Conference paper

Martensite Transformations in the TiNi(Fe,Mo)Ag Alloys After Thermal Cycling

G.A. Baigonakova[1*], E.S. Marchenko[1], L.A. Kolomiets[2], A.L. Chernysheva[2], V.N.Iliushenov[1], V.E.Gunther[1]

*Corresponding author: G.A. Baigonakova, email: gat27@mail.ru

[1] Tomsk State University, Research Institute of Medical Materials and Implants with Shape Memory, Tomsk, Russia
[2] Oncology Research Institute of Tomsk Scientific Research and Marketing Centre, Tomsk, Russia

Received: 23 March 2017
Accepted: 9 April 2017
Published: 16 July 2017

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the SMBIM Conference Committee.

Abstract

This paper presents the results on influence of thermal cycling on martensite transformations in (TiNiFeMo)Ag alloys with silver additive up to 1.5 at.%. The analysis of temperature dependences of the electrical resistivity allows to determine the characteristic temperatures and construct the diagram of martensite transformations. The thermal cycling leads to the reduce in Mstemperature stabilizing the parent B2 phase in all considered cases of Ag additive. The strongest influence of thermal cycling on the Ms temperature was founded in alloy with 1 at.% Ag. Authors describe the factors leading to a change of the characteristic temperatures of martensite transformations during thermal cycling.

1 Introduction

At present the biocompatible (TiNiMoFe) based alloys are demanded materials to manufacture implants in various fields of medicine. The perspective direction for improvement of TiNi implant materials is Ag introduction into the alloy. It is established that the silver additive into TiNi with concentration (C= 0.6-1.3; 1.7; and 1.9 at. %) influences on the durability and plasticity of the material, keeping high parameters of shape memory effect with the maximum reversible deformation to 6.4% in ternary (TiNi)Ag alloys [1,2]. Furthermore, a possibility of emergence of antibacterial properties in TiNi alloy with 1.4 - 3 at. % Ag was showed in [3]. The antibacterial effect is attributed to the free Ag+ ions leaving from the secondary phases of pure silver which are crystallized in the TiNi matrix.

It is necessary to consider the properties stability of the used material during creation of the designs from TiNi-based alloys. It is known that the characteristic temperatures of martensite transformations (MT) B2↔B19' and B2↔R↔B19' are very sensitive to thermal cycling. The TiNi-based alloys are characterized by the high stability level at thermal cycling through the MT area [4] when complex processes of accumulation and stabilization of defects are occurring in the alloys.

The studies of thermocycling effect on phase transformations in the multicomponent (TiNiFeMo)Ag alloys were not conducted in previous works. The objective of the present study is the research of influence of phase hardening on the MT characteristic temperatures in the multicomponent (TiNiFeMo)Ag alloys with silver additive (C= 0, 0.1, 0.2, 0.5, 1 and 1.5 at. %).

2 Experimental

The studied $Ti_{50}Ni_{49.7-x}Mo_{0.3}Fe_{0.2}Ag_x$ alloys were made by means of the vacuum induction melting (VIM) technology in a graphite crucible by remelting the Ti sponge and electrolytic Ni plates with the addition of Mo, Fe and Ag alloying elements.

Table 1 shows the composition of the studied alloys determined by the charge. The losses in weight during melting did not exceed 0.01 %.

The produced ingots with a weight of ≈ 650 g, length of 150 mm and a diameter of 20 mm were spark cut by the electric-discharge wire-cut to make (50×1×1) mm samples.

Table 1. Composition of the studied alloys

№ of alloy	Concentration of elements [at. %]				
	Ti	Ni	Mo	Fe	Ag
1	50	49,5	0,3	0,2	0
2	50	49,4	0,3	0,2	0,1
3	50	49,3	0,3	0,2	0,2
4	50	49,0	0,3	0,2	0,5
5	50	48, 5	0,3	0,2	1
6	50	48, 0	0,3	0,2	1, 5

The temperature dependence of the resistivity curves was measured by the four-point-probe method. Current and potential conductors made of nickel wire (d=0.5 mm) were soldered to the studied sample. A chromel-alumel thermocouple was fixed in the middle of the sample to measure the actual temperature. Liquid nitrogen was used as a coolant for tests below room temperature down to −180°C. Heating above room temperature was performed using an electrically heated air bath with adjustable power input. Cycling was carried out under condition (heating - cooling - heating), 1 and 10 cycles were registered.

