Specific features of the physicochemical properties of welded titanium nickelide

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Abstract. The paper analyzes the strength characteristics of welded joints made of TiNi alloy with a shape memory effect. Comparison of the level of tensile strength of welded samples made by the TIG method in an Ar and He medium was carried out using a universal machine Instron 5985. The study of the material structure was carried out on longitudinal sections using a JSM-6490LV electron microscope. The analysis of the chemical composition of the material under study in local volumes was carried out using an INCA Penta FETx3 energy dispersive attachment. The calorimetric parameters of the original and welded samples were obtained using a differential scanning calorimeter METTLER TOLEDO 822e.

1. Introduction
The application of mechanisms operating with the use of the shape memory effect (SME) in technological processes has shown the advisability of their development [1]. The enjoyment of miniature presses of the SHeR type with ring-shaped bundle force elements (“metal muscles”) made it possible to increase the productivity of the key technological operation - the manufacture of multilayer materials. Expansion of possibilities and scope of application of “metal muscles” required the approbation of welding technology during their production to close circular contours. Studies of new samples of force elements [2] have shown the possibility of their operation not only in the SME mode, but also in the two-way shape memory mode. However, when operating in the mode of cyclic deformation-strength loads in these structures, the possibility of destruction of “metal muscles” in the welding zone was found even at their relatively low values [3].

2. Strength properties
In recent decades, various methods of welding of titanium nickelide have been investigated. Along with electric welding [4–6], the technology of laser welding [7–11], friction welding [12] and explosion [13] were studied. As a rule, the strength of the welded joint was lower than the strength of
the initial material. To clarify the reasons for this and search for methods to increase the resistance of “metal muscles” to breaking loads, the welded joints of a wire 2 mm in diameter made of TiNi55.42wt.% alloy were studied. Welding was carried out in two modes.

In an argon atmosphere, the wire was welded with a constant electric current \( I = 10 \) A. The technological operation lasted \( \sim 3 \) s. Welding was carried out in a helium atmosphere for 1.5 s. In this case, the DC current was 45 A.

The deformation and strength properties of welded samples under tension were studied on an Instron 5985 testing machine. Before testing, some of the samples was exposed to additional heat treatment in the form of annealing at 773 K for 30 min, followed by cooling together with the furnace. Curve 1 in figure 1 illustrates the development of the deformation process and the rupture of the initial material that was exposed to the above heat treatment. With an increase in stresses \( \sigma \) up to 118 MPa, the sample was deformed in the elastic mode. The value of the deformation limit of elasticity \( \varepsilon_y \) was found to be \( \sim 0.005 \). The behavior of welded samples (curves 2–4, figure 1) at this stage of deformation turned out to be close to the behavior of the initial material.

The peculiarities of the mutually independent behavior of \( \sigma \) and \( \varepsilon \) shown by curve 5 in figure 1 are due to the fact that this sample after welding in a helium atmosphere was not exposed to annealing procedure. This could lead to the preservation of the structural gradient and residual stress fields arising during the technological operation due to high temperature gradients and high cooling rate of the material in the welding zone. As a result, the stress initiating the plastic flow process turned out to be somewhat higher.

**Figure 1.** Strength properties of wire samples of TiNi55.42wt.%: 1 – initial, 2–5 – samples welded in Ar (2), He (3), He + 30 thermocycles (4), He (5); 1–4 – with anneal \((T = 773 \) K\), 5 – without anneal. The motion speed of the movable holder is 4 mm/min for curves 1, 2, and the speed is 1 mm/min in the rest of cases.

The stage of deformation in the plastic flow regime up to \( \varepsilon = 0.045 \) is the same for all samples. Then, in the samples welded in a helium atmosphere, an increase in stresses begins with an increase in \( \varepsilon \). And in the samples from the initial material and welded in an argon atmosphere, the plastic flow continued to a value of \( \varepsilon \) equal to 0.055.

