The influence of forging and extrusion on the microstructure and martensitic transformation in Ni-Mn-Ga alloys

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Abstract. The work presents the comparative analysis of the microstructure and character of martensitic transformation in Heusler Ni-Mn-Ga alloys subjected to plastic deformation by forging and complex treatment by forging with subsequent extrusion. It is shown that the treatment by forging leads to the formation of a bimodal structure with large grains of several micrometres surrounded by a fine-grained structure. After a complex treatment, a bimodal structure is also observed. But the volume fraction of the fine-grained structure is larger than in the previous case. Analysis of the martensite transformation temperature shows that thermomechanical treatment by both methods leads to a slight shift in the martensite transformation temperature to the low temperature region.

1. Introduction

Ni₂Mn-X (X=Ga, In, Sn, Co, Fe, etc.) alloys have a combination of simple and unique physical properties. In particular, the ferromagnetic shape memory effect [1-3] and the magnetocaloric effect [4-7] are observed in the region of martensitic and magnetic phase transformations. As a result, these alloys belong to the class of promising functional materials. One of the main directions of the studies is the search for ways to improve the mechanical properties of these alloys, because the multiple occurrence of martensitic transformation (MT) leads to fracture along the boundaries of crystallites. The most promising way to solve this problem is the thermomechanical treatment (TMT) of as-cast polycrystalline alloys [8-11]. The authors of the work carry out research on TMT of Heusler alloys using multiple isothermal forging (MIF) [12, 13] and extrusion (EXT). The advantage of MIF is the possibility of obtaining a massive workpiece with the required structure and a high level of internal stresses. In order to enhance the anisotropy of the alloy in the MT region, it is possible to carry out complex treatment by forging with subsequent extrusion (MIF+EXT).

2. Experimental

Two Ni-Mn-Ga alloys for the investigation were prepared by the method of arc-melting in an argon atmosphere. The elemental composition was analyzed by energy dispersive X-ray spectroscopy on a TESCAN Vega 3 SBH scanning electron microscope. The first alloy, marked as Ga16/6 has the composition Ni₅₄,Mn₁₉,Ga₂₄,₆Si₁₇, the second alloy marked as Ga17/3 - Ni₅₂,9Mn₂₁,1Ga₂₄,₆Si₁₅. The presence of Si in the alloy is explained by its diffusion from quartz glass during vacuum remelting.
Detailed information about this procedure is described in previous works [12, 13]. The Ga16/6 alloy in the initial state was subjected to TMT by MIF, and the Ga17/3 alloy in the initial state was subjected to complex TMT by MIF+EXT. The temperatures of phase transformations (martensitic and magnetic) were determined by measuring the temperature dependences of the specific magnetization and electrical resistance. The magnetization of the alloy was studied with a vibration magnetometer. The installation allows measuring the specific magnetization of the sample in magnetic fields up to 2 T in the range from liquid nitrogen temperatures to +150 °C. The electrical resistivity of the sample was measured by the four-probe method on a sample of 1 mm x 1 mm x 7 mm with a current of 70 mA. The thermocouple and the voltage drop across the sample were measured by two voltmeters V7-78/1. The microstructure of the alloys was investigated by a TESCAN Mira 3 LMH scanning electron microscope in the backscattered mode. MIF was carried out on the machine of complex loading Schenck Trebel RMC 100. Forged alloy was also extruded on a special tool, in which the output circular section has a transition 10 mm→8 mm with an extrusion ratio of 1.6.

3. Results and discussion

3.1. The analysis of phase transitions temperatures in various structural states

The curves of the temperature dependence of the specific magnetization of the Ga16/6 alloy in the initial state and after MIF are presented in figure 1 a. The curves were obtained by heating the sample in the temperature range from –100 °C to +60 °C in an external magnetic field of 80 kA/m.

![Figure 1. Temperature dependences of the specific magnetization of the Ga16/6 alloy in different states (a) and the electrical resistivity of the alloy in the initial state and after MIF+EXT (b); the specific magnetization is normalized to its value at -100°C](image-url)

On the curve for the initial state in the interval of the reverse MT, a jump-like change in the magnetization characteristic of Heusler alloys is observed. The temperatures of the phase transformation have the following values: \( A_S = -54 \) °C, \( A_F = -44 \) °C. Transformation to the paramagnetic phase occurs at 43 °C. This temperature can be roughly called the Curie point, since its precise determination must be carried out by non-magnetic methods. Analysis of \( \sigma(T) \) after forging shows that the characteristic temperatures are shifted to low temperatures by ~7 °C.

The temperature dependence curves of the electrical resistivity of the Ga17/3 alloy in the initial state and after MIF+EXT are presented in figure 1 b. The \( \rho(T) \) curves are recorded when the sample is heated and cooled from –100 °C to –40 °C. It can be seen that in the initial state there is a deviation from a monotone increase in the electrical resistivity of the alloy in the martensitic transformation region. In the process of reverse martensitic transformation, this increase slows down slightly. There is
a bend on the curve. It is known that the high temperature phase is more symmetric, and its specific electrical resistance is lower. The temperatures of the beginning and end of the transformation in the initial state are $A_S = -72 ^\circ C$ and $A_F = -57 ^\circ C$. After TMT by MIF+EXT the transformation on the $\rho(T)$ curve is weaker. The electrical resistance in the treatment state is higher than in the initial state. This indicates an increased density of defects in the treatment state. Subsequently, the electrical resistance of the martensitic and austenitic phases differs less as compared with the initial state. As in the case of TMT by MIF of the Ga16/6 alloy, after MIF+EXT, on the curves, there is also some displacement (~11 °C) of the characteristic temperatures in the downward direction.

