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Thermodynamic calculations of the effect of B and Ta on magnetically induced phase separation in Co–Cr–Pt alloys

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In order to clarify the relation between the magnetically induced phase separation and the recording media characteristics, the thermodynamic calculations of Co–Cr–Pt–B and Co–Cr–Pt–Ta systems have been carried out by using the available binary assessment data and Miedema’s semiempirical values. B is segregated to the boundary in a similar manner as Cr, which makes the boundary region paramagnetic. This result is consistent with available data that B weakens the intergranular magnetic coupling and increases the magnetic anisotropy in Co–Cr–Pt recording media. By adding Ta, the Cr content in the paramagnetic phase is also increased, reducing the intergranular magnetic coupling. However, the Ta content in the ferromagnetic phase is higher than in the paramagnetic phase, decreasing the magnetic anisotropy. Accordingly, the thermodynamic calculations successfully explain experimental magnetic data for Co–Cr–Pt–B and Co–Cr–Pt–Ta recording media. © 2002 American Institute of Physics. [DOI: 10.1063/1.1469684]

Co–Cr-based sputtered films are the current materials of high-density longitudinal recording media,\(^1\) and also considered as the most promising perpendicular recording media.\(^2\) The microstructures of Co–Cr-based films have Co-rich ferromagnetic hcp grains surrounded by a Cr-rich paramagnetic hcp phase.\(^3\) This compositional modulation is spontaneously developed in Co–Cr-based films deposited on heated substrates around 200–400 °C and has an important influence on a high coercivity and a high magnetization in high-density recording media. In the Co–Cr binary phase diagram, a two-phase separation into the ferromagnetic and paramagnetic phases occurs, which is closely correlated with the magnetic transition of Co. That is, it has been considered that the compositional heterogeneity of Cr in Co–Cr-based films is caused by this magnetically induced phase separation in the hcp phase.\(^4\) This phase separation has been thermodynamically calculated along the Curie temperature in the hcp phase as well as the fcc phase.\(^5\) Very recently, we have experimentally demonstrated that this phase separation occurs in bulk alloys and determined the composition of phase boundaries at various temperatures.\(^6\) The experimental data agree well with the thermodynamic calculations,\(^7\) implying strongly that the magnetically induced phase separation should be responsible for the compositional heterogeneity in Co–Cr-based films.

Recently, the first-principles approach has been developed for calculations of phase diagrams.\(^8\) However, it should be pointed out that this method is not so helpful at present for the quantitative description of experimental phase diagrams composed of several kinds of elements. On the other hand, the thermodynamic method is suited for the calculations of the magnetically induced phase separation in Co–Cr-based multi-component alloys.\(^9\) The microscopic compositional heterogeneity in Co–Cr-based films, depending on the additional elements, causes a significant change in magnetic properties.\(^10,11\) In our previous works,\(^9,12–14\) the thermodynamic calculations of the magnetically induced phase separation in Co–Cr–X ternary systems have been conducted in order to discuss the relation between the effects of the additive X on the magnetically induced phase separation and the recording media characteristics. From these results, we have predicted the effective additive for Co–Cr-based recording media. The calculation results could clarify the effects of Pt and Ta on the compositional modulation of Co–Cr–Pt\(^9\) and Co–Cr–Ta\(^12\) recording media.

A remarkable increase in the recording density in hard disks earnestly requires improvements of recording characteristics of Co–Cr-based magnetic media. Co–Cr–Pt films have been getting much attention as high-density recording media, because of their high magnetic anisotropy and high coercivity, though the films bring about higher media noise. In order to reduce such a media noise, the addition of B\(^15\) or Ta\(^16\) to Co–Cr–Pt films has been examined. In the present study, the thermodynamic calculations on the magnetically induced phase separation in Co–Cr–Pt–B and Co–Cr–Pt–Ta systems are carried out and the effects of B and Ta on the magnetic properties of Co–Cr–Pt films are discussed on the basis of the thermodynamic calculations.

