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High-throughput screening of magnetic properties of quenched metallic-alloy thin-film composition spreads

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Abstract

A novel method for capturing and characterizing high-temperature phases of metallic-alloys in thin-film composition spreads has been developed. A high-vacuum (10^{-8} Torr) high-temperature annealing and quenching furnace system has been developed that allows formation of high-temperature phases in thin-film composition-spread samples deposited on 3 in. silicon wafers. Scanning SQUID microscopy and magneto-optical Kerr effect measurements were used to map the remnant magnetization and the hysteresis loops of the spreads of magnetic materials quenched at high temperatures. The combination of these techniques can be used to obtain comprehensive information on the magnetic properties of various metallic-alloy systems.
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1. Introduction

In the study of intermetallic materials, it is often the high-temperature phase that is technologically interesting. As an example, in the Fe–Pd system, it is well known that there exists a region of ferromagnetic shape memory alloys (FSMA) for compounds containing about 30 at.% Pd [1]. The realization of the FSMA phase, however, requires that the alloy be annealed in solid solution (generally 1173 K) and then quenched in ice water to preserve the solid solution phase. If the sample is allowed to cool slowly down to room temperature, the alloy decomposes around 873 K into a mixture of α-Fe and fct equiatomic Fe–Pd and no longer exhibits martensitic transformation [2]. Fig. 1 shows the binary phase diagram of Fe–Pd [3]. The need to quench samples from solid solution is not unique to the Fe–Pd system, and is considered imperative for obtaining high-quality properties in other systems such as FSMA Ni_2FeAl, high magnetostriction Fe–Ga, and the hard magnet MnAl [4–6]. In bulk systems, this is readily accomplished by encapsulating the sample in a quartz ampoule during annealing and then shattering the ampoule during the quench.

In typical combinatorial metallic thin-film experiments requiring heat treatments, the library is mounted on a substrate heater that is contained within a vacuum deposition chamber. The placement of the sample on a substrate heater within a vacuum chamber hampers the rate at which the sample can be cooled following annealing. The ''quickest'' cooling rate can be achieved by simply turning the heater off, but this means it will take the sample as long as 2 or 3 h to reach room temperature. During this time any decomposition process that is kinetically favored can occur and may prevent the desired phase from being present for later measurements. To this end, we have developed a high-vacuum quenching chamber, which allows us to capture high-temperature phases in combinatorial libraries.

In this study, Fe–Pd–Ga was chosen as an example system for quenching because two of the binary edges of the ternary are

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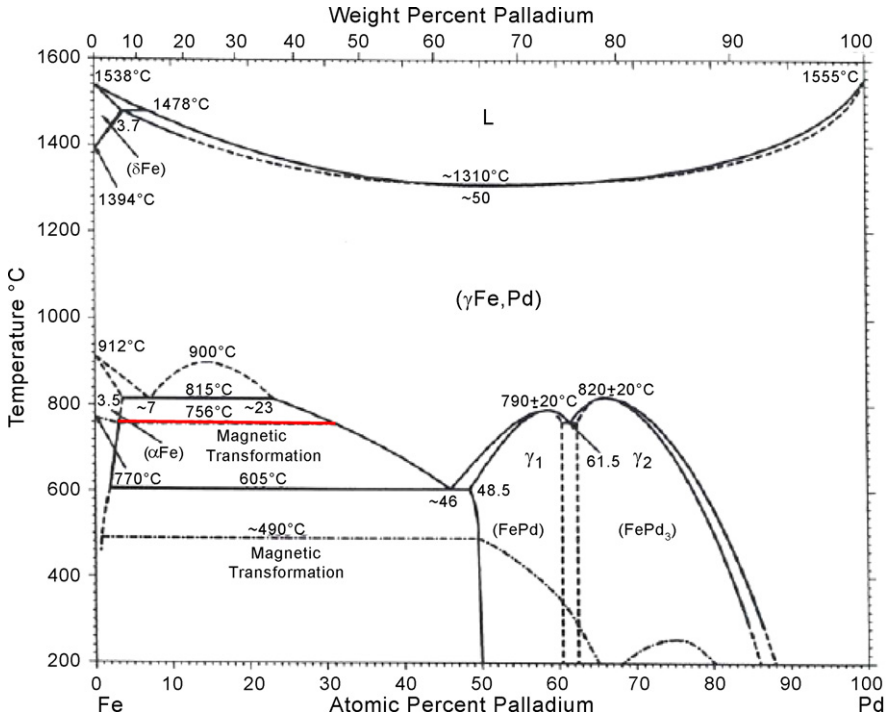

