# Effects of B and C on the ordering of L10-CoPt thin films

# Effects of B and C on the ordering of L1$_0$-CoPt thin films

H. Yamaguchi, O. Kitakami,[a)] S. Okamoto, and Y. Shimada
*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*

K. Oikawa
*National Institute for Advanced Industrial Science and Technology, Sendai 983-8551, Japan*

K. Fukamichi
*Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan*

We have investigated the effects of B and C on the ordering of L1$_0$-CoPt films and confirmed the following quite different role between B and C in CoPt. A small amount of B considerably decreases the temperature for ordering and is interstitially incorporated into L1$_0$-CoPt along its c axis due to the large negative heat of solutions with Co and Pt. X-ray photoelectron spectroscopy analyses have revealed that B atoms combine with Co and Pt. In contrast, C is not incorporated into the CoPt lattice due to its positive heat of solution, resulting in no decrease in the ordering temperature. The present results reveal that CoPt films containing a small amount of B are promising for high density recording media. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1408605]

Magnetic recording is a predominant data storage technology and continues to make rapid advances in data densities. In the near future, however, achievable data densities will be restricted by fundamental magnetic phenomena such as superparamagnetism, resulting in bit instability. The superparamagnetism is the consequence of random field fluctuations due to overcoming the activation energy $Kv$ by thermal energy $k_B T$. Here, $k_B$ and $K$ are the Boltzmann constant and the anisotropy constant per unit volume, respectively, and $v$ is the volume of a reversal unit. Equiatomic Co– and Fe–Pt alloy films with an L1$_0$-ordered structure have been attractive as ultrahigh–density magnetic recording media,[1,2] because the thermal agitation of spins would be suppressed by their very large magnetic anisotropy with a level of $10^7$ ~ $10^8$ erg/cc.[3,4] In general, however, high temperature processes above 600 °C are indispensable for ordering in CoPt and FePt.[5–8] From a practical view point, such a high temperature process is unsuitable for mass production of magnetic recording media. There have been a few attempts to reduce the ordering temperature. In our previous paper,[9] we reported that some additives, such as Sn, Pb, Sb, and Bi, were very effective to reduce the ordering temperature of L1$_0$–CoPt. These additives were found to easily diffuse and segregate onto the film surfaces by postannealing because of their very low surface free energy and low solubility in Co and Pt, resulting in large diffusivities of Co and Pt associated with defects caused by the excreted additives. In contrast with the above additives with a large atomic radius, some elements with a small atomic radius, such as B, C, etc., could be interstitially incorporated into CoPt.

In this letter, we show how B and C affect the ordering of equiatomic CoPt films. We have found quite different behaviors between B and C in CoPt.

The Co$_{0.45}$Pt$_{0.55}$-M (M=B and C) films were prepared on fused quartz substrates in a rf magnetron sputtering system under an argon gas pressure of 5 mTorr at a substrate temperature of 25 °C. A CoPt target with M chips placed uniformly on it was used. The film thickness was fixed at 50 nm. Annealing was performed in a vacuum chamber of 5 $\times 10^{-7}$ Torr at the temperature of 25–650 °C for 1 h. The crystal structure and the lattice parameters were determined by x-ray diffractometry (Cu $K\alpha$ radiation) with symmetric $\theta–2\theta$ scan and asymmetric $2\theta$ scan at the fixed incidence angle of $\theta\sim 8°$. The lattice parameters $a$ and $c$ were accurately evaluated by Cohen's method using the Nelson–Reily function.[10,11] The film compositions and chemical bonding states were investigated by x-ray photoelectron spectroscopy (XPS) with Al- or Mg $K\alpha$ radiation. The room temperature magnetic properties were measured with a vibrating sample magnetometer in a maximum field of 15 kOe.

