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FORMATION AND MAGNETIC PROPERTIES OF $Dy_2Fe_{17-x}Mn_xC(x = 0–17)$ PREPARED BY ARC-MELTING*

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We report on alloys formed by replacing iron with manganese in the compound $Dy_2Fe_{17}C_{1.0}$. Samples were characterized by X-ray diffraction and magnetic measurements. The 2:17-type structure can be crystallized in the whole range of manganese substitution. The Curie temperature of the series of $Dy_2Fe_{17-x}Mn_xC_{1.0}(x = 0–17)$ drops down considerably from 515 K for $x = 0$ to about 20 K for compounds with high manganese concentration, and the compensation point was observed in a narrow range of $x \approx 4–6$. The rapid decrease of the magnetization shows that the manganese substitution is not a simple magnetic dilution to the transition-metal sublattice moment, it indicates that the moment of Mn may be antiparallel to that of Fe. The field dependence of the magnetization of $Dy_2Fe_{17-x}Mn_xC_{1.0}$ may indicate the existence of the nonlinear magnetic structure for the samples with high Mn concentrations.

PACC: 7530C; 7550B

I. INTRODUCTION

The nitrides[1,2] and carbides[3,4] of R_2Fe_{17} intermetallic compounds (R=rare earth) have attracted more attention recently because introducing the interstitial atoms improves the intrinsic hard-magnetic properties significantly, and these materials are the expected candidates for permanent magnets. Unfortunately, these nitrides or carbides prepared by the gas-solid reaction are unstable at high temperatures, and decompose into rare-earth nitrides or carbides and α-Fe on heating to above 600°C. In order to obtain R_2Fe_{17}-type compounds which possess superior magnetic properties as well as better thermal stability, other methods have been adopted, such as the melt-spinning[5,6] and the substitution of iron.[7–9] Many studies[10–14] have been done on 2:17 compounds containing high concentration of the substitutive atoms to explore the effect of substitution on magnetic properties.

The Mn-based 2:17-type carbides $R_2Mn_{17}C_y(y = 1–3)$ have been reported by Block *et al.*[15] and Dirken *et al.*[16] It will be expected to form solid solutions $R_2Fe_{17-x}Mn_xC_y(y = 1–3)$ in the whole range of $x = 0–17$. In this work, we investigate the effect of Mn substituted for Fe in $Dy_2Fe_{17}C$ on its synthesis and magnetic properties in detail.

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II. EXPERIMENTAL

The alloys of $Dy_2Fe_{17-x}Mn_xC_{1.0}$ ($x = 2, 4, 6, 8, 10, 12, 14, 17$) were prepared by arc melting in a highly pure argon atmosphere according to the chemical compositions $Dy_2Fe_{17-x}Mn_{1.1x}C_{1.0}$. The raw materials used were highly pure (at least 99.9%), and an extra 10 at% of manganese were provided to compensate for the loss of it during melting. The phase component and the lattice parameters were deduced from X-ray diffraction using a Rikagu X-ray diffractometer with Cu$K\alpha$ radiation. Curie temperature T_C was inferred from the temperature dependence of the magnetization (i.e., M-T curve) measured under a field of 40 kA/m by use of the vibrating sample magnetometer for samples with T_C above 300 K and the extracting sample magnetometer for samples with T_C below 300 K. In order to observe the compensation point, M-T curves were recorded again for some samples at 40 kA/m from 1.5 to 300 K after the samples had been cooled to 1.5 K in an applied field larger than 3.2×10^6 A/m. M-H curves were recorded from zero up to 5.2×10^6 A/m at 1.5 K using the extracting sample magnetometer.

III. RESULTS AND DISCUSSION

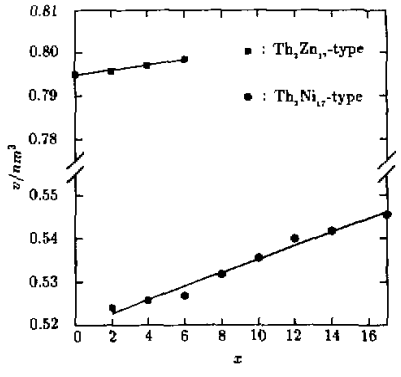

Fig. 1. The unit cell volume v of $Dy_2Fe_{17-x}Mn_xC$ as a function of the manganese concentration.

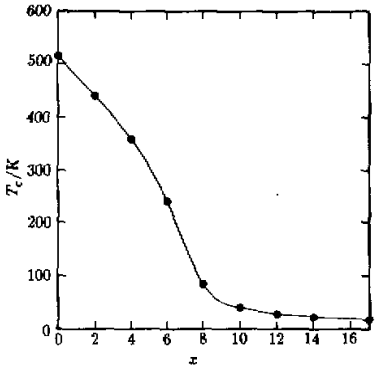

Fig. 2. The composition dependence of the Curie temperature T_C of $Dy_2Fe_{17-x}Mn_xC$.

