Effect of alloying Ni-Mn-Ga with Cobalt on thermal and structural properties

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Abstract. Materials showing a large magnetic field induced strain can potentially substitute giant magnetostrictive materials as well as piezoelectrical ceramics in actuating devices. However the magnetic shape memory alloys face several problems for an industrial application. Besides the well known brittleness the temperature-range is still limited due to the structural and magnetic phase transition around 75°C. By alloying one of the most common systems Ni-Mn-Ga with 4.8 at% and 6 at% Cobalt the Martensite temperature was increased up to 422K and the Curie temperature up to 432K. Neutron diffraction experiments were performed on these Ni-Mn-Ga-Co single crystalline samples at room temperature, which show the existence of two different non-modulated martensitic structures. Dependent on the composition, a tetragonal and an orthorhombic structure in single crystalline samples were verified. Furthermore intermartensitic phase transitions above room temperature were determined in several samples alloyed with 6 at% cobalt. A temperature dependent measurement of the structure of Ni₄₄.₆Mn₂₉.₁Ga₂₀.₁Co₆.₂ showed an orthorhombic phase from room temperature up to 379K changing to a tetragonal intermartensitic phase before reaching the austenitic phase above 389K.

1. INTRODUCTION

Materials, which show a magnetic field induced strain (MFIS) a magnitude higher than piezo- or magnetostrictive materials became a research topic of high interest for applications in sensors or actuators. One of the most promising materials is Ni-Mn-Ga, due to their MFIS of up to 6.8% in low magnetic fields i.e. less than 0.5T [1]. However the brittleness and the low phase transition temperatures limit the application. The replacement of Nickel by other elements like rare earth-elements, iron or aluminum leads to an improvement of the mechanical properties. The systems are less brittle which results in a longer lifetime [2]. Beside the brittleness, the thermal, structural and mechanical properties are affected by the alloying. Iron replacing nickel for example increases the Curie temperature while the substitution of manganese increases the Martensite temperature [3]. The same behavior has been expected in the case of cobalt as the substitute. Like in Ni-Mn-Ga – single crystals, the composition also influences the martensitic structure [4]. The results of the thermal and
structural properties of Ni-Mn-Ga-Co single crystals with two different amounts of cobalt and changing Mn/Ga – ratio will be presented here.

2. Experimental

Using the Bridgeman-like technique Slag Remelting and Encapsulation (SLARE) [5] two single crystalline rods with the weighted compositions Ni$_{45}$Mn$_{31}$Ga$_{19.2}$Co$_{4.8}$ and Ni$_{44}$Mn$_{31}$Ga$_{19}$Co$_{6}$ were grown. The rods were cut into several 6x4x3mm samples along the 100 and 010 direction in the cubic phase.

The composition of the samples was verified by a calibrated Energy Dispersive X-Ray spectrometer (EDS), while the structural and magnetic phase transition temperatures were determined by Differential Scanning Calorimetry (DSC) cycling the temperature from 30 to 250°C one time with 10K/min and afterwards with 5K/min.

The martensitic structures of selected Ni-Mn-Ga-Co – single crystals were determined by neutron diffraction at the Instruments E3 with a perfectly bents silicon monochromator with a wavelength of 1.468Å of the Helmholtz-Center Berlin of Materials and Energy [6] at room temperature and temperatures up to 400K.

3. Results

3.1 Thermal properties of Cobalt alloyed Ni-Mn-Ga single crystals

The high vapor pressure of manganese causes a concentration gradient developing during the growth process along the growth axis of the single crystalline rod. The composition of the samples cut out of the rod along the growth axis shows a deviation of manganese and gallium of more than 3 at%, whereby the amount of manganese increases with the decrease of gallium (see Tab.1). Nickel and cobalt are well distributed over the whole rod. The concentration of both elements remains nearly constant in the determined samples.

| Sample | Co [at%] | Ni [at%] | Mn [at%] | Ga [at%] | Mn/Ga |
|--------|----------|----------|----------|----------|-------|
| Ni$_{45}$Mn$_{31}$Ga$_{19.2}$Co$_{4.8}$ |      |          |          |          |       |
| 1-A    | 5.0      | 45.7     | 29.4     | 19.9     | 1.477  |
| 1-B    | 4.8      | 45.4     | 30.2     | 19.6     | 1.540  |
| 1-C    | 4.8      | 46.0     | 30.6     | 18.6     | 1.645  |
| 1-D    | 4.9      | 45.1     | 30.9     | 19.1     | 1.618  |
| 1-E    | 4.9      | 44.7     | 31.7     | 18.7     | 1.695  |
| Ni$_{44}$Mn$_{31}$Ga$_{19}$Co$_{6}$ |      |          |          |          |       |
| 2-A    | 5.8      | 45.0     | 27.5     | 21.7     | 1.264  |
| 2-B    | 6.0      | 45.2     | 27.6     | 21.2     | 1.299  |
| 2-C    | 6.2      | 44.9     | 28.2     | 20.7     | 1.362  |
| 2-D    | 6.2      | 44.6     | 29.1     | 20.1     | 1.443  |
| 2-E    | 6.0      | 44.6     | 29.5     | 19.9     | 1.481  |
Due to this concentration gradient along the rod, the samples show different structural phase transitions temperatures. Samples containing approximately 4.8% cobalt show a Curie-temperature ($T_C$) of around 420K, while samples with the higher cobalt content of around 6 at-% exhibit a higher $T_C$ of approximately 435K independent from the Mn/Ga ratio (see Fig. 1).

