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Preparation and magnetic property

of MN_y (M=Mn, Co, Ni)

Mitsuharu Tabuchi

Osaka University February, 1994

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Chapter 1 General introduction

1. Historical background of this study

"Nitride" is the compound consist of nitrogen and metal elements (M). Metal nitrides are classified by bonding nature into three categories, i.e., ionic nitride, covalent nitride and interstitial nitride. The constituent elements of ionic nitrides are alkaline and alkaline earth metals. The chemical formula of most ionic nitrides are given by M_3N or M_3N_2 and their chemical compositions are close to be stoichiometric. In ionic nitride, the valence state of nitrogen is only minus three as N^{3-} . The ionic nature of M–N bonding reflects their characteristic properties such as high melting point in nitrogen atmosphere (Ca₃N₂ (1173K), Mg₃N₂ (1573K)), ionic conductivity and easy oxidation in air.

Covalent nitrides refer to the compounds containing later metals than copper in the periodic table. Most of these nitrides possess the stoichiometric composition as predicted from the valence of constituent elements, as well as ionic nitrides. The crystal structures of AlN, BN and GaN are wurtzite-type structure with M_4N tetrahedron. Such the structural feature in AlN, BN and GaN suggests the covalent nature of metal-nitrogen bonding. The electronic properties of covalent nitrides are characterized to be semiconductor or insulator. Covalent nitrides are stable in air compared with ionic nitrides and have high melting point or high decomposition temperature (AlN (2473K), Si₃N₄ (2173K), etc.).

Transition metal nitrides (MN_y) are so-called interstitial nitrides. Most of MN_y have crystal structures such as NaCl type (TiN, VN), anti-NiAs type (Fe₂₋₃N, Cr₂N) anti-perovskite type (Fe₄N) structures and so on, in which M atoms form the nearly closest packed structure such as hcp or fcc and N atoms occupy partially the octahedral interstitial sites of M lattice as shown in Fig. 1. MN_y can possess the variety of crystal phases with the large nonstoichiometry compared to other nitrides. Various crystalline phases of 3d transition metal nitrides MN_y have been reported [1] and are shown in Table 1. The



Fig. 1. Representative 3d transition metal nitrides M_4N (a), $M_{2-3}N$, M_2N (b) and MN (c). Open and closed circles denote 3d metal (M) and nitrogen (N), respectively. M_6N octahedron are also shown in this figure. Octahedral interstitial sites are indicated in (b) by crosses. representative crystal structure of MN_y are classified into three categories, M_4N (anti-Perovskite type structure), $M_{2-3}N$ (anti-NiAs type structure) and MN (NaCl type structure), as shown in Table 1. CoN [2] and FeN [2] possess zincblende type structure with M_4N tetrahedron and differ from other nitrides such as TiN and VN with NaCl-type structure. Covalent nature of M-N bonding in MN_y is presumed by the crystal structure of CoN and FeN. MN_y exhibits diverse properties such as high melting point (e.g., TiN (3223K), ZrN (2973K)), brittleness, electric conductivity, superconductivity (NbN, TiN, MoN), ferromagnetism (Fe₄N, Fe₁₆N₂) and antiferromagnetism (CrN). These properties result from the coexistence of M-M bonding and M-N bonding in MN_y . In particular, 3d metal nitrides (MN_y) have the diversity of magnetic properties. Table 2 depicts the magnetic properties of MN_y ($0 \le y \le 1$) [4–18]. The magnetism of most of 3d metal nitrides but for CoN_y and NiN_y are consistent with the magnetism of their mother metals as shown in Table 2.

 $Cr_2N_{0.88}$ differ from Cr and CrN in the magnetism [4]. CrN exhibit the structural change at Néel temperature. The low temperature phase of CrN has an orthorhombic lattice with a deformed NaCl-type structure [19]. Antiferromagnetic structure of Mn_3N_2 was determined previously [6]. However, magnetic transition temperature (T_{mag}) of Mn_3N_2 and the magnetism of Mn_6N_5 is still unresolved.

The investigation of magnetic property of 3d metal nitrides has been focused mainly on the iron nitrides. Most of FeN_y exhibits ferromagnetism analogous to α -Fe (bcc) but the magnetism of FeN_y in which Fe atoms take hcp or fcc lattice differs from antiferromagnetism of γ -Fe (fcc) and ϵ -Fe (hcp). The difference in the magnetism between Fe₄N and γ -Fe was explained by magnetovolume effect, i.e., the lattice expansion accompanied by inclusion of N atoms caused the increase in magnetic moment per a metal atom (μ_M) and Curie temperature (T_c) of Fe₄N [20]. The magnetovolume effect has been also observed on Y₂Fe₁₇N_y and Y₂Fe₁₇C_y as shown in Fig 2 [21]. It has been reported

Τi	V	C r	M n	Fe	Со	Ň i	
 	(Fe ₁₆ N ₂)						
			Mn ₄ N	Fe ₄ N	(Co_4N)	(Ni ₄ N)	
Ti ₂ N	V_2N	C r ₂₋₃ N	M n ₂₋₃ N	F e ₂₋₃ N	C o 3 N	Ni ₃ N	
				Fe ₂ N	Co_2N	N i 2N	•
			Mn ₃ N ₂				
ΤiΝ	VN	CrN	Mn ₆ N ₅	(FeN)	(C o N)		

Table. 1 Crystal structure of 3d transition metal nitrides. The compounds designated in parentheses are only obtained by non-thermalequilibrium reaction processes.

Compounds	Structure	Magnetism	T _{mag} /K	$\chi \times 10^6$ / cm ³ g ⁻¹	μ _м /μ _в	μ.,,/μв	Ref.
TiN	NaC1	PP	-	1. 0	-	ICW	
Ti	hcp	PP	-	3. 2	-	ICW	
		· <u>·</u> ··································					
VN	NaC1	PP		2.0	-	ICW	
V2N0.88	ε-Fe ₂₋₃ N	PP	-	3. 7	-	ICW	
Ŷ	bcc	PP	~	4.5	-	ICW	
CrN	NaCl	AF	283	3. 98	2.4 (77K)	ICW	<u>. </u>
Cr ₂ N _{0.88}	ε-Fe₂-₃N	PP	-	5.25	-	ICW	
Cr	bcc	AF	311	3.17	0.4	ICW	
Mn ₆ N ₅	Mn: fct-fcc N : ambiguous	_	-	_	_	-	[5]
Mn ₃ N ₂	Mn: fct N : ordered	AF	-	9.2	4.3, 3.4 (11K)	-	[6]
Mn ₂ N	ζ -Fe ₂ N(ortho)) AF	301	15	1.6	ICW	[7]
Mn₄N	Fe ₄ N	FI	738	-	3. 85	ICW	[8]
•	•				0.9 (77K)		
γ -Mn	fct-fcc	AF	480	8.5	2.4	ICW	
α -Mn	α -Mn	AF	95	8.9	1.9, 1.7,	ICW	
					0.6, 0.2.		
FeNo. o	Zinkblende	Р	-	15	-	1.7	[3]
Fe₂N	ζ-Fe₂N(ortho)	F	4	2.9	0.13	3.0	[9]
Fe2N0.78	ε-Fe ₂₋₃ N	F	398	-	1.9, 0.7	D	[7, 10]
Fe₄N	Perovskite	F	761	D	3.0, 2.0	D	[11]
Fe ₁₆ N ₂	Fe: bct	F	813	D	1.36, 2.56	, D	[12]
	N : ordered				3.86.		
ε-Fe	hcp	AF	100	-	0.1	ICW	
γ-Fe	fcc	AF	115	-	0.6	ICW	
α-Fe	bcc	F	1043	-	2.2	3. 20	
CoN	Zinkblende or NaCl	-	-	.	-	-	[2, 13]
CoaN	Anti-CaCl	_	-	- *	-	-	[14]
CO3N1 55	ε-Fe _{2-a} N	AF	11	23	-	3	[15]
CoaN	Fe₄N	F	D	-	-	-	[16]
Co	hcp-fcc	F	1388	-	1.7	3.15	2-02
Ni ₂ N	Ni:bct	Р	-			0.14	[17]
N1: N1	N: ordered	D			0 10		נטז י
N13N1.16	$\varepsilon - f e_{2-3} N$	r	-	· -	0.13	-	[9] [10]
191419 N i	re₄N foo	- F	-		0.6	-	, LIQ]
111	100	Г	021	-	U. 0	1.01	

Table 2 Crystal structure and magnetic properties of MN_y $(0 \le y \le 1)[4]$.

 T_{m*g} ; Magnetic transition temperature (K), χ ; Magnetic susceptibilities (cm³/g) at 300K, μ_M ; Magnetic moment per a metal atom (μ_B), μ_{eff} ; Effective magnetic moment per a metal atom.

P; Paramagnetism, PP; Pauli paramagnetism, AF; Antiferromagnetism, FI; ferrimagnetism, D; Decomposition at high temperature, ICW; Independence of Curie-Weiss law.

 T_{m*e} of Fe₁₆N₂ were estimated by temperature dependence of magnetization below 673K. Plural values of μ_M for Mn₃N₂, Mn₄N, Fe₂N_{0.78}, Fe₄N and Fe₁₆N₂ are attributed to the presence of different metal sites in their structures. that the insertion of small atoms such as H, C and N, into the R₂Fe₁₇ compounds (R=Y and rare earths) produce the volume expansion which increases the magnetic interaction between iron atoms and elevates Curie temperature of the compounds [21]. The increase in magnetic moment of Fe–N martensite with increasing nitrogen content has been explained by the use of the magnetovolume effect [22]. Values of T_c and μ_{Fe} of FeN_y with $y \le 0.5$ have been found to decrease with increasing y [4], as shown in Fig. 3. Mekata *et al.* [23] concluded that the N atoms suppressed magnetic ordering in consequence of the reduction of their magnetic moments. However, it has been found recently that the magnetic properties of FeN_y with y > 0.5 deviate from those tendency in the composition range of $y \le 0.5$ [3].

Recently, Kim and Takahashi reported first that $Fe_{16}N_2$ exhibited a giant magnetic moment ($\mu_{Fe}=2.9\mu_B$) [24]. Since this finding, much interest have been paid on $Fe_{16}N_2$. The crystal structure of $Fe_{16}N_2$ is shown in Fig. 4 [25], and $Fe_{16}N_2$ have the three magnetic moments (1.3, 2.5 and $3.8\mu_B$) corresponding to the different Fe sites [26] in analogy with Fe_4N . The spin polarized band calculations for $Fe_{16}N_2$, Fe_4N and Fe_3N have been carried out [27].

While a little investigation has been reported on Co and Ni nitrides so far. The magnetic properties of Co_{N} have been rarely studied except those of Co_{3} N [15] and Co_{4} N [16]. The chemical composition of Co_{3} N [15] was reported to be Co_{3} N_{1.55} and deviates from that of previous data [28]. The lattice parameter of Co_{4} N [16] was quite small, compared to that of Co_{4} N_{1.0} [1] and is close to that of fcc-Co. The magnitude of the magnetization for Ni₃N_{1.16} has been reported to be compatible with paramagnetism {9], but the detailed magnetic property has not been reported so far.



