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The thermal radiation processes in the Sc–H system

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Abstract

The thermal-radiation processes in the system Sc–H_2 have been investigated. The high-current 4 MeV electron accelerator LAE-5 has been used with a focused electron beam. As a result of experiments at different doses and dose rates (0.025–1.5 Mrad/s) in vacuum and in a hydrogen atmosphere, the main peculiarities of the thermal-radiation processes in Sc–H_2 have been obtained. It was shown that at irradiation of Sc in H_2 environ, the thermal-radiation synthesis (TRS) of Sc hydride, $ScH_{1.92}$, occurred. It was established that on increase of irradiation dose, the temperature of the sample increases to 200–300 °C, after which a sharp temperature jump was observed. Actually, the reaction Sc+H_2 proceeded in a thermal explosion regime. It was shown that the characteristics of TRS depend essentially on irradiation dose rate.

Keywords: Irradiation; Electron beam; Metal hydrides; Self-propagating high temperature synthesis

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1. Introduction

The group III metals and the lanthanides form hydrides of composition from MeH_2 up to MeH_3. But, it has to be noted that from these metals, Sc and Eu can be hydrogenated only up to MeH_2. The structure of Sc hydride is a face-centered (f.c.c.) lattice. Its homogeneity area is in $MeH_{1.65-1.93}$ depending on the purity of used Sc. The reaction of Sc with H_2 is an exothermic one. Traditionally, the Sc hydride is synthesized from purified metal Sc in 'Sieverts' equipment: Sc is preliminary evacuated at 800 °C during 30 min then, H_2 is supplied to the system at 1 atm, afterwards, the temperature is reduced to 450 °C (1 atm=101,325 Pa). The process duration is 16 h [1].

Thermal-chemical-radiation processes in Sc–H systems in the accelerated electron beam have not been previously investigated. In this work, the results of investigations of Sc interaction with H_2 under the action of the accelerated electron beam (thermal-radiation synthesis, TRS), and in the combustion regime (self-propagating high temperature synthesis, SHS) are presented.

2. Experimental

In the investigations, the linear high-current electron accelerator LAE-5 was used. The experiments were performed by the procedures described in Refs. [2,3] with the following accelerator parameters: energy of electrons—4 MeV, average current—150 μA. The special hermetic chamber for the materials processing in the electron beam in vacuum and under pressure (up to 2 H_2 atm) was worked out and placed in the front of the LAE-5 in the focused electron beam. The collimated beam ensures even irradiation of the entire sample volume. The system for measuring the temperature and the heat effects during irradiation was elaborated. The 'S' type Pt/Pt–Rh thermocouple was used. A tablet (d=20 mm, h=5 mm) was pressed from a metal shave, placed in the chamber, and evacuated. Irradiation of the sample in vacuum or in a H_2 atmosphere was carried out with different doses (up to 100 Mrad) and dose rates.

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The investigation of the SHS process in Sc–H_2 was performed in the 'high pressure bomb', provided by the sensors for regulation of the process parameters (pressure, temperature, velocity, etc.) [4,5].

A characterization of the obtained materials was accomplished using physicochemical analyses. It allowed to describe with certainty all the processes and the final products of synthesis. The chemical composition was determined using the methods of classical chemical analysis: pyrolysis in dry oxygen flow (to determine hydrogen contents), X-ray analysis on a DRON-2 diffractometer. The estimation of the thermal stability, the analysis of the heat effects and the study of decomposition mechanism of the obtained hydrides were performed by differential thermal analysis (DTA) and dynamic gravimetry (TG) on a Derivatograph Q-1500 instrument. A temperature range of the instrument from ambient up to 1500 °C and heat rates between 10 and 30 °C/min were used. The mass of the samples was 700–800 mg. Platinum and alundum crucibles were used.

