High-throughput analysis of magnetic phase transition by combining table-top sputtering, photoemission electron microscopy, and Landau theory

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Abstract

Recent progress in materials informatics has triggered growing interest in combinatorial experimental systems for materials development. We demonstrate a novel high-throughput experiment combining compact materials synthesis, synchrotron radiation measurements, and statistical data analysis. This technique focuses on not only drawing phase diagrams but also analysing phase transitions for exploring the functions of magnetic materials. This study involved the rapid preparation of a composition-gradient Fe–Co–Cr ternary thin film using a table-top sputtering system and 3D printer, followed by measurement of the chemical components and magnetic contrast by photoemission electron microscopy, through the acquisition of one million spectral datasets within 10 min. The ternary magnetic phase diagram of Fe–Co–Cr obtained by statistical analysis of the magnetic circular dichroism (MCD) contrast images was in perfect agreement with previous studies. The MCD histogram was fitted based on Landau theory, and the estimated critical exponent β (0.36 ± 0.028) showed excellent agreement with previous theoretical and experimental studies. This study successfully demonstrates universal physical parameter analysis that characterizes magnetic properties by a high-throughput approach combined with a simple experimental apparatus.

Introduction

The development of high-throughput experiments has attracted tremendous attention in materials informatics to discover novel functional materials^{1–4}. Integrating materials synthesis, physical property measurement, and data science is crucial to accelerating materials discovery^{5–7}. Technological development in these individual areas has recently seen dramatic progress, for example, the automation of materials synthesis^{2,5–10}, building materials databases^{11–13}, and predicting physical properties by machine learning^{14–16}. However, many issues remain in high-throughput experiments. The traditional integration of synthesis, measurement, and data analysis is insufficient^{9, 10}; moreover, many combinatorial studies have focused exhaustively on the drawing of phase diagrams. Great efforts have been devoted to studying specific material problems^{4,5}; but the analysis of intrinsic physical properties has been overlooked—few studies have focused on exploring phase transition as an origin of novel function in materials.

In this study, we developed a novel high-throughput experimental method by combining compact materials synthesis, physical property measurement, and statistical analysis (Figure 1). The fusion of these three techniques will accelerate the exploration of materials. Therefore, we focus on not only drawing phase diagrams but also analysing phase transitions as a key part of exploring material functions. For rapid combinatorial sample preparation, we utilised a table-top sputtering instrument with a custom 3D-printed sputter beam aperture (Figure 1(a)) to rapidly deposit a Fe–Co–Cr ternary alloy thin film with a continuous composition gradient in the micro-region. Fe–Co–Cr was chosen as a typical 3d metal alloy system exhibiting a ferromagnetic–paramagnetic phase transition^{17–19}. It is well known that the Fe-rich α_1 phase is ferromagnetic, but at higher Cr concentration the Curie temperature decreases and

the alloy becomes antiferromagnetic; therefore, Fe-Co-Cr is a suitable system for the demonstration of our approach to high throughput experiments. The physical properties of the thin film were analysed using photoemission electron microscopy (PEEM) (Figure 1(b)), a powerful full-field-type microscopy allowing for simultaneous measurement of the chemical composition, magnetic properties, and electronic structure of a specimen. PEEM is a useful technique for analyzing thin films' magnetic properties, and there have been many successful studies of the spin-reorientation transition of magnetic multilayers^{20, 21}. The X-ray absorption intensity is recorded for each pixel of the observed image, and one million X-ray absorption spectra (XAS) and magnetic circular dichroism (MCD) contrast images can be acquired in 10 min. We used these micro-spectroscopic data sets to conduct a high-throughput experiment. X-ray structure analysis was not included in this high-throughput analysis because of the pinpoint measurement. For data analysis, we statistically examined the chemical composition and MCD contrast images recorded in the microscopic image (Figure 1(c)). The information in each pixel was sorted according to the chemical compositional ratio, MCD contrast histograms were prepared depending on the Fe–Co–Cr compositional ratio, and a ternary phase diagram of the MCD histograms was prepared. Finally, we applied Landau theory, a typical model of magnetic phase transitions, to interpret the MCD histograms and magnetic phase transition. The approach is to analyse the pseudo-free energy landscape from MCD image contrast data using the fact that the MCD histogram is the probability distribution function of the magnetisation. We also demonstrated the capability of quantitatively extracting the critical exponent β , a universal parameter in phase transitions, solely from the image information.

