EFFECT OF HEAT TREATMENT ON THE SURFACE STRUCTURE OF Ti–Ni ALLOYS

RyklinaE.P., Prokoshkin S.D.

National University of Science and Technology "MISIS", Moscow, Russia

ryklina@tmo.misis.ru

Surface structure in binary TiNi alloys containing 50.0 at.% Ni and 50.7 at.% Ni after low-temperature thermomechanical treatment (LTMT) and post–deformation annealing (PDA) was studied. A 0.4 mm diameter wire with was subjected to LTMT by cold drawing to diameter 0.3 mm without intermediate annealing (the accumulated strain e = 0.6). Post-deformation annealing (in the case of the Ti–50.7 at.% Ni, aging) was performed in the temperature range 350–700 °C for 20–60 min [1]. The elemental composition of the oxide layer was studied on a "CamScan-4" electron microscope equipped with an "Inca Energy 300" device for energy dispersion electron-probe microanalysis (EPMA) operated at accelerating voltage of 15 kV and a probe current of 1 nA.

Figure 1 shows micrographs of cross sections of the modified surface layers in Ti – 50.7 at.% Ni alloy after various PDA treatments. Using these micrographs, we measured the minimum and maximum depths of the visible change in the layer and calculated the average depth. From these results, the appearance, structure and depth of the oxide layer depend substantially on the preliminary heat treatment schedule. After LTMT + PDA at 430 °C for 10 min, the oxide layer is non-uniform in depth and has a "zonal" character: light and dark fields are clearly visible inside the layer (the picture is not presented). As the PDA time increases from 10 min to 1 h (Fig. 1, schedule 1), the average layer depth increases by about 1.5 times (from 4 to 6 μm); surface regions in the layer have a loose structure (separated fragments are clearly visible over the sample surface). As the annealing time increases to 10 h (Fig. 1, schedule 2), a qualitatively different result is achieved: approximately half the surface does not have an oxide layer, and oxide film regions have a very small depth – up to 3 μm. Evidently, after such long-term heat treatment, the oxide layer becomes so loose that it is almost completely spalled during the preparation of a polished section. High-temperature annealing at 700 °C for 20 min (Fig. 1, schedule 3) followed by quenching leads to the formation of an oxide layer with a qualitatively different structure: it is separated into two zones, namely, a dark near-surface zone and a light zone in contact with the matrix. Both zones are rather dense and uniform. The depth of the dark zone varies in the range 5–13 μm and the depth of the light-zone varies in the range 3–9 μm. Generally, the modified layer has a rather uniform depth of 14–15 μm. Light regions are visible inside the

dark zone; they are located closer to the boundary with the light zone. Long-term annealing of the Ti–50.7 at.% Ni alloy at 430 °C for 10 h after quenching (the micrograph is not presented) leads to a denser layer; however, its thickness is about three times smaller than the thickness after quenching. As noted above, PDA at 430 °C for 10 h results in embrittlement and exfoliation of the oxide layer. Therefore, the layer formed upon PDA at 700 °C loses part of its mass after additional annealing at 430 °C for 10 h. After heating of the Ti–50.0 at.% Ni alloy for quenching, the dark zone in the oxide layer has a structure that is not as homogeneous as that in the Ti-50.7 at.% Ni alloy (see the picture in [2]). Its density is also significantly lower. Separation and exfoliation traces are visible, which are likely to be related to a longer holding time during annealing (30 min).

With EPMA, one can trace the distribution of individual elements across the oxide layer using cross sections of samples treated according to various schedules (Fig. 2). An analysis demonstrates that the depth distribution of oxygen atoms is almost the same after annealing according to all schedules: its content is maximum (40–55%) in the surface layer and then decreases gradually on approach to the boundary with an unoxidized matrix.

