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HEAT-RESISTANT NIOBIUM-BASED ALLOY FOR ROCKET SPACE TECHNOLOGY

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In papers [1, 2] for the first time, theoretically and experimentally it was discovered one of the most, as it may seams, easiest self-oscillatory reactions of oxygen interaction with metals that is most probably is chemical and afterwards biological evolution foundation. Exactly in the mechanism of this reaction laid down different evolution patterns that translated in particular result. Whether dense oxide film is formed protecting the material from further destruction or thermo kinetic vibrations are arise, that may lead to its destruction. Therefore, the main task of research that includes the development of topochemical interaction models of molecular gases, experimental study of the oxidation process, is the establishment of formation mechanisms of dense oxide film.

This paper includes theoretical as well as experimental study of oxidation processes of specific materials based on niobium, impact of alloying components and ingredients on heat-resistance and formation of necessary physical, mechanical and exploitation properties of compositions. Besides, two important technological aspects were reviewed. The first is based on introduction of disperse reinforced additives in nano-dispersive state, for example yttrium oxide or lanthanum, that allow to increase resistance at elevated temperatures saving high technological plasticity. Another technological aspect is connected with development of reactive sintering methods that allow to effectively use the impact of irreversible process of reaction interaction to powdered material consolidation [3], and formation of structure and new properties. Therefore, during application of such method in [4], the material based on nichrome was obtained, which plasticity properties are in two times higher than its analog that was received under traditional metallurgical technology, and cyclic heat-resistance at temperatures up to 1200 ^{0}C more than 10 times higher.

In papers [3, 4] scientific bases of reactive sintering of powder compositions, under the conditions of high inner energy discharge of powder bled, were developed. Special advantage of such technology is high speed of process [5] and absolute erase of heritage effect of initial powdered object.

Materials and study methodology

Initial blends of clean components were prepared by mixing in eccentric mixer during 6 hours together with ШХ15 metal balls. In order to develop alloy based on niobium, it was used powdered electrolytical niobium of fineness less than 63 mμ, thermal titanium sodium – less than 10 mμ and dispersed aluminum – less than 63 mμ. In order to exclude inhomogeneity of charge stock, 0.05% of glycerin was added during mold filling. The samples were molded in metal mold with both sides load on precision mechanical press.

Behavior of sintering and oxidation was studied using namely thermal analysis. For this purpose, into the samples chromel-alumel thermocouples were installed that were placed in a row lengthwise at a pitch of 4 mm (the first one is at 2 mm distance from the surface). Unilateral heating was performed on solar power plant. Temperature changes recording of reaction system was carried out by quick-operating computer-aided system for recording signals based on analog digital transducer.

Solar power plant represents parabolical incident energy concentrator of 2 m in diameter. Installation is equipped with automatic Sun tracking system providing constant value of heat flow that is directed on the sample surface during the whole test period. Adjustment of heat flow density was performed by changing the angle of blinds opening and distance to focus concentrator
(Fig. 1). Main studies of heat-protection materials ablation were performed on this installation [6].

The value of heat flow was selected with regard to necessary speed and heating of samples and generally was not exceeding 3000 kW/m^2.

Study of thermo kinetics reactionary interaction with liquid phase participation was also carried out in pipes type resistance furnace by gradient heating of 10 mm diameter and 12-15mm length samples from cylinder edge side during their way to the heating zone. Initialization was performed in pipes type resistance furnace with specified isothermal temperature that exceeded or would be close to melting temperature of the most low-meling eutectics or peritectic.

Laws of powder mixtures molding based on niobium

At the initial stage of the work it has been studied behavior during pressing of the niobium powder and its binary mixtures with titanium, which is a major alloying component of the developed material. As it turned out, due to the high ductility of niobium its powder is compressed perfectly (Fig. 2). The maximum relative density of the compacts is 92.5 %.

When introducing titanium in the range of 30-45 % the decrease of compacts compressibility throughout the range of compression pressures is observed. Mixtures formability is limited to the lower boundary of the pressing pressure of 200 MPa. In the area of compression pressures of 500-700 MPa it is observed inflection on the compression curves, which is probably due to the destruction of surface oxide films. Metals of periodic system VA group have this tendency - vanadium, niobium and tantalum.

The need for a detailed study of the individual components effect of the developed material is also associated with the behavior of compacts made of mixtures during sintering. Not all components can activate sintering, on the contrary, growth of compacts is most frequently observed. This is caused by alloy homogenization during sintering and unipolar diffusion can result in billets growth due to pores formation. Therefore it was studied compressing laws of intended compounds mixtures of the developed material.