Fig. 2. Volume (V) dependence of Curie temperature (T_c) of $Y_2Fe_{17}N_x$ (\blacktriangle) and $Y_2Fe_{17}C_y$ (\bullet) [21]. The broken line represents the volume dependence of Y_2Fe_{17} .



Fig. 3. Plots of the magnetic moments (μ_{Fe} : O) and Curie temperature (T_c : ×) against the nitrogen contents of FeN_y (y≤0.5) [4].



Fig. 4. Crystal structure of $Fe_{16}N_2$ [25]. Open and closed circles denotes Fe and N atoms, respectively.

• : :

2. Purpose of this study

Although numerous investigations in connection with the magnetic properties of 3d metal nitrides have been carried out so far, as described above, there remains several problems about the effect of nitrogen content on the magnetism of MN_y . N atoms in MN_y have been said to suppress magnetic ordering in consequence of the reduction of their magnetic moments [23]. This concept can explain the decrease in the magnetic moment and magnetic transition temperature with increasing nitrogen content in Fe₂₋₃N [23] (See Fig. 3.). However, the magnetic moment and magnetic transition temperature of Fe₄N and Fe₂N_{0.78} is larger than γ -Fe and ϵ -Fe, respectively, as shown in Table 2, can not be explained by this concept. This tendency has been well explained by the use of another concept, "magnetovolume effect". The effect of the nitrogen content on the magnetic properties of MN_y has been interpreted coordinately. That is, some idea besides two concepts is required to understand the effect of nitrogen content on the magnetic properties of MN_y .

In this work, it is purposed that the effect of nitrogen content on the magnetic properties of MN_y are understood comprehensively. In order to achieve this purpose, the following problems were elucidated systematically, (1) the determination of the factors which govern magnetic transition temperature, (2) the relation between the magnetic moment per a metal atom and N-coordination number and (3) the effect of the number of valence electrons per a metal atom on the magnetic properties.

In order to resolve these problems, the factors governed the magnetic transition temperature were first examined in MnN_y , because of the presence of various equilibrium phases over the wide range between 0 and 1 as compared to CrN_y , FeN_y , CoN_y and NiN_y . The determination of T_{mag} for Mn_3N_2 and Mn_6N_5 was carried out through measurements of temperature dependence of magnetic susceptibility, because the magnetic properties of Mn_6N_5 and Mn_3N_2 have not been clarified in detail. These results is described in chapter

2. The idea obtained by the examination of the factors affected the magnetic transition temperature of MnN_y , i.e., the relation between the magnetic transition temperature and the magnetic moment, is extended to other nitrides in chapter 3. The effect of number of valence electrons per a metal atom on the magnetic properties is investigated in chapter 4 by the use of $M_{2-3}N$ and M_2N which exist over the many kinds of 3d metals. Temperature dependence of magnetic susceptibility for Co_3N , Co_2N and Ni_3N were also studied because of the lack of their magnetic property. Furthermore, MnN_y films with various nitrogen content prepared by reactive vapor deposition method and the effect of ordering of nitrogen atoms on the electrical property are examined through temperature dependence of electrical resistivity of MnN_y film (chapter 5). Finally, in chapter 6 is given the general discussion which based on the information of chapter 2, 3, 4 and 5.

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Chapter 2 Relation between magnetic transition temperature and magnetic moment for manganese nitrides MnN_y (0<y<1)

1. Introduction

The magnetic properties of transition metal nitrides MN_y are similar to those of their mother metals [1]. In particular, some of iron nitrides FeN_y exhibit ferromagnetism in analogy with the magnetism of α -Fe. The magnetic properties of iron nitrides FeN_y, such as Fe₄N [2], Fe₂₋₃N [1] and Fe₂N [1] have been well studied so far. Curie temperatures T_c for FeN_y ($y \le 0.5$) show a tendency that T_c decrease with increasing y [1, 3]. However, it has been found recently that one of phases of FeN_y with y>0.5 indicates a deviation from the tendency in the composition range of $y \le 0.5$ [4]. The study on magnetic properties of FeN_y (y>0.5) has been rarely investigated because FeN_y with y>0.5 are formed only by applying non-thermal equilibrium reaction processes. In the case of chromium nitrides CrN_y, only Cr₂N and CrN exist, respectively, as the phases on the Cr-N phase diagram and as regards cobalt nitrides CoN_y and nickel nitrides NiN_y, only Co₃N, Co₂N and Ni₃N are stable phases in the Co-N and the Ni-N system. Consequently, discussions on the relation between the magnetic properties of metal nitrides and their nitrogen content, y have been restricted within the range of y less than 0.5.

On the other hand, the various crystal phases of MnN_y with a variety of nitrogen content, such as Mn_4N , $Mn_{2-3}N$, Mn_3N_2 and Mn_6N_5 were reported on the Mn--N phase diagram [5]. The magnetic properties of Mn_4N [6, 7] and $Mn_{2-3}N$ [1, 8] which have, respectively, the similar crystal structures as those of Fe₄N and Fe₂₋₃N were clarified previously. The antiferromagnetic structure of Mn_3N_2 below 291K was analyzed by unpolarized neutron diffraction measurements at 11 and 291K, and also by magnetic susceptibility measurement between 3.5K and room temperature [9], but magnetic transformation temperature of Mn_3N_2 was not determined. The magnetic property of

 Mn_6N_5 was still remains unresolved. In this work, the magnetic properties of both Mn_3N_2 and Mn_6N_5 were clarified by magnetic susceptibility measurements from 100K to 958K, and then the magnetic transition temperature T_{mag} of MnN_y with y ranging from 0 to 1 was discussed in connection with the shortest Mn–Mn distance and the magnetic moment per a Mn atom.

2. Experimental

 Mn_6N_5 were prepared by heating α -Mn powder (99.9% in purity, Furuuchi Chemical Co.) at 873K for 3h in NH₃ gas flow, followed by annealing at 673K for 20h in the same atmosphere. Mn_3N_2 was obtained by heating α -Mn at 873K for 3h in NH₃ gas flow, followed by annealing in H₂ flowing at 873K for 1.5h. MnO, existed as a second phase in Mn_6N_5 and Mn_3N_2 was removed by washing with successive HCl aqueous solution, distilled water and ethanol. The concentration of HCl aq. solution used was 1.0 moldm⁻³ and 0.1 moldm⁻³ for Mn_6N_5 and Mn_3N_2 , respectively.

The identification of products was carried out using a X-ray diffractmeter (CuK α radiation, Rotaflex/RINT, Rigaku Co). The lattice parameters of products were obtained from X-ray diffraction (XRD) measurement using silicon as an internal standard. The nitrogen and oxygen contents in products were determined by means of the apparatus for nitrogen and oxygen analysis (EMGA-2800, Horiba Co.).

The magnetic susceptibility of a sample was measured at 10.5kOe by a Faraday balance (MB-3, Shimazu Co.) in He atmosphere between 100 and 300K and in N₂ atmosphere between 300 and 958K, respectively. Mn Tutton's salt was used as a standard substance of magnetic susceptibility. The temperature was calibrated by magnetic transition temperatures of MnO (117.8K [10]), Ni (631.0K [10]) and α -Fe₂O₃ (953K [10]) used as standard materials. As trace amounts of spontaneous magnetization σ_s from ferromagnetic impurity was observed, the external magnetic field dependence of the

magnetization σ of samples was measured at 80K, 300K, and in the vicinities of 740K and of 950K, respectively. The values of saturation magnetization σ_s of the ferromagnetic impurity was evaluated from the value of σ extrapolated to zero magnetic field, H=0 in the $\sigma-H$ curve between 1.8 and 12.5kOe at each temperature.

Thermal gravimetry and differential thermal analyses, TG–DTA measurements for Mn_6N_5 and Mn_3N_2 were accomplished by using the instrument for thermal analysis (TG81110, Rigaku Co.) between 300 and 973K under N_2 gas flow and Ar gas flow, respectively.

3. Results and discussion

3.1 Structure, composition and magnetic susceptibilities of Mn_6N_5 and Mn_3N_2

Powder XRD patterns of Mn_6N_5 and Mn_3N_2 are shown in Fig. 1 (a) and (b), respectively. All diffraction lines of Mn_6N_5 could be indexed with a face centered tetragonal (fct) cell and those of Mn_3N_2 was indexed with three fold fct cell along the caxis direction as reported previously [11], showing that ordering of nitrogen atoms in the fct Mn lattice took place in Mn_3N_2 . The chemical composition of both samples was determined to be $Mn_6N_{5.35}$ and $Mn_3N_{1.93}$ by nitrogen and oxygen analysis. These values agreed, respectively, with $Mn_6N_{5.32}$ and $Mn_3N_{1.91}$ evaluated from the relationship between lattice parameter and composition of MnN_y [12].

The DTA measurements of both Mn_6N_5 and Mn_3N_2 indicated that they took place the phase transition at 660–663K and 913–923K, respectively. Otsuka *et al* [13] found that Mn_6N_5 films transformed from fct to fcc at 683 ± 20 K by the electron diffraction measurement, and Jacobs and Stübe [11] observed the reversible phase transition of Mn_3N_2 at 903–928K by means of DTA measurement. The phase transition temperatures observed in this work agreed with these previous results. Mn_3N_2 possesses the fct structure of Mn atoms with the ordering of nitrogen atoms. Therefore, it could be presumed that crystal



Fig. 1. Powder X-ray diffraction patterns of Mn_6N_5 (a) and Mn_3N_2 (b). In (a), all diffraction peaks were indexed as Mn taking fct cell ; a=0.4221nm, c=0.4137nm, c/a=0.980. In (b), all diffraction peaks were indexed as Mn taking three fold fct cell along c-axis direction ; a=0.4205nm, c=1.2128nm, c/a=0.961.

ructure transformation like order-disorder transition or fct-fcc transition such as Mn_6N_5 occurred in Mn_3N_2 .

Fig. 2 depicts the temperature dependence of the magnetic susceptibilities χ of Mn₆N₅ and Mn₃N₂ from 100 to 958K on heating process. Values of σ_s at room temperature of ferromagnetic impurity in Mn₆N₅ and Mn₃N₂ were estimated to be 0.025–0.031 and 0.030– 0.084Gcm³/g by extrapolation to a zero field from σ -H curves, respectively. T_c of the ferromagnetic impurity was observed to be about 740K indicating that the ferromagnetic impurity was Mn₄N (T_c =738K, σ_s =27.0Gcm³/g [2. 7, 10]). An amount of Mn₄N in Mn₃N₂ or Mn₆N₅ was evaluated to be less than 0.3% by the values of σ_s . The magnetic susceptibilities of Mn₆N₅ and Mn₃N₂ were calculated after correcting the observed value with σ_s . The magnetic susceptibilities of Mn₆N₅ and Mn₃N₂ at 298K were

 $(10.6\pm0.2)\times10^{-6}$ cm³/g and $(7.5\pm0.5)\times10^{-6}$ cm³/g, respectively. That for Mn₃N₂ was close to the previously reported value of 9.2×10^{-6} cm³/g [9].

