Prediction of Effective Elements for Magnetically Induced Phase Separation in Co-Cr-based Mangetic Recording Media

Prediction of effective elements for magnetically induced phase separation in Co–Cr-based magnetic recording media

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Thermodynamic calculations of the magnetically induced phase separation of the hcp phase in Co–Cr-based alloy systems, which is the origin of the compositional modulation observed in magnetic recording media, have been carried out. The magnetic and nonmagnetic terms in the Gibbs energy are evaluated from available thermodynamic data and Miedema's semiempirical values. It is demonstrated that the phase separation in Co–Cr–X ternary alloys can be classified into four types, depending on the values of interaction energies between Co and/or Cr and X atoms. Existing magnetic data on Co–Cr-based recording media are discussed in terms of the phase stability of the hcp phases. The present calculations would be useful for development of high-density magnetic recording media. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1389067]

Co–Cr-based sputtered thin films have a high coercivity H_c with a high magnetization M, and have been widely used as magnetic recording media of hard disks. The thin films have a hcp structure and a fine microstructure with the Co-rich ferromagnetic phase precipitated in the Cr-rich paramagnetic matrix.[1] Thermodynamic calculations of the phase equilibria in the fcc and hcp phases of the Co–Cr system show a two-phase separation into the ferromagnetic and paramagnetic phases formed along the Curie temperature[2,3] as recently confirmed experimentally by Oikawa *et al.*[4] It has been explained that this phase separation is induced by the magnetic transition of Co.[5] This magnetically induced two-phase separation of the hcp phase has been attributed to a compositional modulation of Cr in Co–Cr-based sputtered thin film.[3,6]

It is well known that the distribution of Cr in each phase and the microstructure has a significant effect on the recording properties of this alloy. Pt and/or Ta have been added for modification of the recording characteristics resulting in a drastic change in the distribution of Cr.[7,8] According to thermodynamic calculations of Co–Cr–Pt and Co–Cr–Ta ternary systems,[9,10] both the miscibility gap of the hcp phase and the Cr content in the ferromagnetic hcp phase are reduced with increasing Pt content, resulting in increases of the coercive force and media noise level, whereas the addition of Ta results in the promotion of the Cr distribution in the paramagnetic phase and isolation of magnetic grains from each other results in a reduction of media noise. Consequently, the effect of the addition of Pt or Ta on Co–Cr-based recording media is strongly related to the stability of the magnetically induced miscibility gap and can be explained by thermodynamic calculations.

Recently, the first-principle approach has been developed.[11] However, this method is not so helpful at present for the quantitative description of the experimental phase diagram. In the present study, therefore, thermodynamic calculations of the magnetically induced phase separation in Co–Cr–X ternary systems have been conducted to predict the stability of the miscibility gap by using the available binary assessments[9,12–24] and Miedema's values.[25] The effects of alloying elements X on the phase boundaries and the magnetic properties are herein discussed on the basis of the thermodynamic calculations.

The Gibbs energy of the ternary solution was described by dividing it into magnetic (G^{mag}) and nonmagnetic contributions. The molar Gibbs energy of a ternary solution is given by

$$G = G^{\mathrm{mag}} + [G^{\mathrm{ex}} - TS^{\mathrm{mix}}]^{\mathrm{nonmag}},$$

where S^{mix} is the ideal entropy of mixing and T is the temperature. G^{ex} is the excess free energy term which includes deviations from the ideal solution. G^{ex} is expressed by the Redlich–Kister description[26] as

$$G^{\mathrm{ex}} = \sum_{i=0} \{(x_{\mathrm{Co}} - x_{\mathrm{Cr}})^i {}^i\Omega_{\mathrm{CoCr}} x_{\mathrm{Co}} x_{\mathrm{Cr}} + (x_{\mathrm{Co}} - x_{\mathrm{X}})^i \times {}^i\Omega_{\mathrm{CoX}} x_{\mathrm{Co}} x_{\mathrm{X}} + (x_{\mathrm{Cr}} - x_{\mathrm{X}})^i {}^i\Omega_{\mathrm{CrX}} x_{\mathrm{Cr}} x_{\mathrm{X}}\},$$

where x_{Co}, x_{Cr}, and x_{X} are the atomic concentrations of Co, Cr, and X, respectively. The interaction energy between i and j atoms is given by Ω_{ij}. The magnetic contribution term to the Gibbs energy is expressed by the mathematical description given by Hillert and Jarl[27] where the compositional dependence on the Curie temperature and the Bohr magneton number are taken from the experimental data. Details of the calculation method have been reported.[9]

