

ノート

TiFe_{0.9}Co_{0.1} 水素化物の磁気特性

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Magnetic Properties of Hydrogenated TiFe_{0.9}Co_{0.1}

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Abstract

The thermodynamic properties of the TiFe_{0.9}Co_{0.1}-H system and its magnetic properties with various hydrogen contents were examined. The pressure-composition isotherm curves showed a plateau region, and the change in the enthalpy with monohydride formation was similar to that of TiFe. From the conventional magnetic properties examinations, TiFe_{0.9}Co_{0.1} was found to show no magnetic transition down to 10 K. The magnetic susceptibility of TiFe_{0.9}Co_{0.1} increased with hydrogen uptake, but no ferromagnetic behavior was observed up to the hydrogen content of TiFe_{0.9}Co_{0.1}H_{0.6} at room temperature. The change in magnetic susceptibility with hydrogen uptake could be explained qualitatively by the band structure calculation.

1. Introduction

TiFe is a candidate for hydrogen storage material consisting of abundantly existing,

inexpensive elements [1]. This intermetallic compound is also expected to be a magnetic material because of its iron-rich composition, and to be a functional material applied to hydrogen sensing. However, no magnetic order has been found to occur in TiFe down to 4.2 K [2]. It was reported that TiFe_{0.74}Co_{0.26} with the partial substitution of Co for Fe showed ferromagnetic behavior at the temperature of 36 K [2,3]. A problem with this substitution is that Co is an expensive element, and the use of Co results in a cost increase.

The appearance of the magnetic transition of TiFe_{0.74}Co_{0.26} was caused by the addition of an electron to the intermetallic compound; the substitution of Co for Fe introduces one more electron per atom without changing the electronic band structure. Hydrogen also contributes to the addition of electrons [4]. A synergistic effect on magnetic properties can, therefore, be expected with only modest substitution of Co atoms. Although TiFe_{1-y}Co_y absorbs hydrogen under high hydrogen gas pressure [5,6], it quickly releases hydrogen under normal pressure. Therefore, the magnetic properties of hydrogenated TiFe_{1-y}Co_y must be examined *in-situ* under high hydrogen pressure.

The aim of this paper is to report the results of preliminary examination on hydrogen-induced large magnetic moments in TiFe_{1-y}Co_y compounds. The magnetic susceptibility of TiFe_{0.9}Co_{0.1} under high hydrogen pressure and the pressure-composition isotherm curves were measured. The relationship between hydrogenation and magnetic properties were also discussed.

2. Experimental

Ti, Fe and Co grains, the initial materials used for preparing TiFe_{0.9}Co_{0.1}, were purchased from Kojyundo Kagaku Co. Ltd. All these materials had 99.9% purity.

Stoichiometric amounts of the grains were weighed out, and melted together in an arc furnace under an argon atmosphere. To obtain a homogeneous sample, the ingot was turned upside down and melted again, and this process was repeated 5 times. After the arc melting, the surface of the ingot was grinded to remove any impurities on the surface. The TiFe_{0.9}Co_{0.1} ingot thus obtained was mechanically crushed into powder. X-ray diffraction (XRD) measurement for the prepared powder was performed using an X'pert system (Panalytical). In the measurements, crystallized Si powder was added to the sample powder for diffraction angle calibration.

Pressure-composition isotherm curve measurements were performed using an automated measurement system (Suzuki Syokan Co. Ltd.). Approximately 1 g of TiFe_{0.9}Co_{0.1} powder was placed in a stainless steel vessel, which was attached to the system. The powdered sample was activated in the following procedure. First, the sample was heated up to 673 K for 2 hours in a vacuum given by an oil-sealed rotary pump. Then, hydrogen gas was introduced stepwise up to 4 MPa (40 atm) at room temperature, and the hydrogen gas was evacuated at 473 K. The hydrogenation process was repeated 5 times to stabilize hydrogen absorption characteristics. The amount of absorbed hydrogen was estimated as follows. In closed system, the hydrogen pressure decreased when the sample contacted to hydrogen gas. The consumption of hydrogen gas by contacting the sample was regarded as the amount of hydrogen in the sample, which was calculated by applying the pressure difference, temperature, and a volume in the closed system to ideal gas law.

The magnetization measurement of TiFe_{0.9}Co_{0.1} was performed by SQUID magnetometer MPMS-7 (Quantum design) at temperatures from 10 to 300 K under the magnetic field up to 7 T. The alternating-current magnetic susceptibility of

TiFe_{0.9}Co_{0.1}H_x was measured by using a system specially prepared for the measurements of magnetic susceptibility under high hydrogen pressure. The detail of the system are described elsewhere [4,7].