Figure 1 shows the variation of in-plane coercivity $H_c$ for CoPt-$x$ at. % M (M=B and C) films as functions of annealing temperature $T_a$. It is obvious that C scarcely gives forth influence on $H_c$. In contrast, the addition of B significantly lower the annealing temperature necessary for high $H_c$, compared with that for pure CoPt. Further increase in $T_a$ above 550 °C drastically decreases $H_c$. Such a remarkable
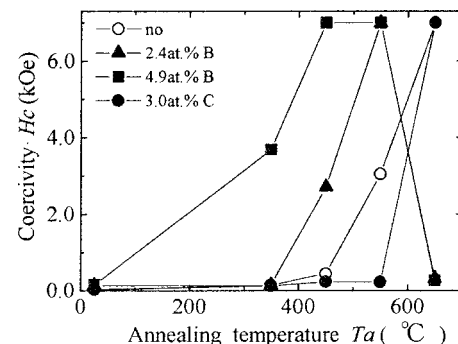


FIG. 1. Variation of in-plane coercivity $H_c$ for 50 nm thick CoPt–B, C films as a function of annealing temperature $T_a$.

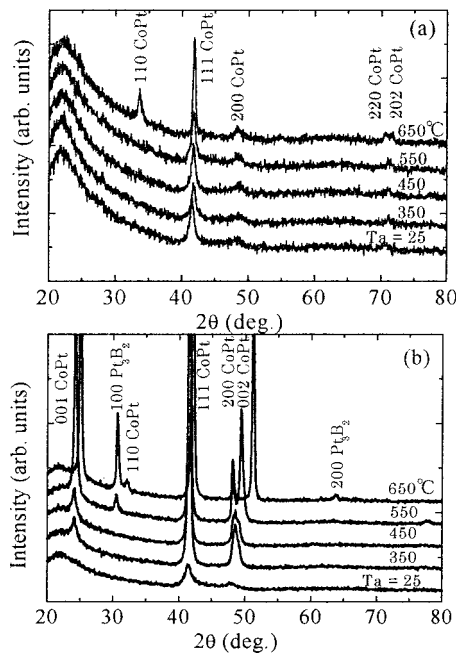[a)]Electronic mail: kitakami@tagen.tohoku.ac.jp

FIG. 2. Typical $\theta$–$2\theta$ scans for 50 nm thick (a) CoPt-3.0 at. % C and (b) CoPt-4.9 at. % B films annealed at various temperatures. Note that strong superstructure line 001 from the ordered $L1_0$-CoPt is clearly observed in the CoPt–B film.



FIG. 3. Variation of 111 diffraction peak with annealing temperature for (a) CoPt, (b) CoPt-4.9 at. % B, and (c) CoPt-3.0 at. % C.

effect of B on the magnetic properties can be understood from the $\theta$–$2\theta$ scans shown in Fig. 2(b). In contrast with CoPt and CoPt-3.0 at. % C in Fig. 2(a), the superstructure line 001 from the ordered $L1_0$-CoPt appears at $T_a = 350\,°C$ by addition of 4.9 at. % B, indicating that disorder–order transformation starts to occur around this temperature. Such a low-temperature ordering due to B is responsible for high coercivity. Further increase in $T_a$ above $550\,°C$ forms $Pt_2B_3$, accompanied by a shift of CoPt diffraction peaks toward higher angles. This result indicates that Co–Pt becomes Co-rich due to formation of $Pt_2B_3$. Such deviation from equi-atomic composition decreases $H_c$ due to a significant reduction of magnetic anisotropy.[4,12]