![Fig 1: Phase transition temperature of A: Ni$_{45}$Mn$_{31}$Ga$_{19.2}$Co$_{4.8}$ and B: Ni$_{44}$Mn$_{31}$Ga$_{19}$Co$_{6}$ determined by DSC versus the Mn/Ga ratio of the particular samples. The black squares indicate the Martensite temperature, the red circles the intermartensitic phase transition temperature and the blue triangles the Curie temperature.](image)

The Martensite-temperature in both alloys is highly affected by the Mn/Ga-ratio. While the structural phase transition from the Martensite to the Austenite in samples with 4.8 at% Co is shifted from 350K in the Ga-richest sample to 435°C in the sample from the other side of the rod. (see Fig.1) In samples containing around 6 at% Co accompanied by a decreasing Ga-content an increasing Martensite temperature from 340 to 400K was verified.

Furthermore most of the determined samples with 6 at% Cobalt show a second intermartensitic phase transition, also increasing from 340K to 370K with the decreasing Ga-content.

### 3.2 Structural properties of Co-alloyed Ni-Mn-Ga single crystals

#### 3.2.1 Martensitic structure of samples with 4.8 at% Co

The martensitic structures of sample 1-D and 1-E from the single crystalline rod with the weighted composition Ni$_{45}$Mn$_{31}$Ga$_{19.2}$Co$_{4.8}$ were determined by neutron diffraction. Both samples have exactly the same amount of cobalt, but with a different Mn/Ga – ratio.

Sample 1-D shows a tetragonal martensitic structure with the lattice parameters $a = b = 6.56\text{Å}$ and $c = 5.49\text{Å}$, which results in a cell volume of 236.25Å$^3$. For the second sample 1-E with a higher Mn/Ga – ratio an orthorhombic unit cell was verified. The experiment showed the three different cell-parameters $a = 6.62\text{Å}$, $b = 5.58\text{Å}$ and $c = 5.48\text{Å}$ and therefore a slightly smaller unit cell volume of 212.22Å$^3$.

#### 3.2.2 Martensitic structure of samples with 6 at% Co

Two samples of the single crystalline rod with the weighted composition Ni$_{44}$Mn$_{31}$Ga$_{19}$Co$_{6}$ were chosen for the neutron diffraction experiments. The martensitic structure of sample 2-A and 2-D was determined at room temperature. Both samples show an orthorhombic nonmodulated structure with similar cell parameters. The longest axis of sample 2-A is $c = 6.53\text{Å}$ and for the shorter axis the values $b = 5.57\text{Å}$ and $c = 5.40\text{Å}$ were verified. The measurements on sample 2-D resulted in the cell parameters $a = 6.58\text{Å}$, $b = 5.52\text{Å}$ and $c = 5.51\text{Å}$.

Since this sample shows an intermartensitic phase transition at 379K, temperature dependent diffraction pattern showed a change in the lattice constants (see Fig. 2). With increasing temperature,
the c-axis becomes smaller, while the length of a and b increases. Above the phase transition temperature a tetragonal nonmodulated structure with \(a = 6.54\text{Å}\) and \(b = c = 5.54\text{Å}\) was determined. By increasing the temperature up to 408K, again a decrease of the lattice constant \(c\) and an increase of \(a\) and \(b\) was verified.

![Fig. 2 Lattice constants of Sample 2-D dependent on the temperature. Above the intermartensitic phase transition the structure changes from an orthorhombic nonmodulated structure to a tetragonal nonmodulated structure. The diffraction experiments were done at the HZB Instrument E3 with a wavelength of 1.486Å.](image)

4. Conclusion

Replacing nickel with cobalt in Ni-Mn-Ga strongly influences both phase transition temperatures. The Curie temperature is shifted from approximately 380K [7] in Ni-Mn-Ga alloys with 50 at% Ni up to 435K in Ni-Mn-Ga alloyed with 6 at% Co. Comparing the Martensite temperature of Ni-Mn-Ga alloys with similar Mn/Ga-ratios and the Co-alloyed samples, an increase of around 20K is found [1]. Besides the nonmodulated tetragonal structure also found in Ni-Mn-Ga alloys, a nonmodulated orthorhombic structure was verified. The cell volume of Ni-Mn-Ga alloyed with 6 at% Co increases with the Mn/Ga ratio, which can be explained due to the higher amount of Mn, which has a bigger radius than Ga.

References

[1] K Rolfs, A Mecklenburg, J-M Guldbakke, R C Wimpory, A Raatz, J Hesselbach and R Schneider 2009 Mag. Mag. Mater. 321 1063
[2] S H Guo, Y H Zhang, Z Q Zhao, J L Li, and X.L. Wang 2004 J. Rare Earths 22 632
[3] G H Wu, W H Wang, J L Chen, L Ao, Z H Liu, W S Zhan, T Liang and H B Xu 2002 Appl. Phys. Lett. 80 4 634
[4] N Lanska, O Söderberg, A Sozinov, Y Ge, K Ullakko and V K Lindroos 2004 J. Appl. Phys. 95 8074
[5] A Mecklenburg, S Fiechter, H-P Nabein, R Schneider 2005 DE102004018664A1
[6] R C Wimpory, P Mikula, J Saroun, T Poeste, J Li, M Hofmann and R Schneider 2008 Neutron News 19 (1) 16
[7] V. V. Khovailo, V. Novosad, T. Takagi, D. A. Filippov, R. Z. Levitin and A. N. Vasil'ev, Phys.Rev. B 70, 174413 (2004)