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ABSTRACT OF DOCTORAL THESIS

Structural, Magnetic and Micromechanical Properties of Multifunctional Ni-Mn-Ga Heusler Alloys Influenced by Elemental Doping

Magnetic shape memory alloys (MSMAs) have recently emerged as one of the most extensively researched groups of modern functional smart materials. This is due to the fact that their complex magnetostructural nature is very often associated with a variety of significant properties that may be influenced by different stimuli, including thermal, magnetic and mechanical field. Among the relatively narrow group of MSMAs, NiMnGa-based Heusler alloys stand out as one of the post promising candidates for many future multifunctional applications, due to the numerous magneto-thermo-mechanical properties, including magnetic field-induced strains, thermal and magnetic pseudoelasticity, giant magnetoresistance, magneto- and mechanocaloric effects or exchange bias. All of the multifunctional properties of Ni-Mn-Ga alloys stem from the reversible first-order martensitic transformation and the reversible second-order magnetic transformation. The martensitic transformation undergoes from high-symmetry austenite phase to low-symmetry martensite phase, whereas the magnetic transformation undergoes from paramagnetic to ferromagnetic state. The main characteristic feature of the Ni-Mn-Ga compound is that both transformations are independent and can be shifted individually through compositional tunning, introduction of additional alloying elements or proper heat treatment. As a result, the functional properties of the final material may be adjusted to the particular application, which is the main idea of modern material engineering. However, in order to establish the consistent designing rules for some future potential applications, a detailed knowledge of the complex magnetostructural behaviour of doped Ni-Mn-Ga compounds is required.

The purpose of this thesis is to investigate the influence of elemental doping and atomic ordering on the magneto-thermo-structural behaviour of NiMnGa-based magnetic shape memory alloys. To achieve this, the series of polycrystalline Ni-Mn-Ga alloys doped with Co and/or Fe were produced by the arc-melting technique. All samples were carefully annealed and subjected to a cooling procedure involving three different cooling rates realized by water, air and furnace cooling, which simulates the different atomic ordering. The presented comprehensive characterization of microstructure, magnetic and micromechanical properties of the produced multifunctional alloys is carried out in terms of the electronic parameters, including the valence electron concentration and the non-bonding electrons concentration.

In the presented dissertation, two main parts can be distinguished: the theoretical framework and the experimental part. The theoretical part provides an introduction to the topic of multifunctional NiMnGa-based magnetic shape memory Heusler alloys. This part mainly focuses on microstructural features of the investigated materials and the corresponding complex nature of the reversible martensitic transformation. Furthermore, the introduction

includes detailed information on the major functional properties of Ni-Mn-Ga compounds, including thermal and magnetic shape memory, giant magnetoresistance, exchange bias and mechanocaloric effects. Particular emphasis is also placed on the compositional dependence of off-stoichiometric alloys and the influence of selective alloying elements. The last parts of the theoretical introduction present the different forms of Ni-Mn-Ga materials and describes some recent advanced promising applications of different types of NiMnGa-based Heusler alloys.

The research part of the dissertation is divided into two areas. The first one includes the characterisation of the production process of the polycrystalline NiMnGa-based materials, as well as the description of the characterization methods used in the presented studies. The second part of the research area is entirely devoted to the presentation of the investigation results and the broad discussion of the emerging outcomes.

The first section of the research chapter is dedicated to microstructural and crystallographic investigations conducted on polarised optical microscope, SEM/EDS, XRD and AFM. These studies reveal the single phase microstructure for all fabricated materials and confirm the obtained chemical composition with the designed ones, which validates the production process of NiMnGa-based materials in bulk polycrystalline form. The detailed temperature dependent Rietveld refinement analysis allows to identify the crystal lattice parameters for cubic austenite, tetragonal non-modulated martensite and five-layered modulated martensite, and demonstrates the clear dependence of structural properties of Ni-Mn-Ga Heusler alloys on the considered electronic parameters. The additional, supporting, AFM investigation reveals the complex microstructure of self-accommodated martensitic structures observed at three different length scales and manifested by various twinning models. Moreover, a quantitative approach to the analysis of AFM profiles for martensitic relief is also proposed to distinguish the non-modulated and modulated types of martensite.

The second section of the research chapter is focused on both the reversible martensitic transformation and magnetic transformation observed in the fabricated multifunctional alloys. In this case, the magneto-thermo-structural behaviour of the produced samples was investigated with the help of DSC, M-TG and VSM, which allows for extensive characterization of first- and second-order transformations. These studies clearly show that the structural transformation in Ni-Mn-Ga-Fe-Co system is strongly dependent on the elemental doping and can alter over a wide range of temperature, independently of the magnetic transformation. Moreover, it is also demonstrated that the temperature of martensitic transformation may be predicted by the electronic parameters, regardless of the type of dopant.

The third part of the research chapter is strictly focused on the magnetic properties of the studied alloys estimated on the basis of VSM measurements carried out at wide ranges of temperatures and external magnetic fields. In this section, the atomic ordering of differently cooled samples is discovered to greatly influence the magnetic properties of the samples, such as coercivity. Moreover, the investigation of the martensite and austenite hysteresis loops clearly depicts the considerable magnetostructural anisotropy of the low-symmetry martensite phase in comparison to the high-symmetry austenite phase. To quantitatively describe the observed differences, the low of approach to magnetic saturation model were used to estimate the energy of magnetocrystalline anisotropy in all fabricated NiMnGa-based materials. The strong relationship between magnetocrystalline anisotropy, chemical composition and electronic parameters is also described in detail in this section.

The last part of the research chapter considers the micromechanical properties of the produced polycrystalline samples investigated by instrumented nanoindentation mapping. The presented studies reveal considerable anisotropy of the elastic and plastic properties of neighbouring grains and twins in the austenite and martensite phase, respectively. The statistical approach based on the 2D Gaussian mixture model used for clustering, labelling and calculating the mechanical parameters of individual grains is also proposed and comprehensively discussed in this section. In the case of micromechanical properties, the obtained vales of hardness, elastic modulus and elastic energy ratio are once again discussed with respect to the examined electronic parameters. Lastly, the additional AFM investigation of the residual imprints displays two significant phenomena: reorientation of twins in self-accommodated martensite and mechanical stress-induced martensitic transformation, which is widely reviewed in this section.

The submitted dissertation contains a comprehensive and methodological examination of the microstructure and magneto-thermo-mechanical characteristics of Ni-Mn-Ga magnetic shape alloys influenced by Co and Fe doping. The provided results and accompanying discussions demonstrate that correct elemental doping results in a substantial change in all of the crucial multifunctional features of final material, including structural, magnetic and mechanical properties. The established influence of Co and/or Fe on the Ni-Mn-Ga composition, as well as the effect of varied cooling conditions, can be exploited to modify and alter the necessary functional properties of the material to make it suitable for a certain demanding application. Furthermore, in the Ni-Mn-Ga-Co-Fe system investigated in this thesis, the universal approach regarding both the valence electron concentration and the non-bonding electron concentration may be used to determine the specific multifunction functional characteristics. The extensive research presented in this dissertation makes a distinct and original contribution to the future development of polycrystalline NiMnGa-based Heusler alloys, especially in the promising Ni-Mn-Ga-Co-Fe system.

Keywords: *magnetic shape memory alloys*; *multifunctional materials*; *reversible martensitic transformation*; *twinned martensite*; *magnetocrystalline anisotropy*; *nanoindentation mapping*