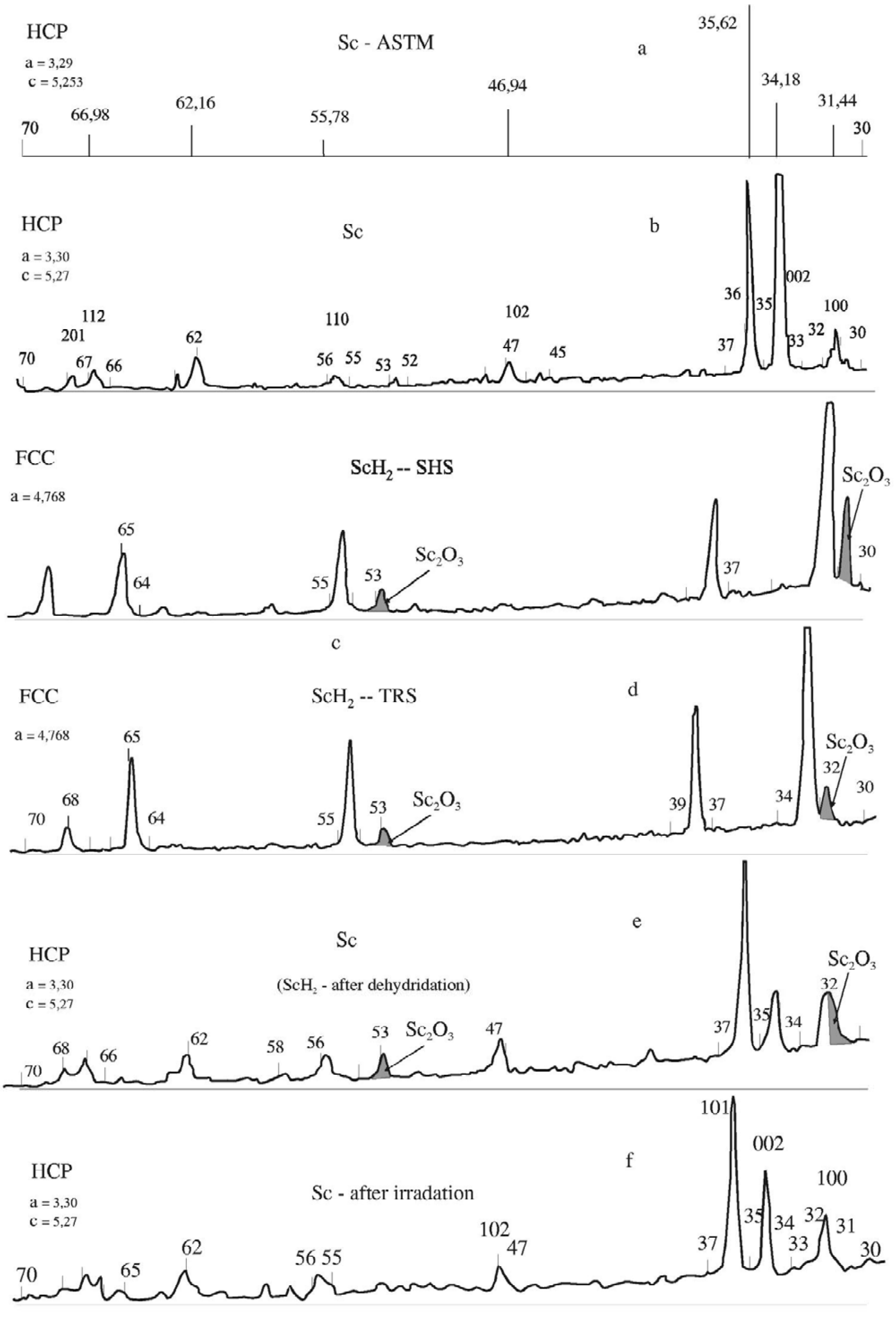

Fig. 1. The diffraction patterns of scandium and its hydrides.

In the present experiments, scandium of ScM-2 grade was used in the form of druse and shattered pieces of 1–10 mm. The diffraction pattern of the h.c.p. lattice of this sample differed from the ASTM standard (Fig. 1a, b).

2.1. SHS processes in the Sc–H system

Earlier, the Sc hydride, ScH_2, of f.c.c. structure (a= 4.782) with a hydrogen content of 4.25 wt.% had been obtained [4,5] by the SHS method from the shavings obtained by mechanical treatment of a scandium ingot (ScM-1 grade).

In these experiments, the f.c.c. hydride of scandium, ScH_2 (a=4.77 Å) and, apparently a scandium oxide were obtained at hydrogenation of ScM-2 grade (druse) by the SHS technique (Fig. 1c). The temperature and the combustion rate were changed, respectively, between 1300 and 1550 °C and 3–5 cm/s depending on the hydrogen pressure.

The hydrogen content of the obtained products was close to 3.45 wt.%. It is worthy to note that the hydrogen content is calculated for all over the sample weight, including the scandium oxide (Table 1). Unfortunately, the used methods of chemical analysis do not allow to evaluate the hydrogen content in the oxide and hydride phases separately. Surely, the hydrogen content in the obtained hydride is higher: taking into account that the hydrogen absent in the oxide phase, its content in hydride phase actually is 3.82 wt.%. It is lower than in early obtained SHS hydride of scandium—4.25 wt.% [3,4].