Rupture of the welded annealed samples occurred when a strain of \( \sim 0.08 \) was reached. In this case, the stress level \( \sigma_{TS} \) in the sample welded with a current of 45 A (helium atmosphere) was \( \sim 580 \) MPa, and in the sample fabricated with \( I = 10 \) A (argon atmosphere) it was 140 MPa less. A sample prepared in a helium atmosphere and subjected to 30 thermal cycling after annealing in the temperature range from 270 K to 400 K turned out to be less durable. Its destruction occurred at \( \sigma_{TS} \sim 460 \) MPa, and the deformation turned out to be less than 0.07. Curve 5 in figure 1 shows that the
rupture of the unannealed sample took place at close values of $\sigma_{TS}$ and $\varepsilon$. Rupture of all welded samples occurred in the boundary layer, i.e. on the border of initial and welded materials.

3. Structural analysis
To analyze the reasons for the results obtained, the structure of the material on longitudinal thin sections was studied using a JSM-6490LV electron microscope. The presence of the INCA Penta FETx3 energy dispersive attachment made it possible to analyze the chemical composition of the material under study in local volumes. Figure 2 shows thin sections of the fracture zone of the initial material (a) and a sample welded in an argon atmosphere (b), as well as a thin section of the wire welding zone in a helium atmosphere (c).

![Figure 2](image)

**Figure 2.** Longitudinal thin sections of the fracture zones of the initial material (a), a sample welded in an Ar atmosphere (b), a thin section of a welded joint obtained in an He atmosphere (c).

The rupture of the sample from the initial material occurs with the formation of a neck. The rupture surface can coincide with the boundaries of the inclusions (figure 3a). Chemical analysis of these formations showed that the content of Ti in them may be 6 – 10 times higher than Ni. Occasionally this superiority becomes twentyfold. Additional studies of such inclusions in the materials under study showed that oxygen can enter the composition with Ti and Ni. Its concentration varies in such formations from a few tenths to 10%, and in exceptional cases up to 20%. The characteristic size of these grains can reach 3 $\mu$m. But most of them do not exceed a few tenths of a micrometer in diameter. The distance between such grains in the original material, according to the data from the obtained images, varies mainly from 5 $\mu$m to 10 $\mu$m.
Figure 3. Zones of a thin section of destroyed initial material: a - point B, b - point D, c - point H (figure 2a).

The sample surface at the base of the neck (figure 3b) is cut by small cracks ~ 1 μm deep. In the near-surface layer, there are zones in the chemical composition of which the concentration of nickel is three times higher than that of titanium. It can be assumed that the state of the alloy is determined by the TiNi$_3$ composition. Outside the neck area, the sample surface (figure 3c) is also covered with fine cracks. The layer thickness of the TiNi$_3$ composition can reach 5 μm. Crack depth reaches nickel-rich layer thickness.

When the sample welded in an argon atmosphere breaks down, necking is not observed. In the welded material, along with the grains described above, consisting mainly of titanium, inclusions with a highly indented surface are noted (figure 4a). Probably, in this way the dendritic morphology characteristic of the cast material appears. In such structural elements, large gradients of chemical composition can be observed. In particular, it was possible to detect a change in the Ni content in the inclusion material from 13 at.% to 31 at.%. That is, in such microvolumes, the presence of titanium and its oxides, as well as compositions of Ti$_2$Ni and TiNi, is possible.
In the boundary layer of the initial and welded materials, a crack was found (in addition to micron-sized cracks), which is directed from the surface of the welded joint to the center. The depth of such a crack exceeds 40 μm (figure 4b). Along with inclusions enriched in titanium, the presence of chains of inclusions (bright white in contrast) of a eutectic character, precipitated along the grain boundaries, was noted on the surface of the thin section. The transverse size of such inclusions is ~ 0.5 μm, and the nickel concentration in them can reach 70 at.%. In this case, the grain boundary can be completely covered by them. The composition of grains surrounded by such a "garland" contains ~ 55 at.% nickel and, accordingly, 45 at.% titanium. It can be assumed that the main component of the grain chain material is TiNi₃. Apparently, its presence is also possible in the grains from Ti₄₅Ni₅₅at.%. The crack surface largely coincides with the boundary of the clusters with an increased nickel concentration. In the surface layer, cut by microcracks, chemical analysis showed the presence of zones with a concentration of titanium ~ 60-65 at.% and nickel ~ 35-40 at.%. In the initial material of the welded sample (figure 4c), the chemical composition of which is close to equiatomic titanium nickelide, inclusions enriched in titanium were observed. The nickel content in them varies from 16 to 35 at.%