Results And Discussion

Figure 2(a–c) depicts the chemical composition maps obtained by PEEM, which illustrate that the chemical composition of Fe, Co, and Cr spatially and continuously changes. The line profiles of the compositional distribution of Fe, Co, and Cr are shown in the lower part of Figure 2 (a), (b), and (c), respectively. Each element's composition varies continuously in a roughly linear fashion, confirming that the composition distribution is adequately prepared. A ternary composition map of Fe–Co–Cr obtained by superimposing the three images is displayed in Figure 2(d), where the overlapped region at the centre shows the alloying of the three elements. Figure 2(e) depicts the MCD image of the same area as the composition map, indicating a clear magnetic contrast in the centre and upper-right region of the sample. In the superimposed composition and MCD images, the appearance and disappearance of magnetic contrast aligns with variations in the chemical compositional ratio of Fe–Co–Cr (Figure 2(f)). The MCD contrast appears in regions of intermediate concentration of all three elements and regions of high Co concentration, whereas the contrast disappears in regions of high Cr and Fe concentrations. This suggests that a ferromagnetic–paramagnetic phase transition occurs depending on the Fe–Co–Cr composition. We confirm the reproducibility of the appearance and disappearance of the MCD contrast in 5 adjacent island thin films. (Supplementary Figure 1.) We obtained these magnetic phase transition data in approximately 30 min with the proposed high-throughput measurement system.

Next, the ternary phase diagram of the MCD histogram is depicted in Figure 3, which was obtained simultaneously by the statistical analysis of MCD contrast depending on the Fe–Co–Cr compositional ratio. We divided the image into 40 regions of interest (ROIs) according to compositional ratio with steps of 5 at%, The spatial distribution of ROIs is shown in supplementary Figure 2, showing that a reasonably continuous compositional distribution is formed. One histogram typically contains MCD information corresponding to as many as approximately 10,000 pixels. Herein, we focus on the MCD contrast to discuss the ferromagnetic/paramagnetic transition, and discussing the construction of magnetic domains due to the loss of spatial information is beyond the scope of this study. We generated a histogram as a function of MCD asymmetry for each ROI. A single-peaked MCD histogram, as depicted in the example in Figure 3(b), corresponds to a paramagnetic state because no net magnetisation exists for the corresponding composition (monotonic grey contrast). A double-peaked MCD histogram, such as depicted in Figure 3(c), corresponds to a ferromagnetic state because the constituent spontaneous magnetisations oriented parallel or antiparallel to the X-ray direction split the MCD signal into positive and negative values (white and black contrast in the grey-scale image, respectively). The structure of the MCD histogram is a useful feature to classify the magnetic state. A misfit in several MCD histograms is probably due to the effect of the magnetic domain structure on parameter such as magnetostatic energy and magnetization direction. In this study, we have used two simple measures, the presence/absence of peak splitting in the histogram and the full width at 20% of maximum of the histogram, to discuss the ferromagnetic/paramagnetic states. The analytical parameters of the MCD histogram have been previously examined in an Fe–Cr binary alloy (Supplementary Figure 3). The 40 MCD histogram panels were categorised by colour (ferromagnetic: red, paramagnetic: green) and overlaid on the previously established Fe–Co–Cr ternary phase diagram (Figure 3(a))^{17–19}. This confirmed that the ferromagnetic and paramagnetic phase distributions determined from the MCD histograms are in perfect agreement with the known phase boundaries of the ferromagnetic–paramagnetic transition and the miscibility gap. Although pure Fe is a well-known ferromagnet, it is outside the range of this phase diagram. We performed an examination experiment for an Fe–Cr binary alloy using the same experimental technique and confirmed that the ferromagnetic transition occurs as the Fe concentration increases (Supplementary Figure 3). We have also twice confirmed the reproducibility of the magnetic phase diagram drawing (Supplementary Figure 4). Therefore, we successfully demonstrated the high-throughput experimental determination of a ternary magnetic phase diagram.