Thus, when studying compressibility of niobium alloy initial composition it was revealed that partial replacement of titanium by zirconium analogue leads to an increase in density throughout the range of compression pressures starting from formability limits due to the greater ductility of zirconium powder. Comparing the previous data on niobium compressibility it can be concluded that the other additive components in the specified amounts do not substantially affect the nature of the compression, but increase the pressure value corresponding to the lower formability boundary.

Within variation limits of main components composition and various additives content there is no significant change of niobium based mixtures compressibility. This is because high ductility margin of niobium powder. Therefore there is a sufficiently large interval of dopants variation during the material composition optimization. It should be noted that the fundamental differences from the general laws of powder compositions molding based on niobium is not observed in the framework of classical concepts developed in the works of M. Balshina, I. Radomyselskogo, M. Stern and others.

Laws of sintering processes of the powder mixtures based on niobium

When placing the samples in a heated oven and initiating reacting interaction and up to its end, the sintering process is in non-isothermal mode, during which the temperature change trajectory is determined not only by external heat, but also by internal heat generation (Fig. 3). It should be noted that during reacting interaction self-steepening phase the nonlinear behavior of the temperature is observed, that confirms the synergistic nature of the reacting interaction.

In accordance with the objective the density of niobium based material shall be not more than 6 g/cm^3, which imposes certain limits on the concentration ranges of the main alloying components responsible for properties such as high-temperature strength, heat resistance, and the density of the final product. Actually, for this purpose the dependencies of ternary alloys theoretical density from content of the main alloying components - aluminum and titanium were developed (Fig. 4).

These results allow us to determine variation ranges of titanium and aluminum content.

The required properties of powder complex functional material are formed exactly during sintering. Diffusion homogenization is taking place, interparticle contacts are developed, material structure is formed, other processes occur as well.

Technological behavior during sintering can not be unmistakably identified basing on the alloy composition of the main alloying components. Niobium and titanium form a continuous series of solid solutions. However, due to the increase or decrease of titanium concentration and thus homologous solidus temperature, heterodiffusion parameters are also change, which will affect in one or another way on the character of the volume changes of binary alloys. Indeed the study of compression patterns during sintering indicates that when titanium content increase in the binary alloy, an increase of shrinkage at low densities of preform is observed. Thus during sintering of niobium alloy with 30 % titanium the shrinkage is observed only at relatively low density compacts, which is caused by a well-developed internal surface of the porous body. However, with an increase in compacts' density more than 77.5 % due to heterodiffusion of components the shrinkage is suppressed and the samples growth is observed.

Increased of titanium content up to 35 % enhances expansion of observed shrinkage field until the samples with 87.5 % porosity. With further increase of the raw compacts density the heterodiffusion of components begins again suppress shrinkage, which again leads to samples growth. That is, with such titanium content the samples growth is possible only with high relative density of compacts, which is achieved with pressing pressures close to the capabilities limits of standard molds used in the technological process of material obtaining.

Increase in alloy content of titanium up to 45 % leads to shrinkage in a whole range of density ratio wet compact, obtained during at process. Also it should be pointed that increase in alloy content of titanium leads not just only to a qualitative change of growth process to shrink process, but also significantly increases the shrinkage quantitatively. Thus, increase of titanium content from 30 to 45 % the maximum observable shrinkage changes from 4.7 to 18 %.

Therefore, the clear dependence between the titanium content in alloy and amount of shrinkage is being traced.

Aluminum is a reaction component for this system, considering that there are several intermediate phases as well as in titan-aluminum system and in niobium-aluminum system. Fundamentally new mass transfer mechanisms can be actuated during sintering. As shown earlier [3], reactive interaction process starts from the most fusible component, in this particular case from aluminum. Certainly, dissolution rate of refractory materials in liquid melt far exceeds the dissolution rate of solid components in refractory base. In this respect aluminum injection leads to burst growth of compacts and samples porosity correspondingly. Consequently blanks consolidation problems arise. So far as for the additional densification other mold with large dimensions is needed so that sample could be housed. Moreover as a result of reaction diffusion accelerated homogenization and, correspondingly, the material hardening take place, for that reason larger pressures should be used for remolding, and in case of this alloy – post –ultimate strength of steel mold.