Welding the wire in a helium atmosphere resulted in the formation of pores in the welded material and in the boundary layer (figure 2c). Perhaps this is due to local boiling of the superheated melt. Figure 5a shows that, along with pores in the boundary layer near the sample surface, there are parallel cracks ~ 10 μm and ~ 20 μm deep. This sample was not loaded. Therefore, the size of cracks is significantly smaller than the size of a similar defect in figure 4b. In the near-surface layer of the sample, grains with an increased nickel content (up to 65 at.%) can be found. These grains have an

Figure 4. Zones of a thin section of a fractured and welded joint in an Ar atmosphere: a – point A, b – point G, c – point H (figure 2b).

In the boundary layer of the initial and welded materials, a crack was found (in addition to micron-sized cracks), which is directed from the surface of the welded joint to the center. The depth of such a crack exceeds 40 μm (figure 4b). Along with inclusions enriched in titanium, the presence of chains of inclusions (bright white in contrast) of a eutectic character, precipitated along the grain boundaries, was noted on the surface of the thin section. The transverse size of such inclusions is ~ 0.5 μm, and the nickel concentration in them can reach 70 at.%. In this case, the grain boundary can be completely covered by them. The composition of grains surrounded by such a "garland" contains ~ 55 at.% nickel and, accordingly, 45 at.% titanium. It can be assumed that the main component of the grain chain material is TiNi₃. Apparently, its presence is also possible in the grains from Ti₄₅Ni₅₅at.%. The crack surface largely coincides with the boundary of the clusters with an increased nickel concentration. In the surface layer, cut by microcracks, chemical analysis showed the presence of zones with a concentration of titanium ~ 60-65 at.% and nickel ~ 35-40 at.%. In the initial material of the welded sample (figure 4c), the chemical composition of which is close to equiatomic titanium nickelide, inclusions enriched in titanium were observed. The nickel content in them varies from 16 to 35 at.%

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elongated shape. However, the transverse size is equal to the characteristic size of formations similar in chemical composition in samples welded in an argon atmosphere. Oxygen was found in nickel-enriched grains of material welded in a helium atmosphere, the concentration of which reaches several atomic percent.

**Figure 5.** Zones of a thin section welded in an He atmosphere: a - point C, b - point F, c - point G (figure 2c).

In the central zone of the welded material, both near the surface (figure 5b) and in the inner region (figure 5c), inclusions with a high titanium content are transformed into groups of new formations of smaller sizes. In the first case, they resemble “garlands” of grains scattering from a single center. In the second case, they are chains and crystals of a dendritic structure. In the central part of the welded material (figure 5b), there are no cracks on the sample surface.

If we consider the bulk of the material, in which the alloy is made of titanium nickelide close to the equiatomic composition, then a scatter in the ratio of Ti and Ni is observed in it. In the initial material, a selective analysis of chemical elements showed the possibility of changing the Ti concentration from 49.06 at.% to 50.55 at.% In the central part of the weld penetration in an Ar atmosphere, the Ti content ranges from 48.83 at.% to 52.40 at.%. Welding in a helium atmosphere with higher amperage reduces the spread of Ti content. Its concentration varies in the range from 49.26 at.% to 52.16 at.%.