3. Results and Discussion

Figure 1 shows the XRD pattern of the prepared powder sample without hydrogen. The diffraction peaks from crystallized Si powder are labeled by “Si” in this figure. The diffraction angles of the observed peaks almost exactly corresponded to those of TiFe, which has a CsCl type crystal structure (JCPDS database no. 01-083-1653). The lattice constant of TiFe_{0.9}Co_{0.1} was calculated to be 0.2978 nm, which was also the same as that of TiFe reported elsewhere (0.2975 nm). No other peaks were detected in this measurement, indicating that Co atoms formed a complete solid solution with Fe and the crystal structure remained unchanged after substitution of Co for Fe [6].

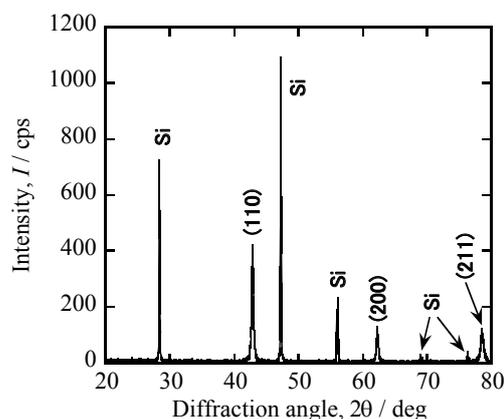


Figure 1. X-ray powder diffraction pattern of TiFe_{0.9}Co_{0.1}. The label “Si” means the diffraction peaks from crystallized Si powder.

The temperature dependence of the magnetization for TiFe_{0.9}Co_{0.1} was measured under the external magnetic field of 0.1 T. The result is shown in Figure 2(a). Magnetization decreased steeply with increase in temperature up to about 30 K, and its temperature dependence was far weaker above 30 K. It seemed that the magnetization was in inverse proportion to temperature, but it did not obey exactly the Curie-Weiss law. No magnetic phase transition appeared in the measurement. The magnetic field

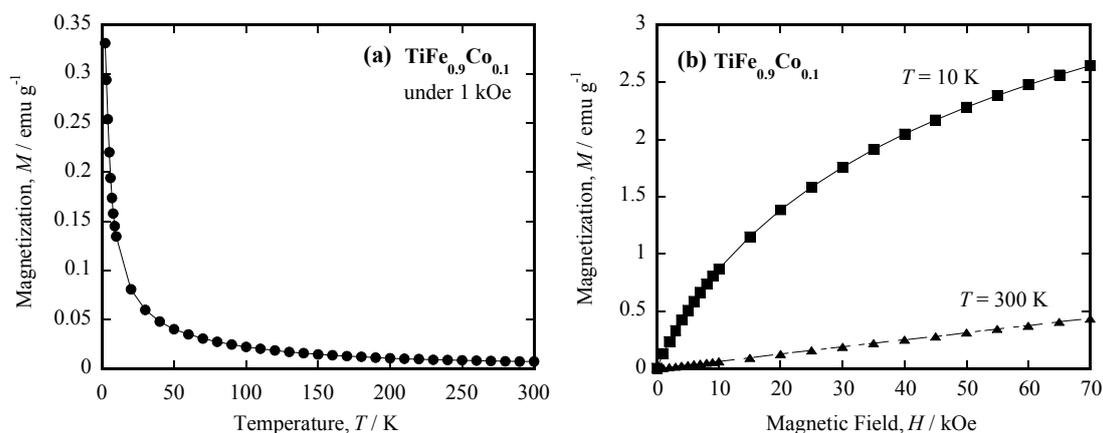


Figure 2. Magnetic properties of TiFe_{0.9}Co_{0.1} measured by using SQUID magnetometer.

dependence of magnetization at 10 K and 300 K is shown in Figure 2(b). The magnetization at 300 K increased linearly with the magnetic field. The magnetization at 10 K showed the saturation behavior, but did not reach the saturated value up to 7 T. In addition, no metamagnetic transition was observed, suggesting that TiFe_{0.9}Co_{0.1} showed paramagnetic behavior at 10 K. From these results, we confirmed that TiFe_{0.9}Co_{0.1} has a non-magnetic ground state [3].

