestion that TRS processes at irradiation of $ZrN_{0.17}$ in hydrogen can be considered as a 'thermal explosion'.

For comparison, let us consider the temperature profiles in Fig. 2. They are obtained at formation of hydridonitrides in the SHS mode. In the $ZrN_{0.17} + H_2$ system after local instantaneous initiation in a thin layer of sample with a tungsten spiral, the exothermal reaction propagates from layer to layer due to heat transfer. The rate of combustion is within the limits of 1 cm/s. Therefore, in the thermogram, a jump of temperature to 470°C is observed. As a result of this reaction, the zirconium hydridonitrides with HCP structure are synthesized [1,2].

Another series of experiments intended to describe the influence of preliminary irradiation with different dose powers (0.025–0.9 MRad/s) on $ZrN_{0.17}$. At irradiation of $ZrN_{0.17}$ in vacuum as mentioned above, the sample temperature rises from 175 to 650°C, depending on the radiation dose (Table 1). After turning off the beam and cooling the sample down to room temperature, the chamber was filled up by hydrogen. In a few seconds, the temperature of the sample sharply increased to 500–600°C. In fact, it was the same exothermal reaction, as in TRS or SHS, but it started at room temperature without any external initiation of reaction. As a result of this reaction, zirconium hydridonitride $ZrN_{0.17}H_{1.63}$ was obtained (Table 1). The same phenomenon, earlier called 'cold synthesis' (CS), was observed in the interaction of group IV metals with hydrogen. The temperature developed at CS slightly varies with the increase of dose power of the preliminary irradiation, but remains nearly 100°C below the temperature at TRS.

In Fig. 3, the thermograms of CS at dose power of preliminary irradiation 0.2 MRad/s are presented. In this experiment hydrogen filling is performed in 1550 s after the beam is switched off, at a sample temperature close to 40°C.

Notice that the CS in the $ZrN_{0.17}$–H system also proceeds at room temperature. This reaction could be realized for an hour after irradiation. The obtained product is always a hydridonitride of identical composition.

3.2. Synthesis of zirconium carbohydrides

Earlier it was shown that the carbohydrides of FCC structure are formed by SHS mode at combustion of mixture Zr + 0.4C in hydrogen [3]. During irradiation of this mixture, TRS takes place, but the reaction $Zr + H_2$ is preferred and the carbon remains free. Considering this, to carry out the TRS of carbohydride, previously synthesized

Table 1
Characteristics of thermal-radiation synthesis and of cold synthesis of zirconium hydrides, hydridonitrides and carbohydrides