As shown in Fig. 2, a slightly swelled part around 750K in the χ -*T* curve of Mn₃N₂ on heating was probably due to the small amount of Mn₄N (T_c =738K) [2, 7, 10]. Except this region, χ -*T* curves indicate maxima in the temperature ranges of 655 to 660K for Mn₆N₅ and 914 to 936K for Mn₃N₂, respectively. The same maxima are also found in the χ -*T* curves on cooling in the temperature range of 627 to 636K and 859 to 869K for Mn₆N₅ and Mn₃N₂, respectively. It is found from the χ -*T* curves that the magnetism of both Mn₃N₂ and Mn₆N₅ is antiferromagnetic. This results on Mn₃N₂ is consistent with the magnetic structure of Mn₃N₂ [9]. Each maximum point in the χ -*T* curves of Mn₆N₅ and Mn₃N₂ was close to each phase transition temperature of 660–663K and 913–923K obtained by DTA, respectively. Therefore the temperature. However many evidences that the magnetic transition temperature is comparable to the phase transformation temperature have been observed, e.g. on γ -Mn [14–16], MnPt [17], Mn₃GaN [18] CrN [19] and so



Fig. 2. Temperature dependence of magnetic susceptibility for Mn_6N_5 and Mn_3N_2 . Arrows indicate the maximum point in χ -*T* curve. χ for Mn_6N_5 and Mn_3N_2 were obtained by correction of σ_s . σ_s in Mn_6N_5 and Mn_3N_2 powder obtained from values of σ extrapolated to zero magnetic field, *H* in σ -*H* curves at various temperatures, respectively, see text.

TABLE. 1 Crystal structure, shortest Mn-Mn distance r_{Mn-Mn} , magnetism, magnetic transition temperature T_{mag} , and magnetic moment per a Mn atom, μ_{Mn} for γ -Mn and MnN_y.

Species	Crystal structure	$r_{\rm M}$ $\gamma_{\rm m}/\rm nm$	Magnetism	<i>T</i> /K	$\mu_{\rm M}/\mu_{\rm P}$
-		MI-MI		- mag	
γ–Mn	fct (<480K)	0.2592	Antiferro	480	2.4 (0) at 0K
	fcc (>480K)				,
		••			
Mn₄N	Fe₄N type	0.273	Ferri	738	3.85 (0)
					0.9 (2) at 77K
Mn ₂ N	ζ-Fe ₂ N type	0.2797	Antiferro	301	1.6 (3) at 120K
Mn ₃ N ₂	Mn: fct at 295K	0.2916	Antiferro	≧925±11	4.3 (2)
	N · ordered				34 (5) at 11K
					5.1 (5) u 111
Mn_6N_5	Mn : fct (<683±20K)	0.2955			
	fcc (>683±20K)		Antiferro	≧655±3	unknown
	N : ambiguous	·			

The value of r_{Mn-Mn} correspond to the shortest Mn-Mn distance in a plane parallel to the c-axis. In the μ_{Mn} column, the number of nitrogen atoms neighboring a Mn atom with the value of μ_{Mn} , z_N are designated in parentheses.

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on. Mn_6N_5 and Mn_3N_2 as well as γ -Mn seem to take place the magnetic transition accompanied by the structural change. Néel temperatures of Mn_6N_5 and Mn_3N_2 were estimated to be 655-660K and 914-936K, respectively. Such the fact that each magnetic transition temperatures on cooling is lower than each on heating of Mn_6N_5 and Mn_3N_2 , may reflect the hysteresis accompanying the structural change. In subsequent sections, the Néel temperatures of Mn_6N_5 and Mn_3N_2 on heating are used as magnetic transition temperature T_{mag} .

3.2 Consideration with respect to magnetic properties of MnN_y with 0 < y < 1

Though it was clarified that Mn_4N possess the band like electronic structure, electronic structure of other MnN_y is not still revealed. The magnetic transition temperature T_{mag} is generally represented by molecular field theory based on localized spin model [20] as follows,

$$T_{mag} = \frac{2z |J_{M-M}| S(S+1)}{3k}$$
(1).

Where z represent the coordination numbers, J_{M-M} is the exchange coupling constant between the nearest neighboring magnetic atoms, S is spin quantum numbers, and k is Boltzmann constant. In the case of 3d transition metal, the term S(S+1) is equals to the square of magnetic moment per a metal atom, μ_M^2 .

 $T_{\rm mag}$ and $\mu_{\rm Mn}$ of MnN_y and γ -Mn are given in Table 1 with the shortest Mn-Mn distance, $r_{\rm Mn-Mn}$ and with the crystal structure of them. The values of $r_{\rm Mn-Mn}$ correspond to the shortest Mn-Mn distance in a plane parallel to the c-axis. Where the crystallographic data and magnetic properties of γ -Mn [14-16], Mn₄N [2, 6, 7] and Mn₂N [8], $\mu_{\rm Mn}$ of Mn₃N₂ [9], and the phase transition temperature of Mn₆N₅ [13] were referred to those of published data.

The values of r_{Mn-Mn} of γ -Mn and MnN_y differed from each other in Table 1. As

the relation between y and r_{Mn-Mn} of MnN_y ($0 \le y \le 1$) was revealed, the r_{Mn-Mn} for them were plotted against the nitrogen content y, as shown in Fig. 3. The r_{Mn-Mn} of $Mn_{2-3}N$ were calculated from the lattice parameter of the previous data [5]. It is found from Fig. 3 that there is a linear relationship between y and r_{Mn-Mn} in spite of different crystal structure.

In order to discuss the variation of T_{mag} with the r_{Mn-Mn} for MnN_y , the magnetic transition temperature are plotted against each shortest M-M distance (M=Mn, Fe, Co) on Mn_6N_5 , Mn_3N_2 , $Mn_{2-3}N$ [1, 8], Mn_4N [6, 7] and manganese alloys with fcc or fct lattice, such as y-Mn [14-16], MnNi [17], MnPd [17], MnPt [17], CoMn [21], FeMn [22], $Mn_{3}Rh$ [23], $Mn_{3}Pt$ [23], $(CoMn)_{0.75}Fe_{0.25}$ [21], $Fe_{0.82}Mn_{0.14}C_{0.04}$ [24] and $Fe_{0.89}Mn_{0.07}C_{0.04}$ [24] as shown in Fig. 4 (a). Adachi et al. [21] found that T_{mag} of disordered antiferromagnetic fcc alloys increase with increasing their lattice parameter. Their observation corresponds to the change of T_{mag} against $r_{\text{M-M}}$ ranging from 0.25 to 0.257nm in Fig. 4 (a). The data of Mn alloys in Fig. 4 (a) are rather scattered, but there is obviously the trend that T_{mag} of alloys with $r_{M-M} < 0.27$ nm increase with an increase in r_{M-M} , but T_{mag} of the alloys with r_{M-M} >0.27nm decrease with increasing r_{M-M} . The T_{mag} vs r_{M-M} plots for Mn₄N, Mn₃N₂ and Mn_6N_5 with fct or fcc lattice are found to exist in a convex band appeared in the T_{mag} vs r_{M-M} plots for the Mn alloys. However, the T_{mag} vs r_{M-M} plots of Mn₂₋₃N which have Mn lattice near to hcp deviate from the convex band for Mn alloys in Fig. 4 (a). By Cluster-Variation method on the basis of Ising model of ferromagnetism in fcc Pt-Mn alloys, Sato [25] found that $|J_{Mn-Mn}|$ became smaller with an increase in the ratio of atomic distance to d-shell radius, r/R. It is predicted by this concept and eq. (1) that T_{mag} decrease However, the result shown in Fig. 4 (a) is monotonously with increasing r_{M-M} . inconsistent with the above prediction. Some factors other than $|J_{M-M}|$ are required to interpret the tendency in the T_{mag} vs

r_{м-м} plot.



Fig. 3. The relation between nitrogen content y and the shortest Mn–Mn distance, r_{Mn-Mn} . Closed circle denotes that Mn has fcc or fct lattice, and closed triangle denotes that Mn takes hcp lattice. The values of r_{Mn-Mn} correspond to the shortest Mn–Mn distance in a plane parallel to the c-axis. The dashed line indicates the line obtained by least square fitting between y and r_{Mn-Mn} with 0.986 of correlation coefficient.



Fig. 4. Plots of magnetic transition temperature T_{mag} (a) and magnetic moment per a metal atom μ_{M} (b) against the shortest M-M distance r_{M-M} (M=Mn, Fe and Co) for MnN_y and Mn alloys with fcc or fct lattice. Small circle denotes T_{mag} vs r_{M-M} or T_{mag} vs r_{M-M} plots for Mn alloys. In Fig. 4 (a), the values of r_{Mn-Mn} for MnN_y was taken from Table. 1 and T_{mag} vs $r_{\text{Mn-Mn}}$ plots for Mn₂₋₃N were from previous data. The part which is surrounded with dashed lines in Fig. 4 (a), shows the correlation between T_{mag} and $r_{\text{M-M}}$. The larger value of μ_{Mn} as shown in Table. 1 utilizes as μ_{Mn} of each Mn_4N and Mn_3N_2 . The part which is surrounded with dashed lines in Fig. 4 (b) exhibits the correlation between $\mu_{\rm M}$ and r_{M-M} .

According to eq. (1), the magnetic moment per a M atom (M=Mn, Fe, Co), μ_M is thought as a factor responsible for T_{mag} of MnN_y and alloys. The magnetic moments of a M atom in MnN_v and the manganese alloys with fcc or fct lattice are plotted against the r_{M-M} in Fig. 4 (b). The value of μ_{Mn} for Mn_6N_5 was estimated to be 3.4 μ_B [9] which correspond to smaller one of $\mu_{Mn}(z_N=5)$ for Mn₃N₂ in Table. 1, because a Mn atom in Mn_6N_5 with tetragonally distorted NaCl structure [9, 13] have probably five nearest neighboring nitrogen atoms. In both cases of Mn₄N and Mn₃N₂, Mn atoms with two different lattice sites has been observed as shown in Table 1. The magnetic moment of the Mn atom with smaller N-coordination number z_N is larger than that of Mn atom with The value of μ_{Mn} in MnN_y may be affected by the larger N-coordination number. formation of Mn-N bond and also by the expansion and deformation of lattice accompanied by an increase in its nitrogen content. Such facts were observed previously in Fe-N and Fe-C system. In α '-martensite [26], though the magnetic moment of Fe atom adjacent to nitrogen or carbon atoms decrease by the formation of Fe-N and Fe-C bonds, those of the second or third neighboring Fe atoms also increase by the expansion and deformation of lattice. Nakajima et al. [27] found that Fe atoms at remoter lattice sites from nitrogen atoms in $Fe_{16}N_2$, have the larger magnetic moments. The mechanism which $\mu_{\rm Fe}$ of a Fe atom with smaller N-coordination number is larger than that of a Fe atom with larger N-coordination number will be described by exemplifying Fe₄N in appendix. Sakuma [28] calculated the density of state for Fe_4N , Fe_3N and $Fe_{16}N_2$ using the linearized muffin-tin orbital (LMTO)-the atomic sphere approximation (ASA) method and concluded that the N atom is to bring about the large magnetic moments through lattice expansion (magnetovolume effect) and prevent the exchange-splitting by promoting the itineracy of electrons. If the larger μ_{Mn} were used for Mn₄N and Mn₃N₂, the relation between μ_{Mn} and r_{Mn-Mn} is similar to that between T_{mag} and r_{M-M} . However, a remarkable deviation from the tendency in the μ_M vs r_{M-M} plot is observed using the small and

averaged μ_{Mn} for Mn₄N and Mn₃N₂. Consequently, the large μ_{Mn} for Mn₄N and Mn₃N₂ were adopted in the μ_M vs r_{M-M} plot in Fig. 4 (b).