Finally, we analysed the MCD histograms near the magnetic phase transition using Landau theory, an excellent model that can describe the pseudo-free energy F of a system based on the mean field approximation. The following simple fourth-order polynomial of the magnetisation m can represent the magnetic phase transition^{22,23}.

$$F = -hm + Am^2 + Bm^4$$

The second-order term Am^2 is the exchange energy term, and the sign of the coefficient A corresponds to the ferromagnetic–paramagnetic transition. The fourth-order coefficient B is the magnetic anisotropy energy term and h is the magnetic field. Note that the experimental MCD histograms remained

asymmetric due to the remanent magnetisation. Therefore, we left the first-order term hm as a correction term to perform fitting. It should also be noted that Landau theory cannot wholly treat spatial inhomogeneity in magnetic domain structures because of the mean field approximation²⁴. Therefore, we abandoned the spatial information in the MCD-PEEM image and statistically treated the MCD data to investigate only the presence of a ferromagnetic–paramagnetic transition. As a result of fitting the MCD histograms, the coefficient A changed from 2.00×10^{-3} in the ferromagnetic phase ($\text{Fe}_{25}\text{Co}_{40}\text{Cr}_{35}$) to -6.99×10^{-3} in the paramagnetic phase ($\text{Fe}_{30}\text{Co}_{30}\text{Cr}_{40}$), where the change in sign indicates a magnetic phase transition. The coefficient B ranged from 1.90×10^{-5} ($\text{Fe}_{25}\text{Co}_{40}\text{Cr}_{35}$) to 9.43×10^{-5} ($\text{Fe}_{30}\text{Co}_{30}\text{Cr}_{40}$). The critical exponent β was examined using the equation

$$\sqrt{A/2B} = |T_c - T|^\beta$$

with the experimental A and B values for $\text{Fe}_{40}\text{Co}_{45}\text{Cr}_{15}$. The Curie temperature T_c for the corresponding composition (210 °C) was taken from a previous study¹⁹, and we verified the reproducibility of the results by repeating the same experiment for several different viewing fields. The b value obtained by this procedure was 0.36 ± 0.028 . Comparison with b values determined with the three-dimensional Ising model (0.365) and for $\text{Fe}_{78-x}\text{Cr}_x\text{Si}_4\text{Nb}_5\text{B}_{12}\text{Cu}_1$ (0.367–0.376)^{23,25,26} showed that our results are in good agreement. As mentioned above, there remains an issue with using Landau theory to treat spatial inhomogeneity. The introduction of a correction term describing the inhomogeneity of the magnetic domain structure would be useful to correct the landscape of free energy and improve the accuracy of b ^{27,28}. It is noteworthy that our method can determine b without temperature-dependent measurements. Moreover, the extraction of such a universal parameter from image information is a unique feature of this technique, unlike conventional exhaustive combinatorial analyses. Our proposed system is a starting point to realize efficient and inexpensive high-throughput experiments. Although it is currently performed ex-situ, the in-situ combination with beamline instruments will accelerate database construction, and enables efficient materials discovery.

In summary, this study involved the integration of a simple combinatorial thin-film deposition technique using a 3D-printed sputtering aperture and high-throughput measurements of both the chemical composition and magnetic contrast of a Fe–Co–Cr ternary gradient thin film by PEEM. The appearance and disappearance of MCD contrast were clearly confirmed depending on the chemical compositional ratios. As a result, we successfully composed the magnetic phase diagram of the Fe–Co–Cr ternary system simultaneously by statistical analysis of the acquired image information, and the ternary diagram was in excellent agreement with the established ferromagnetic–paramagnetic transition and miscibility information. Finally, the evaluation of the critical exponent b based on Landau theory, and the results showed quantitatively good correspondence to previous studies. This study has successfully established a novel high-throughput experimental method combining materials synthesis, physical property measurement, and statistical analysis for exploring material functionalities. In addition, it has focused

not only on drawing the phase diagram but also on analysing the magnetic phase transition as a key component of exploring the material functions.

