Combinatorial Development of Fe-Pd-X thin film systems with improved intrinsic properties

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The development of new ferromagnetic shape memory alloys (FSMA) using ab initio calculations, combinatorial fabrication and investigation methodologies, is the subject of this contribution. A systematic investigation for new FSMA with improved intrinsic properties is performed by fabrication of ternary materials libraries based on the binary alloy Fe₈₀Pd₂₀. Suggested by ab initio calculations, Cu, Mn and Pt were chosen as alloying elements. For all Fe-Pd-X (Cu, Mn and Pt) systems, a broadening of the transformation region and a shift in transformation temperatures was observed. Unlike Pt, only small amounts of Cu and Mn were soluble in Fe-Pd without formation of precipitates. A composition-dependent change of Curie temperature and saturation polarization was found for all systems.

1 Introduction

Ferromagnetic shape memory alloys (FSMA) exhibit a magnetic field induced strain (MFIS) effect, which in the case of Ni₂MnGa gives a maximum of up to 10% [1]. However, Ni₂MnGa suffers also from several drawbacks, e.g. a low Curie temperature, low saturation polarization and brittleness. The FSMA Fe₈₀Pd₂₀ is interesting due to its enhanced magnetic properties like saturation polarization and Curie temperature, although it undergoes a martensitic transformation (MT) slightly below room temperature. In order to develop new FSMA with enhanced intrinsic properties (increased transformation temperatures, Curie temperature and saturation polarization and to stabilize the transforming meta-stable fcc phase) the alloying of Fe₈₀Pd₂₀ with third elements is a promising route. The investigation of new ternary Fe-Pd based FSMA is performed by using the combinatorial fabrication and investigation methodology, whereby the samples are fabricated as materials libraries consisting of more than 300 samples per library and then investigated by fully automated high-throughput characterization techniques.

2 Experimental

The materials libraries were fabricated by using a combinatorial magnetron sputtering system (CMS 600/400LIN, DCA), where the films were deposited by co-sputtering from elemental targets (100 mm diameter, purity 99.99%, focal point at the middle of the substrate, 45° tilt, target-substrate distance 185 mm) on thermally oxidized 4 inch Si substrates [2]. The 1.5 m thick SiO₂ layer serves as a diffusion barrier between Fe–Pd–X films and Si during later annealing. A lift-off process was used to structure the films into arrays of discrete 3 mm x 3 mm squares. After deposition, the materials libraries were annealed in a furnace (Schmetz IU 54 1F) at 1123 K for 0.5 h under N₂ atmosphere at 80 kPa and then quenched to room temperature with an N₂ overpressure (40 kPa) at a cooling rate of approximately 15 K/s to achieve the metastable transforming phase. Sample compositions were determined by automated energy dispersive X-ray spectroscopy (EDX) using a Jeol JSM 5800LV equipped with an Oxford Inca system (accuracy 0.5 at.% after calibration with alloy EDX standard). Fully automated temperature-dependent electrical resistance, R(T), and magneto-optical Kerr effect (MOKE) measurements were performed [3] in order to determine sample properties such as occurrence of an MT and ferromagnetism. X-ray diffraction (XRD) and synchrotron measurements at various temperatures were conducted to investigate structure and residual stress of the samples. Saturation polarization and Curie temperature were determined by using a Physical Property Measurement System (PPMS, Quantum Design) equipped with a temperature-dependent vibrating sample magnetometer (VSM).

3 Results and Discussion

For the Fe-Pd system it is known that structure and magnetic properties can be adjusted by varying the c/a ratio of the lattice along the Bain-path from fcc to bcc structure due to the adaptive character of this alloy [4]. A flattening of the energy-landscape slope can stabilize the fct structure leading to an increase of transformation temperatures. Further ab initio calculations can be used to calculate the change of total energy with the c/a ratio along the Bain-path, as an indicator for the stability of the different phases in the resulting energy-landscape [5]. Thus different routes for selecting promising third elements can be defined in order to optimize FSMA properties.

A change of the energy-landscape can be induced by varying the effective structure of Fe-Pd systematically. This can be achieved by the addition of Cu, in order to increase the 3d electron concentration in the Fe-Pd based alloy, which effectively varies the electron to atom (e/a) ratio while keeping the Fe content constant.

Figure 1: Partial Fe–Pd–Cu composition diagram showing the compositional area covered by the materials libraries with light grey circles denoting the fabricated samples. Constant e/a ratios are visualized by black lines. Transforming samples are indicated by squares with colour-coding indicating the martensite start temperature Ms.
For the Fe-Pd-Cu system a broadening of the region undergoing a MT was found, as depicted in Figure 1. A transforming Fe-Pd-Cu single phase occurs for Cu contents < 5 at.%, where Cu is added to Fe-Pd in expense of Pd. Magnetic investigations showed a decrease of saturation polarization and Curie temperature in good accordance with calculated values from ab initio simulation. An increase of the Invar-type behaviour and a further stabilization of the meta-stable transforming fcc parental phase of Fe-Pd due to the addition of Cu was found. In Figure 2, thin film results are compared to bulk (splat-samples) results, finally giving an indication that Fe is the decisive factor controlling the MT in this alloy. To conclude, the addition of Cu allows an increase in the transformation temperatures as function of the Fe content [6].

A further way to favour the fct structure in this alloy and achieve higher transformation temperatures can be realized by alloying inherently antiferromagnetic admixtures as Mn into Fe-Pd.

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Figure 2: Martensite start temperatures (Ms) as a function of e/a ratio and Fe content presented as projections onto the planes in a 3D graph with colour-coded Cu content. Binaries are shown by black symbols (bulk by squares and films by triangles), while circles refer to Fe-Pd-Cu thin film experiments in this study. Diamonds refer to values obtained for both binary and ternary bulk samples. For comparison literature data of binary alloys [7,8] are included (black open squares and black filled triangles). Black lines visualize the general compositional trends for the three kinds of data.

From the Fe-Pd-Pt system, a path connecting both binary alloys was found to exhibit a reversible transformation while saturation polarization was significantly increased. Here, Pt substitutes for Pd for all samples within the region of interest.

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