From Fig 4, $\mu_{\rm M}$ was presumed to contribute more greatly to $T_{\rm mag}$ than $|J_{\rm M-M}|$ of MnN_y and Mn alloys. In the case of Mn alloys, $T_{\rm mag}$ is sensitively affected by the coordination number of magnetic atoms and the degree of ordering of Mn and non-magnetic atoms, depending on chemical composition of Mn alloys. Therefore, the relation between $T_{\rm mag}$ and $\mu_{\rm M}$ is shown only for MnN_y in which each Mn is surrounded with 12 neighboring Mn atoms.

Fig. 5 depicts T_{mag} vs μ_{Mn} plots for γ -Mn and MnN_y. Here, larger magnetic moments were used as μ_{Mn} for Mn₄N and Mn₃N₂. It was found that there is a obviously linear relationship between the T_{mag} and the μ_{Mn} . Probably, T_{mag} of MnN_y depend on the value of μ_{Mn} of the Mn atoms with smaller N-coordination number as can be seen from Table 1.

A linear relation between magnetic moments per a metal atom and the magnetic transition temperature were observed at the Cr base alloys which contain 1 at% of V, Mo, W, Mn, Ru and Re, respectively [29]. It has been reported also in Mn-Ni alloy [30] that the μ_{Mn} and T_N of Mn-Ni alloy decrease linearly with increasing Ni content. The linear relationships in $T_N - \mu_{Mn}$ plots have been reported only in the range of 1.7 to 2.4 μ_B , so far [30]. The most interesting aspect of present result is that the linear relationship between T_{mag} and larger μ_{Mn} is kept over the wide range from about 1.6 to 4.3 μ_B , though the reason why the T_{mag} for MnN_y depends on larger μ_{Mn} is still unresolved. The relationship between the magnetic transition temperature and the larger magnetic moment for MnN_y may be interpreted by clarifying their electronic structure through band calculation.



Fig. 5. The relation between larger magnetic moments μ_{Mn} and magnetic transition temperature T_{mag} for MnN_y with $0 \le y < 1$. The dashed line indicates the line obtained by least square fitting between μ_{Mn} and T_{mag} with 0.994 of correlation coefficient. The magnetic moment in Mn₆N₅ was assumed to be $3.4\mu_B$ corresponding to that of the Mn atom surrounding with five nitrogen atoms in Mn₃N₂ as shown in Table 1.

4. Summary

The magnetic susceptibility measurements for Mn_6N_5 and Mn_3N_2 prepared by nitriding α -Mn powder in NH₃ flow were carried out between 100 and 958K to clarify the magnetic properties of manganese nitrides. The magnetism of both Mn_6N_5 and Mn_3N_2 are antiferromagnetic below 655-660 and 914-936K, respectively, and their antiferromagnetic interaction disappeared with accompanying the phase transition. The change of T_{mag} with r_{M-M} was found to correspond considerably to that of μ_M with r_{M-M} of MnN_y and Mn alloys. Linear relationship between T_{mag} and larger μ_{Mn} of MnN_y with $0 \le y < 1$ obtained experimentally.

Appendix

The crystal structure of Fe₄N is shown in Fig. 1 (a) of chapter 1. It can be visualized as an fcc Fe lattice with an additional N atom at the center of the cell. Whereas only one Fe sublattice is observed in fcc Fe (γ -Fe), two Fe sublattice can be accounted for in Fe₄N; (i) the Fe atoms at the cube corner positions (hereafter referred to as Fe(1)); (ii) the Fe atoms at the face center positions (hereafter referred to as Fe(2)). The crystallographic position of N lead to six Fe(2)-N distances shorter than eight Fe(1)-N ones (d(Fe(2)-N)~0.190nm; d(Fe(1)-N)~0.329nm). These geometrical considerations suggest that Fe-N interactions would preferentially occur between face-center Fe and central N atoms rather than between corner Fe and N atoms.

The magnetism of Fe₄N has been reported to be ferromagnetic with T_c of 761K [2] and two different values of μ_{Fe} have been observed [3] ($\mu_{Fe(1)}=3\mu_B$; $\mu_{Fe(2)}=2\mu_B$). The occurrence of two different μ_{Fe} can be explained the following mechanism [31, 32]. Fig. 6 depicts the changes of the local densities of states D(E) of Fe 3d bands at Fe(2) (a) and Fe(1) (b) in Fe₄N, accompanying the Fe-N interaction, respectively. N 2p bands are situated in the top of the partially filled Fe(2) 3d band and overlap with them. p-d mixing occur mainly between N 2p and Fe(2) 3d bands. The level repulsion due to the p-d mixing will cause a downward shift in energy of the D(E) of Fe(2) 3d band in the down spin state to place them lower than the D(E) of Fe(1) atoms more distant from the N site. In other words, the D(E) of Fe(2) atoms in down spin state are changed from dotted lines to solid ones with the Fe-N interactions. The degree of the shift in E of D(E) of Fe 3d band in the down spin state is larger than that of Fe 3d band in the up spin state, because Fe 3d band in down spin state possess more 3d holes than that in the up spin state. Accompanying the energy shift of Fe(2) 3d band, the center of D(E) of Fe(1) atoms in down spin state is changed from dotted lines to solid ones. The electron transfer from the Fe(1) 3d bands to the Fe(2) ones result from the shift of that of Fe(1) atoms in down spin state. As a result, the local magnetic moment of a Fe(1) atoms raised, while that of a Fe(2) atom is lowered.



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Fig. 6. The local densities of states (D(E)) of N 2p band and Fe 3d bands in Fe₄N at the face center positions (Fe(2)) (a), and at the cube corner ones (Fe(1)) (b) [31]. D(E) of Fe(1) and Fe(2) atoms are changed from dotted lines to solid ones with the inclusion of N atoms, and the electrons of down spin states are then transferred from Fe(1) 3d bands to Fe(2)ones. As a result, μ_{Fe} of a Fe(1) atom is raised, while that of a Fe(2) atom is lowered.

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Chapter 3 Application of the relation between the magnetic moment and the magnetic transition temperature to MN_y besides MnN_y

3d Metal atoms in 3d metal nitrides often distribute at different lattice sites which take different N-coordination number each other. In such a case, magnetic moment of metal atoms in a nitride varies with depending on N-coordination number of metal atom (z_N) , i.e. the metal atom with larger N-coordination number possesses smaller magnetic moment. A linear relationship between the magnetic transition temperature (T_{mag}) and the largest magnetic moment $(\mu_{(max)})$ of metal atoms in metal nitride was found out in the Mn and N system as described in chapter 2.

It is interesting whether the linear correlation can apply to other metal nitrides MN_y besides MnN_y or not. To examine of the linear correlation between $\mu_{M(max)}$ and T_{mag} , MN_y with the ordered arrangement of N atoms are desired.

 CrN_y are unsuitable for this purpose, because all Cr atoms occupy the same lattice site in both Cr [1] and CrN [2]. The values of $\mu_{M(max)}$ and T_{mag} of metal nitrides with ordered arrangement of N such as Co_4N and Ni_4N are not yet decided. The magnetic data of CoN_y and NiN_y are insufficient to examine the relation between $\mu_{M(max)}$ and T_{mag} .

On the other hand, there are many data about the magnetism of FeN_y in analogy with MnN_y as shown in Table 2 of chapter 1. Each of crystal phases such as Fe₄N [3], Fe₁₆N₂ [4] and Fe₂N_{0.78} [5] with the ordered structure of nitrogen atoms, possess the two or three kinds Fe atoms with different μ_{Fe} . In Fe₄N and Fe₂N_{0.78}, the μ_{Fe} of the Fe atom with smaller N-coordination number is larger than that of the Fe atom with larger one. In Fe₁₆N₂, the first neighbor Fe atom of nitrogen has the least magnetic moment, and the third one has the maximum moment. Consequently, the relation between T_{mag} and $\mu_{\text{Fe}(\text{max})}$ in FeN_y is examined. Fig. 1 depicts the plots of T_{mag} against $\mu_{\text{Fe}(\text{max})}$ of γ -Fe (fcc), ε -Fe and FeN_y (0<y<0.5) with the hcp or fcc lattice of M atoms. T_{mag} and μ_{Fe} of α -Fe γ -Fe [7], ε -Fe [8], Fe_{2.04}N [8], Fe_{2.5}N [5, 8] and Fe₄N [3, 9] are previous data. In the case of





Fe₄N and Fe_{2.5}N, the values of the largest μ_{Fe} were adopted. It is found that T_{mag} changes linearly with $\mu_{Fe(max)}$ in γ -Fe, ε -Fe and FeN_y in a similar manner to as γ -Mn and MnN_y. However, the T_{mag} vs $\mu_{Fe(max)}$ plots for α -Fe and Fe₁₆N₂ with bcc or bct Fe lattice as the primitive structure deviated considerably from the linear relation between T_{mag} and $\mu_{Fe(max)}$ as shown in Fig. 1. The deviation from the linear relationship in the T_{mag} vs $\mu_{Fe(max)}$ plots for Fe₁₆N₂ and α -Fe may be attributed to the difference in Fe-coordination number of the Fe atom between the crystal phases of FeN_y. That is, it is shown that the linear relation between T_{mag} and $\mu_{Fe(max)}$ are only maintained in FeN_y with the nearly close-packed structure of Fe atoms such as hcp or fcc. It is found that the linear correlation in the T_{mag} vs $\mu_{Fe(max)}$ plot, which was observed in MnN_y, can apply to FeN_y with close-packed structure of Fe atoms.