Methods

We developed a compact combinatorial instrument for the rapid synthesis of Fe–Co–Cr ternary thin films with a composition gradient. The system consists of a table-top multi-source DC magnetron sputtering instrument, a custom-manufactured sputter beam aperture made by a 3D printer for controlling the direction and diffusion of the sputtered particles, and a commercially available transmission electron microscopy (TEM) grid. The beam aperture was 3D-printed using titanium powder and was designed such that the three cylindrical entrance holes converge into one exit hole. The individual hole diameters are 2.3 mm, and the aperture is 4 mm thick as shown in Fig. 1(a) and 4(a). The creation of the aperture began with the design of a 3D model of the jig using Autodesk MAYA, fabrication of a resin jig prototype in Da Vinci 1.0AiO, and then fabrication of the metal jig on a metal 3D printer. A TEM grid with $30\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$ square holes was attached to the exit side of the aperture. We used a commercially available copper TEM grid by VECO (400 mesh, thickness $25\text{ }\mu\text{m}$). Fe, Co, and Cr were deposited obliquely on a SiO_2/Si substrate by DC magnetron sputtering to prepare a ternary thin film with a composition gradient. The typical sputtering conditions were as follows: base pressure of $9.03 \times 10^{-4}\text{ Pa}$, Ar^+ pressure of 1.0 Pa , sputtering current of 25 mA , and room temperature. Multicomponent layered films with 2 nm -thickness were deposited for each element and the procedure repeated 10 times to obtain a multi-layered film with 30 total layers and a thickness of 60 nm . Subsequently, the specimen was annealed at 600°C for 1 h *in-situ* to promote alloying. The annealing temperature and time were determined based on the diffusion coefficient of Fe–Cr ($7.8 \times 10^{-9}\text{ m}^2/\text{s}$), and a sufficient diffusion length ($1.78\text{ }\mu\text{m}$) compared to the film thickness (60 nm)¹⁸.

As a prior experiment, we examined two standard Fe–Cr binary thin films with and without annealing. Specimens were prepared as a homogeneous film without the use of the beam aperture and TEM grid. XRD analysis confirmed that the Fe(110) and Cr(110) double peaks merge into a single FeCr(110) peak upon annealing, suggesting that Fe and Cr are intermixing and alloying during annealing (Figure 4 (b)).

For Fe–Co–Cr alloys, chemical maps and magnetic contrast images were measured using a spectroscopic PEEM instrument (Elmitec, SPELEEM) installed at BL17SU of SPring-8^{29–31}. Prior to XAS/MCD-PEEM measurement, the surface oxide layer was removed by gentle sputtering with Ar^+ ions at 1 kV acceleration voltage, 15 mA of emission current, $P = 2.0 \times 10^{-5}\text{ Torr}$ for about 90 minutes, with gentle annealing at 400°C . The XAS and MCD signals were acquired in the same field of view, and the photon energy was continuously scanned at the L absorption edges of Fe, Co, and Cr. The energy scan ranges for Fe, Co, and Cr were $700\text{--}730$, $770\text{--}805$, and $570\text{--}600\text{ eV}$, respectively, with a step size of approximately 0.14 eV . The composition ratio was determined from XAS absorption and photoionization cross-section of each element³³. The edge height of the L_3 absorption peak was normalized by the photoionization cross-

section, and the chemical composition of the three elements was given by the ratio of the normalized intensities by following formula.

$$I_{\text{nom}}^{\text{Fe}} = I_{\text{XAS}}^{\text{Fe}} / CS^{\text{Fe}}$$

$$\text{Comp}^{\text{Fe}} = I_{\text{nom}}^{\text{Fe}} / (I_{\text{nom}}^{\text{Fe}} + I_{\text{nom}}^{\text{Co}} + I_{\text{nom}}^{\text{Cr}}),$$

