Magnetocrystalline anisotropy of Ni-Mn-Ga-Co-Cu martensite

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Abstract

The martensites of Heusler alloys based on Ni-Mn-Ga exhibit magnetically-induced reorientation resulting in giant field-induced strain. Up to 12 % strain was observed in Ni-Mn-Ga-Co-Cu with 4 at.% of Co and Cu. The driving force of the phenomenon is the magnetocrystalline anisotropy. We studied the evolution of the anisotropy with temperature and compositions using magnetization curve measurements in four different single crystalline Ni-Mn-Ga-Co-Cu and compared with pure Ni-Mn-Ga. The anisotropy of martensite decreases with increasing average doping (Cu+Co)/2 but it does not scale with valence electron concentration or tetragonal ratio.

**Keywords**: Martensite; Magnetocrystalline anisotropy; Heusler alloys, Ni-Mn-Ga.

Introduction

Ni-Mn-Ga is a Heusler alloy which can be considered as a prototype of magnetic shape memory alloys. One of the magnetic shape memory phenomena is the magnetic-field-induced strain (MFIS) [1]. MFIS strain highly exceeds that obtained as a result of magnetostriction and occurs only in martensitic phase. Martensitic transformation temperature in Ni-Mn-Ga alloys depends on their chemical composition. It was found that copper doping of Ni-Mn-Ga can increase the martensitic transition temperature, but also decreases the saturation magnetization *M*s. The *M*s decrease can be compensated by additional cobalt doping. The composition affects the martensite structure as well, and can lead to modulated (10M or 14M) structure, non-modulated (NM) structure, commensurate or incommensurate structures. The 10M and NM martensites can be modelled as tetragonal crystals with lattice parameters *a* and *c* with *c* < *a*, and *c* > *a*, respectively. A breakthrough was achieved in Ni46Mn24Ga22Co4Cu4 alloy with NM structure, where MFIS of 12% was reached [2]. Driving force of MFIS is the magnetocrystalline anisotropy (MCA). In tetragonal crystals the anisotropy energy is described by anisotropy constants *K*1, *K*2, and *K*3. For 10M structure the anisotropy constant *K*1 is positive, *K*1 > 0, and an easy axis of magnetization occurs. In NM structure *K*1 is negative, *K*1 < 0, and thus the material exhibits an easy plane of magnetization. Our study aims at MCA of non-modulated Ni-Mn-Ga-Co-Cu martensites, which – as mentioned above – can exhibit high MFIS, which is attractive for applications.

Experiment

The Ni-Mn-Ga-Co-Cu single crystals were prepared by directional solidification [2]. The composition, listed in Table 1, was checked by X-ray fluorescence spectroscopy. The X-ray diffraction confirmed tetragonal structure of the crystals, and the lattice parameters *a* and *c* were measured at temperature *T* = 300 K, with tetragonality ratio *c*/*a* given in Table 1. Since Ni-Mn-Ga alloy belongs to Hume-Rothery phases, the valence electron concentration *e*/*a* given in Table 1 is expected to be important for their physical properties.

The MCA of our crystals was determined from magnetization curves measured by vibrating sample magnetometer PPMS (Quantum Design). The samples were mechanically compressed to obtain almost single variant microstructure of the martensite prior to magnetization measurements. The martensite was magnetized along hard axis of magnetization up to field of 9 T for temperatures between 10 and 400 K. Since the samples were magnetically open, the shape anisotropy had to be taken into account by correcting the measured loops for demagnetization. To obtain the correction a hysteresis loops in austenite phase were measured. We assumed negligible anisotropy of cubic austenite and thus the low-field slope of the austenite loop determines the demagnetization factor. Since martensitic transition affects macroscopic sample dimensions only slightly, the obtained factor can be used for correction of magnetization curves of martensite.

From the corrected curves the anisotropy constants *K*1 and *K*2 were determined using Sucksmith-Thompson method [5], which for our non-modulated tetragonal martensites can be expressed as

 *H*i/*I* = -[(2*K*1+4*K*2)/*I*s2] + (4*K*2/*I*s4)*I*2 (1)

Here *H*i is the internal magnetic field in units of A/m, *I* and *I*s are magnetization and spontaneous magnetization in Tesla. The quantity *I*s was determined from high-field linear regression of the measured magnetization curves as an intercept of the regression line.