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Chapter 4 Preparation and magnetic properties of cobalt nitrides CoN_y and nickel nitrides NiN_y (0<y<0.5)

1. Introduction

There are four crystal phases, Co_4N , Co_3N , Co_2N and CoN in the cobalt and nitrogen system. Co_4N with an antiperovskite type structure, which is isostructural to Fe_4N [1], can be obtained only non-thermoequilibrium processes such as reactive sputtering method [2]. Both Co_3N and Co_2N possess the basic structure of hcp arrangement of metal atoms like $Fe_{2-3}N$ and Fe_2N [3]. The fine Co powder obtained by reduction of Co_3O_4 in H₂ flowing in the temperature region between 623 and 673K, can convert to Co_3N and Co_2N in NH₃ flow at temperatures of 653 to 663K [3]. CoN with NaCl type structure was synthesized by thermal decomposition of $Co(NH_2)_3$ in vacuo in the temperature region between 323 and 343K [4] and CoN with a zinkblende structure was prepared by the non-explosive decomposition of $[Co(NH_3)_6](N_3)_3$ in the temperature region between 368 and 423K in vacuo [5].

Recently, the magnetic properties (saturation magnetization, coercivity and perpendicular magnetic anisotropy) of sputter-synthesized Co-N films were studied for use as media for high density magnetic recording [6-8]. However, the magnetism of individual CoN_y phases was not so clearly analyzed in these studies. Oda *et al.* [2] presented that saturation magnetization of Co₄N films were 46.5-85.1Gcm³/g at room temperature. The magnetism of Co₃N_{1.55} has been reported to be antiferromagnetic below 11K [9].

There are several phases of nickel nitrides NiN_y such as Ni_4N , Ni_3N , Ni_2N and Ni_3N_2 . Ni_3N with a hexagonal structure which is analogous to Co_3N and $Fe_{2-3}N$ could be only obtained by nitrizing Ni powder in NH₃ flow. Dorman and Sikkens [10] prepared Ni_4N , Ni_3N and Ni_2N films by reactive sputtering using Ni target and an $Ar-N_2$ gas

mixture. Ni₄N are a fcc [10, 11] or a fct [10, 12] phases and are metastable above about 523K [13]. Ni₂N with a bct unit cell is only obtained by reactive sputtering method [10]. The presence of Ni₃N₂ is quite unlikely [14, 15]. The magnetism of Ni₃N has been referred to be non-ferromagnetic or paramagnetic [16–18] but has not been clarified in detail.

Mekata *et al.* [19] reported that hexagonal $(M_{2-3}N)$ and orthorhombic (M_2N) nitrides such as $V_{2-3}N$, $Cr_{2-3}N$, $Mn_{2-3}N$, $Fe_{2-3}N$ and Fe_2N were similar to their mother metals in magnetisms, but magnetic moment of these nitrides was reduced by producing metalnitrogen bonding. However, the influences of the number of valence electrons of a M atom (*e/a*) on the magnetic properties of $M_{2-3}N$ and M_2N have not been investigated so far. In this chapter, Co_3N , Co_2N and Ni_3N were prepared by thermal decompositions of $CoCl_2$ and $NiCl_2$ in NH_3 flow. Magnetic susceptibility (χ), for them were measured in the temperature region between 83 and 298K to reveal their magnetic properties. Magnetic properties of $M_{2-3}N$ and M_2N (M=Mn, Fe, Co, Ni) were studied in relation to the number of valence electrons per a M atom. Finally one of the role of nitrogen in the magnetisms of $M_{2-3}N$ and M_2N were considered.

2. Experimental

 Co_3N and Co_2N powder were obtained by thermal decomposition of about 0.1g and 0.05g of $CoCl_2$ (anhydrous, Nakarai Tesque) at 663K for 12h in NH₃ flow and at 663K for 2.5h in the same atmosphere, respectively, and samples were quenched to room temperature after heating. About 0.1g of NiCl₂ converted to Ni₃N at 623K for 20h in NH₃ flow.

The identification of products were carried out using a X-ray diffractmeter (Rigaku Rotaflex/RINT CuK α radiation). The lattice parameters of products were obtained from X-ray diffraction (XRD) measurements using silicon as an internal standard. The nitrogen

and carbon contents in products were determined by thermal conductivity method (240C, Perkin Elmer Co.) and the chroline contents in them were analyzed by Stragand's method (MX-3 Yanagimoto Seisakusho).

Temperature dependence of magnetic susceptibilities (χ) of the samples was measured at 12.5kOe by magnetic balance (MB-3, Shimazu Co.) between 83 and 298K in He atmosphere. Mn Tutton's salt was used as the standard substance of χ . Temperature was calibrated by values of χ for Mn Tutton's salt at various temperatures. The magnetic field (*H*) dependence of magnetization (σ) for samples was measured in the magnetic field between 1.8 and 12.5kOe to evaluate the spontaneous magnetization σ_s of some ferromagnetic impurity.

3 Results and discussion

3.1 Structure and composition of Co_3N , Co_2N and Ni_3N

Fig. 1 shows the XRD patterns of Co₃N and Co₂N. XRD patterns of Co₃N and Co₂N were indexed by using a hexagonal (a=0.4608nm, c=0.4361nm) and an orthorhombic (Pnnm [20], a=0.2853nm, b=0.4606nm and c=0.4305nm) unit cells, respectively. Lattice parameters of both Co₃N and Co₂N agreed with previous data [3, 20]. The relation between hcp arrangement of Co atoms and both unit cells of Co₃N and Co₂N were shown in Fig. 2 (a) and (b), respectively. The relations between the cell dimensions of Co₃N and Co₂N, and those of the hcp arrangements of Co atoms were as follows, $a=\sqrt{3}a_0$ and $c=c_0$ in Co₃N, and $a=a_0$, $b=\sqrt{3}a_0$ and $c=c_0$ in Co₂N, respectively. It is implied that N atoms in Co₃N and Co₂N occupy regularly the octahedral interstitial sites in hcp Co structure. Such the regular occupation of N atoms have been observed in Fe₂N, Fe₂₋₃N and Ni₃N [17]. The crystal structure of Co₂N was reported to be CaCl₂ antitype [20]. An ordered arrangement of N atoms in Co₂N result in an orthorhombically deformed cell of a CaCl₂ antitype cell [20].



Fig. 1. X-ray diffraction patterns of Co_3N and Co_2N .

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Fig. 2. Metal arrangements and unit cells of Co_3N (a) and Co_2N (b). Open circle denotes a Co atom. The unit cells of Co_3N and Co_2N are expressed by dotted lines. a_0 and c_0 correspond to the lattice parameters of Co_3N and Co_2N . The relations between cell dimensions of them and hcp arrangement of Co atoms were as follows, $a=\sqrt{3}a_0$ and $c=c_0$ in Co_3N , and $a=a_0$, $b=\sqrt{3}a_0$ and $c=c_0$ in Co_2N , respectively.

Carbon and Chlorine impurities in Co_3N and Co_2N were not detected. The chemical composition for Co_3N and Co_2N were evaluated to be $Co_3N_{1.02}$ - $Co_3N_{1.18}$ and $Co_2N_{0.98}$, respectively, by thermal conductivity method. The composition range for Co_3N was close to the previous data of $Co_3N_{1.05}$ - $Co_3N_{1.10}$ [3]. It was found that Co_3N contained excess N atoms, but Co_2N with N deficiency was close to stoichiometric.

Fig. 3 displays the XRD pattern of Ni₃N. This pattern was indexed by a hexagonal unit cell (a=0.8010nm, c=0.4309nm). However, the value of the a-parameter for Ni₃N correspond to 3 times that for hcp arrangements of Ni atoms. This result is contrary to those of Co₃N, Ni₃N and Fe₂₋₃N [17]. The fact suggests that the arrangements of N atoms in Ni₃N slightly differ from those in Fe₂₋₃N, Ni₃N and Co₃N. The presence of C and Cl in Ni₃N were also not observed. Ni₃N possessed the N content corresponding to Ni₃N_{1.00}-Ni₃N_{1.01}. Consequently, Ni₃N prepared by firing NiCl₂ in NH₃ flowing contains excess nitrogen but very close to stoichiometric.

3.2 Magnetic properties of Co₃N, Co₂N and Ni₃N

Temperature dependence of magnetic susceptibility of Co_3N and Co_2N were shown in Fig. 4. Values of σ_s at 293K for Co_3N and Co_2N were estimate to be $3.6\pm0.4\text{Gcm}^3/\text{g}$ and $0.23\pm0.05\text{Gcm}^3/\text{g}$ by extrapolating σ to zero magnetic field in σ -H curves, respectively. Amounts of α -Co impurity in Co₃N and Co₂N were in the order of 2.0-2.5wt% and 0.11-0.16wt%, respectively, on assuming that the ferromagnetic impurity was only α -Co (σ_s =161.85Gcm³/g, T_c =1394K [21]). The magnetic susceptibilities of Co₃N and Co₂N were calculated after correcting the observed values of σ with σ_s . Values of χ at room temperature for Co₃N and Co₂N were (20±4)×10⁻⁶cm³/g and (3.3±0.2)×10⁻⁶ cm³/g, respectively. The higher value of χ for Co₃N than that for Co₂N were found. Fig. 4 shows that both χ for Co₃N and Co₂N increase with decreasing temperature down to 83K. It is suggested that both nitrides exhibit paramagnetic behavior above 83K. It



4 2.







is also found from Fig. 4 that the temperature dependence of χ for Co₂N is smaller than that for Co₃N. Fig. 5 (a) and (b) depicts the temperature dependence of inverse molar susceptibilities $1/\chi_m$ for Co₃N and Co₂N, respectively. On the basis of linear relationships between $1/\chi_m$ and T for both Co₃N and Co₂N, the magnetism for both compounds are found to be paramagnetism which follows Curie-Weiss law above 83K. The values of effective magnetic moments (μ_{eff}) of Co₃N and Co₂N were calculated to be $1.4\pm0.1\mu_B$ and $0.65\pm0.5\mu_B$, respectively. The values are smaller than about $3\mu_B$ for $Fe_{2-3}N$ and Fe_2N [19] and $3.15\mu_B$ for Co [22]. The values of the Weiss temperature (θ) for Co₂N and Co₂N were +45±15K and -27±7K, respectively, as seen from Fig. 5. The ferromagnetic couplings in Co₃N is expected below 60K. The Weiss temperature of Co₂N is small and negative. It is presumed that the magnetic susceptibility is influenced by temperature independent paramagnetism such as Pauli paramagnetism or antiferromagnetic coupling takes place below 33K. The values of θ and μ_{eff} of Co nitride denoted as Co₃N were reported to be -500K and $3\pm0.3\mu_{\rm R}$. The difference in the magnetic properties between the present result and the previous data [9] for Co₃N is attributed to a difference in chemical composition between them, i. e. real chemical composition is $Co_3N_{1.55}$.