X-ray analysis of the $Dy_2Fe_{17-x}Mn_xC_{1.0}$ ($x = 0$–17) powder specimens reveals that the main phase is 2:17-type for all samples. Moreover, there has been a change from the rhombohedral Th_2Zn_{17}-type for $x = 0$[3] to the hexagonal Th_2Ni_{17}-type for $8 \leq x \leq 17$, the coexistence region of these two structures being $x = 2$–6. The lattice constants a, c and the unit-cell volume v derived from X-ray diffraction are listed in Table 1. We can find that the unit-cell volume increases linearly with increasing manganese concentration (Fig. 1) although the lattice parameters a, c do not vary linearly. Some papers[5,11,14] have reported that the structure changes from Th_2Ni_{17}-type to Th_2Zn_{17}-type with an expansion of the

unit-cell volume caused by the interstitial atoms or the substitution element such as Ga, Al, etc. But it is contrary in the series of $Dy_2Fe_{17-x}Mn_xC_{1.0}$.

Figure 2 shows the manganese concentration dependence of the Curie temperature T_C of $Dy_2Fe_{17-x}Mn_xC_{1.0}$. It can be found that T_C drops drastically with slight deviation from straight line at an average rate of about 50 K per Mn atom for $x = 0$–8, then decreases much slowly as it approaches a lower limit of 20 K. This variation of T_C is similar to that in the series of $Er_2Fe_{14-x}Mn_xB$.[17] It is well known that Curie temperature is determined by the Fe-Fe, R-Fe and R-R interactions in the rare-earth iron intermetallic compounds, and the Fe-Fe interaction is dominant. Thus, the marvelous drop of T_C of $Dy_2Fe_{17-x}Mn_xC_{1.0}$ for $x = 0$–8 indicates that manganese decreases largely the transition-metal interaction. This may be due to the negative coupling between Mn and Fe. The T_C is determined by the Dy-Dy interaction in samples of high manganese concentration because the interaction in transition metal sublattice is almost negligible, so the change of T_C is small.

Table 1. The lattice parameters a and c, unit cell volume v, Curie temperature T_C, compensation temperature T_{comp} and magnetization M per unit formula at 1.5 K in an applied field 5.2×10^6 A/m for compounds $Dy_2Fe_{17-x}Mn_xC$.

x	Structure	a/nm	c/nm	v/nm^3	T_C/K	T_{comp}/K	$M/(\mu_B$/f.u.)
0*	Th_2Zn_{17}	0.8585	1.2454	0.7949	515		17.0
2	Th_2Zn_{17}	0.8586	1.2462	0.7956	440		10.4
	Th_2Ni_{17}	0.8516	0.8345	0.5241			
4	Th_2Zn_{17}	0.8598	1.2448	0.7970	359	23	−2.1
	Th_2Ni_{17}	0.8527	0.8351	0.5258			
6	Th_2Zn_{17}	0.8596	1.2475	0.7984	240	161	−3.5
	Th_2Ni_{17}	0.8539	0.8343	0.5268			
8	Th_2Ni_{17}	0.8563	0.8376	0.5319	84		−5.5
10	Th_2Ni_{17}	0.8573	0.8413	0.5355	40		−8.4
12	Th_2Ni_{17}	0.8601	0.8428	0.8399	28		−10.0
14	Th_2Ni_{17}	0.8617	0.8424	0.5417	23		−10.5
17	Th_2Ni_{17}	0.8631	0.8455	0.5455	18		−9.3

*Taken from Ref. [3].

The measurements of M-T curves of the samples at 40 kA/m, after having been cooled to 1.5 K in an applied field of 3.2×10^6 A/m, show the existence of compensation points: 23 K for $x = 4$ and 161 K for $x = 6$ (Fig. 3). At lower Mn concentration ($x = 0, 2$), the magnetization of the transition-metal sublattice is dominant at all temperatures. At higher Mn concentrations ($x \geq 4$), the transition-metal sublattice moment is smaller than the Dy-sublattice moment at 1.5 K. And for $x \geq 8$ the curie temperature is too low, the magnetization of the Dy-sublattice dominates the net magnetization. Only in a narrow range of the Mn concentration ($x \approx 4 - 6$), the two sublattice moments cancel out each other at a certain temperature (i.e., T_{comp}) because the Dy-sublattice moment decreases faster as a function of temperature than the transition-metal sublattice moment.

