Crystal Structures and Magnetic Properties of the System $\text{Rh}_1\text{Mn}_{1-x}\text{Sb}_x$ *

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Crystal structures and magnetic properties of Rh-Mn-Sb alloys have been investigated by means of X-ray diffraction and magnetic measurements. It has been found that alloys in the composition range of $\text{Rh}_{1.00}\text{Mn}_{0.66}\text{Sb}_{0.34} \sim \text{Rh}_{1.00}\text{Mn}_{0.55}\text{Sb}_{0.45}$ are a solid solution of the face-centered tetragonal L1_0 -type with lattice parameters of $4.200 \sim 4.182 \text{ \AA}$ and axial ratios of $0.806 \sim 0.829$. The typical $\text{Rh}_{1.00}\text{Mn}_{0.55}\text{Sb}_{0.45}$ alloy has a saturation magnetization of 52.3 emu/g at absolute zero, a magnetic moment of $3.20 \mu_B$ per Mn atom, a Curie point of 330°K and a paramagnetic Curie point of 286°K . The observed relationship between reciprocal susceptibility and temperature indicates weak ferrimagnetic behavior of this alloy.

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I. Introduction

Previous work on the crystal structures and magnetic properties of the intermetallic compounds in a series of Rh-Mn-Sb alloys⁽¹⁾ has shown that Cl_b -type compounds are formed near the composition $\text{Rh}_1\text{Mn}_1\text{Sb}_1$, whereas at higher Rh concentrations the alloys indicate the X-ray diffraction patterns indicative of the presence of a new crystal structure type in addition to the Cl_b -type. A feature of interest also is the strong magnetization of these alloys.

The present work is concerned with the experimental results on alloys of the new crystal structure type.

II. Experimental Procedure

The alloy specimens were prepared from 99.99% Rh and Mn and Sb of the same purities as reported previously⁽¹⁾. Carefully weighed quantities of Rh, Mn and Sb were sealed in evacuated silica tubes 6~7 mm in inner diameter and 50~70 mm long, melted at $1150 \sim$

1350°C for 1 hr in an electric furnace and then quenched in iced water. For the purpose of further homogenization, the alloys were pulverized, resealed in evacuated silica tubes and quenched in iced water again. The alloys thus obtained were examined by means of X-ray diffraction, and the above-mentioned operation was repeated until sufficient homogenization was realized. Finally, the alloys were prepared in the form of powder, bulk matter or rods, then homogenized at $700 \sim 1000^\circ\text{C}$ for 40~100 hr and cooled slowly at a rate of 100°C/hr .

The X-ray analysis of the crystal structures, and the lattice constant and magnetic measurements were entirely the same as described in a previous paper⁽¹⁾.

III. Results and Discussion

1. Crystal structure

X-ray diffraction studies on crystal structures of Rh-Mn-Sb alloys were performed using 29 alloys whose compositions are shown in Fig. 1. Figure 2 shows the diffraction patterns of the typical alloys $\text{Rh}_{1.00}\text{Mn}_{0.50}\text{Sb}_{0.50}$ (No. 19), $\text{Rh}_{1.00}\text{Mn}_{0.55}\text{Sb}_{0.45}$ (No. 18), $\text{Rh}_{1.00}\text{Mn}_{0.66}\text{Sb}_{0.34}$ (No. 13) and $\text{Rh}_{1.00}\text{Mn}_{0.70}\text{Sb}_{0.30}$ (No. 11) which were held at 1000°C for 98 hr and then slowly cooled. These alloys have compositions indicated by the open circles in the figure. Alloys No. 18 and No. 13 exhibit a single phase of the *fcc* lattice type, while alloy No. 19 with a higher Sb concentration than alloy No. 18 shows the *fcc*

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Fig. 1 Compositions of Rh-Mn-Sb alloys tested.

- : L1₀(CuAu)-type
- ◐: B2(CsCl)-type
- : Two or three phases

phase together with a weak second phase corresponding to the RhSb compound⁽²⁾. This second phase cannot be removed by any heat treatment. Alloy No. 11 exhibits fairly strong diffraction lines of the B2-type that correspond to those of the RhMn compound^{(3)~(5)}. Next, the

Fig. 2 X-ray diffraction pattern of Rh₁Mn_{1-x}Sb_x alloy cooled at a rate of 50°C/hr after heating at 1000°C for 98 hr Cu-Kα radiation.

Table 1 Comparison of observed and calculated data for X-ray (Cu-Kα) diffraction lines of Rh_{1.00}Mn_{0.55}Sb_{0.45} alloy.