3 Results and discussion

The study of the temperature dependence of the resistivity curves ρ(T) allows to determine the MT characteristic temperatures (TR, MS, Mf) in a static state and to estimate qualitatively the MT type (B2→R→B19′ or B2→B19′) by the shape of ρ(T) curves. The start and finish temperatures of direct MT are well identified on inflection points of ρ(T) curves whereas it is difficult to implement under reverse MT. It is caused by the asymmetric nature of their ρ(T) changes.

Fig. 1 illustrates the temperature dependence of the resistivity curves for (TiNiMoFe)Ag alloys with different silver concentrations (1 cycle). They show the structural changes which are happening in the MT range of the studied alloys. The ρ(T) curves indicate that under cooling the beginning of the parent B2 phase transition to the R-phase corresponds to an increase in the TR temperature. The sharp decrease in the resistivity under cooling on ρ(T) curves corresponds to the MS point of direct R→B19′MT. The Mf point shows the end of the direct MT. When TiNi-based alloys are doped with Ag (0–1.5 at. %), the martensite transformation results are rhombohedral R and monoclinic B19′phases.

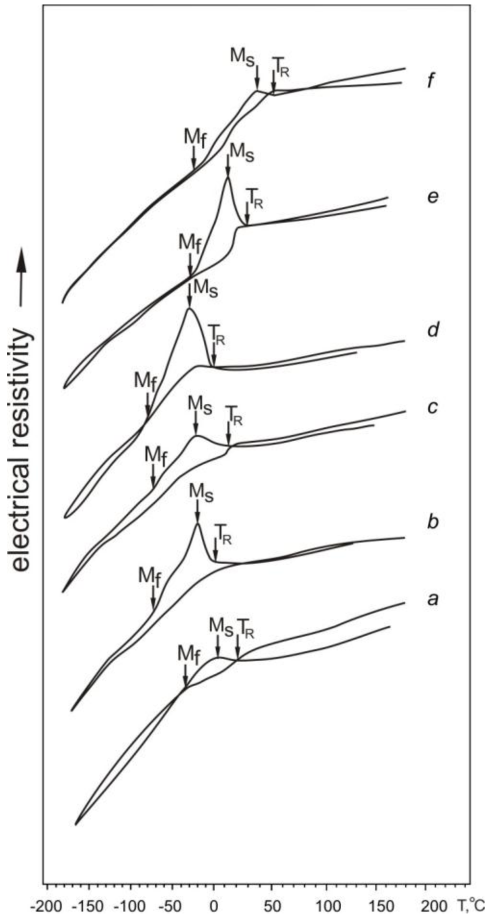

Fig. 1. Temperature dependences of the resistivity curves for (TiNiMoFe)Ag alloy: a) 0; b) 0.1; c) 0.2; d) 0.5; e) 1; f) 1.5 at.% Ag

The electrical resistivity value ρ is a characteristic of material properties and it characterizes the ability of a substance to prevent a current flow. In TiNi-based alloys at austenite-martensite phase transition the growth of ρ defines a presence of R phase. It is known [4] that formation of R-phase structure is followed by a high density of the intercrystalline twinning antiphase boundaries, elastic-plastic lattice distortions in the field of interphase boundaries and mainly by the increase of distortions in R-phase. All these structural changes during the formation of R-phase crystals lead to the growth of ρ(T) at a decrease of temperature.

Table 2.The value Δρ for (TiNiMoFe)Ag alloys

Concentration of Ag (at.%)	0	0.1	0.2	0.5	1	1.5

Δρ (1 cycle), [μΩ×sm]	3	5	2	10	13	5
Δρ (10 cycle), [μΩ×sm]	3.5	8	7	12	15	6

For all studied alloys the value Δρ=ρMs-ρTR which changes depending on the alloy composition has been calculated (Table 2).

The maximum value of Δρ (13 μΩ×sm) is in the alloy with 1 at.% Ag. It can characterize more disordered structure of solid solution than in alloys with different Ag contents.

Based on the analysis of ρ(T) curves, the MT characteristic temperatures (TR, MS, Mf) were determined and the diagram of martensite transformations was constructed (Fig. 2).