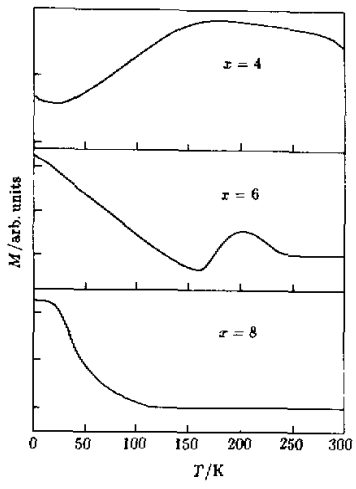

Fig. 3. Temperature dependence of the magnetization of $Dy_2Fe_{17-x}Mn_xC$ ($x = 4, 6, 8$) measured from 1.5 to 300 K by using the extracting sample magnetometer in an applied field of 40 kA/m. The samples were cooled to 1.5 K under a field greater than 3.2×10^6 A/m before measurement.

In Fig. 4 the field dependence of the magnetization at 1.5 K for several values of x can be seen. The sample with $x = 2$ shows nearly a saturation behavior, while a linear component of the magnetization is observed for $x = 4, 6$ and more complex magnetization procedure for $x \geq 8$. These samples with $x \geq 4$ are unsaturated in a high field of 5.2×10^6 A/m because the moments rotate away from their zero-field orientation in the lattice when a field is applied on samples. Such a behavior may be caused by (a) rotation of the net moments of Dy and transition-metal sublattices toward each other, or (b) nonlinear moment structure. In the pattern of the high resolution neutron diffraction at 10 K for $Er_2Fe_{14}Mn_3C$[18], there are not any additional diffraction peaks, thus we can conclude the magnetic moments of all atoms align linearly in the lattice of $Dy_2Fe_{17-x}Mn_xC_{1.0}$ with low Mn content. Therefore, the phenomenon of non-saturation of low Mn sample arises from the rotation of the net moments of Dy and transition-metal sublattices. In $Dy_2Fe_{17-x}Mn_xC$ with high Mn content, the dominant Dy-Dy interaction and the complex magnetic action of manganese would cause the nonlinear magnetic structure which results in the complex field dependence of magnetization.

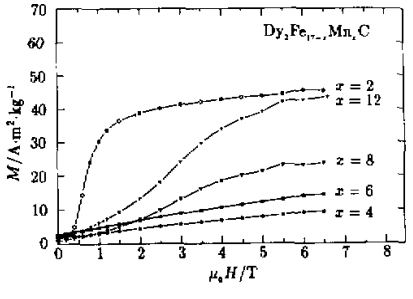

Fig. 4. The field dependence of the magnetization of $Dy_2Fe_{17-x}Mn_xC$ ($x = 2, 4, 6, 8, 12$) recorded at 1.5 K.

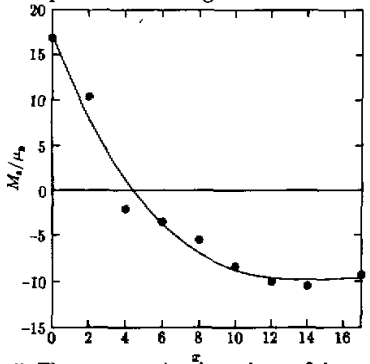

Fig. 5. The concentration dependence of the magnetization of $Dy_2Fe_{17-x}Mn_xC$ at 1.5 K in an applied field of 5.2×10^6 A/m. The line is provided as a guide to the eye.

Data of magnetization of $Dy_2Fe_{17-x}Mn_xC$, measured in an applied field 5.2×10^6 A/m at 1.5 K, are listed in Table 1, and the concentration dependence of it is plotted in Fig. 5.

Here, we have assumed that the net magnetization is negative if it is parallel to the rare-earth sublattice moments. In Fig. 5, it can be seen clearly that the magnetization decreases successively. The initial drop is faster than the case of simple magnetic dilution. This may be due to that the moment of manganese is antiparallel to that of iron.

IV. SUMMARY

The 2:17-type structure can be synthesized in the whole range of manganese substitution for iron in $Dy_2Fe_{17}C$. Curie temperature of $Dy_2Fe_{17-x}Mn_xC$ drops rapidly at a rate of about 50 K per Mn before $x = 8$, then slowly as it approaches a lower limit of 20 K per Mn, indicating that Mn reduces the interaction of the transition-metal significantly with increasing Mn concentration until the Dy-Dy interaction dominates. Magnetization decreases faster than that in the case of simple magnetic dilution with low Mn concentration, possibly resulting from the antiferromagnetic coupling between Mn and Fe. Collinear magnetic structure for samples with low Mn concentration can be concluded from neutron powder diffraction, while the complex field dependence of the magnetization implies the nonlinear magnetic structure for samples with high Mn concentration.

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