Temperature dependence of magnetic susceptibility (χ) and inverse molar susceptibility ($1/\chi_m$) for Ni₃N were shown in Fig. 6 (a) and (b), respectively. The values of σ_s at room temperature for Ni₃N samples varied in the range between 3.2×10^{-3} and 6.2×10^{-3} Gcm³/g. Ni metal impurity in Ni₃N was evaluated as less than 0.01wt%, on assuming that the ferromagnetic impurity in samples was only Ni ($\sigma_s = 55.01$ Gcm³/g, $T_c = 631.0$ K [22]). The value of χ for Ni₃N at room temperature was (1.12 ± 0.01)× 10^{-6} cm³/g and which was fairly smaller than that for Co₃N. χ of Ni₃N increases with decreasing temperature as seen in Fig. 6 (a). The linear relationship in the $1/\chi_m - T$ plot in Fig. 6 indicates that the magnetism of Ni₃N is paramagnetic above 83K which obeyed



Fig. 5. Temperature dependence of inverse molar susceptibility for Co_3N (a) and Co_2N (b). Weiss temperature, θ and the effective magnetic moment per a metal atom, μ_{eff} were described in this figure.



Fig. 6. Temperature dependence of magnetic susceptibility (a) and inverse molar susceptibility (b) for Ni_3N .

Curie-Weiss law. The values of μ_{eff} and θ for Ni₃N were $0.48\pm0.04\mu_{B}$ and $-210\pm20K$, respectively, depending on the nitrogen content. The value of μ_{eff} for Ni₃N is very small compared with $1.61\mu_{B}$ for Ni [22]. The Values of μ_{eff} for M₃N (M=Fe, Co, Ni) decrease in order of Fe₂₋₃N, Co₃N and Ni₃N. This tendency is analogous to that for their mother metals, where the μ_{eff} decrease with increasing number of valence electrons per a metal atom (*e/a*).

3.3 Consideration in terms of magnetic properties of $M_{2-3}N$ and M_2N

The magnetisms of most of $M_{2-3}N$ and M_2N are usually discussed in connection with those of their mother metals [19] and alloys. In general, magnetic susceptibility of a transition metal consists of the terms of Larmor diamagnetism (χ_d), temperature dependent paramagnetism (χ_c) and temperature independent paramagnetism (χ_{PL}) as follows [23],

$$\chi = \chi_{\rm d} + \chi_{\rm c} + \chi_{\rm PL} \tag{1}.$$

 χ_d of a compound is equal to the sum of diamagnetic susceptibilities of constituent atoms. The values of χ_d for M₃N were calculated to be $(-2.5\pm0.5)\times10^{-5}$ cm³/mol by the sum of χ_m of M and N atoms. The value of χ_d is smaller by one or two orders than those of χ for M₃N. χ_c is the temperature dependent term which obeys Curic-Weiss law as follows [23],

$$\chi_c = \frac{N\mu_{eff}^2}{3k} \frac{1}{T-\theta}$$
(2).

Where k, θ and N are Boltzmann constant, Weiss temperature and Avogadro number, respectively.

 χ_{PL} corresponds to the terms of sum of Pauli paramagnetism and Landau diamagnetism. The relation between χ_{PL} and the density of state at Fermi level $D(E_F)$ holds as follows [22],

$$\chi_{PL} = \frac{2}{3} D(E_F) \mu_B^2$$
 (3).

Where $\mu_{\rm B}$ is Bohr magneton. Since $\chi_{\rm PL}$ is independent on temperatures, the contribution of $\chi_{\rm PL}$ to χ becomes large at high temperature. The values of $\chi_{\rm PL}$ obtained by subtracting the $\chi_{\rm d}$ and $\chi_{\rm c}$ from χ , are $(3.1\pm0.8)\times10^{-4}$ cm³/mol for Co₃N and $(8.2\pm0.7)\times10^{-5}$ cm³/mol for Ni₃N, respectively. The decrease in the values of $\chi_{\rm PL}$ from Co₃N to Ni₃N can be understood by relating to the decrease in $D(E_{\rm F})$ with increasing 3d electrons in their 3d bands.

It was considered that the magnetic properties of these nitrides are mainly contributed with the 3d bands consist of metal valence electrons. Therefore, the values of μ_{eff} were plotted against valence electrons per a metal atom, e/a of Mn₂N [24], Fe₂₋₃N [19], Fe₂N [19], Co₃N, Co₂N and Ni₃N in Fig. 7. It were worth noting that the overall feature in the μ_{eff} -e/a relations for M₂₋₃N and M₂N lines is similar to those for 3d transition metal alloys [25]. This fact supported also experimentally the large contribution of 3d bands to the magnetic properties for M₂₋₃N and M₂N. This behavior, which magnetic moments per a metal atom (μ_M) and μ_{eff} varied with e/a like Slater-Pauling curve as shown in Fig. 8, were observed in 3d transition metal phosphide, M₃P [26] and boride, M₂B and MB [27].

 Co_3N , Co_2N and Ni_3N possessed considerably lower μ_{eff} and magnetic transition temperatures compared to those of their mother metals and that the value of μ_{eff} for Co_2N was smaller that for Co_3N as mentioned previously. The effect of N atom on magnetic moment of metal nitride was also observed in the Fe and N system, in which μ_{Fe} and T_c decreased with an increase of nitrogen content [19, 28].

Mekata *et al.* attributed the difference in the magnetic properties between $Fe_{2-3}N$ and Fe_2N to the difference of environment around a metal site between them [19]. The difference of the magnetic properties between Co_2N and Co_3N may be understood on the



Fig. 7. The relation between the formal valence electron number per a metal atom, e/a and the effective magnetic moment per a metal atom, μ_{eff} for $M_{2-3}N$ (\bigcirc [19], \bullet ; present results) and M_2N (\triangle [19], \blacktriangle ; present results). Dot-dashed line and dotted curves show that μ_{eff} of M_2N and $M_{2-3}N$, respectively, exhibit the behavior such as Slater-Pauling curve observed in 3d metal alloys.



Fig. 8. The relation between magnetic moment per a metal atom (μ_M) and number of valence electrons per a M atom (e/a) in 3d metals and their alloys "Slater-Pauling curves" [22].

viewpoint of N-coordination number around a M atom. Fig. 9 depicts the types of environments around a metal site in M₃N and M₂N. A metal atom occupies at the body center of trigonal prism consist of octahedral interstitial sites which are partially occupied by N atoms. Since N atoms in M₃N and M₂N are surrounded by six metal atoms, one of the type of environment in Fig. 9 (a) is dominant at the composition near to M₃N and the other type in Fig. 9 (b) present primarily at the composition close to M₂N. Mössba uer spectrum for Fe_{2.5}N confirmed the presence of Fe atoms with two different internal fields [19], indicating that Fe atoms in Fe_{2.5}N possess different magnetic moments which reflect the environments around a Fe atom. On the basis of the values of magnetization and internal field for Fe_{3.2}N, Fe₂₋₃N and Fe₂N [18, 19, 28, 29], the values of μ_{Fe} of Fe atoms with two and three neighboring N atoms were evaluated to be $1.9-2.0\mu_{\text{B}}$ and $0.12-0.19\mu_{\text{B}}$, respectively. It is thought that the difference in μ_{eff} for Co₃N and Co₂N is analogous to the variation of magnetic moment in FeN_y described above, i.e. Co₃N possesses larger μ_{Co} compared with Co₂N, since Co₃N surpasses Co₂N with regard to the proportions of a Co atom with two neighboring N atoms.

4 Summary

Magnetic properties of $M_{2-3}N$ and M_2N were studied to elucidate the effect of the kind of M and N-coordination number around a M atom on their effective magnetic moment.

 Co_3N , Co_2N and Ni_3N were prepared by the thermal decompositions of $CoCl_2$ and $NiCl_2$ in NH_3 flow, were investigated to clarify through the measurements of magnetic susceptibilities in the temperature region between 83 and 293K. All of Co_3N , Co_2N and Ni_3N exhibit paramagnetism which obeyed Curie-Weiss law above 83K. The Values of effective magnetic moments for Co_3N , Co_2N and Ni_3N are estimated to be 1.4 ± 0.1 , 0.65 ± 0.05 and $0.48\pm0.04\mu_B$, respectively. In the system of M_2N (M=Mn, Fe, Co), the



Fig. 9. Two types of environments around a metal site in M_3N (a) and M_2N (b).

effective magnetic moments were observed to be varied with the number of valence electrons of the M atom. In the system of $M_{2-3}N$, (M=Fe, Co, Ni), the effective magnetic moments, decreased monotonously with increasing the number of valence electrons of the M atom. It was found that these tendency of the relations between the effective moments and the number of valence electrons per a M atom for M_2N and M_3N are similar to those for 3d metals and their alloys whose the effective magnetic moments vary with the number of valence electrons of a 3d metals like "Slater-Pauling curves".

The difference in the effective magnetic moments between Co_3N and Co_2N may be related to that in N-coordination numbers around the Co atom between them, i.e. μ_{eff} of Co_3N with the two nitrogen atoms adjacent to the Co atom is larger than that of Co_2N with three nitrogen atoms adjacent to the Co atom. This result is consistent with the tendency observed at MnN_v described in chapter 2.

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Chapter 5 Preparation and their electric properties of manganese nitride MnN_y (0<y<1) thin films by reactive vapor deposition method

1. Introduction

Manganese nitrides (MnN_y) (0<y<1) have been reported to take four crystal phases, $Mn_4N,\ Mn_{2-3}N,\ Mn_3N_2$ and Mn_6N_5 so far. The powders and single crystals of MnN_y were prepared by nitrizing manganese amalgams [1], the thermal decomposition of $Na_2[Mn(NH_2)_4]$ [2] and the reaction between MnI_2 and $NaNH_2$ in high NH_3 pressure [2]. Mn_4N and Mn_6N_5 films were obtained by reaction of α -Mn film with NH₃ gas at 573K The magnetic properties of Mn_4N [5, 6] and $Mn_{2-3}N$ [7, 8] with the crystal [3, 4]. structures analogous to Fe_4N and $Fe_{2-3}N$, respectively, were clarified previously. The antiferromagnetic structure of Mn₃N₂ was determined by the measurement of unpolarized neutron diffraction at 11 and 291K [2]. There are many reports on electrical resistivity of TiN film [9], CrN film [10] Fe_aN sheet [11] and Ni₃N powder [12]. However, electrical resistivity of MnN, have scarcely been investigated, except a report describing that Mn₃N₂ exhibits a metallic conductivity [13]. The serious problem on preparation of Mn nitrides is coexistence of manganese oxides as a by-product which hamperes characterization of Mn nitrides.

In this work, MnN_y films were prepared by reactive vapor deposition method. Since this vapor deposition process is distinct in the point of reaction temperature from the direct nitrization process of Mn powder with NH_3 or N_2 flowing, this process can be expected for the formation of MnN_y with large nonstoichiometry of nitrogen and also for elimination of by products such as MnO. The electrical properties of MnN_y films were clarified by measurement of electrical resistivity of the Mn oxides free samples.