It is known that in Ni-Mn-Ga alloys, a decrease in the average grain size as a result of TMT leads to a gradual suppression of the martensitic transformation [14]. This is manifested in the reduction of the transformation temperature and its severity in the analysis of magnetic, electrical or dilatometric properties. With a decrease in the grain size of less than 1 µm, the phase transformation is practically not observed. In the investigated Ga16/6 and Ga17/3 alloys TMT by forging and forging with subsequent extrusion do not lead to suppression of the martensitic transformation, but only shifts it by 7-10 °C to the region of lower temperatures.

3.2. The microstructure of the alloy after treatment by multiple isothermal forging

Microstructure of the Ni-Mn-Ga alloys in the initial cast state (after vacuum melting) was described by us earlier in [12, 13] Therefore, this paper presents the results of microstructural studies of the alloys only after TMT. Figure 2 a shows the microstructure of the Ga16/6 alloy after MIF, characterized by a bimodal distribution of grains. In this structure, large grains of several hundred microns are surrounded by a fine-grained structure. In the body of large grains there is a blurred contrast indicating the presence of a substructure and/or internal stress fields as a result of the treatment.

![Figure 2](image1.png)

**Figure 2.** SEM image of the Ga16/6 alloy after MIF (a) and the Ga17/3 alloy after MIF+EXT (b).

3.3. The microstructure of the alloy after complex treatment by forging and extrusion

The microstructure of the Ga17/3 alloy after complex TMT by MIF+EXT is shown in figure 2 b. The axis of the extrusion is horizontal relative to the image. The bimodal distribution of the grains formed during the treatment by forging is not eliminated in the structure after hot extrusion. So, there are still large grains of several hundred micrometers in size, surrounded by a fine-grained layer. However, compared to the forged state, the layer of small grains has a greater width. That is, the volume fraction of small grains after extrusion deformation increases.

Thus, after forging and extrusion, the martensitic transformation is not suppressed, despite the grinding structure, and, accordingly, the manifestation of functional effects in it can be maintained. This is probably due to the fact that the layer of fine-grained structure serves as an area of relaxation of stresses arising in the process of martensitic transformation and prevents the accumulation of
excessive density of defects and the development of microcracks in the material. It can be assumed that in this way it will be possible to increase the stability of the functional properties of alloys with multiple cycles of phase transformation.

4. Conclusions
Thermomechanical treatment of Ni-Mn-Ga alloys by forging and forging with subsequent extrusion leads to the transformation of a cast coarse-grained structure into a bimodal structure consisting of large grains several hundred micrometers in size, surrounded by layers of a fine-grained structure. As a result of the formation of such a structure, the martensitic transformation shifts by ~7-11 °C to the region of lower temperatures.

It is expected that due to the creation of a bimodal grain structure, it will be possible to significantly increase the thermal stability of the functional properties of Heusler alloys during cycles of multiple martensitic transformation.

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References
[1] Pagounis E, Chulist R, Szczesnit M J and Laufenberg M 2014 Appl. Phys. Lett. 105 052405
[2] Barmina E, Kosogor A, Khovaylo V, Gorshenkov M, Lyange M, Kuchin D, Dilmieva E, Koledov V, Shavrov V, Taskaev S, Chatterjee R and Varga L K 2017 J. Alloys Comp. 696 310
[3] Li Z, Yang B, Zou N, Zhang Y, Esling C, Gan W, Zhao X and Zuo L 2017 Materials 10 463
[4] Pandey S, Quetz A, Aryal A, Dubenko I, Mazumdar D, Stadler S and Ali N 2017 J. Magn. Magn. Mater. 444 98
[5] Zhukova A, Rodionova V, Ilyin M, Aliev A M, Varga R, Michalkis S, Aronin A, Abrosimova G, Kiselev A, Ipatov M and Zhukova V 2013 J. Alloys Comp. 575 73
[6] Arumugam S, Devarajan U, Muthu S E, Singh S, Thiyagarajan R, Raja M M, Rama Rao N V and Banerjee A 2017 J. Magn. Magn. Mater. 442 460
[7] Rodionova I D et al 2015 JETP Letters 101(6) 38
[8] Kourov N I, Korolev A V, Pushin V G and Marchenкова E V 2012 Phys. Solid State 54 2128
[9] Chulist R, Skrotzki W, Oertel C.-G, Bohm A, Lippmann T and Rybacki E 2010 Scripta Mater. 62 650
[10] Chulist R, Bohm A, Rybacki E, Lippmann T, Oertel C.-G and Skrotzki W 2012 Mater. Sci. Forum 702–703 169
[11] Chulist R, Potschke M, Boehm A, Brokmeier H.-G, Garbe U, Lippmann T, Oertel C.G and Skrotzki W 2007 MRS Proc. 1050 BB09-03
[12] Musabirov I I, Safarov I M, Galeyev R M, Afonichev D D, Koledov V V, Rudskoi A I and Mulyukov R R 2017 Mater. Phys. Mech. 33 124
[13] Musabirov I I, Safarov I M, Galeyev R M, Gaisin R A, Koledov V V and Mulyukov R R 2018 Phys. Solid State 60(6) 1061
[14] Musabirov I I, Safarov I M, Mulyukov R R, Sharipov I Z and Koledov V V 2014 Letters on Materials 4 265