Fig. 1. The Fe–Pd binary phase diagram taken from [3]. The curie temperature of the high-temperature phase has been marked with a red line.

of technological interest as magnetostrictors. $Fe_{70}Pd_{30}$, as discussed above, is a well-known FSMA when it is annealed at high temperatures and then quenched [1]. There have been several reports of synthesizing single composition thin-film samples of this system by quenching [7,8]. However, to our knowledge this has not been attempted with composition spreads. The other system is Fe–Ga, a well-known magnetostrictive material that shows strictions as high as 300 ppm with 20 at.% Ga content [5]. These two systems are ideal for the present study as they exhibit rich binary phase diagrams, and have properties that depend strongly on heat treatments. Ternary studies of these systems offer the opportunity to possibly expand the region exhibiting the FSMA property in Fe–Pd. In addition, the abnormally high magnetostriction in $Fe_{80}Ga_{20}$ is attributed to the sudden decrease of the shear modulus C' [9]. The addition of Pd to $Fe_{80}Ga_{20}$ could further soften C' and hence increase magnetostriction.

We have captured the high-temperature phases in sputtered thin-film composition-spread samples of Fe–Pd–Ga using our high-vacuum quenching chamber. X-ray diffraction was used to confirm the successful formation of the high-temperature phase by quenching a $Fe_{70}Pd_{30}$ thin-film sample. In order to map the magnetic properties of the spread samples, a combination of scanning SQUID microscopy and magneto-optical Kerr effect (MOKE) measurements were employed.

2. Experimental methods

All the composition-spread samples were deposited in an ultra-high-vacuum (10^{-9} Torr) magnetron co-sputtering chamber [10,11]. The chamber has the ability to sputter up to three elemental targets in a non-confocal geometry, allowing for a natural composition-spread to be formed across a 3 in. wafer. In this experiment, 3 in. (1 0 0) Si wafers with 3 μm of amorphous SiO_2 were used. Here, the SiO_2 layer acted as a diffusion barrier to prevent the formation of silicides at the interface. All samples were gridded into 535 2 mm × 2 mm [2] areas during deposition through the use of a Si physical mask. The targets used in this study were Fe, Pd and intermetallic Fe_2Ga_3. Both RF and DC power supplies were used with typical powers being in the range of 10–70 W. Depositions were conducted using ultra-high purity Ar (99.9995%) at 4.6 mTorr, with a target-substrate distance of 12.5 cm. The deposition lasted 1.5 h and yielded typical film thickness of 0.6 μm. Wavelength dispersive spectroscopy (WDS) was used to map the composition across the spread before and after annealing.

After deposition the samples were placed into the quenching chamber, schematically represented in Fig. 2, to be post-annealed and quenched. The chamber incorporates a cryopump allowing its base pressure to be as low as 10^{-8} Torr. The cryopump is open

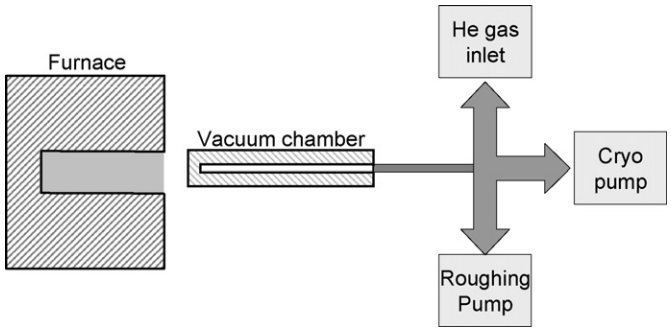

Fig. 2. A schematic representation of the high-vacuum annealing/quenching furnace system.

to the chamber throughout annealing so that even during annealing at 1273 K the pressure never exceeds 10^{-5} Torr. After pumping down, the chamber can be backfilled with inert gases to help trap high vapor pressure materials. The chamber weighs about 30 lbs, and during annealing the portion containing the sample is placed directly into a modified high-temperature furnace. Cooling water is constantly run through the handle grips of the chamber to ensure the handles and the rest of the vacuum equipment remain at room temperature during annealing. Upon completion of annealing, the end of the chamber containing the sample is immersed in ice water, quenching the chamber to 273 K in less than 2–3 s. The sample is in constant contact with the bottom side of the chamber during the quench so that it quenches as quickly as the chamber wall. The advantage of this technique is that the sample never comes in direct contact with either the atmosphere or water during the quench.