2. Experimental

Fig. 1 shows the schematic drawing of the apparatus used for preparation MnN_y films. The reaction chamber was made of pyrex glass. The reaction chamber consists of two gas inlets, a W filament for vaporizing Mn metal and electrodes for glow discharge, which is made of W rods and Ta plates. N2 gas (99.9999% in purity, Osaka Sanso Kogyo Co.) and α -Mn flakes (99.9% in purity, Nakalai Tesque Co.) were used as the source of the reaction. The reaction chamber were evacuated down to a pressure of $\leq 6.5 \times 10^{-3}$ Pa by oil rotary pump and oil diffusion pump through a liquid nitrogen trap. The α -Mn flakes placed on the W filament were preheated under vacum of 0.13Pa to remove the contamination such as oxigen and water on their surface with closing the shutter. After the reaction chamber was evacuated again down to 6.5×10⁻³Pa, nitrogen gas flow into the chamber was initiated and then nitrogen gas pressures was kept constant at desired one by regulating the leak valve (LV in Fig, 1). Nitrogen gas was activated by the glow discharge induced by high voltage of 10kV. Then the shutter was opened and α -Mn was vaporized by applying electric power to the W filament. The electric power (E_n) between 100 and 300W was regulated in order to control nitrogen content of products. The deposition time of film was varied from 5 to 30 min. The bright emission like plasma was observed during the deposition. Slide glasses or polystyrene coated slide glasses were used for the substrates. A Chromel-Alumel thermocouple was put over the substrate. No efforts were made to heat substrates. The substrate temperature during the deposition was in the range between 373 and 523K. The nitrogen gas pressure (p_N) during the deposition was set at desired pressures between 1.3 and 26Pa and the fluctuation of $p_{\rm N}$ was depressed within ±0.65Pa. The thickness of the films ranged from 0.2 to 0.8µm. The powder samples were obtained by dissolving the polystyrene films between the deposited film and the substrate in tetrahydrofuran.

The crystalline phase in both the deposited films and the powders was identified



Fig. 1 Schematic drawing of the apparatus used for the reactive vapor deposition. (a); W filament where α -Mn flakes are placed, (b); shutter, (c); substrate, (d); thermocouple, (e); Ta electrode for glow discharge, (f); neon transformer, (g); electric power supply, A; ammeter, V; voltmeter, G1; pirani gauge, G2; ionization gauge, LV; leak valve, SV; stop valve, R; regulator for N₂ gas cylinder, V; main valve, and conductance valve, DP; oil diffusion pump, RP; rotary pump.

using a X-ray diffractmeter (CuKα radiation, Rotaflex/RINT, Rigaku Co.). The lattice parameters of powder samples were determined from X-ray diffraction (XRD) measurement by using silicon as an internal standard. The nitrogen content in the powder samples was determined by CHN analysis using 240C, Perkin Elmer Co. The electrical resistivity of deposited films was measured by four point probe method in the temperature range between 5 and 295K, and film thickness was measured with using nanoscope (Model 911–9150, Anelva Co.).

3. Results and discussion

3.1 Structure and composition of the deposited films

The crystalline phase in the films varied with depending on deposition parameters, E_p and p_N . The films contained both phases of α -Mn and Mn₄N only when depositing the films without glow discharge and the bright emission. Figs. 2, 3 and 4 show XRD patterns of the films deposited at various conditions comparing with those of Mn₆N₅, Mn_3N_2 and Mn_4N obtained by heating α -Mn powder in N_2 or NH_3 flow, respectively. In all XRD patterns of the films, no peaks of Mn oxides were detected. Mn₂₋₃N with hexagonal lattice has not been obtained in the present work. The XRD patterns of Mn₃N₂ and Mn₆N_{6.42} films exhibit a strong preferred orientation with the closest packing plane of Mn atoms parallel to the substrate, but the powder samples of Mn₃N₂ and Mn₆N_{6.42}, which were obtained by tearing off the films from the substrates, showed the same XRD patterns to those of Mn_3N_2 and Mn_6N_5 , respectively. The XRD patterns of the Mn_4N films agrees with that of Mn₄N, but no preferred orientation is observed as shown in Fig. 2. The width of XRD peaks of the Mn₄N film were broader than those of the Mn₆N₅ and Mn₃N₂ films, in spite of the no difference in film thickness among them. These results imply that the crystallinity of the Mn₄N film is poorer than those of the others. The Mn₄N film was obtained only in the case when glow discharge was blinking because of low E_p and



Fig. 2 X-ray diffraction patterns for the Mn_4N film deposited at E_p of 155W and p_N of 1.3Pa, and Mn_4N powder obtained successively firing α -Mn powder at 1073K in N_2 and H_2 flow.



Fig. 3 X-ray diffraction patterns for the Mn_3N_2 film deposited at E_p of 240W and p_N of 2.6Pa and Mn_3N_2 powder obtained successively firing α -Mn powder at 873K in NH₃ and H₂ flow.



Fig. 4 X-ray diffraction patterns for the $Mn_6N_{6.42}$ film deposited at E_p of 186W and p_N of 25Pa and (b) Mn_6N_5 powder obtained firing α -Mn powder at 873K in NH₃ flow.

low $P_{\rm N}$. Such the fact suggests that the stability of the glow discharge during the deposition affects micro structure of the films.

Deposition conditions, nitrogen contents and lattice parameters for the MnN_v films are listed in Table 1. Values of the lattice parameters of Mn_3N_2 , Mn_4N and Mn_6N_5 films are consistent with previous reported data [1], respectively, as shown in Table 1. One third of the c axis of Mn_3N_2 is also shown in parentheses. As seen in Fig. 5. the XRD pattern of MnN_{0.64} powder, which was obtained by tearing off the films from the substrates, is different from that of Mn₃N₂ but the pattern is similar to that of Mn₆N₅ with no superlattice diffractions which are observed of Mn₃N₂ with an ordered arrangement of nitrogen atoms. Furthermore, it is found that values of lattice parameters of MnN_{0.64} and $MnN_{0.71}$ films were comparable to those of Mn_6N_5 reported previously [1] rather than the value of c/3 of the Mn_3N_2 , in spite of their nitrogen contents close to that of Mn_3N_2 . Though Mn_6N_5 and Mn_3N_2 have the fct lattice (c/a<1) of Mn atoms, it was pointed out that they differ in the arrangement of nitrogen atoms [2, 4, 13] each other. Nitrogen vacancies at octahedral site in Mn₃N₂ arrange regularly to result in the c axis of 3×c (primitive fct lattice of Mn), while those in Mn_6N_5 were presumed to distribute randomly [2, 4, 13]. Because of the ordering of nitrogen vacancies in Mn_3N_2 , the value of c/3 of Mn_3N_2 is smaller, compared to the c axis of Mn_6N_5 . Thus, the $MnN_{0.64}$ and the $MnN_{0.71}$ films can be thought to be Mn_6N_5 -type compounds. In the subsequent descriptions, that $MnN_{1.07}$ and $MnN_{1.08}$ films are called $Mn_6N_{5+\delta}$ film and $MnN_{0.64}$ and $MnN_{0.71}$ films are referred to as $Mn_6N_{5-\delta}$ film. The Mn_6N_5 -type compound has been reported to be stable in a composition range between MnN_{0.84} and the composition range MnN_{0.95} at 573K and becomes narrow with increasing temperature [14]. The X-ray data on MnN_{0.64}, MnN_{0.71}, MnN_{1.07} and MnN_{1.08} films indicate that the composition range for Mn₆N₅-type compound is much wider than that reported previously. One of the reasons for existence of the large nonstoichiometry of Mn₆N₅ may be attributed to low deposition temperature.

					or fct lattice	e			
Phase	E_{p}/W	p _N /Pa	y in MnN _y	Observed value			Reported value		
				a/nm	c/nm	c/a	a/nm	c/nm	c/a
Mn ₄ N	155	1.3–2.6	<u> </u>	0.3865		1.000	0.3864ª		1.000ª
Mn ₃ N ₂	240	2.6-3.9		0.4206	1.3162 (0.4054 [*])	2.832 (0.964**)	0.4206 ^b	1.3132 ^b (0.4044 [*])	2.883 ^b (0.961 ^{**})
<u></u>	143	6.5	0.64	0.4199	0.4140	0.986			
$Mn_6N_{5\pm\delta}$	160	9.1	0.71	0.4221	0.4161	0.986	0.4221°	0.4115°	0.975°
	174	. 25	1.07	0.4219	0.4151	0.984			
	186	25	1.08	0.4218	0.4155	0.985	0.4214 ^d	0.4148 ^d	0.984 ^d

Table 1 Deposition conditions, nitrogen contents and lattice parameters for MnN_y films.

 $a : Mn_4N_{1.0} \ (MnN_{0.25}), \ b : Mn_3N_{1.97} \ (MnN_{0.66}), \ c : Mn_6N_{5.07} \ (MnN_{0.85}) \ and \ d : Mn_6N_{5.52} \ (MnN_{0.92}).$

The composition range of Mn_6N_5 phase was reported to be in a range between $MnN_{0.84}$ and $MnN_{0.95}$ at 573K in previous data [14]. *; the value of c/3a and **; the value of c/3.



Fig. 5 X-ray diffraction patterns for the $MnN_{0.64}$ film deposited at E_p of 143W and p_N of 6.5Pa (a) and Mn_3N_2 powder deposited at E_p of 240W and p_N of 2.6Pa (b).

ი ნ Fig. 6 depicts the variation of crystal phase as functions of E_p and p_N . The $Mn_6N_{5\pm\delta}$ films were obtained over the relatively wide range of E_p and p_N , especially in a larger p_N region compared to Mn_4N and Mn_3N_2 . However, Mn_3N_2 became easy to deposit at the large E_p region, even though p_N was also large, because evaporation rate of Mn increased with a increase of E_p . While, in lower p_N region, deposition of Mn_3N_2 preferred, but Mn_4N was obtained only at low E_p and p_N region where the glow discharge was blinking.

3.2 Electrical resistivity for the MnN_v films

Temperature dependence of the ratio of electrical resistivity to that at 295K, ρ/ρ_{295} , for the MnN_y films is shown in Fig. 7. All of the MnN_y films exhibited low resistivity in a range of $10-100\mu\Omega m$ at room temperature. These values for MnN_y films are comparable to those of Ni₃N powder ($28\mu\Omega m$ at 273K) [12], but higher than those of TiN film (0.5-7 $\mu\Omega$ m) [9] and Fe₄N sheet (1.62 $\mu\Omega$ m) [11]. It is seen in Fig. 7 that the temperature dependence of ρ/ρ_{295} above 50K for Mn₃N₂ and Mn₆N_{5+ $\delta}$} are metallic, but the Mn_4N films exhibits semiconductive behavior. The metallic behavior of the Mn_3N_2 film is consistent with previous data for Mn_3N_2 [13]. The increase in ρ/ρ_{295} of the Mn_3N_2 and $Mn_6N_{5+\delta}$ films with decreasing temperature below 50K may be related to the presence of the localized magnetic moments giving rise to the other scattering mechanism as Can't effect [15], because the magnetisms of Mn_3N_2 was reported to be antiferromagnetic [2]. Mn_6N_5 was presumed to be an antiferromagnetic compound [16]. The semiconductive behavior of $\rho/\rho_{295}-T$ curve of the Mn₄N film may not reflect inherent property of Mn₄N because of poor crystallinity. The value of ρ/ρ_{295} of $Mn_6N_{5+\delta}$ films is found to keep almost constant close to 1 in the temperature region between 5 and 295K. Such a fact, i. e. small temperature dependence of ρ is similar to temperature dependence of ρ above superconducting transition temperature of some NaCl type compound with a lot of



Fig. 6 The relation among crystal phase in products, nitrogen gas pressure during deposition (p_N) and electric power applied to W filament (E_p) .