As mentioned above, the ability of scandium to hydrogenate strongly depends on the purity of used scandium. The obtained results manifest it.

In Fig. 2, the thermogram of the SHS process, and in Fig. 3 the derivatograms of the SHS scandium hydride are presented. The latter shows that decomposition of the scandium hydride occurs by endoeffects at 960±10 °C.

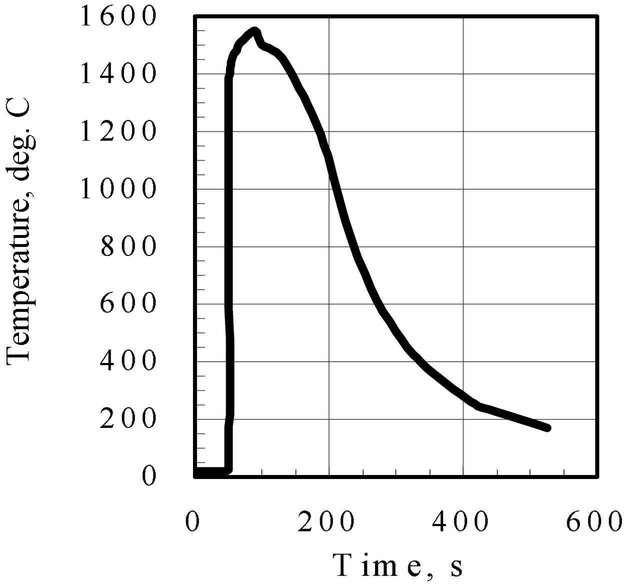

Fig. 2. The thermogram of SHS process in the $Sc–H_2$ system.

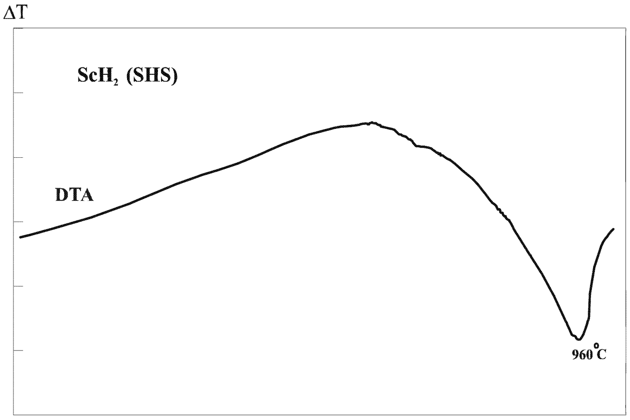

Fig. 3. DTA of SHS hydrides of scandium.

2.2. Thermal-radiation synthesis of scandium hydride

It is interesting to follow the metamorphosis of used scandium. At irradiation of scandium in vacuum by a dose rate of 1.3 Mrad/s up to the total dose of 100 Mrad (the achieved temperature is 960 °C), the crystal lattice became ordered and its diffraction pattern became similar to that of the ASTM standard. The parameters of the lattice after irradiation did not vary: a=3.30; c=5.27 Å (Fig. 1e). Upon irradiation of ScM-2 in a H_2 environment, TRS took place only at high dose rates, 1–1.5 Mrad/s, forming scandium hydride with an f.c.c. structure (Fig. 1d) as for

Table 1
Characteristics of thermal-radiation synthesis of scandium hydride

Dose rate (Mrad/s)	Dose, (Mrad)	$T_{heating}$ (°C)	T_r (°C)	Hydrogen content*, in the end product (wt.%)	Phase composition
SHS	–	–	1550	3.45	$ScH_2+Sc_2O_3$ (~10%)
0.2	200	190	–	0.86	$Sc+Sc_2O_3$
0.3	200	225	–	0.67	Sc
0.5	180	385	–	0.57	Sc (ordered)
0.8	280	520	–	0.8	Sc (ordered)+ScH_x
1.0	120	560	>900	3.42	$ScH_2+Sc_2O_3$ (~10%)
1.3	100	–	>900	3.45	$ScH_2+Sc_2O_3$ (~10%)
1.5	100	305	1135	3.41	$ScH_2+Sc_2O_3$ (~10%)

* Taking into account that the hydrogen is only in the hydride phase, its content in this phase really is 3.82 wt.% H_2.