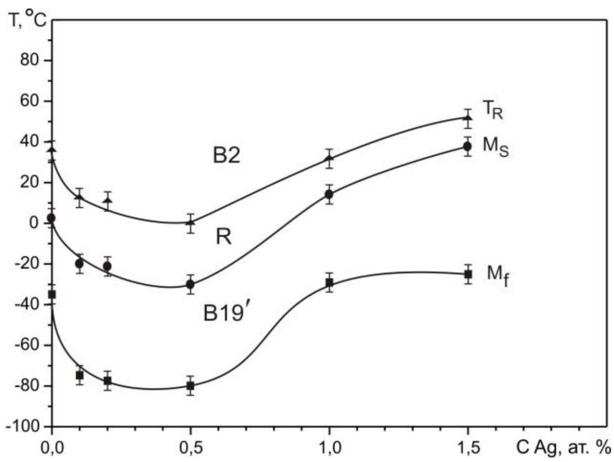

Fig. 2. Dependence of the characteristic temperatures TR, MS and Mf on silver concentration in the (TiNiMoFe)Ag alloys

The doping of TiNiMoFe with insignificant Ag concentrations (up to 0.5 at. %) leads to a decrease in the MT characteristic temperatures (TR,MS, Mf) by 20–30 °C. Higher Ag concentrations (1 and 1.5 at. %) increase the MT characteristic temperatures and shift the phase transitions B2→R→B19′to the high-temperature region(Fig. 2). The revealed feature of the silver-doped TiNi-based alloys is the decrease of the MT characteristic temperatures at concentrations of up to 0.5 at.% Ag and the increase of MT temperatures at concentrations above 0.5 at.% Ag. It has a practical significance, since Ag element allows controlling and shifting slightly the phase transformation temperatures.

One of the important parameters of shape memory materials in particular TiNi-based alloys is the ability to change its shape under the constant loading, both upon cooling and heating, i.e. to be deformed during thermal cycling through the phase transformation intervals.

Influence of thermal cycling on the characteristic temperatures of phase transformations is evident in many factors.

The first one relates to the fact that the formation of the martensite phase is accompanied by the latent heat release of phase transformation at the B2=B19 transition which causes the formation of secondary phase precipitates in the form of Ti_2NI, Ni_3Ti and others in the conditions of a higher temperature on the interface boundary. Particles primarily change composition of the matrix in TiNi alloy, increasing or decreasing the concentration of the elements Ti and Ni. In accordance with this, MS temperature is decreased at excess Ni or increased at excess of Ti in the phase matrix.

The second factor is related to the formation and growth of the martensitic crystals under loading, which is accompanied by plastic deformation of the phase matrix. The plastically deformed areas of the phase matrix are not involved in the restructuring of the structure at the phase transition and prevent the movement of the interface boundary.

The third factor is connected with the creation of highly stressed areas in the phase matrix during the formation of martensite crystals. These areas lead to a shift of the phase transition temperature to higher temperatures accordaning to the Clausius–Clapeyron relation.

All the factors introduce contribution to the change of the MT characteristic temperatures of TiNi-based alloy during thermocycling under loading. Thermocycling leads to a stabilization of contributions gradually with the increase of cycle's number. Therefore, alloy will take on more stable properties if we carry out the thermal cycling before it is application [5].