 $\bullet : Mn_6N_5, O : Mn_3N_2, \blacksquare : Mn_4N, \blacktriangle : Mn_6N_5 + Mn_3N_2, \bigtriangleup : Mn_3N_2 + Mn_4N.$


Fig. 7 Temperature dependence of electrical resistivity ratios (ρ/ρ_{295}) for MnN_y films. ρ_{295} denotes the electrical resistivity at 295K. The value of $\rho_{295}/\mu\Omega m$ for each samples is designated in parentheses.

vacancies such as TiO [17] and NbN [18]. The reason why TiO and NbN have little temperature dependence of ρ , is due to the large contribution of the electron scattering term by vacancies to ρ , because the term has little temperature dependence. While the $Mn_6N_{5-\delta}$ film exhibits a semiconductive behavior in temperature dependence of ρ , even though crystallinity, preferred orientation and thickness of the film are very similar to those of the Mn₆N_{5+ δ} films. The $\rho/\rho_{295}-T$ curves of Mn₆N_{5± δ} films imply that they possess a lot of vacancies. There was a remarkable difference in sign of the temperature coefficient of ρ (TCR) between the Mn₆N_{5+ δ} films and the Mn₆N_{5- δ} films. The semiconductive behavior of temperature dependence of ρ/ρ_{295} for the $Mn_6N_{5-\delta}$ film may be attributed to the presence of too much number of N vacancies to exhibit metallic conductivity, because the vacancies scatter carriers. Such the difference in TCR between the $Mn_6N_{5\pm\delta}$ films is still unresolved. However, it have been reported that the sign of TCR of TiO or NbN is variable depending on their oxygen [17] or nitrogen content [18]. The differences in the signs of TCR of TiO with the different oxygen contents were attributed to a distinction in the electronic structures [17]. The difference in TCR between the $Mn_6N_{5\pm\delta}$ films may reflect that between their electric structures.

4. Summary

 Mn_4N , Mn_3N_2 and Mn_6N_5 films were obtained by reactive vapor deposition method. The chemical composition of the films was controlled by regulating both of electric power applied to W filament and nitrogen gas pressure during the deposition. Deposited Mn_6N_5 films possessed the large nonstoichiometry of nitrogen. Temperature dependence of electrical resistivity for the Mn_3N_2 and the $Mn_6N_{5+\delta}$ films exhibit a metallic behavior. However, the $Mn_6N_{5-\delta}$ films exhibit a semiconducting behavior, even though the microstructure of $Mn_6N_{5-\delta}$ film is quite similar to that of $Mn_6N_{5+\delta}$ film. The slight dependence of ρ/ρ_{295} of the $Mn_6N_{5+\delta}$ films may attributed to a lot of Mn and N'vacancies.

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Chapter 6 Concluding Remarks

The magnetism of 3d metal nitrides MN_y is generally similar to that of mother metals. On the other hand, the magnetic transition temperature of MN_y varies greatly with their nitrogen content. In spite of the importance of the effect of nitrogen content on the magnetism, the relation between the number of nitrogen atom per a metal atom and the magnetism of MN_y has been rarely studied except FeN_y . Furthermore, the magnetic properties of MN_y with the same crystal structure were affected considerably by a kind of metal. In order to clarify the effect of nitrogen content on the magnetism of 3d metal nitrides, the relationships between nitrogen content and the magnetic property and also the relationship between the number of valence electrons and magnetism are necessary to examined systematically.

Metal atoms in 3d metal nitrides often distribute at different lattice sites which take different N-coordination number each other. In such a case, magnetic moment per a metal atoms in a nitride varies with the N-coordination number of metal atom (z_N) , i.e. the metal atom with larger N-coordination number possesses smaller magnetic moment. The mechanism of such the different magnetic moments of atom by atom in MN_y was explained on Fe₄N as follows [1, 2]. The crystal structure of Fe₄N is shown in Fig. 1 (a) in chapter 1. It can be visualized as an fcc sublattice of Fe with an additional N atom at the center of the cell. There are two kinds of Fe atoms occupy different lattice sites each other, i.e., (i) the Fe atoms at the cube corner positions (hereafter referred to as Fe(1)) and (ii) the Fe atoms at the face center positions (hereafter referred to as Fe(2)). The crystallographic position of N results in shorter Fe(2)-N distances than Fe(1)-N ones $(d(Fe(2)-N) \sim 0.190$ nm; $d(Fe(1)-N) \approx 0.329$ nm). These geometrical considerations suggest that the Fe-N interactions would preferentially occur between face-centered Fe and central N atoms rather than between corner Fe and N atoms. The magnetism of Fe₄N was ferromagnetic with T_c of 761K [3] and different values of magnetic moment for Fe(1) and

Fe(2) atoms was observed [4] $(\mu_{Fe(1)}=3\mu_B; \mu_{Fe(2)}=2\mu_B)$. The occurrence of larger μ_{Fe} is explained by a band theory appeared at Appendix in chapter 2 [1, 2]. Consequently, the distribution of μ_M have to be taken into account for the consideration of the magnetic property. The effect of nitrogen content on the magnetism was examined in the Mn-N system, because manganese nitrides MnN_v possess various crystal phases over a wide range of *y* (0<*y*<1). The shortest Mn-Mn distance in MnN_v increases linearly with increasing The interatomic distance r_{M-M} between paramagnetic atoms their nitrogen content. generally correlate to not only exchange coupling constant $|J_{M-M}|$ and but also magnetic moment per a M atom ($\mu_{\rm M}$). A strong correlation between $T_{\rm mag}$ and $r_{\rm M-M}$ was observed in MnN_y and Mn alloys, both of which have fcc and fct Mn-sublattice. However, the $T_{\text{mag}}-r_{\text{M-M}}$ plot of $Mn_{2-3}N$ and Mn_2N , which have hep Mn sublattice, deviated from a tendency in the $T_{\text{mag}} - r_{\text{M-M}}$ plot of fcc or fct MnN_y and Mn alloys. Therefore the correlation between $\mu_{\rm M}$ and $T_{\rm mag}$ was examined. The magnetic moment of the Mn atom at the lattice site in MnN_v is strongly affected by numbers of nitrogen adjacent the Mn atom above described on Fe₄N. As seen in the result of neutron diffraction of Mn₃N₂, the largest $\mu_{\rm M}$ in MnN_y generate on the Mn atom with the smallest $z_{\rm N}$ in any cases. The following magnetic moment of Mn atom were used for each N-coordination number z_N ; 2.4 $\mu_{\rm B}$ for $z_{\rm N}$ =0, 0.9 $\mu_{\rm B}$ for $z_{\rm N}$ =2, 1.6 $\mu_{\rm B}$ for $z_{\rm N}$ =3, 3.4 $\mu_{\rm B}$ for $z_{\rm N}$ =5. In this work, a linear relationship between T_{mag} and the largest μ_{M} in MnN_{y} with $0 \leq y \leq 1$ is first discovered. Through the investigation of the effect of nitrogen on the magnetic properties of MnN_v $(0 \le y \le 1)$, the μ_{Mn} of the Mn atom with smaller N-coordination number were found to relate to T_{mag} . Such a linear relationship between the largest μ_{M} and T_{mag} was also observed for FeN_v $(0 \le y \le 0.5)$ with the nearly closest-packed structure such as of Fe atoms. These findings indicate that T_{mag} of MN_v with nearly closest-packed structure of 3d metals correlate closely to the largest μ_{M} in MN_y, which is its magnetic moment of the M atom with smallest N-coordination number. Consequently, it may be concluded

that the magnitude of largest μ_{M} is important parameter rather than r_{M-M} correlated to "magnetovolume effect" to explain the effect of nitrogen on the magnetic transition temperature of MN_{y} .

In the system of M_2N (M=Mn, Fe, Co), the effective magnetic moments were observed to be varied with the number of valence electrons of the M atom. In the system of $M_{2-3}N$, (M=Fe, Co, Ni), the effective magnetic moments decreased monotonously with increasing the number of valence electrons of the M atom. These relations between the effective moments and the number of valence electrons per a M atom for M_2N and M_3N are similar to those for 3d metals and their borides and phosphides, in which the effective magnetic moments or the magnetic moments varies with the number of valence electrons in such a way "Slater-Pauling curves".

The values of effective magnetic moments for Co_3N , Co_2N and Ni_3N are determined to be 1.4±0.1, 0.65±0.05 and 0.48±0.04 μ_{B} , respectively. The difference in the effective magnetic moments between Co_3N and Co_2N may be related to the difference in Ncoordination numbers around the Co atom between them, i.e. μ_{eff} of Co_3N with the Ncoordination number of 2 is larger than that of Co_2N with the N-coordination number of 3. This result is consistent with the tendency observed at MnN_v and FeN_v.

 Mn_4N , Mn_3N_2 and Mn_6N_5 films free from oxides which hampers characterization of MnN_y were prepared successfully by reactive vapor deposition method, and their electric resistivity were measured. The chemical composition of the films was controlled by regulating both of electric power applied to W filament and nitrogen gas pressure during the deposition. Deposited Mn_6N_5 films possessed the large nonstoichiometry of nitrogen. Temperature dependence of electrical resistivity for the Mn_3N_2 and the $Mn_6N_{5+\delta}$ films exhibit a metallic behavior. However, the $Mn_6N_{5-\delta}$ films exhibit a semiconducting behavior, even though the microstructure of $Mn_6N_{5-\delta}$ film is quite similar to that of $Mn_6N_{5+\delta}$ film. The slight dependence of ρ/ρ_{295} of the $Mn_6N_{5+\delta}$ films may be attributed

to a lot of Mn and N vacancies.

It is found as the effect of nitrogen content on the magnetic transition temperature that the magnitude of the largest magnetic moment of the M atom with smallest N-coordination number correlates closely with the magnetic transition temperature of MN_y with nearly closed-packed arrangement of M atoms.

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Paper relevant to this study

M. Tabuchi, M. Takahashi and F. Kanamaru, "Relation between magnetic transition temperature and magnetic moment for manganese nitrides MnN_y (0<y<1)" J. Alloys. Comp., in press.

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