Dose power (Mrad/s)	Thermal-radiation synthesis				Cold synthesis					
	T_{begin} (°C)	$T_{reac.}$ (°C)	H_2 (wt.%)	Formula and phase content	Dose (MRad)	T_{heat} (°C, in vacuum)	T_{begin} CS (°C)	$T_{reak.}$ (°C)	H_2 (wt.%)	Formula and phase content
Zr–H_2										
SHS	300–500	900	2.07	ZrH_2, FCT $a = 4.976$ Å $c = 4.457$ Å						
0.1					No reaction					
0.2	250	700	2.15	ZrH_2, FCT	70	400	50	680	2.15	ZrH_2
0.3	250	700	1.96	ZrH_2, FCT	47	650	25	720	2.08	ZrH_2
0.4	250	730	2.06	ZrH_2, FCT	65	680	25	700	2.09	ZrH_2
0.5	250	730	2.07	ZrH_2, FCT	60	720	25	680	2.1	ZrH_2
0.6	280	750	2.06	ZrH_2, FCT	40	800	25	620	2.1	ZrH_2
0.7	255	760	2.04	ZrH_2, FCT	70	840	25	625	1.97	ZrH_2
0.8	280	800	1.99	ZrH_2, FCT	60	910	30	650	2.05	ZrH_2
0.9	280	790	2.04	ZrH_2, FCT	70	895	25	620	1.92	ZrH_2
1.0	280	790	2.11	ZrH_2, FCT	–	–	–	–	–	–
$ZrN_{0.17}$–H										
		700	1.61	$ZrN_{0.17}H_{1.53}$						
0.05			No reaction		100	175	35	560	1.6	$ZrN_{0.17}H_{1.50}$
0.1			No reaction		100	310	35	575	1.65	$ZrN_{0.17}H_{1.57}$
0.2	165	620	1.73	$ZrN_{0.17}H_{1.65}$	100	645	35	560	1.75	$ZrN_{0.17}H_{1.66}$
0.3	235	580	1.54	$ZrN_{0.17}H_{1.46}$						
0.4	280	612	1.45	$ZrN_{0.17}H_{1.37}$						
0.5	295	650	1.46	$ZrN_{0.17}H_{1.39}$	100	610	35	610	1.69	$ZrN_{0.17}H_{1.61}$
0.6	300	660	1.47	$ZrN_{0.17}H_{1.39}$						
0.7	300	670	1.5	$ZrN_{0.17}H_{1.46}$						
0.8	300	675	1.47	$ZrN_{0.17}H_{1.39}$						
0.9	300	700	1.45	$ZrN_{0.17}H_{1.37}$	100	590	35	590	1.64	$ZrN_{0.17}H_{1.56}$
1.0	300	765	1.54	$ZrN_{0.17}H_{1.46}$						
$ZrC_{0.4}$–H										
	–	1950	1.0	$ZrC_{0.4}H_{0.97}$						FCC
0.025			No reaction		70	110	55	395	1.12	$ZrC_{0.4}H_{1.09}$
0.05			No reaction		70	220	55	422	0.99	$ZrC_{0.4}H_{0.96}$
0.1	95	405	1.29	$ZrC_{0.4}H_{1.25}$	70	320	55	422	1.11	$ZrC_{0.4}H_{1.08}$
0.2	135	427	1.06	$ZrC_{0.4}H_{1.03}$	70	463	55	437	1.01	$ZrC_{0.4}H_{0.98}$
0.3	160	487	1.01	$ZrC_{0.4}H_{0.98}$	40	535	55	385	0.95	$ZrC_{0.4}H_{0.92}$
0.4	185	520	0.99	$ZrC_{0.4}H_{0.96}$	50	490	55	457	0.96	$ZrC_{0.4}H_{0.93}$
0.5	210	535	0.97	$ZrC_{0.4}H_{0.94}$	70	540	55	420	0.98	$ZrC_{0.4}H_{095}$
0.6	–	–	–	–	70	715	55	437	1.01	$ZrC_{0.4}H_{0.98}$
0.7	237	628	1.06	$ZrC_{0.4}H_{1.03}$	70	803	55	443	0.95	$ZrC_{0.4}H_{0.92}$
0.8	–	–	–		70	850	55	437	1.03	$ZrC_{0.4}H_{1.0}$
0.9	248	635	0.99	$ZrC_{0.4}H_{0.96}$	–	–	–	–	–	–

by SHS, non-stoichiometric zirconium carbide $ZrC_{0.4}$ was used as starting material.

Similarly to the $ZrN_{0.17}$–H system, the zirconium carbide $ZrC_{0.4}$ interaction with hydrogen in the accelerated electron beam was studied. In the $ZrC_{0.4}$–H system, TRS takes place in the range of irradiation dose power 0.1–1 MRad/s, forming zirconium carbohydrides. In Table 1, several TRS characteristics of this system are presented.

In Fig. 4, the thermograms of TRS in the system $ZrC_{0.4}$–H are presented at irradiation by a dose power of 0.4 MRad/s. It is obvious that the temperature of the sample increases with the increase of the radiation dose. Reaching 185°C (at dose power 0.4 MRad/s), a sharp temperature jump up to 520°C is observed, followed by a smooth decrease, though the irradiation is continued up to 100 MRad ($t = 250$ s). The formation of carbohydrides $ZrC_{0.4}H_{0.96}$ with FCC structure occurred at the end of this process.

In a series of experiments, samples of $ZrC_{0.4}$ were first irradiated in vacuum. After cooling of the sample, the chamber was filled with hydrogen. CS was observed. In Fig. 5, the thermograms of CS are presented.