As a result of growth mechanism identification during reaction sintering a new method of sintering activation was developed [7]. A large number of fine pores is generated during the reaction sintering in reaction liquid, which coagulate fast in large caverns indigenous during the sintering. There is an ample quantity of local flows in reaction liquid, which provide fine pores coagulation. Injection of inert additive nanosized powders, like fluorides or oxides at fixed proportion leads to breaking-up or inhibition of caverns formation. The growth observed in the initial phase, when fine pores are generated. Then they effectively participate in composition sintering activation. Therefore the appropriate quantity ratio of yttrium oxide inert additive and reaction component was found that led to composition compound (Fig. 5).

In the present case the compound process has much in common with sintering character of one-component metal-powder, i.e. it is correspondent to the patterns specific to phenomenological sintering model [7]. Increase of shrinkage amount is typical as the result of billets' porosity increase or their density ratio decrease.

Mass-loss rate, related with separation of adsorbed gases of oxygen, nitrogen, carbon dioxide and water, also depends on density ratio. All of them refer to interstitial impurities, which reduce metal ductility of VA group and their alloys. Indeed mass-loos dependences studying in sintering revealed their essential meaning. Thus at relative compact density about 67 % losses will be slightly over 1 %, while at relative density about 70 % they will be already over 2 %. This means that the main part of interstitial impurities is remained in material composition.

Selecting optimal technology it is necessary to know not just only the shrinkage amount, but also density ratio, which is reached at set-up technological process parameters. Thus porosity less than 90 % means occurrence of apparent porosity that means that it is necessary to apply the protective agents during the further hot rolling in order to avoid internal oxidation. It significantly increases technology cost. The example of this alloy development shows that despite large shrinkage at low compact densities, maximum required density is achieved just only in large densities compact domain. This achieved due to maximum molding forces, that places special requirements to steel mold materials, used during material blanks cold. The most appropriate is usage of not just only У8-type carbon steels but at least of ХВГ high-hardness steels. Their service life will be essentially more lasting.

An X-ray diffraction analysis of the sintered alloy based on niobium showed a fairly good homogenization of the alloy at different temperatures [5]. However, due to its composition the alloy falls into the two-phase field, and lines of intermetallic compounds appear. It is possible that stable structures of intermetallic compounds surrounded by titanium oxides are formed in the course of the reacting, as observed on the X-ray diagram (Fig. 6). Indeed, the lower titanium oxide reflections are seen, Ti_3O in particular. Sintering temperature increase up to 1375 ^{o}C leads to disappearing of intermetallic compounds, however titanium oxide remains. It is noteworthy that the line of intermetallic compounds expands due to nonequilibrium pattern of their formation. Apparently, they are the primary products of sintering reaction, i.e. they are synthesized in the initial period of the exothermic reaction initiated by contact melting of aluminum in the powder mixture.

On the basis of breaks and fracture pattern analyzing of such material composition the conclusion could be made that the alloy is highly crack-sensitive and has low ductility properties.

Taking these circumstances into account, new material on the basis of niobium with high contain of titanium was developed. Study of molding sand mixture compactibility during cold molding has shown that increasing of titanium containing resulting in decreasing of compact density. At the same time study of sintering process of this composition has shown that titanium concentration increasing of 8 % provides significant increasing of shrinkage. Amount of shrinkage increase almost twice throughout all variation rate of compact density ratio. Single sintering provides target density of blank > 90 %. Therefore there is no need to integrate second compaction of blanks operation.

Increasing of titanium consisting lead to improvement of material ductility, that allows increase volume ratio of indifferent dispersion-strengthening admixture of yttrium oxide and therewith increase heat resistance of the alloy.

Studying of physical and mechanical properties and heat resistance of the material

Cyclic heat resistance of niobium alloys with density 5.788 g/cm^3 and 5.558 g/cm^3 was studied. Experiments was conducted on cylindrical test-piece with diameters 1.994; 0.992 cm and height 0.294; 0.481 cm for niobium alloys with density 5.788 g/cm^3 and 5.558 g/cm^3 respectively. During research work 100 twenty-minute cycles of test-pieces oxidation was conducted in electrically heated furnace at a temperature 1200 ^{o}C.

After each 20ty minutes cycle was performed weighing operation of cooled to room-temperature work-pieces on high-accuracy electronic weighing machine with precision of one tenthousandth of a gramm. Alloy with lower content of titanium less heat resistant (Fig. 7) than alloy, that consist 45 % Ti.