The Gibbs energy of the hcp solution phase is represented by dividing it into magnetic (\(G^{\text{mag}}\)) and nonmagnetic parts. The nonmagnetic part consists of the ideal mixing entropy (\(G^{\text{id}}\)) and the excess Gibbs energy (\(G^{\text{ex}}\)) terms. The excess Gibbs energy and the magnetic terms are expressed by the Redlich–Kister\(^17\) and the Hillert–Jarl\(^18\) description,
respectively. The molar Gibbs energy of the hcp solution phase is given by
\[ G = G^{id} + G^{ex} + G^{mag} \]
with
\[ G^{id} = RT \sum x_i \ln x_i, \]
\[ G^{ex} = \sum x_i x_j \left( 0 \Omega_{ij} + 1 \Omega_{ij} (x_i - x_j) + 2 \Omega_{ij} (x_i - x_j)^2 + 3 \Omega_{ij} (x_i - x_j)^3 \right), \]
\[ G^{mag} = RT \ln (\beta + 1) - f(\tau), \]
where \( R \) is the gas constant and \( T \) is the temperature; \( x_i \) and \( x_j \) are, respectively, the atomic concentrations of elements \( i \) and \( j \) with \( i, j = B, Co, Cr, Pt, \) and \( Ta. \) The Bohr magneton number is denoted as \( \beta, \) and \( f(\tau) \) is given by the polynomial expression with the normalized temperature \( \tau = T/T_C \) derived from the specific heat formulas of the magnetic transition. The Curie temperature \( T_C \) and \( \beta \) are expressed by the phenomenological function of composition. Details for the calculations were given in other articles. Since there are no available experimental thermodynamic data on B–Pt and Ta–Pt systems, the interaction energies between Pt and B, and Pt and Ta is negatively large. Some parts of the calculated magnetically induced phase separation include metastable phase equilibria.

In our previous letter, we demonstrated that the types of the magnetically induced phase separation in ternary systems could be classified into four groups. Type I: the Cr contents in both the ferromagnetic hcp, hcp\textsubscript{ferro}, and paramagnetic hcp, hcp\textsubscript{para}, phases decrease with increasing additive. Type II: the Cr content in the hcp\textsubscript{ferro} phase decreases and that in the hcp\textsubscript{para} phase increases with increasing additive. Type III: the Cr content in the hcp\textsubscript{para} phase is increased by additive, whereas that in the hcp\textsubscript{ferro} phase is not effectively reduced. Type IV: the three-phase separation occurs into one hcp\textsubscript{ferro} phase and two hcp\textsubscript{para} phases. The calculated results were consistent with the experimental observations and explained well the effects of the addition of Pt, Ta or Ge on the magnetic properties of Co–Cr-based recording media, though the films were not fully in the equilibrium state. The present Co–Cr–Pt, Co–Cr–B, and Co–Cr–Ta ternary alloys belong to the type I, II, III, respectively, because the relation of the interaction energies are \( \Omega_{CoB} < \Omega_{CoPt} < 0, \Omega_{CrB} < \Omega_{CoB} < 0 \) and \( \Omega_{CoTa} < 0, \Omega_{CrTa} > 0 \) as discussed in our previous letter.

Figure 1(a) shows the calculated Cr content in the hcp\textsubscript{para} phase at 400 °C for Co–20 at. % Cr–(0–20) at. % Pt-based alloys with various B contents. The Cr content in the hcp\textsubscript{para} phase decreases with increasing Pt in Co–Cr–Pt ternary alloys. However, the addition of B considerably increases the Cr content in the hcp\textsubscript{para} phase because the interaction energy between B and Cr is negatively large, which promotes the magnetically induced phase separation. It has been reported that the addition of B to Co–Cr–Pt alloys effectively reduces both the intergranular exchange coupling and the media noise. The present calculated results suggest that the reason for the media noise reduction by the addition of B is due to the reduction of the intergranular exchange coupling through the increase of the Cr content in the hcp\textsubscript{para} phase. In addition, B is preferentially distributed to the hcp\textsubscript{para} phase, promoting the magnetic decoupling among the hcp\textsubscript{ferro} grains. As pointed out by Kubota, Folks, and Marinero this preferential distribution would bring about a severe distortion of the hcp\textsubscript{para} lattice.

