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Characterization and thermodynamic study of ultra-fine particle of Ni–B amorphous alloy[1]

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Abstract

Ultra-fine particle of Ni–B amorphous alloy was prepared by chemical reduction of Ni^{2+} with $NaBH_4$ and characterized with TEM and XRD. The heat capacity and thermal stability were measured with a high-precision automatic adiabatic calorimeter and DTA. The upper limit of applied temperature of the substance was found to be 684 K for use as catalyst.

Keywords: Ni–B alloy; Ultra-fine particle; Amorphous alloy; Heat capacity; DTA

1. Introduction

Ultra-fine particle of Ni–B amorphous alloy is a kind of metal catalyst used in the hydrogenation of benzene [1]. In recent years, considerable attention has been paid to the preparation of the alloy by reduction of metal salts using borohydride in an aqueous solution [1–3]. Each catalyst has its activation range of temperature, while few attentions were devoted to the thermodynamic properties of the amorphous Ni–B alloy. In the present research, thermodynamic parameters like the heat capacity and phase-transition temperature of the amorphous and crystal alloys, as well as the preparation and characterization of the sample are studied, in order to understand comprehensively the chemical and physical properties of the ultra-fine particles of Ni–B alloy.

2. Experimental

2.1. Sample preparation

The ultra-fine particles were prepared by adding dropwise an aqueous solution of 100 ml 1.8 mol l^{-1} $NaBH_4$ to an aqueous solution of 500 ml 0.2 mol l^{-1} $NiSO_4$ under vigorous stirring for 4 h at room temperature. The black precipitate was washed thoroughly with distilled water in order to remove residual ions from the reaction mixture, followed by washing with acetone to remove the water.

The chemical composition of the prepared sample, determined by chemical analysis with dimethylglyoxime, has been reported previously in detail [1]. The sample contained 80.05% of nickel and 19.95% of boron (in weight), respectively.

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2.2. Sample characterization

Transmission electronic microscope (TEM) of Philips EM420 was used to determine the morphology and grain size of the alloy. The result indicates that the average grain size of the sample is 15.1 nm and scattered as Boltzmann distribution, which proves that the Ni–B alloy sample is nanostructural material. The X-ray diffraction (XRD) measurement was performed with an instrument of Rikagu D/max-VB revealing that the sample is a typical amorphous substance without any sharp crystalline peaks.

2.3. Heat-capacity measurement

The heat capacity of the sample was measured with a small sample adiabatic calorimeter which has been described previously in detail [4]. The uncertainty of temperature measurement in the calorimeter is ca. 1 mK. Heat-capacity measurements of α-Al_2O_3 over the temperature range of 60–350 K indicate that deviation of the experimental results from the smoothed curve lie within $\pm$0.2%, while the inaccuracy is within $\pm$0.5%, as compared with those of the National Bureau of Standards [5]. The sample mass used for the calorimetric study is 2.943 g (0.094 mol based on the molar mass of 31.148 g mol^{-1}).

2.4. Thermal analysis

Differential thermal analysis (DTA) was carried out with a differential thermal analyzer (Setaram, Lyon, France) in a nitrogen atmosphere with a heating rate of 5 K min^{-1} (sample mass 22.6 mg).

3. Results and discussion

The experimental data of heat capacities were listed in Table 1, which demonstrates that no phase transition took place in the low temperature range of 80–350 K.

A distinct exothermic peak was observed in the DTA curve shown in Fig. 1. This peak lies in the temperature range of 620 to 725 K with a peak temperature of 684 K, and no other thermal anomaly was found below this temperature. The result can be explained that the ultra-fine particles of amorphous Ni–B alloy are in a metastable phase, and becomes crystals as the temperature is higher than 684 K.

Table 1
The experimental heat capacities of the ultra-fine particles of amorphous Ni–B alloy (Ni-80.05%, B-19.95% in wt.)

T/K	C_p/(J K^{-1} g^{-1})	T/K	C_p/(J K^{-1} g^{-1})	T/K	C_p/(J K^{-1} g^{-1})	T/K	C_p/(J K^{-1} g^{-1})
80.236	0.1900	153.587	0.3737	227.089	0.4934	291.225	0.5987
85.221	0.2109	157.337	0.3810	230.504	0.5128	294.174	0.6069
89.230	0.2200	161.049	0.3818	233.921	0.5059	297.120	0.6042
92.543	0.2301	164.717	0.3950	237.337	0.5210	300.382	0.6216
95.693	0.2388	168.367	0.4001	240.719	0.5169	303.980	0.6342
99.003	0.2487	171.920	0.4090	244.092	0.5168	307.568	0.6033
102.478	0.2615	175.466	0.4145	247.474	0.5277	311.148	0.6246
106.106	0.2715	178.982	0.4180	250.843	0.5337	314.705	0.6343
110.670	0.2797	182.868	0.4275	254.209	0.5363	318.246	0.6375
113.867	0.2868	187.125	0.4285	257.540	0.5619	321.788	0.6263
117.574	0.2987	191.312	0.4414	260.850	0.5486	325.325	0.6400
121.205	0.3018	195.231	0.4479	264.380	0.5666	328.832	0.6504
124.763	0.3153	198.881	0.4580	267.197	0.5710	332.408	0.6590
128.257	0.3195	202.502	0.4641	270.225	0.5627	336.074	0.6629
131.696	0.3291	206.096	0.4700	273.251	0.5682	339.755	0.6624
135.079	0.3347	209.661	0.4798	276.282	0.5793	343.459	0.6566
38.411	0.3412	213.194	0.4877	279.312	0.5868	347.193	0.6500
142.035	0.3494	216.701	0.4929	282.322	0.5804	350.976	0.6639
145.944	0.3603	220.193	0.4973	285.309	0.5887		
149.792	0.3687	223.600	0.5160	288.273	0.6015		

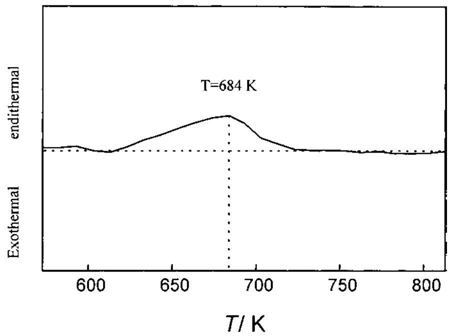

Fig. 1. The DTA curve of ultra-fine particles of Ni–B amorphous alloy.

Another experiment [1] has proved that the crystalline Ni–B alloy does not possess catalytic activity, that is in order to ensure the catalytic activity of the Ni–B alloy the applied temperature of the substance cannot be higher than the phase-transition temperature.

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