Table 2
Characteristics of TRS of scandium hydride at preliminary irradiation of Sc

Dose rate of preliminary irradiation (Mrad/s)	Dose (Mrad)	T_{heat} (°C)	Dose rate of TRS in H_2 (Mrad/s)	T of reaction beginning (°C)	T_{react} (°C)	*H_2 content, in the end product (wt.%)	Phase composition
1.3	80	960	0.5	275	945	3.41	$ScH_2+Sc_2O_3$ (~10%)
1.0	100	780	0.5	280	>900	3.35	$ScH_2+Sc_2O_3$ (~10%)
1.0	100	870	0.2			TRS did not proceed	
1.0	75	755	Without beam	530	950	3.32	$ScH_2+Sc_2O_3$ (10%)
0.5	100	465	0.2			TRS did not proceed	

* Taking into account that the hydrogen is only in the hydride phase, its content in this phase really is 3.82 wt.% H_2.

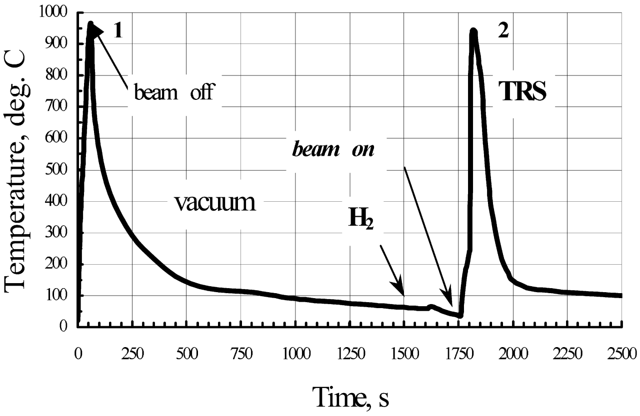

Fig. 4. The temperature profile of TRS process in the Sc–H_2 system.

SHS. Similarly to the four group metals [2,3] after heating of scandium in the accelerated electron beam, a thermal explosion happens. It was not possible to fix precisely the temperature of the thermal explosion. However, a sharp jump of temperature up to T_{max}=1010–1130 °C was observed. These temperatures of scandium hydride creation in the TRS mode were lower than the combustion temperature in SHS by 200–300 °C. In TRS products, the hydrogen content reached 3.4–3.45 wt.%. On the X-ray pattern of the obtained product, alongside the f.c.c crystal lattice of scandium hydride, an oxide phase Sc_2O_3 (about ~10%) was always detected. In Table 1, the characteristics of TRS process for the given system are presented.

2.3. Radiation activation of scandium

The following series of experiments manifested that the scandium was activated under preliminary irradiation, allowing the TRS implementation at lower dose rates. As can be seen in the thermogram in Fig. 4, the hydrogen giving (shown by arrow) after preliminary irradiation of scandium in vacuum at a dose rate of 1.3 Mrad/s (curve 1), the TRS became possible at a dose rate of 0.5 Mrad/s (curve 2). The TRS temperature profile is like that for the group IV metals [3]. Fig. 4 shows also that for the initiation of the exothermal reaction, a rather low temperature (about 275 °C) is needed. The hydrogen content in the obtained products is 3.45 wt.%, the calculated phase composition correspond to formula $ScH_{1.79}$+~10% Sc_2O_3 (Table 2).

At a preliminary irradiation dose rate of 1 Mrad/s in vacuum followed by irradiation in hydrogen at a dose rate of 0.2 Mrad/s, TRS did not happen.

It is known that using the furnace technique, the hydrogenation of scandium is impossible without long-time vacuum annealing. The conditions used in our experiments preliminary irradiation of scandium in vacuum, is somewhat reminiscent of vacuum annealing, but in this case, it proceeds under the action of accelerated electron beam in a few seconds.

It was not possible to implement the Cold Synthesis described in Refs. [2,3] in the Sc–H system under any conditions. After irradiation of scandium in vacuum at 0.2 Mrad/s up to 200 Mrad (305 °C) followed by hydrogen exposure at 100 °C the diffraction pattern practically did not vary, and hydrogenation was not observed. Even at hydrogen exposure at 345 °C in a similar experiment, hydrogenation almost did not occur, but the diffraction pattern became ordered.

The decomposition of TRS of scandium hydride occurs by endoeffect at 960 °C, analogous to SHS scandium hydride.

Acknowledgements

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