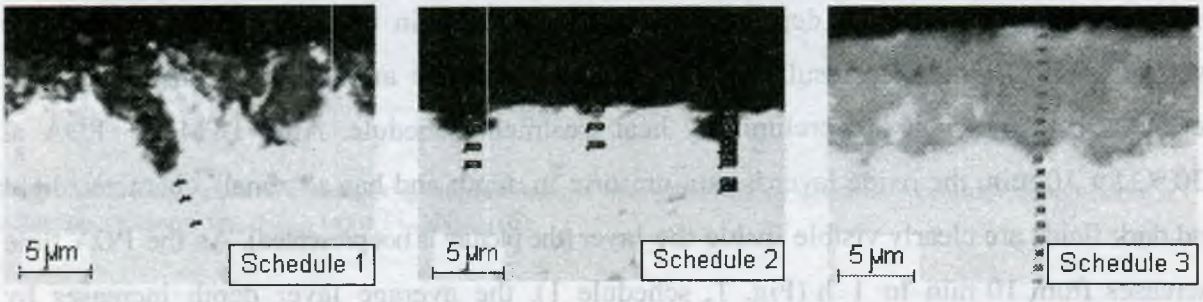

Figure 1. Micrographs of the PDA oxidized surface layers in Ti–50.7 at.% Ni alloy samples taken with reflected electrons after LTMT. Points indicate the EPMA sites analysed to determine the oxygen, nickel and titanium contents. PDA schedules: 1 – 430 °C, 1 h; 2 – 430 °C, 10 h; 3 – 700 °C, 20 min

The depth profiles of nickel and titanium are more complex and their characters depend substantially on the PDA schedule (Fig. 2). The depth profiles of nickel and titanium in an oxide layer after annealing at 430 °C for 1 hour are rather chaotic (Fig. 2, schedule 1) but quite regular after annealing at 430 °C for 10 hours (Fig. 2, schedule 2). PDA at 700 °C (Fig. 2, schedule 3) is characterised by clear oxide layer depth profiles of nickel and titanium. The near-surface dark layer is enriched in titanium: its content in this layer reaches 60% (i.e., significantly higher than in the unoxidised matrix). The nickel content in this layer approaches zero. In contrast, the light layer in contact with the matrix is enriched in nickel: its content in this layer reaches 90% and the titanium content is almost zero.

In all cases, the titanium content in the near-surface layer correlates with the content of

oxygen having diffused from the surface (Fig. 2). Obviously, this directional migration of titanium atoms is caused by the interaction of titanium with oxygen to form oxides. In this case, nickel atoms are mainly retained in the unbound state and their migration is directed from the surface towards the bulk of the sample.

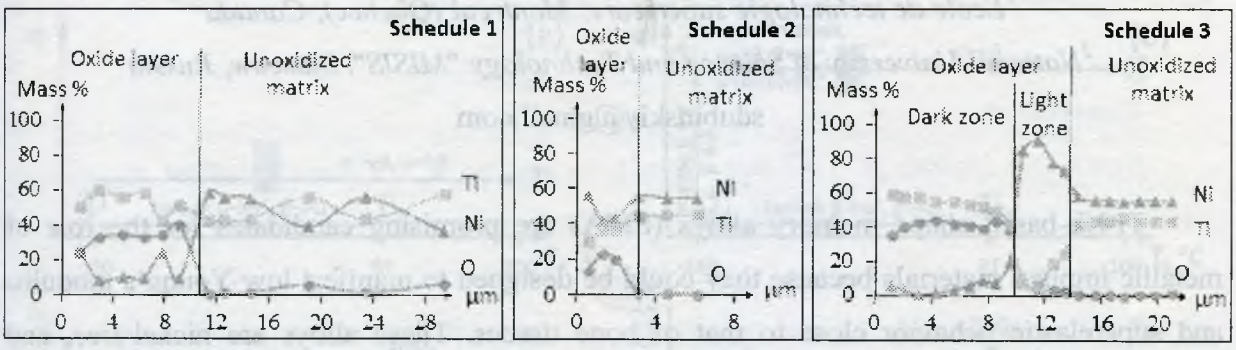

Figure 2. Depth profiles of the element concentrations in the oxidized surface layers in Ti–50.7 at.% Ni alloy samples. The curves correspond to the PDA schedules and micrographs shown in Fig. 1 and are plotted using EPMA data

Summarizing the results, one can conclude that the depth, structure, composition and properties of the oxide layer that forms on the surface of Ti–Ni alloy products during PDA depend substantially on the annealing temperature and time. Compared to quenching, the application of LTMT can improve the state of the alloy surface due to a decrease in the oxide-layer depth by more than an order of magnitude. Under annealing at high temperatures a layer of uncombined nickel forms, which is inadmissible for articles applied in medicine.

The present work was carried out under financial support of the Ministry of Education and Science of Russian Federation

1. V. Brailovski., I.Yu. Khmelevskaya, S.D. Prokoshkin, V.G. Pushin, E.P. Ryklina, R.Z. Valiev. Phys. Met. and Metallogr. 97, Suppl. 1 (2004) 3–55.
2. S.D. Prokoshkin, E.P. Ryklina, A.A. Chernavina, V.Ya. Abramov, N.S. Krestnikov. Russian Metallurgy (Metally), 6 (2009) 519–526.