where $I_{\text{XAS}}^{\text{Fe}}$ is the edge height of L_3 peak of Fe, CS^{Fe} is the photoionization of Fe, $I_{\text{nom}}^{\text{Fe}}$, $I_{\text{nom}}^{\text{Co}}$, $I_{\text{nom}}^{\text{Cr}}$ are the normalized intensity of each element, and Comp^{Fe} is resulting composition ratio of Fe. The composition of Co and Cr are determined in the same manner. The absence of an oxidized layer was confirmed from the edge shape of the XAS plot, indicating that the sample was not oxidized (Figure 4 (c))³⁰. MCD contrast was determined by the asymmetry caused by the difference in the helicity of circularly polarised X-rays. The field of view was set to a diameter of 100 μm so that the entire island with a composition gradient was in the viewing field. The resolution of the charge-coupled device (CCD) camera was 1024×1024 pixels with 16 bit grey-scale, and the exposure time was 3 s per image. Thus, micro-spectroscopic data composed of approximately 200 images (energy points) were acquired in 10 min. The signal-to-noise (S/N) ratio of a single-pixel spectrum is at most 10%, and the S/N ratio can improve by integrating the pixel information (Figure 4 (d)). Although the typical ROI contains 10,000 pixels, 100 pixel is enough to obtain sufficient S/N for compositional analysis. We prepared semi-automatic macros using the Python modules, namely numpy and pandas, to load the PEEM data, evaluate the composition ratio, analyze MCD signal, and set the ROIs.

The MCD contrast data were correlated with the Fe–Co–Cr composition (divided with a step size of 5 at%) determined from the XAS intensity at the corresponding area. Then, each MCD data cluster was converted into a histogram indicating the distribution of the number of pixels as a function of MCD intensity. The magnetic phase (ferromagnetic or paramagnetic) for each composition was determined from the number of peaks appearing in the histogram. The obtained MCD histograms were quantitatively organised on a Fe–Co–Cr ternary phase diagram. Finally, the MCD histograms were analysed using Landau theory and the critical exponent β was extracted. Landau theory can describe the pseudo-free energy of the system by a simple fourth-order polynomial of an order parameter, which is magnetisation in the case of a magnetic material. Since the specimen may practically have a remanent magnetisation, we left the first-order term as the internal magnetic field for fitting.

Declarations

Data Availability Statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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Author contribution statement

M.K. designed and directed the experiments. T. N. and M. Y. prepared specimens, performed PEEM measurements, and analysed the data. T. O carried out the PEEM experiment. D. N. and A. F. contributed to preparatory experiment and discussions. All authors discussed the results and contributed the final manuscript.

Additional Information

The authors declare no competing interests.

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Figures

Figure 1

Workflow of high-throughput experiment combining materials synthesis, physical property measurement, and statistical analysis. (a) A 3D-printed sputter beam aperture was used to deposit a Fe–Co–Cr ternary thin film with a continuous composition gradient. (b) Photoemission electron emission microscopy (PEEM) obtained one million X-ray absorption spectra (XAS) and magnetic circular dichroism (MCD) contrast images in 10 min. (c) The MCD histogram dependence on compositional ratio was used to

construct the ternary magnetic phase diagram of Fe–Co–Cr and determined the critical exponent from Landau theory. Autodesk Maya 2018, Shade 3D Standard ver.14, Igor Pro 4.0 , Wolfram Alpha (<https://www.wolframalpha.com/>) are used for the preparation of the figure.

Figure 2

Chemical compositions, MCD contrast images, and superimposed maps obtained by PEEM of the Fe–Co–Cr thin film. (a–c) Chemical composition maps and line profiles of Fe, Co, and Cr. (d) Superimposed chemical map of Fe, Co, and Cr with an overlapped region at the centre and (e) MCD image in the same area showing the magnetic contrast around the centre. (f) Superimposed image of chemical compositional ratio and MCD.

Figure 3

Magnetic phase transition in the Fe–Co–Cr thin film. (a) Fe–Co–Cr ternary phase diagram overlaid with MCD histograms. (b, c) MCD histograms near the magnetic phase transition, where single and double peaks correspond to paramagnetic and ferromagnetic states, respectively. The MCD histograms were analysed by Landau theory. Igor Pro 4.0 is used for the preparation of Figure 3a.

Figure 4

Experimental setup and evaluation measurement results. (a) Schematic drawing of sputtering beam aperture. (b) XRD pattern of homogeneous Fe-Cr binary alloy film for with and without annealing specimen. (c) XAS spectra of Fe L edge obtained on Fe-Co-Cr ternary thin film. The spectral shape corresponds to non-oxidized Fe. (d) Signal-to-noise ratio in XAS spectra versus the number of integrating pixels. Autodesk Maya 2018 is used for the preparation of Figure 4a.

Supplementary Files

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