Index	Spacing $d(\text{\AA})$		Intensity	
	Meas.	Calc.	Obs.	Calc.
001	3.466	3.467	vw	13
110	2.956	2.957	vw	15
111	2.253	2.250	vs	1815
200	2.091	2.091	s	745
201	1.800	1.791	vw	8
002	1.734	1.734	m	205
220	1.478	1.479	m	237
202	1.333	1.335	m	336
311	1.235	1.236	s	510
222	1.127	1.125	m	194
400	1.045	1.046	w	83
331	0.948	0.948	m	154
420	0.935	0.935	m	155

vs: very strong, s: strong, m: middle, w: weak and vw: very weak.

crystal structure in alloy No. 18 with the typical *fcc* single phase has been analyzed. Table 1 shows a comparison between the calculated and experimental values of the interplanar spacing d and the observed intensity of each diffraction line. There is excellent agreement between the calculated and observed values of the interplanar spacings. Assuming that the crystal structure of the alloy is of the *fcc* L1₀ type (CuAu type) and that the Rh atom and the Mn and Sb atoms occupy the sites, $(000, \frac{1}{2}\frac{1}{2}0)$ and $(0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2})$, respectively, the crystal structure factor F of this alloy can be given as follows:

When $h + K$ is even with $\begin{cases} h = 2n \\ l = 2n \end{cases}$ and $\begin{cases} h = 2n + 1 \\ l = 2n + 1 \end{cases}$,

$$F = 2[f_{\text{Rh}} + f_{(\text{Mn} + \text{Sb})/2}].$$

In the case of $\begin{cases} h = 2n \\ l = 2n + 1 \end{cases}$ and $\begin{cases} h = 2n + 1 \\ l = 2n \end{cases}$,

$$F = 2[f_{\text{Rh}} - f_{(\text{Mn} + \text{Sb})/2}].$$

Here f is the atomic scattering factor. The integral intensity of each diffraction line calculated from the F , the results are in excellent agreement with the observed intensity. Therefore, the crystal structure of this alloy is determined to be of the *fcc* L1₀-lattice type as shown in Fig. 3.

Figure 4 shows the lattice parameter for Rh₁Mn_{1-x}Sb_x alloys where x is varied from 0.3 to 0.6. As can be seen from the figure, the crystal

Fig. 3 Crystal structure of L1_0 -type.

structures of alloys with $x=0.30\sim 0.33$ show the coexistence of the two phases of the L1_0 - and B2-types. The lattice parameter of the L1_0 -type is $a=4.200\text{ \AA}$, which is nearly constant against composition. On the other hand, higher Sb-concentration alloys with $x=0.50\sim 0.60$ show the coexistence of the two phases of the L1_0 - and B31-types, and the lattice parameter of L1_0 -type is almost constant at $a=4.182\text{ \AA}$. The crystal structures of intermediate alloys with $x=0.34\sim 0.45$ alloys out of the range of coexistence of the two phases are in the single phase state of the L1_0 -type. The values of the lattice parameter a in these alloys decreased linearly with increase in x , and both the lattice parameter c and the atomic ratio c/a increased appreciably with increase in x . The single-phase alloy No. 18 of the L1_0 -type which is nearest to

Fig. 4 Lattice parameters and axial ratios of $\text{Rh}_1\text{Mn}_{1-x}\text{Sb}_x$ alloys.

the stoichiometric composition has $a=4.182\text{ \AA}$, $c=3.467\text{ \AA}$, and $a, c/a$ ratio of 0.829.

Figure 1 shows the relation between the alloy phase and composition, where $\bigcirc$ indicates the single phase of the L1_0 -type, $\bullet$ the coexisting state of the L1_0 -type with an additional crystal structure type phase, and $\odot$ the single phase of the B2-type.

2. Magnetic properties

Figure 5 shows the relation between the saturation magnetization σ_s in a field of about

Fig. 5 Temperature dependence of saturation magnetization of $\text{Rh}_1\text{Mn}_{1-x}\text{Sb}_x$ alloys cooled at a rate of 50°C/hr after heating at 1000°C for 98 hr.

10.6 kOe and the temperature T for seven $\text{Rh}_1\text{Mn}_{1-x}\text{Sb}_x$ alloys with $x=0.34\sim 0.45$ slowly cooled after a homogenizing treatment at 1000°C for 98 hr. The saturation magnetization of these alloys is as low as about 3 emu/g for the composition at $x=0.34$, whereas the value of σ_s for the alloys with the compositions $x=0.36$ increases to about 10 emu/g at low temperature. Further, the alloy with the composition $x=0.37$ increases σ_s up to about 27 emu/g, and all the alloys with more than $x=0.40$ have constant σ_s values of about 50 emu/g at low temperature. The Curie points T_c in these alloys increase gradually with increase in x . The alloy with $x=0.45$ which is in the single phase of the L1_0 -type and is nearest to the stoichiometric composition shows the highest temperature of 330°K .