As mentioned above, the addition of B is found to be very effective to promote the ordering of CoPt. In order to investigate the role of B and C in CoPt, we traced variation of the fundamental line 111 for CoPt–B and –C films annealed at various temperatures. From Fig. 3(b), the lattice spacing (111) of CoPt-4.9 at. % B remains very large for $T_a \leq 550\,°C$ compared with that of pure CoPt, and then abruptly decreases for $T_a > 550\,°C$ due to formation of $Pt_2B_3$. In contrast, 111 peak from CoPt-3.0 at. % C behaves similarly as that for pure CoPt, although it is very weak and broad. All these results indicate that B is interstitially incor-porated into CoPt and decreases the ordering temperature. At higher annealing temperature above $550\,°C$, ordered $L1_0$-CoPt(B) decomposes into $Pt_2B_3$ and Co-rich $L1_0$-CoPt. On the other hand, C is hardly incorporated into CoPt lattice. Figure 4 shows the variation of the lattice parameters $a$, $c$ and tetragonality $c/a$ for CoPt-4.9 at. % B as a function of annealing temperature. Comparing with the values of $a = 3.776\,Å$, $c = 3.662\,Å$, and $c/a = 0.9698$ for CoPt and CoPt–C annealed at $T_a = 650\,°C$, the fct lattice of $L1_0$-CoPt(B) is obviously elongated along $c$ axis, yielding a large $c/a$. This result suggests that B is interstitially incor-
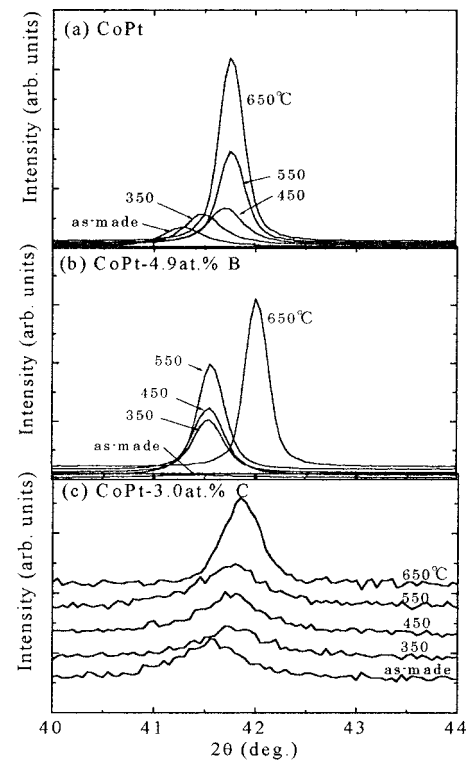
porated along the c axis of $L1_0$-CoPt. Further increase in $T_a$ above $550\,°C$ enhances the tetragonality due to Co enrich-ment in CoPt by formation of $Pt_2B_3$.[12]

The quite different behaviors between B and C men-tioned above are explained from the thermodynamical point of view. In the equilibrium phase diagrams,[13] C is almost insoluble in both Co and Pt, and the heat of solution of C in Co[14] and Pt[15] are positive, implying that there are strong repulsive atomic interactions between C and Co, and Pt. Therefore most C atoms are considered to decompose in the films without any alloying. In fact, XPS analyses have re-vealed that C atoms in the as-made and annealed CoPt-3.0 at. % C films hardly show a chemical shift of the C $1s$ line. [Fig. 5(a)]. On the other hand, the B $1s$ line in CoPt-4.9 at. % B showed that B atoms combine with Co and Pt, as can be seen from Fig. 5(b). In accordance with Miedema's formula on heat of solution,[16] the atomic interactions for Co–B and Pt–B are attractive and their interaction energies $\Omega$ in the conventional regular solution model are evaluated to be
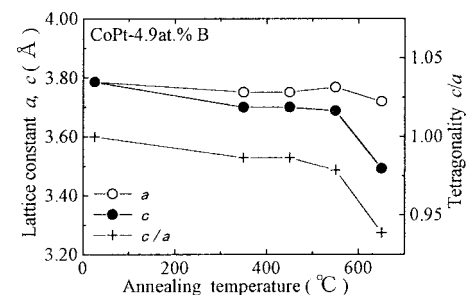


FIG. 4. Lattice parameters $a$, $c$, and the tetragonality $c/a$ vs annealing temperature for CoPt-4.9 at. % B. Note that the fct lattice of $L1_0$-CoPt–B is obviously elongated along the $c$ axis, compared with the values of $a = 3.776\,Å$, $c = 3.662\,Å$, and $c/a = 0.97$ for $L1_0$-CoPt and CoPt–C.

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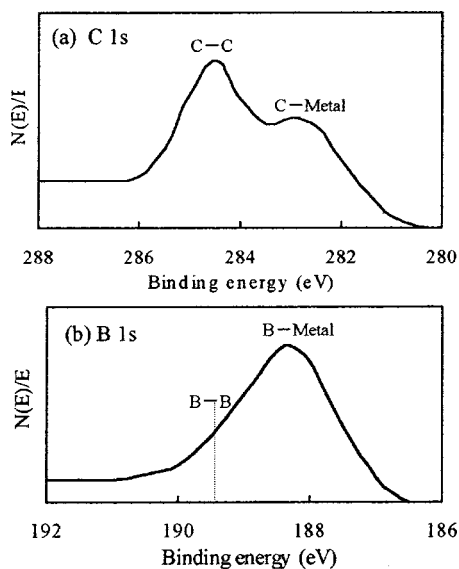
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FIG. 5. C $1s$ and B $1s$ photoelectron spectra for (a) CoPt-3.0 at. % C and (b) CoPt-4.9 at. % B films, respectively.