Figure 3 shows the pressure-composition isotherms for TiFe_{0.9}Co_{0.1}-H system at different temperatures. The isotherm at each temperature showed a plateau region, which shifted upwards in pressure and shrunk in width with the increase in temperature. The single β phase (monohydride phase) appeared at $[\text{H}]/[\text{TiFe}_{0.9}\text{Co}_{0.1}] > 0.55$. The pressure-composition isotherm curves at 303 K and 313 K showed slight swelling at $[\text{H}]/[\text{TiFe}_{0.9}\text{Co}_{0.1}] \approx 0.60$ and 0.55,

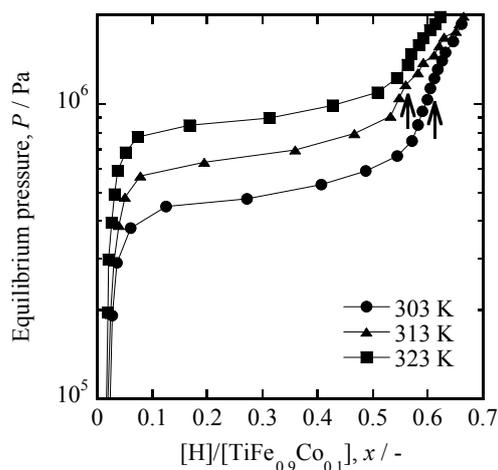


Figure 3. Pressure-composition isotherm curves for the TiFe_{0.9}Co_{0.1}-H system.

respectively (indicated by arrows in figure 3). The swelling probably reflected the appearance of a dihydride phase as reported for TiFe [1]. The changes in standard enthalpy ($\Delta H^\circ_{\alpha-\beta}$) and entropy ($\Delta S^\circ_{\alpha-\beta}$) for monohydride formation were estimated by the van't Hoff plot using the plateau pressures at $[H]/[TiFe_{0.9}Co_{0.1}] = 0.2$; the $\Delta H^\circ_{\alpha-\beta}$ and $\Delta S^\circ_{\alpha-\beta}$ were -25 kJ/molH_2 and $-95 \text{ J/K}\cdot\text{molH}_2$, respectively. The obtained value for $\Delta H^\circ_{\alpha-\beta}$ was in a range of scattering of reported values for TiFe (from $-22 - -28 \text{ kJ/molH}_2$) [1,5,6,8].

Figure 4 shows the magnetic susceptibility of hydrogenated $TiFe_{0.9}Co_{0.1}$ at room temperature. The output voltage on the y-axis in the figure is theoretically proportional to the magnetic susceptibility, but the conversion of this voltage to magnetic susceptibility is difficult because of the unknown proportional coefficient and the background signals from the stainless steel vessel. The magnetic susceptibility increased linearly with hydrogen content, but the hydride ($TiFe_{0.9}Co_{0.1}H_{0.6}$) showed only two times as large magnetic susceptibility as $TiFe_{0.9}Co_{0.1}$. It was suggested that $TiFe_{0.9}Co_{0.1}$ monohydride showed paramagnetic behavior at room temperature, and no large magnetic moments appeared by hydrogenation. If the band structure of $TiFe_{0.9}Co_{0.1}$ could be the same as that of TiFe, the enhancement of magnetic susceptibility by hydrogenation could be explained by the electronic band structure of TiFe calculated earlier [9,10]. The results of electronic band structure calculation of TiFe indicated that the Fermi energy was

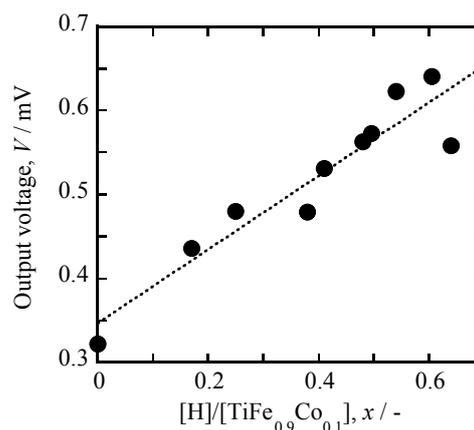


Figure 4. Alternating-current magnetic susceptibility of hydrogenated $TiFe_{0.9}Co_{0.1}$. The dashed line indicates the result of linear fitting by the least-squares method.

positioned near the trough. The density of states rose sharply to reach the peak at an energy level slightly higher than the Fermi energy. Hydrogen provided the doping electrons and lifted the Fermi energy. As a result, the density of states at the Fermi energy increased and the magnetic susceptibility also increased by hydrogenation. To investigate magnetic properties in the ground state, it is necessary to examine the magnetic properties at low temperature under high hydrogen gas pressure.

4. Conclusions

The magnetic susceptibility of hydrogenated TiFe_{0.9}Co_{0.1} was investigated. The hydrogen absorption properties were similar to those of TiFe. TiFe_{0.9}Co_{0.1} had a paramagnetic ground state. The magnetic susceptibility of hydrogenated TiFe_{0.9}Co_{0.1} increased with hydrogen uptake but no large magnetic moments appeared at room temperature by hydrogen uptake. The change in the susceptibility with hydrogen uptake was qualitatively explained by the electronic band structure of TiFe. Consequently, large magnetic moments could not be induced by hydrogenation up to $[H]/[TiFe_{0.9}Co_{0.1}] \simeq 0.60$ for TiFe_{0.9}Co_{0.1} at room temperature.

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