Experiments results shown that during first cycles of oxidation small weight increment appear which not exceed 1 % for niobium with density of 5.788 g/cm^3 and 0.3 % for niobium with density 5.558 g/cm^3 after first cycle and it significantly reducing with every following cycles. Weight increment directly aligned with proof oxide film formation on the material surface. Starting on 6th cycle for more dense alloy on the basis of niobium and from 17th for less dense alloy the trivial loss in weight of test-pieces is occur. It is attributable to oxide film flaking off that almost uniformly continuing through to 100th oxidation cycle (Fig. 7).

Studying of thermokinetics of oxidation process suggest that alloy with lower consistence of titanium is oxidizing in condition of higher thermokinetics variations than tailored composition on the basis of niobium and this fact validate the hypothesis about prominent role of oxidation dynamic [8] for forming of heat resistance composition and selection of its tailored composition (Fig. 8).

At the table shown physical and mechanical properties of developed alloy on the basis of niobium. Material was tested after sintering with density rate 92.5 %.

Testing results suggests about sufficiently high characteristics of the material which can operate in necessary conditions without protective covering. It could be used for metallic thermal protection of reusable spacecraft.

Conclusions

1. New heat resistant dispersion-strengthening alloy on the basis of niobium with reduced density 5.558 g/cm^3 was developed.
2. Technology for reaction sintering of the material on the basis of niobium was implemented.
3. Heat resistance of the alloy was studied. It has been established that material is workable in conditions of cyclic thermal effect up to 1200 ^{o}C as it stand 100 cycles of heating and cooling to room temperature.

4. Throughout tests material lost 11 % of its mass.

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Figures

Fig. 1. Solar power plant for studying of thermokinetics of reactionary interaction in obtaining of alloy on the basis of niobium: 1 – sun louver; 2 – paraboloid reflector ∅ 2 m

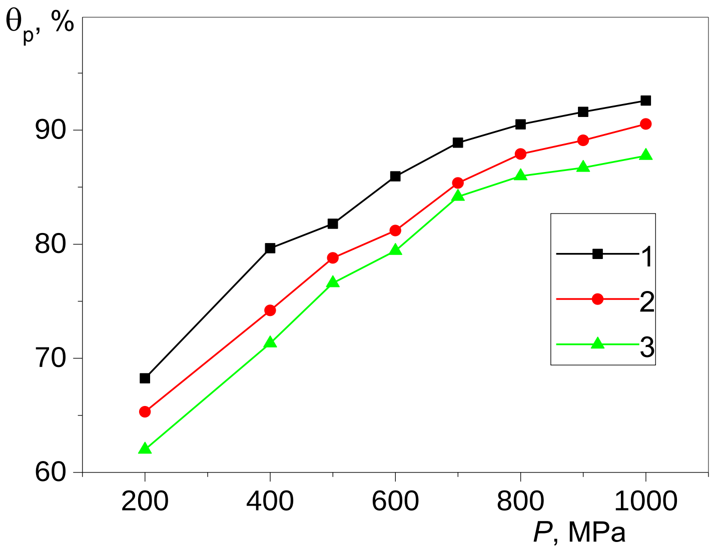

Fig. 2. Dependence of pressing relative density on pressing pressure: 1 – Nb;

2 – Nb+30%Ti; 3 – Nb- 45% Ti. where θ_p – relative density after pressing;