This affects the calorimetric characteristics of the material. The study of these physical parameters was carried out on a METTLER TOLEDO 822e differential scanning calorimeter. The rate of temperature change during heating and cooling was 10 K/min. The initial material was compared with the material of the central penetration zone.
All three samples were preliminarily heated to 723 K and then cooled to 173 K. During reheating, the endothermic reaction of the reverse martensitic transformation in the initial material began to manifest itself at 238 K (figure 6, curve 1). Heat absorption is most intense in the temperature range from ~ 304 K to 324 K with a maximum at ~ 318.5 K. When the temperature reaches 333 K, the phase rearrangement of the crystal lattice ends.

![DSC studies](image)

**Figure 6.** DSC studies: 1 - initial material, 2 - the central part of the sample welded in an Ar atmosphere, 3 - the central part of the sample welded in an He atmosphere.

The endothermic reaction in a material welded in an Ar atmosphere begins at 229 K. The most intense heat energy consumption occurs in the temperature range from 264.5 K to 317.2 K with an extreme value at 307.9 K. The completely endothermic reaction stops at a temperature close to 333 K. However, heat energy consumption in the material of the welding zone was almost three times less heat absorption in the original material.

In titanium nickelide welded in a helium atmosphere, the onset of the reverse martensitic transformation occurs at 228 K. The endothermic reaction proceeds most intensely in the range from 282 K to 320.5 K and completely stops at 328 K. In contrast to the two previous curves, in this case, two peaks were observed. The first was recorded at a temperature of ~ 294.8 K, the second near a temperature of 308 K. Apparently, the transformation in this material proceeds in two stages. At the beginning, the absorption of thermal energy occurs in grains enriched with nickel, and a little later, giving rise to the second extremum, there is a rearrangement of the crystal lattice in microvolumes with a predominant concentration of titanium. Selective analysis showed that the average value of Ti concentration in the first case is 49.63 at.% and in the second - 50.70 at.%. The specific heat of transformation in titanium nickelide welded in a helium atmosphere is ~ 80% of the corresponding parameter of the initial material. This may be due to the fact that in a significant part of the material, martensitic transformation is completely absent. Also, inclusions can hinder deformation processes by increasing the elastic limit \( \sigma_y \). The presence of residual stresses at the boundaries of grains of different chemical composition reduces the strength characteristics of the material (curve 5, figure 1). The performed annealing, which partially reduces the residual stresses, increases the strength of the sample and slightly decreases \( \sigma_y \) (curve 3, figure 1). However, thirtyfold thermal cycling by the transition of the alloy from the martensitic state to the austenitic one and vice versa can again increase the stresses at the corresponding boundaries, lead to the growth of microcracks along the surfaces separating the equiatomic titanium nickelide and microvolumes without transformation of the crystal lattice. The consequence of this can be the behavior of the sample, reflected by curve 4 (figure 1).
4. Conclusion
Selective analysis of the chemical composition showed that the greatest variety of compositions of Ti, Ni and, in some cases, oxygen is present in the transition zones from the initial material to the weld penetration (figure 4b). After welding in an argon atmosphere, it should be noted that there are 4 groups of microvolumes with different ratios of alloy components. Welding in a helium atmosphere results in greater material homogeneity (figure 5b). However, large temperature gradients, due to the significantly superior amperage during welding, are a factor that generates microcracks and residual stresses in this transition layer. As a result, structures appear near the surface of two samples that reduce the level of material resistance to fracture. The results obtained and the analysis performed allow us to make the assumption that when a more homogeneous material structure is achieved as a result of welding, one can expect an increase in its strength and deformation properties. For this, it is necessary, first of all, to reduce temperature gradients in pieces made of titanium nickelide during the operations of the technological process under study. The presence of the TiNi$_3$ compound near the destruction zones remains a separate issue. Determining the role of this composition in deformation processes and fracture requires additional research.

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