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Novel compositions of Heusler-based glass-coated microwires for practical applications using shape memory effect

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ABSTRACT

In the given contribution, the production of shape-memory glass-coated microwires based on Ni_2FeZ (Z = Ga, Sn, Sb) and $Co_2Cr(GaSi)$ alloys is shown, focusing to their repeatable production. Such wires are characterized by monocrystalline structure along entire length. This leads to 1.5% reversible temperature shape memory effect for Ni_2FeGa microwire in the as-cast state without necessity of additional thermal treatment. Moreover, well defined anisotropy results in the variation of permeability up to 550% during the phase transition. On the other hand, $Co_2Cr(GaSi)$ microwires show reversible superelastic straining up to 1.1% with a very small irreversible strain (<0.1%).

1. Introduction

Functional shape memory alloys need to operate reversibly and repeatedly. The most prominent shape memory alloys (SMA) based on titanium-nickel are known due to their good mechanical properties and excellent biocompatibility [1]. Such SMA alloys can be used as actuators. On the other hand, magnetic shape memory alloys (MSMA) are even more interesting, since they can be simultaneously used as micromechanical actuators and sensors [2]. The most familiar MSMA is the alloy with chemical composition Ni_2MnGa. Anyway, this system of alloys has some drawbacks, mainly originating from the loss of Mn during production samples. It causes non-stoichiometry of sample and loss of shape memory effect. One solution is replacement of Mn by Fe in alloys based on Ni_2FeZ (Z = Ga, Sn, Sb) [3,4] or applications of Mn-free composition.

Generally, manufacture of all perspective “smart” alloys has several problems. Firstly, it is production of a large amount of alloy with exact chemical composition accompanied with the same physical properties. The second problem is their brittleness because of the crystalline character. The solution is Taylor - Ulitovsky method, which allows preparation of microwires - composite material that consists of metallic core (diameter ~ 1–100 μm) coated by glass (thickness ~2–20 μm) (Fig. 1) [5]. The huge benefit of microwires is their large production (several kilometers from small bulk (~3 g)) and the straight application. The elastic glass-coating fix the shape of brittle metallic nucleus and does not allow its mechanical decomposition. Moreover, glass-coating provides insulation from electrical short-circuit, allows wire to be used in chemically aggressive environment and provides biocompatibility of usually biologically incompatible composition of Heusler alloys.

In the given contribution, the production of shape-memory glass-coated microwires based on Ni_2FeZ (Z = Ga, Sn, Sb) and $Co_2Cr(GaSi)$ alloys are shown, highly focusing to the repeatable production. It is shown, that Taylor - Ulitovsky method allows production of large amount of wire in a short time that shows 1.5% reversible shape memory effect without additional thermal treatment. Moreover, well defined anisotropy results in the variation of

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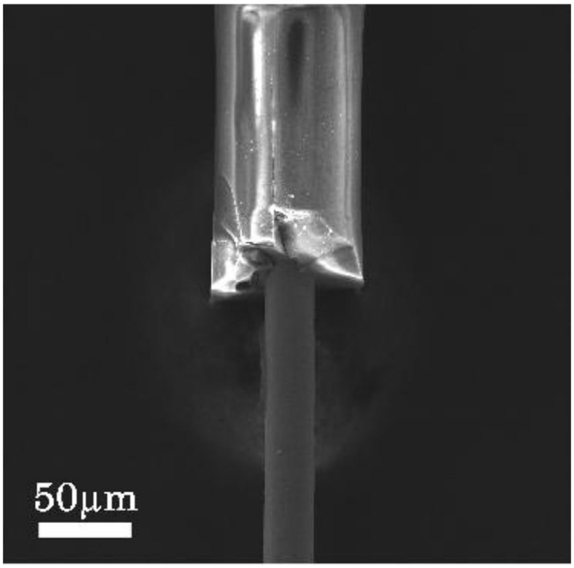

Fig. 1. SEM image of Ni_2FeGa Heusler microwire.

permeability up to 550% during the phase transition. Therefore, such materials can be used as smart actuators that serve as high sensitivity sensors by itself.

2. Experimental

Precursor of master alloys with chemical composition Ni_2FeZ (Z = Sn, Sb, Ga) and $Co_{51}Cr_{27}Ga_{11}Si_{11}$ were prepared by arc-melting method from high-purity elements (99,9%) under argon atmosphere. To obtain the high homogeneity, ingots were four times remelted. Magnetic shape memory microwires coated by Pyrex glass were prepared using Taylor - Ulitovsky method, which is suitable for production of few kilometers of high quality wires. Glass-coated microwires with the metallic nucleus having diameter: d (Ni_2FeGa) ~ 29 µm, d (Ni_2FeSn) ~ 15 µm, d (Ni_2FeSb) ~ 120 µm, d ($Co_{51}Cr_{27}Ga_{11}Si_{11}$) ~ 7 µm and glass thickness from 17 to 80 µm can be easily produced.

