DERIVATOGRAPHIC INVESTIGATIONS INTO THERMAL DECOMPOSITION OF DISPERSED PARTICLES OF METAL-CARBON COMPOSITES

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Introduction

One of the main obstacles in the prolonged reversible use of hydride-forming alloys is their poisoning with electronegative impurities (O,N etc.).

In the course of cycling these impurities arrange on the crystallite surface and take some area on the grain boundaries. This complicates hydrogen diffusion into the crystallite bulk and back and slows down the time for charge-discharge processes. The large accumulation of these impurities (mainly as oxides and oxynitrides) results in the material dispersion, difficulty in heat and mass transfer. Moreover, in some alloys and intermetallic compounds, with increasing temperature, oxygen and nitrogen diffusion along the grain boundaries alternates by volume diffusion of these elements. As a result, the number of interstices capable of placing hydrogen is decreased what leads to the sharp decrease in the material hydrogen capacity [1-23].

We have attempted to prepare the metal-carbon composite in the form of ultradispersed powder of hydride-forming alloys. The surface of particles in these alloys was covered with the thin layer of nanostructural carbon. The nanostructural carbon layer is thought to be penetrable for hydrogen and impenetrable for electronegative impurities.

In this work the investigations into interaction of dispersed powders of metal-carbon composites with air atmosphere are presented. Investigations have been performed in heating from the room temperature to 1000 ^{o}C on Q-1500D derivatograph.

Fig.1 shows the following particles: a - initial particle with a carbon layer; b - after treatment for 1 min by ultrasound. The chip in the piece of the layer is seen.

Table 1. (Values of Temperatures are given in °C)

N	Material	Temperature of beginning the change in mass	DTG				DTA	Change in mass, %	Temperature range of thermal decomposition
			T_1 max	T_2 max	T_3 max	T_4 max	Tmax		
1	Nickel produced in alcohol	230	280				280	-8	230 — 400
2	Nickel produced in toluene	240	310	330	340		345	-24	240 — 400
3	Nickel produced in solvent-2355	240		330	340		340	-23	240 — 460
4	Nickel produced in solvent 2355, additionally purified in toluene	235	310	325			325	-29	235 — 410
5	$LaNi_5$, produced in toluene	240	310	330			340	-33	240 — 430
6	$LaNi_5$, produced in solvent-2355	270		330	340		350	-24	270 — 460
7	$LaNi_5$, produced in solvent 2355, additionally purified in toluene	240	310		340		330	-41	240 — 440
8	$LaNi_5$, produced in toluene and purified by ultrasound	240		325			330	-44	240 — 430
9	Dispersed carbon produced in toluene	210	340	420	500	710	710	-98	210 — 740
10	Dispersed carbon produced in toluene and treated by ultrasound	250	250	550	630	648	648	-98	250 — 680
11	Nickel electrolytic	280	550	660				23	280-750
12	$LaNi_5$ powder produced by mechano-chemical method	280	550				550	45	280-840

Experiment and results

The following composites have been studied: powders of pure nickel and $LaNi_5$; dispersed powders of nickel and $LaNi_5$ produced by the electric spark method in toluene, alcohol, solvent-2355 - unpurified powders and powders purified in pure toluene; powders additionally purified using ultrasound in pure toluene; dispersed powder of spectro-pure carbon.

On the base of the study performed the following has been found: temperature ranges for thermal decomposition of dispersed powders, values of mass loss in heating (due to the evolution of different gases), temperatures for maximum rates of mass loss. The difference-thermal analysis has been performed (Table 1).

It has been found that depending on the powder composition, the technique for its preparation and purification, the temperature for the beginning process of mass loss and the range of its occurrence are different.

Conclusions

The value of mass loss significantly differs for different powders. The experiments performed have allowed us to outline the ways for further investigations directed at the creation of metal-carbon hydrogen-sorbing materials with the enhanced cyclic stability.