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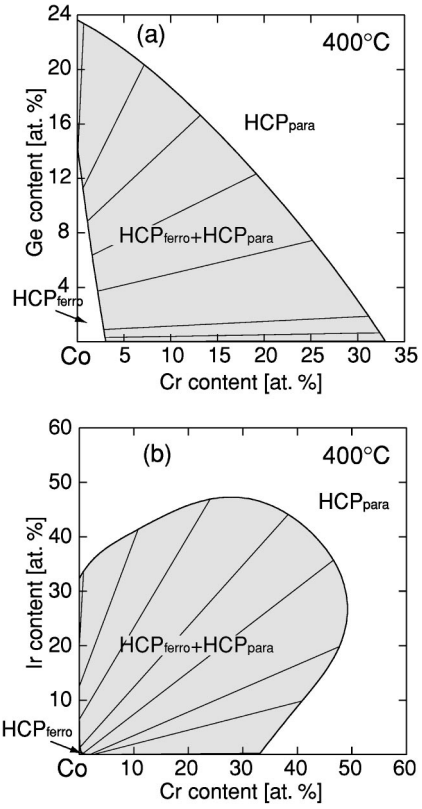

FIG. 1. Calculated phase diagrams at 400 °C including the metastable boundaries: (a) Co–Cr–Ge and (b) Co–Cr–Ir systems.

In the present study, the interaction energies Ω_{ij} of various systems were selected from the available data.[12–24] In some alloy systems where the interaction energies of the hcp phase have not been reported, those values of the fcc or bcc phase have been adopted for the calculations, because the thermodynamic properties of these solution phases generally have similar characteristics. The mixing enthalpy evaluated by Miedema's method[25] was also applied for systems in which no thermodynamic assessment has been done. It should be noted that the calculated magnetically induced phase separation includes the metastable phase boundaries.

Representative results of the calculations are shown in Fig. 1. The isothermal section of the Co–Cr–Ge system at 400 °C is shown in Fig. 1(a). The magnetically induced phase separation is also predicted in the Co–Ge binary system.[28] The miscibility gap is formed along the Curie temperature and the width of the gap of the Co–Cr binary becomes narrower with increasing Ge content. Figure 1(b) shows the isothermal section of the Co–Cr–Ir system at 400 °C. The miscibility gap of the Co–Cr binary is expanded and the Cr content of the ferromagnetic phase is strongly reduced with increasing Ir content.

From these thermodynamic calculations, the shape of the magnetically induced phase separation in the Co-rich portion of the Co–Cr–X ternary system from 200 to 450 °C was classified into four types, as shown in Fig. 2. Type I: The Cr contents in both the ferromagnetic and paramagnetic phases decrease with increasing X, as shown in Fig. 2(a). In this type of phase diagram, the interaction energies Ω_{CoX} and Ω_{CrX} have similar magnitudes of value. Type II: The Cr content in the ferromagnetic phase decreases and that in the paramagnetic phase increases with increasing amounts of X, as shown in Fig. 2(b). The interaction energies Ω_{CoX} and Ω_{CrX} of this type have the relationship of $0>\Omega_{CoX}\gg\Omega_{CrX}$ and the Gibbs energy of the Cr–X system is significantly stabilized, resulting in enhancement of the phase separation of Co–Cr. Type III: The Cr content of the paramagnetic hcp phase is increased by the addition of X, whereas that in the ferromagnetic phase is not effectively reduced, as shown in Fig. 2(c). The interaction energies of this system show the tendency of $\Omega_{CoX}<0$ and $\Omega_{CrX}\gg 0$, and a chemical miscibility gap exists in the Cr–X system and continues to the phase separation of the Co–Cr system. Type IV: The three-phase equilibrium of one ferromagnetic and two paramagnetic phases was calculated in some systems, as shown in Fig. 2(d). In this case, the interaction energies are similar to those for type III in magnitude, but a magnetically induced miscibility gap exists in the Co–X system.