The morphological characteristic and chemical composition of microwires have been studied by scanning electron microscope (SEM) TESCAN VEGA 3 XMU, which includes the energy dispersive X-ray spectroscopy (EDX). EBSD analysis has been performed by SEM TESCAN MIRA 3 to confirm monocrystalline structure as well as crystallographic orientation. The glass was mechanically removed from the microwire. Structure and crystalline phases of Ni_2FeGa and $Co_{51}Cr_{27}Ga_{11}Si_{11}$ have been studied by X-ray diffraction at D/max Rapid II (Rigaku) using Mo-Kα radiation at room temperature. In our case, the XRD was performed on the sheet that consists of parallel ordered wires without the glass-removal. The glass introduces the strong axial stresses that we believed are the reason for preferential crystallographic orientation along the wire's axis. Glass removal and milling of the metallic nucleus could introduce another complex stresses that should influence the measurements. Low temperature crystal structure of Ni_2FeGa microwire has been studied by X-ray diffraction at end station P02.1 situated at synchrotron facility PETRA III in DESY. Diffraction experiment was carried out by X-ray of wavelength 0.20727 Å and recorded on area detector PerkinElmer 1621. Microwire was cooled to a low temperature using a liquid nitrogen blowing cryostreamer.

Hysteresis loops along the parallel direction with respect to the wire's axis were measured using SQUID magnetometer MPMS3 at the different temperatures. Temperature dependence of magnetic moment was measured in the temperature range from 50 to 400 K at magnetic field of 50 Oe and 10 kOe. Susceptibility measurements were done using LCR meter at frequency 100 kHz under magnetic field of 0,5 Oe.

Finally, mechanical properties of Ni_2FeGa and $Co_{51}Cr_{27}Ga_{11}Si_{11}$ were studied by dynamic mechanical analyzer Q800 DMA in temperature range corresponding to the phase transition under constant force 0.01 N and under force ramp up to 3 N at room temperature, respectively.

3. Results and discussion

Taylor - Ulitovsky method allows production of large amount (up to kms) of wire. The dimensions (metallic nucleus diameter and glass coating thickness) can be effectively controlled by wounding speed and glass feeding speed of automated machine. Fig. 1 shows the SEM image of selected pieces of Ni_2FeGa microwire that is characterized within the presented paper. The dimensions of the wires are shown in Table 1.

One of the few disadvantages of Taylor - Ulitovsky method is long-time (few min.) melting of master alloy until whole wire is drawn. This leads to evaporation of Mn out of master alloy in Mn-based microwires. In contrary, Mn-free Heusler microwires have almost excellent correspondence of real composition (obtained by EDX analysis from at least 5 different points) with the desired one — see Table 1.

X-ray analysis of Ni_2FeGa microwire at room temperature (Fig. 2a) reveals that it crystallizes in crystalline structure having $Fm\overline{3}m$ space group. The lattice parameter $a = 5.756$ Å is in a good agreement with other works [6]. The small variation in our result may be a result of strong tensile stress induced by the rapid solidification applied on metallic nucleus by glass due to their different thermal expansion coefficient. Moreover, low temperature Ni_2FeGa phase has been recognized at 95 K (not shown) to be monoclinic structure with lattice parameters $a = 4.15(9)$ Å, $b = 5.37(6)$ Å, $c = 20.76(1)$ Å, $\beta = 86.73°$.

X-ray analysis of $Co_2Cr(GaSi)$ microwire at room temperature and (Fig. 2b) reveals again that it crystallizes in phase with $Fm\overline{3}m$ space group as in the case of Ni_2FeGa. The lattice parameter 5.722 Å is in a good agreement with the previous works [7].

No X-ray analysis has been performed on Ni_2FeSn and Ni_2FeSb till now due to the complexicity of such study. However, it is planned for the future.

It has been shown before [8,9] that production of microwires leads to the appearance of oligocrystalline structure, where large crystals (few tens of µm) appears along the wire. However, when the production is provided carefully with well selected diameter of metallic nucleus and total diameter, the monocrystalline structure can appear. Fig. 3 shows EBSD analysis of Ni_2FeGa that was carried out on a part of the surface of microwire without glass. Firstly, no grain boundary has been found along entire wire. Additionally, various analyses of randomly selected pieces of microwire show the same figures, which point to monocrystalline structure of entire microwire with [111] axis parallel to the wire's axis. Such preferred

Table 1
Real, desired composition, diameter of metallic nucleus *d*, and total diameter *D* of prepared microwires.

Desired composition	Real composition	*d* µm	*D* µm
Ni_2FeGa	$Ni_{50.03}Fe_{25.36}Ga_{24.61}$	29	80
Ni_2FeSn	$Ni_{50.37}Fe_{24.32}Sn_{25.37}$	15	49
Ni_2FeSb	$Ni_{51.5}Fe_{23.44}Sb_{25.06}$	120	280
$Co_{51}Cr_{27}Ga_{11}Si_{11}$	$Co_{51.39}Cr_{25.99}Ga_{11.33}\ Si_{11.29}$	7	25