Table1: Basic characteristics of Ni-Mn-Ga(-Co-Cu) alloys. Non-doped reference alloy was adopted for comparison from ref. [3]

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| Alloy name | Composition according to XRF | Tetragonality ratio c/a at T = 300 K | Electron concentration e/a |
| NMG3 | Ni46.5Mn22.7Ga24.4Co2.9Cu3.5 | 1.148 | 7.62 |
| NMG4 | Ni45.5Mn22.5Ga23.9Co4.0Cu4.2 | 1.148 | 7.64 |
| NMG5 | Ni44.7Mn22.5Ga22.7Co4.9Cu5.2 | 1.158 | 7.74 |
| NMG4.25 | Ni45.9Mn20.6Ga25.1Co4.9Cu3.6 | 1.137 | 7.61 |
| NMG0 | Ni50.5Mn30.4Ga19.1 | 1.207 | 7.75 |

Results and discussion

The examples of magnetization curves of the NMG3 alloy corrected for demagnetization are presented in Figure 1a both for martensite and austenite phases. The curves of martensite were almost hysteresis-free, and hence almost only the rotation of the spontaneous magnetization vector occurred out of easy plane. Magnetic saturation of austenite occurred almost immediately during magnetization process, resulting in square-like magnetization curve.

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**Figure 1** (a) Selected magnetization curves for the NMG3 alloy. The curves were corrected for demagnetization. Anisotropy fields at temperatures *T* = 10 and 300 K are marked *H*A10 and *H*A300, respectively. (b) Temperature dependence of anisotropy constant *K*1 and saturation magnetization *M*s of the NMG3 alloy determined from such curves. The quantity *T*CM is the Curie temperature of the martensite. Both graphs were taken from [4].

From the measured hysteresis loops in different temperatures the temperature dependence of the anisotropy constant *K*1 was determined according to equation (1) shown in Figure 1b. Instead of absolute temperature *T* we used relative temperature *t* = *T*/*T*CM, where *T*CM is the Curie temperature of martensite. *T*CM was estimated from magnetization curves of martensite measured at temperatures near the martensitic transition temperature, using Arrott plot technique [6]. With increasing temperature both *K*1 and *M*s of martensite decrease. Behaviour of the remaining doped alloys was very similar [6]. From the relation *K*1(*T*/*T*CM) ≈ [*M*s(*T*/*T*CM)]*n* and exponent *n* ≈ 3 at low temperatures we can conclude that magnetocrystalline anisotropy in Ni-Mn-Ga-Co-Cu martensite has single-ion origin [4].

The measured anisotropy at *T* = 10 K we correlated with various variables expected from the theory to be significant for the anisotropy. Figure 2 presents the anisotropy constant *K*1 as a function of valence electron concentration *e*/*a* and tetragonality ratio *c*/*a*. To our surprise there is no clear trend with any of the variables. From the calculations [7] we expect monotonous increase of *K*1 with increasing *c*/*a*, but no clear trend is observed.

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Figure 2. Anisotropy constant *K*1 at temperature *T* = 10 K as a function of (a) valence electron concentration *e*/*a*, (b) tetragonality ratio *c*/*a*.



Figure 3. Comparison of experimental (black open circles) and calculated (black solid circles) anisotropy constant *K*1 [4]. Lines connecting the symbols serve only as a guide for the eye.

Finally, we compared the experimentally determined values of *K*1 with the onecalculated from the first principles [4]. Figure 3 shows both experimental and calculated anisotropy constants -*K*1 of doped alloys as a function of averaged dopant concentration of cobalt and copper (Co+Cu)/2. As there is no NM structure at stoichiometric Ni2MnGa we also listed the anisotropy of NM for Mn excess composition (Table 1). The measured anisotropy constant -*K*1 decreases with increasing dopant concentration in agreement with the *ab-initio* calculations [4]. From calculations also follows that the easy plane (*K*1 < 0) anisotropy should change to easy axis (*K*1 > 0) with higher doping. Our experiments, however, confirmed only easy plane in our Ni-Mn-Ga-Co-Cu martensites. Moreover, the calculated magnitude of the anisotropy is smaller than measured. The knowledge of the anisotropy helps to predict the temperature and composition range where magnetically induced reorientation in Ni-Mn-Ga-Co-Cu alloys can occur [8].

## Conclusion

We investigated magnetocrystalline anisotropy of non-modulated tetragonal Ni-Mn-Ga-Co-Cu martensites as a function of composition and temperature. We found that the anisotropy has the single-ion origin. Anisotropy constant *K*1 as a function of valence electron concentration *e*/*a* or of tetragonality ratio *c*/*a* exhibited no clear trends. In agreement with theoretical calculation the easy plane anisotropy decreased with increasing average doping but in contrast to calculation the measured anisotropy was larger and no predicted change to uniaxial anisotropy with easy axis was detected.

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