The Cr content in the hcp\textsubscript{ferro} phase for Co–20 at. % Cr–(0–20) at. % Pt alloys decreases with increasing Pt and B content as shown in Fig. 1(b). The B content in the hcp\textsubscript{ferro} phase also decreases with increasing Pt content. The Pt content in the hcp\textsubscript{para} phase slightly increases by the addition of B, but that in the hcp\textsubscript{ferro} phase remains almost unchanged. From the comparison between our previously calculated results and the experimental results, the effects of Pt on Co–Cr thin films concluded that the decrease of the Cr content in the hcp\textsubscript{ferro} phase results in the enhancements both the magnetic anisotropy and coercivity. The present calculated results elucidate that the simultaneous addition of Pt and B is more effective for the increase of magnetic anisotropy and coercivity. The present calculated results elucidate that the simultaneous addition of Pt and B is more effective for the increase of magnetic anisotropy and coercivity. The present calculated results elucidate that the simultaneous addition of Pt and B is more effective for the increase of magnetic anisotropy and coercivity.
coercivity than the addition of Pt only, in accordance with experimental results of Co–Cr–Pt–B films.15,25

Shown in Fig. 2(a) is the calculated Cr content in the hcp$_{\text{para}}$ phase at 400°C for Co–20 at. % Cr–(0–18) at. % Pt as a function of Ta content. The addition of Ta increases the Cr content in the hcp$_{\text{para}}$ phase, particularly in the low Pt content region. The increase of the Cr content in the hcp$_{\text{para}}$ phase is expected to lead to the reduction of the intergranular exchange coupling as well as the media noise, consistent with experimental data.16,23,26 The present calculated results clarify that the addition of Ta is more effective on the reduction of the media noise in the low Pt content region, in particular, in the Co–Cr–Ta ternary alloys. However, in the Pt content higher than 16 at. %, Ta is not effective to increase the Cr content in the hcp$_{\text{para}}$ phase. Consequently, it is expected that B is more effective to increase the Cr content than Ta in Co–Cr–Pt films, particularly in high Pt content range.

Although Ta tends to be distributed in the hcp$_{\text{ferro}}$ phase, its content in the hcp$_{\text{ferro}}$ phase is not affected by the Pt content as shown in Fig. 2(b), except for above 4 at. % Ta. The Cr content in the hcp$_{\text{ferro}}$ phase slightly decreases with increasing Ta. According to our experimental results, the addition of Ta to Co and Co–Cr films steeply decreases the magnetic anisotropy and coercivity. The present calculated results suggest that the addition of Ta to Co–Cr–Pt alloys reduces the magnetic anisotropy because of the increase of the Ta content in the hcp$_{\text{ferro}}$ phase, though it weakens the intergranular exchange coupling due to the increase of the Cr content in the hcp$_{\text{para}}$ phase.

In summary, the thermodynamic calculations on the magnetically induced phase separation in Co–Cr–Pt–B and Co–Cr–Pt–Ta systems have been carried out by using the binary interaction energies and discussed the magnetic properties of Co–Cr–Pt recording media in terms of the magnetically induced phase separation. B is preferentially distributed to the paramagnetic phase rather than to the ferromagnetic phase, and effectively increases the Cr content in the paramagnetic phase. On the other hand, Ta is distributed to the ferromagnetic phase rather than to the paramagnetic phase and increases the Cr content in the paramagnetic phase. Accordingly, B is more useful than Ta because of the effective suppression of the intergranular exchange coupling without degradation of the magnetic anisotropy.

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