$-5.68 \times 10^5$ and $-6.52 \times 10^5$ J/mol, respectively. Consequently, B is naturally incorporated into CoPt, and forms $Pt_3B_2$ at higher annealing temperatures, because the magnitude of $\Omega_{Pt-B}$ is larger than that of $\Omega_{Co-B}$. From these results, the ordering temperature is significantly reduced by addition of B which is interstitially incorporated along the c axis of the $L1_0$-CoPt. This mechanism is different from the cases of Sn, Pb, Sb, and Bi in which the lattice defects caused by the excreted additives promote the ordering.[9] Such a significant reduction of the ordering temperature by addition of B could be explained by the fact that lattice distortion during the disorder/order transformation is trivial for CoPt–B compared with that for CoPt: tetragonality $c/a$ is 0.9889 for CoPt-4.9 at. % B and 0.9698 for CoPt, as seen from Fig. 4. Owing to this small change of the crystal lattice, the activation energy for the disorder/order transformation would be lowered. We expect that B in $L1_0$-FePt is similar in the effect because the atomic interaction of B with Fe is nearly the same as that with Co.

In summary, we have demonstrated that the annealing temperature for ordering of $L1_0$-CoPt can be significantly lowered down to $T_a \sim 350\,°C$ by addition of B. B atoms are interstitially incorporated along the c axis of the ordered phase. On the other hand, the addition of C is ineffective for ordering. Such a different role between B and C in CoPt can be understood by their atomic interactions with Co and Pt. From the present results, it is concluded that the B added CoPt films are very promising for high density recording media.

[1] K. R. Coffey, M. A. Parker, and J. K. Howard, IEEE Trans. Magn. **31**, 2737 (1995).
[2] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, Science **287**, 1989 (2000).
[3] R. A. McCurrie and P. Gaunt, Philos. Mag. **13**, 567 (1966).
[4] V. V. Maykov, A. Ye. Yermakov, G. V. Ivanov, V. I. Khrabrov, and L. M. Magat, Phys. Met. Metallogr. **67**, 76 (1989); *ibid.* **69**, 198 (1990).
[5] M. R. Visokay and R. Sinclair, Appl. Phys. Lett. **66**, 1692 (1995).
[6] S. Stavroyiannis, I. Panagiotopoulos, D. Niarchos, J. A. Chistodoulides, Y. Yang, and G. C. Hadjipanayis, Appl. Phys. Lett. **73**, 3453 (1999).
[7] V. Parasote, M. C. Cadeville, G. Garreau, and E. Beaurepaire, J. Magn. Magn. Mater. **198–199**, 375 (1999).
[8] R. F. C. Farrow, D. Weller, R. F. Marks, M. F. Toney, S. Hom, G. R. Harp, and A. Cebollada, Appl. Phys. Lett. **69**, 1166 (1996).
[9] O. Kitakami, Y. Shimada, K. Oikawa, H. Daimon, and K. Fukamichi, Appl. Phys. Lett. **78**, 1104 (2001).
[10] B. D. Cullity, *Elements of X-Ray Diffraction* (Addison-Wesley, Reading, MA, 1956).
[11] S. Okamoto, O. Kitakami, and Y. Shimada, J. Magn. Magn. Mater. **208**, 102 (2000).
[12] C. Chen, O. Kitakami, S. Okamoto, and Y. Shimada, J. Appl. Phys. **87**, 6947 (2000); O. Kitakami and Y. Shimada, Mater. Jpn. (in press).
[13] T. B. Massalski, in *Binary Alloy Phase Diagrams*, 2nd ed. (ASM International, OH, 1996).
[14] J. C. Swartz, Metall. Trans. **2**, 2381 (1971).
[15] R. H. Siller, W. A. Oates, and R. B. McLellan, J. Less-Common Met. **16**, 71 (1968).
[16] A. R. Miedema, F. R. de Boer, and R. Boom, J. Less-Common Met. **41**, 283 (1975); *ibid.* **46**, 67 (1976).