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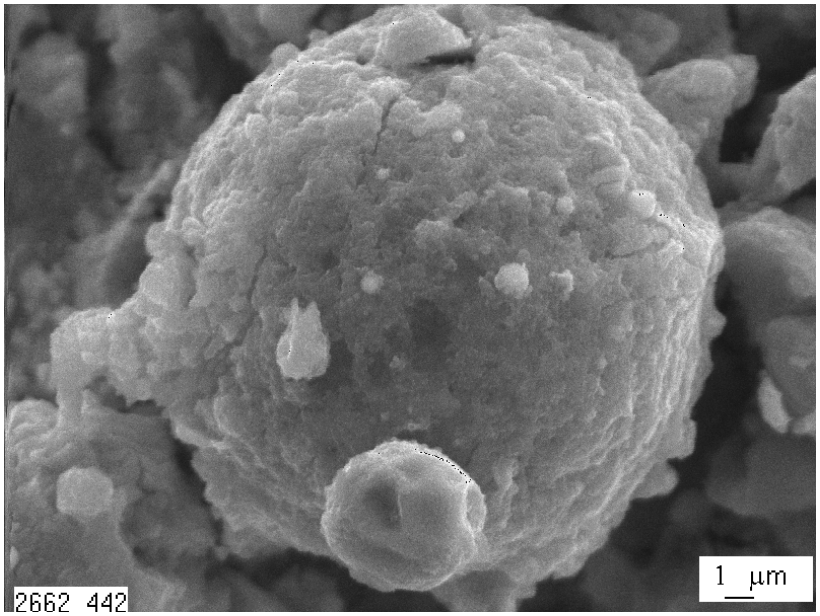

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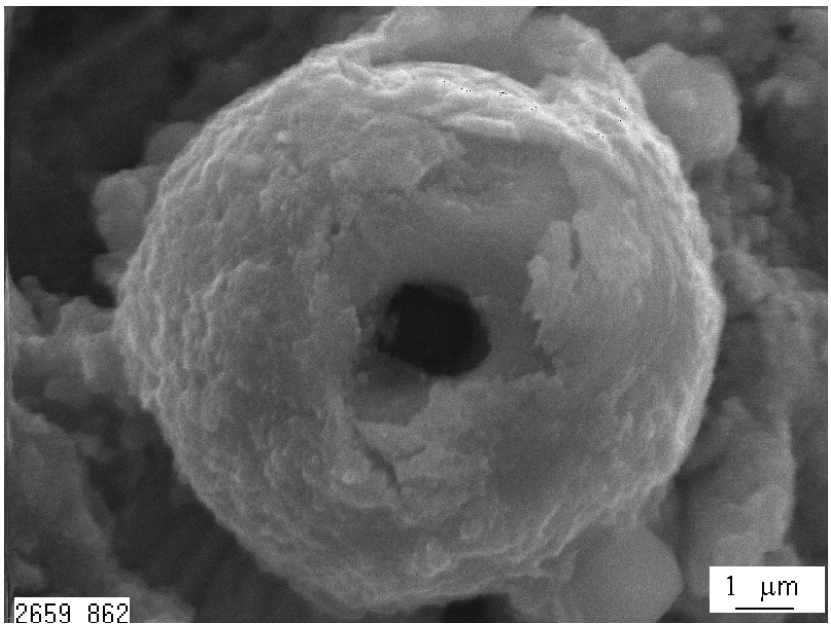

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ДЕРИВАТОГРАФИЧЕСКИЕ ИССЛЕДОВАНИЯ ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ ДИСПЕРСНЫХ ЧАСТИЦ МЕТАЛЛОУГЛЕРОДНЫХ КОМПОЗИТОВ

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Введение

Одним из основных препятствий долгосрочного реверсивного использования гидридообразующих сплавов является их отравление электроотрицательными примесями (O, N и др.).

При циклировании эти примеси располагаются на поверхности кристаллитов, занимая пространство на границах зерен. Этим осложняется диффузия водорода в объем кристаллита и обратно и замедляется время процессов заряда-разряда. Большое скопление этих примесей (в основном в виде оксидов и оксинитридов) приводит к диспергированию материала, затруднению процессов тепло- и массопереноса. Кроме того в некоторых сплавах и интерметаллидах при повышении температуры диффузия кислорода и азота по границам зерен сменяется объемной диффузией этих элементов. В результате этого сокращается количество междоузлий, способных размещать водород, что ведет к резкому снижению водородоемкости материала.

Нами сделана попытка получить металл-углеродный композит в виде ультрадисперсного порошка гидридообразующих сплавов. Поверхность частиц этих сплавов покрыта тонкой пленкой наноструктурного углерода. Предполагается, что наноструктурная углеродная пленка будет проницаемой для водорода и непроницаемой для электроотрицательных примесей.

В настоящей работе проведены исследования взаимодействия дисперсных порошков металлоуглеродных композитов с атмосферой воздуха при нагреве от комнатной температуры до 1000°C на приборе Дериватограф Q-1500Д.