In this system, CS starts with a rather low dose power of the preliminary irradiation (from 0.025 MRad/s). In Table 1, the main characteristics of CS and its products are presented. The increase of dose power brings to a rise of

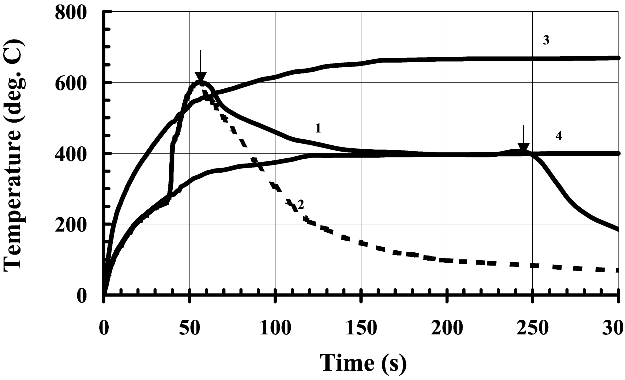

Fig. 1. Temperature profiles of thermal-radiation processes at irradiation of $ZrN_{0.17}$ at dose power 0.4 MRad/s: (1) in hydrogen (TRS); (2) TRS with beam switched off (dashed lines); (3) irradiation in vacuum; (4) irradiation $ZrN_{0.17}H_{1.6}$ in hydrogen.

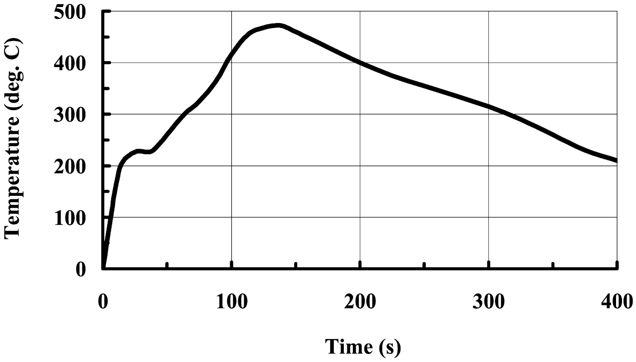

Fig. 2. Temperature profiles of hydridonitrides $ZrN_{0.17}H_{1.6}$ in the SHS mode.

heating temperature of the sample in vacuum from 110 to 800°C. Over the corresponding power range, the temperature developed on the interaction of $ZrC_{0.4}$ with hydrogen increases insignificantly (from 395 to 485°C). As seen from Table 1, the temperature of zirconium carbohydrides formation in the CS mode is lower than the temperature developed in TRS. Yet the carbohydrides, obtained by the two indicated modes, do not differ significantly in chemical or phase composition. The total indexes of the obtained FCC carbohydrides (Me/Non-Me) are always above 1.

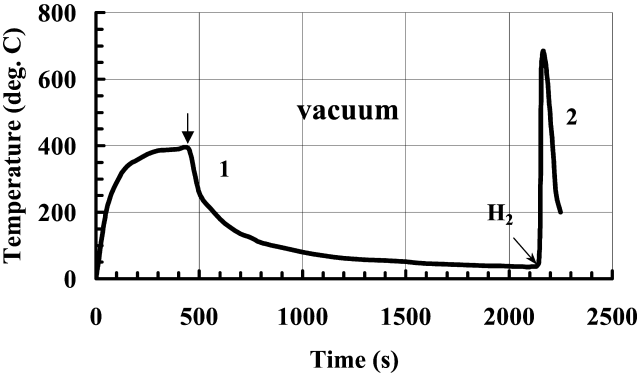

Fig. 3. Thermograms of cold synthesis in the $ZrN_{0.17}$–H system at dose power of preliminary irradiation 0.2 MRad/s: (curve 1) temperature of sample heating in vacuum; (curve 2) temperature profile of CS. Irradiation proceeded for 450 s, after which the beam was switched off. H_2 was given to the chamber after 1550 s.