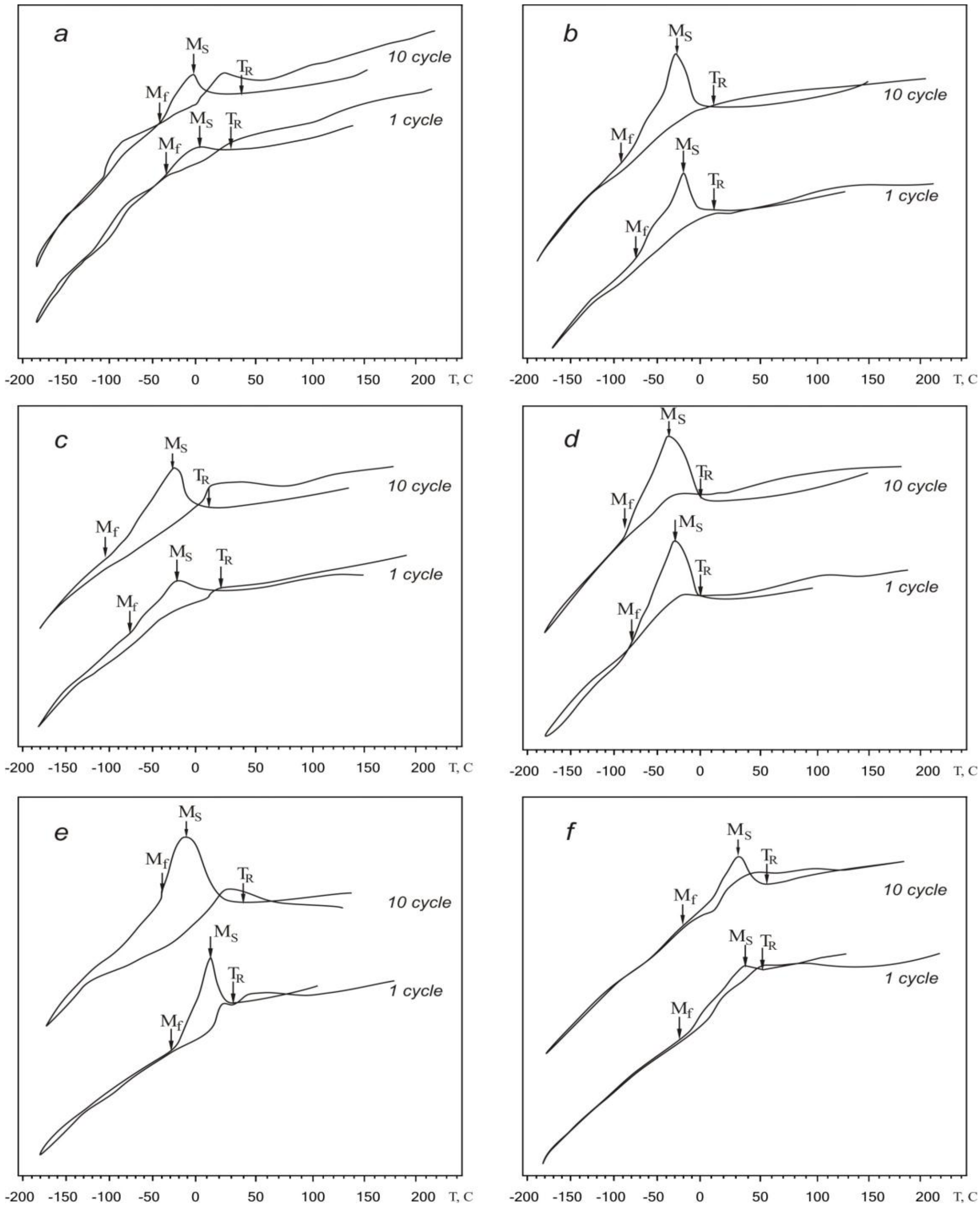

Fig. 3. Temperature dependences of the resistivity curves for 1 and 10 cycles in (TiNiMoFe)Ag alloys: a) 0; b) 0.1; c) 0.2; d) 0.5; e) 1; f) 1.5 at. % Ag

The values of the MT characteristic temperatures for 1 and 10 cycles are given in Table 3.

Table 3. The values of the MT characteristic temperatures for 1 and 10 cycles

The MT characteristic temperatures / Ag [at. %]	MS, [K] (1 cycle)	MS, [K] (10 cycle)	Mf, [K] (1 cycle)	Mf , [K] (10 cycle)	TR, [K] (1 cycle)	TR, [K] (10 cycle)
0	3	-2	-35	-42	21	39
0.1	-20	-29	-154	-119	1	12
0.2	-22	-24	-175	-98	13	12
0.5	-30	-38	-80	-89	0	0
1	13	-11	-29	-88	29	40
1.5	38	32	-25	-23	52	56

During thermocycling of all the alloys a sequence of the B2→R→B19' MT at cooling does not change. At the same time the growth of electrical resistivity valueis observed at low temperatures due to the structural complexity of R-phase crystals and an increase in electron scattering centers.

The thermocycling leads to the reduce in Ms temperature stabilizing the parent B2 phase in all considered cases of Ag additive. The strongest influence of thermocycling on the Ms temperature was founded in alloy with 1 at.% Ag (MS decreases almost by 20 °C). It can be connected with the strongest change in the elastic-plastic properties of the alloy as a result of doping silver. Ag provokes a growth of defects in the matrix phase, and significantly greater undercooling must be for formation of martensite crystals during thermocycling. However an exact reason of the MT characteristic temperatures shift can be established after carrying out researches on a structural and phase condition of system.

4 Summary

In TiNi-based alloys with Ag the growth of electrical resistivity value is observed. It deals with the change of the matrix composition and the increase of electron scattering centers.

The MT characteristic temperatures are sensitive to the composition change of the alloys. The doping of TiNiMoFe with insignificant Ag concentrations (up to 0.5 at.

%) leads to a decrease in the MT characteristic temperature MS by 20–30 °C. Higher Ag concentrations (1 and 1.5 at. %) increase the MS characteristic temperature and shift the phase transitions B2→R→B19 to the high-temperature region.

In all the studied alloys the B2→R→B19 MT sequence does not change at thermal cycling, but it is accompanied by hardening phase with varying degrees of development. The maximum level of phase hardening is observed in the alloy with 1 at.% Ag at a decrease of Ms by 20°. In all other cases of doping the value is up to 8.

5 Acknowledgments

This study was supported by Tomsk State University Mendeleev Fund Program (research grant No 8.2.10.2017)

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