Figure 6 shows the composition dependence of the Curie point for the ten alloys containing those

Fig. 6 Curie points and magnetic moments in $\text{Rh}_1\text{Mn}_{1-x}\text{Sb}_x$ alloys.

in the two-phase state (a) and of the magnetic moment n_B per Mn atom, obtained by extrapolating the saturation magnetization to 0°K, for the alloys in the single phase of the L1_0 -type (b). As regards the relation between the Curie points and composition in (a), the Curie points of the alloys with the compositions $x=0.30$ and 0.33 are about 210°K and those of the alloys with $x=0.50$ and 0.45 have the temperature of 330°K. Next, the magnetic moments of the alloys with $x=0.36$ are as low as 1.4 μ_B , but a large increase in a moment with increase in Sb concentration is observed indicating the highest value of 3.20 μ_B in alloy No. 18 of the nearest stoichiometric composition. Since Mn and Sb atoms in alloy No. 18 of the L1_0 -type are arranged in a disorder state at the sites $0\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}0\frac{1}{2}$, the Mn–Mn pair is considered to possess three different Mn–Mn pairs⁽⁶⁾ interatomic distances of 2.89, 3.47 and 4.18 Å as shown in Fig. 7. However, according to the studies on ferromagnetic and antiferromagnetic Mn base compounds, fluorite-type compounds or Heusler-type compounds, the interatomic distances of these ferromagnetic and antiferromagnetic Mn–Mn pairs are experimentally assigned generally to be of the order of 2.89 and 4.18 Å. Consequently, if the two kinds of the Mn–Mn pairs in the alloys of the L1_0 -type have different magnetic moments and the directions of the spins in the Mn atom are antiparallel to each other, the alloys exhibit

Fig. 7 Distances of pair of Mn–Mn in L1_0 -type alloy $\text{Rh}_{1.00}\text{Mn}_{0.55}\text{Sb}_{0.45}$.

ferrimagnetic properties. Further, if one of the two Mn–Mn pairs is non-magnetic, these alloys appear to have ferromagnetic properties due to the spin of another pair.

In Fig. 8 is shown the relation between the magnetic susceptibility χ_g and the reciprocal susceptibility $1/\chi_g$ above the Curie temperature, and temperature for alloy No. 18 which is a representative *fcc* alloy in the system $\text{Rh}_1\text{Mn}_{1-x}\text{Sb}_x$. As can be seen from the figure, the values of $1/\chi_g$ between 550 and 800°C are varied linearly with temperature obeying a Curie-Weiss law, but at lower temperatures it decreases along the concave curve against transverse axis with decreasing temperature. Therefore, the paramagnetic Curie point θ_p of this alloy show

Fig. 8 Temperature dependence of magnetic susceptibility and reciprocal magnetic susceptibility of the alloy $\text{Rh}_{1.00}\text{Mn}_{0.55}\text{Sb}_{0.45}$.

the low $286 \pm 3^\circ\text{K}$, rather than the Curie point $T_c = 330^\circ\text{K}$. This result shows that this alloy may have some ferrimagnetic properties.

IV. Conclusions

X-ray diffraction and magnetic measurements have been performed on 29 Rh–Mn–Sb ternary alloys after sufficient homogenizing treatment at high temperatures. The obtained results are summarized as follows.

(1) The $\text{Rh}_{1.00}\text{Mn}_{0.55}\text{Sb}_{0.45}$ alloy have the crystal structure of the face-centered tetragonal L1_0 -type, in which the Rh sites are $(000, \frac{1}{2}, \frac{1}{2}, 0)$ and the Mn and Sb sites are $(0, \frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2})$. This alloy has a lattice parameter of $4.182 \text{ \AA}$, its axial ratio c/a being 0.829.

(2) The lattice parameters of $\text{Rh}_1\text{Mn}_{1-x}\text{Sb}_x$ with $x = 0.34$ to $x = 0.45$ in the single phase of the solid solution of the L1_0 -type range from 4.200 to $4.182 \text{ \AA}$. In the lower composition region μ_B $x = 0.34$ the alloys show the coexistence of the two phases of the L1_0 -type and the B2-type (RhMn), whereas in the higher

composition region than $x = 0.45$ the alloys show the coexistence of the two phases of the L1_0 -type and B31-type (RhSb).

(3) The saturation magnetic moment per Mn atom and the Curie point of the $\text{Rh}_{1.00}\text{Mn}_{0.55}\text{Sb}_{0.45}$ alloy are found to be $3.2 \mu_B$ and 330°K , respectively, this alloy has been assumed to have some ferrimagnetic properties from the relation between $1/\chi_g$ and temperature.

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