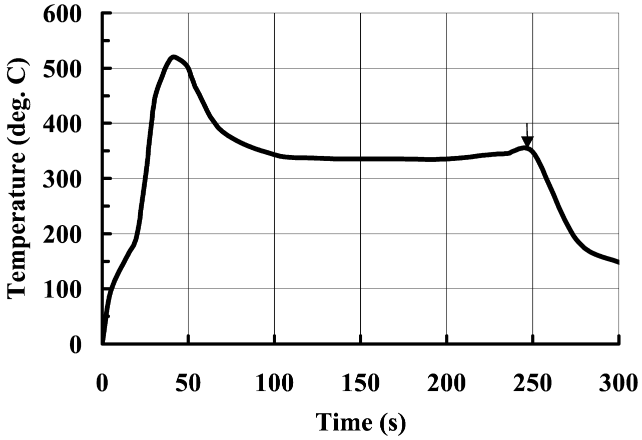

Fig. 4. Thermograms of TRS in the $ZrC_{0.4}$–H system at irradiation by dose power of 0.4 MRad/s.

In the study of the 'lifetime' of the alleged radiation damages in $ZrC_{0.4}$ bringing to CS, it was found that the CS in this system can be observed only at $T = 55$°C, contrary to the Zr–H and $ZrN_{0.17}$ systems, where the CS is observed at temperatures as low as 25°C.

4. Conclusions

The analysis of the experimental results (thermograms, chemical and X-ray analyses data, etc.) has shown that in the systems based on zirconium — (Zr–H, $ZrN_{0.17}$–H and $ZrC_{0.4}$–H) TRS can be realized, as well as the CS phenomenon, resulting in the formation of hydrides. The mechanisms of the interaction of Zr, $ZrN_{0.17}$ and $ZrC_{0.4}$ with hydrogen under accelerated (4 MeV) electron beam are identical. The main features of TRS and CS reactions

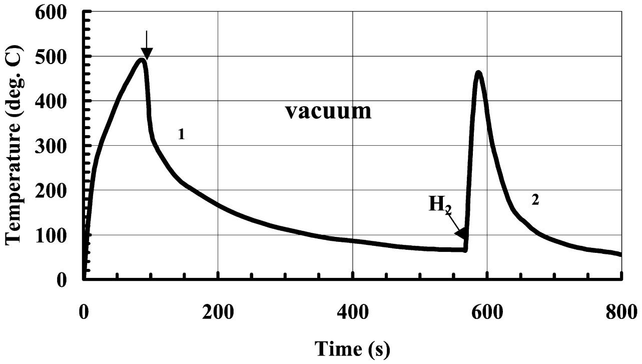

Fig. 5. Thermograms of CS: (curve 1) the temperature profile at irradiation of sample in vacuum; (curve 2) the temperature profile at cold synthesis $ZrC_{0.4}H_{1.0}$. Irradiation was proceeded for 90 s, the beam was switched off and H_2 was admitted to the chamber after 510 s.

in these three systems are similar, except that in $ZrN_{0.17}$–H and $ZrC_{0.4}$–H, CS starts at a significantly lower power dose of preliminary irradiation — 0.025 and 0.05 MRad/s, but in Zr–H the cold synthesis starts at dose powers ten times as high — 0.2 MRad/s (Table 1).

At present it is still impossible to describe the nature of CS. It may be only suggested that at preliminary irradiation in vacuum, the displacement energy is exceeded and a critical concentration of radiation defects in the crystal lattice is created. These defects increase the reactivity of the sample and evidently cause its interaction with hydrogen at room temperature.

Apparently, the presence of a non-metallic sublattice is essential for this effect, as it promotes the saving of structural defects, and essentially influence CS. At the same time it is hard to explain why the 'lifetime' of the accumulated energy in Zr and $ZrN_{0.17}$ is higher, than that in $ZrC_{0.4}$. The type of crystal lattice might account for it. Perhaps Zr and $ZrN_{0.17}$ of the HCP structure might save radiation defects longer, than the FCC structure of $ZrC_{0.4.}$

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