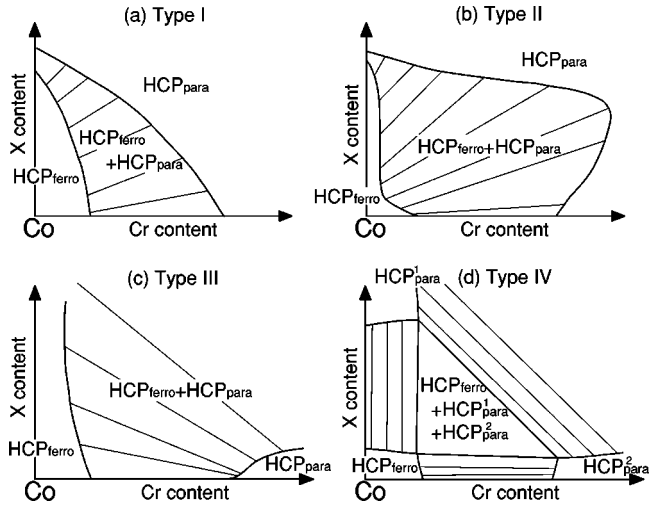

FIG. 2. Schematic miscibility gap boundaries of the hcp phase in the Co–Cr–X isothermal section from 200 to 450 °C.

Figure 3 shows the classification of the phase equilibria for each element in the Periodic Table based on the calculated results. It has been explained that the addition of Pt to the Co–Cr alloy thin film increases the coercive force and the magnetic anisotropy because the Cr content in the ferromagnetic phase significantly decreases with increasing Pt content,[29] which corresponds to the Co–Cr–Pt phase diagram belonging to type I or II. Pd, Rh, and Ir also show a similar type of miscibility gap. Therefore, the magnetic properties of the Co–Cr–Pd thin-film alloy would be expected to

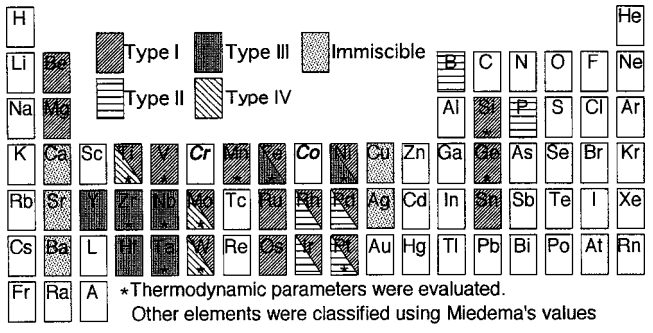

FIG. 3. Classification of elements in the Periodic Table for the miscibility gap of the hcp phase in the Co–Cr–X system.

be similar to those of the Co–Cr–Pt system.[9] On the other hand, the addition of Ir to Co strongly decreases the magnetic anisotropy energy,[30] which in turn would cancel out the beneficial effect of decreasing Cr content in the ferromagnetic phase by alloying of Ir. For the addition of Ta, recording noises are reduced by increasing Cr content in the paramagnetic phase, which promotes the isolation of each ferromagnetic particle.[5,6] Since Hf, Nb, Y, and Zr belong to type III, the same as those of the Co–Cr–Ta system, these elements would be expected to have similar effects on the magnetic properties of the Co–Cr–Ta system. However, the amount of the addition of these elements should be limited to low concentration ranges to avoid the formation of an amorphous phase because of a high forming ability of the amorphous phase.[31] Recently, it has been reported that the addition of B is effective for improvement of the magnetic properties of Co–Cr–Pt alloy thin film.[32] The phase diagram of the Co–Cr–B ternary system belongs to type II. Ueno and Hasebe[24] calculated the distribution of Cr in the Co–Cr–B system and suggested that the Cr content in the paramagnetic phase increases with increasing B content and that the magnetic isolation of the ferromagnetic particles would be promoted. From our calculations, the addition of P is also expected to have similar effects on the magnetic properties. Takahashi *et al.*[33] have reported that the Co–Cr–Ge ternary alloy has a high magnetic anisotropy energy and is reported as a promising high-density recording medium. Since the Co–Cr–Ge system belongs to type I, as shown in Fig. 1(a), the addition of Ge to the Co–Cr thin film would reduce the Cr content in the paramagnetic phase and depress the magnetic isolation of each ferromagnetic particle. In view of the phase equilibria, therefore, further adjustment of selection of alloying elements would be necessary to increase the Cr content in the paramagnetic phase for improvement of the magnetic properties of the Co–Cr–Ge system.

In conclusion, thermodynamic calculations on the magnetically induced phase separation of the hcp phase in Co–Cr–X ternary systems have been conducted. The shape of the miscibility gap of the Co–Cr–X ternary system can be classified into four types. The relation between these phase diagrams and the magnetic properties has been discussed. The present calculations would be useful for design and development of Co–Cr-based high-density magnetic recording media.

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