Scanning SQUID microscopy measurements were carried out using a Neocera Magma C20 room temperature scanning SQUID microscope. The typical scan time for an entire 3 in. wafer was 2 h. The SQUID scans were then combined with WDS results to map out the measured magnetic flux density distribution from the sample, which is proportional to the remnant magnetization, onto the ternary phase diagram.

A high-throughput MOKE system was employed to measure the Kerr intensity hysteresis loops of the samples. The change in Kerr intensity is directly proportional to the magnetization of a sample, and when measured as a function of applied magnetic field it can be used to directly determine the coercive field H_c and saturation field H_s [12].

The MOKE system used in this study was set up in a longitudinal geometry, where the incident beam and the applied magnetic field were in the plane of the sample. A 635-nm power-stabilized diode laser (20 mW), attenuated down to 2 mW/mm to avoid local heating, was used as the light source. A condensing lens was used to focus the spot size down to a diameter of less than 1 mm, allowing individual measurement of squares in gridded libraries. A photoelastic modulator operating at 50 kHz and lock-in detection was used to measure changes in polarization, yielding a sensitivity of about 5 μrad. The penetra-tion depth of the light was estimated to be about 150 nm, much less than the film thickness. The magnetic field was applied by an electromagnet with a field range of ±2 T. An X-Y-Z stage, located at the bottom of the sample stage, was used to scan the spread samples. An automated program was designed to scan through the data and evaluate the H_s and H_c for each curve.

3. Results and discussion

In order to illustrate the ability of the quenching chamber to quench an entire 3 in. wafer, an experiment was first carried out where only Fe and Pd targets were used during deposition in order to create a series of binary spreads. The samples were then annealed in vacuum at 1173 K for 1 h and either slow cooled or quenched in ice water. X-ray diffraction was done on both samples to determine if the high-temperature phase had been preserved. Fig. 3 shows an X-ray

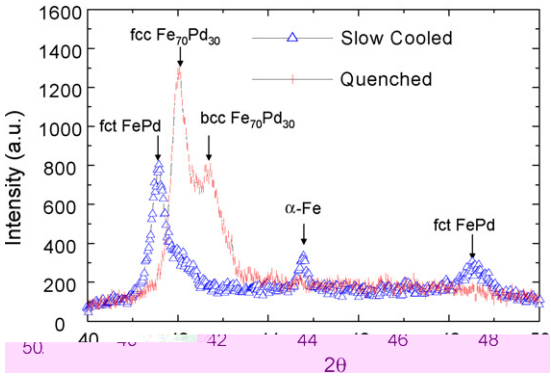

Fig. 3. A comparison of XRD scans from the quenched and slow cooled $Fe_{70}Pd_{30}$ samples. Here the presence of phase decomposition to α-Fe and Fe–Pd is clearly seen in the slow cooled sample. The quenched sample retains the high-temperature fcc/bcc phase.

spectrum comparison of the $Fe_{70}Pd_{30}$ composition spots on the binary spread samples, which have either been slow cooled or quenched. From the X-ray spectra, it is clear that the slow cooled sample underwent decomposition into the α-Fe and equitatomic fct Fe–Pd. The quenched sample meanwhile clearly maintained its high-temperature fcc/bcc phase as dictated by the composition. This is a clear indication that the annealing/quenching chamber can truly trap the high-temperature phases in compositions spreads.

Fe–Ga–Pd composition-spread samples were annealed at 1173 K for a half hour and then quenched in ice water. It was found after high-vacuum annealing of these spreads that a large amount of Ga had evaporated from the wafer due to its high vapor pressure. To prevent Ga deficiency, after pumping down the quenching furnace to its base pressure, the system was then subsequently backfilled with research grade He gas to 1 atm. The positive pressure of He helped to trap Ga in the composition-spread samples and was employed for all subsequent heat treatments.

Fig. 4 shows the mapping of the magnetic flux density in μT using scanning SQUID microscopy of a Fe–Pd–Ga composition-spread plotted in the ternary phase diagram. We focus our discussion here on the range near the Fe–Pd binary. The properties of the Fe–Ga region will be published elsewhere. The field value is proportional to the remnant

Fig. 4. A magnetic flux density mapping of the ternary phase diagram obtained through scanning SQUID. Here the magnetic flux density is related to the remnant magnetization of each sample. The shaded bar beneath the graph indicates the region of the high-temperature phase diagram of binary Fe–Pd that is magnetic. There is good correlation between the areas that exhibit high magnetization in the ternary and the magnetic region of binary Fe–Pd.