Таблица 1 (Значения температур указаны в °C)

N п/п	Материал	Температура начала изменения массы	ДТГ				ДТА	Изменение массы, %	Температурный интервал термического распада
			T_1 max	T_2 max	T_3 max	T_4 max	Tmax		
1	Никель, полученный в спирте	230	280				280	-8	230 — 400
2	Никель, полученный в толуоле	240	310	330	340		345	-24	240 — 400
3	Никель, полученный в растворителе-2355	240		330	340		340	-23	240 — 460
4	Никель, полученный в растворителе-2355, дополнительно очищенный в толуоле	235	310	325			325	-29	235 — 410
5	$LaNi_5$, полученный в толуоле	240	310	330			340	-33	240 — 430
6	$LaNi_5$, полученный в растворителе-2355	270		330	340		350	-24	270 — 460
7	$LaNi_5$, полученный в растворителе-2355, дополнительно очищенный в толуоле	240	310		340		330	-41	240 — 440
8	$LaNi_5$, полученный в толуоле и очищенный ультразвуком	240		325			330	-44	240 — 430
9	Дисперсный углерод, полученный в толуоле	210	340	420	500	710	710	-98	210 — 740
10	Дисперсный углерод, полученный в толуоле и обработанный ультразвуком	250	250	550	630	648	648	-98	250 — 680
11	Никель электролитический	280	550	660				23	280-750
12	Порошок $LaNi_5$, полученный механохимическим способом	280	550				550	45	280-840

На рис. 1 показаны такие частицы: а – исходная, имеющая углеродною пленку; б – после обработки в течение 1 минуты ультразвуком. Виден скол куска пленки.

Условия эксперимента и результаты

Исследованы следующие композиты: порошки чистого никеля и $LaNi_5$, дисперсные порошки никеля и $LaNi_5$, полученные электроискровым методом в толуоле, спирте, растворителе-2355, неочищенные и очищенные в чистом толуоле, а также дополнительно очищенные с помощью ультразвука в чистом толуоле, дисперсный порошок спектрально чистого углерода.

На основании проведенных исследований установлены температурные интервалы термического распада дисперсных порошков, величины убыли их массы в процессе нагрева, обусловленные выделением различных газов, температуры максимальных скоростей убыли массы, проведен дифференциально-термический анализ (см. таблицу 1).

Установлено, что в зависимости от состава порошков, технологии их получения и очистки температура начала процесса потери массы и интервал его протекания различны.

Выводы

Величина потери массы существенно отличается для различных порошков.

Проведенные эксперименты позволили наметить пути дальнейших исследований в направлении создания металл-углеродных водород-сорбирующих материалов с повышенной циклической устойчивостью.

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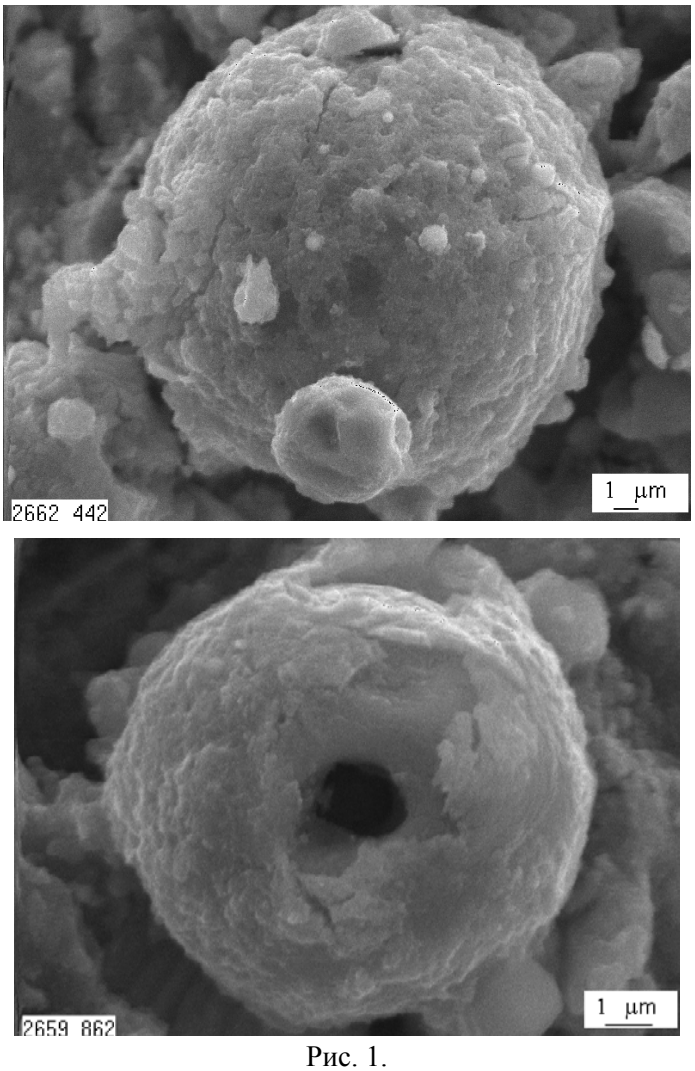

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Рис. 1.