P – pressing pressure

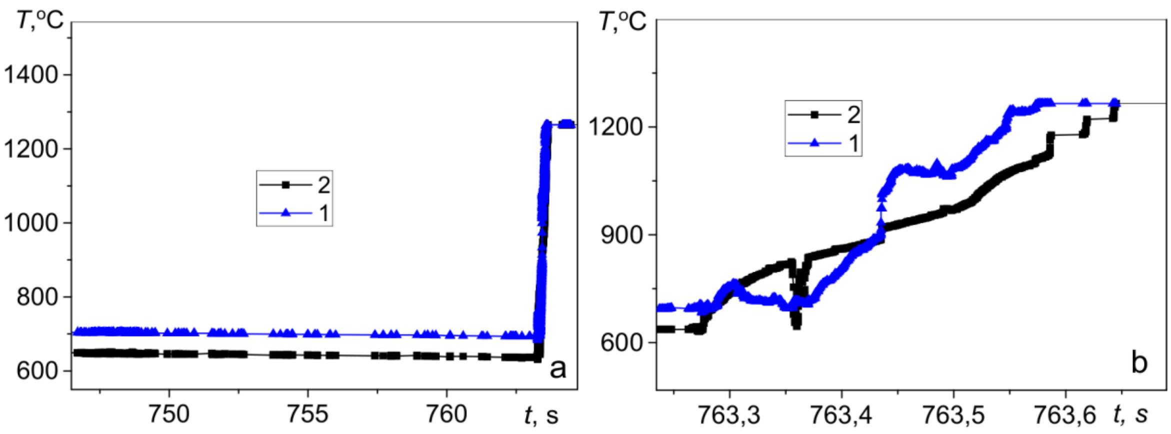

Fig. 3. Thermokinetic of reacting interaction in Nb-Al system: a-general view, b-fragment, indications of thermocouple throughout sample length: 1-2 mm, 2-6 mm.

Where *T* - temperature, *t* – time

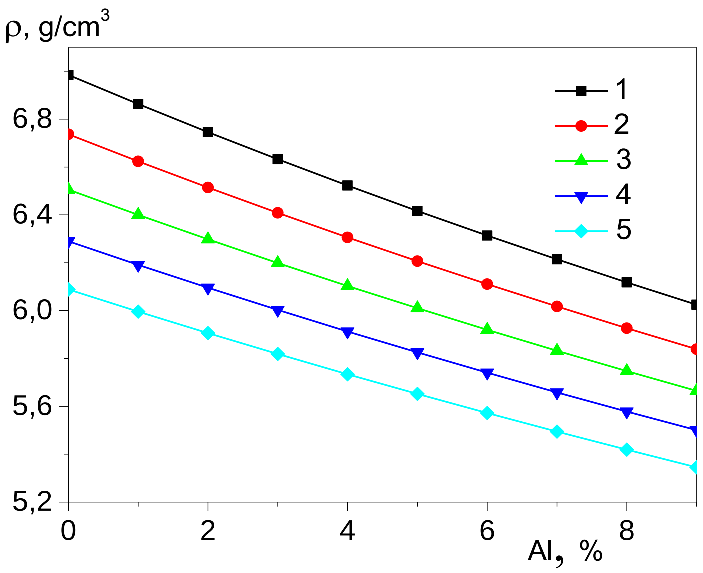

Fig. 4. Dependence of niobium alloys theoretical density on titanium and aluminum containing: 1 – 25% Ti; 2 – 30% Ti; 3 – 35% Ti; 4 – 40% Ti; 5 – 45% Ti.

Where ρ - density; Al – aluminum containment

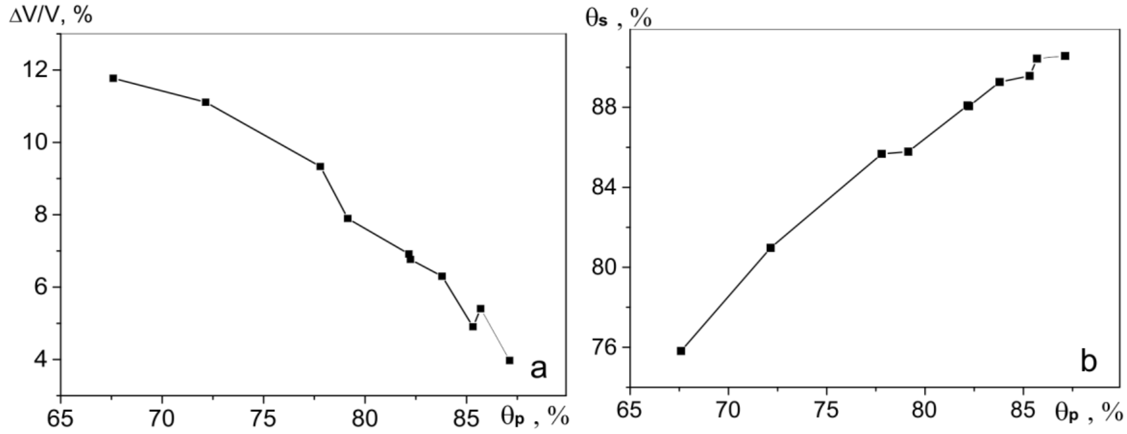

Fig. 5. Dependence of sample(s) shrink-off and its relative density at sintering temperature 1325 ^{o}C on density rate of pressing of composition on the basis of niobium with 37 % Ti, which contain aluminum and yttrium oxide. Where ΔV/V - samples shrink-off; θs – density rate of untreated pressings

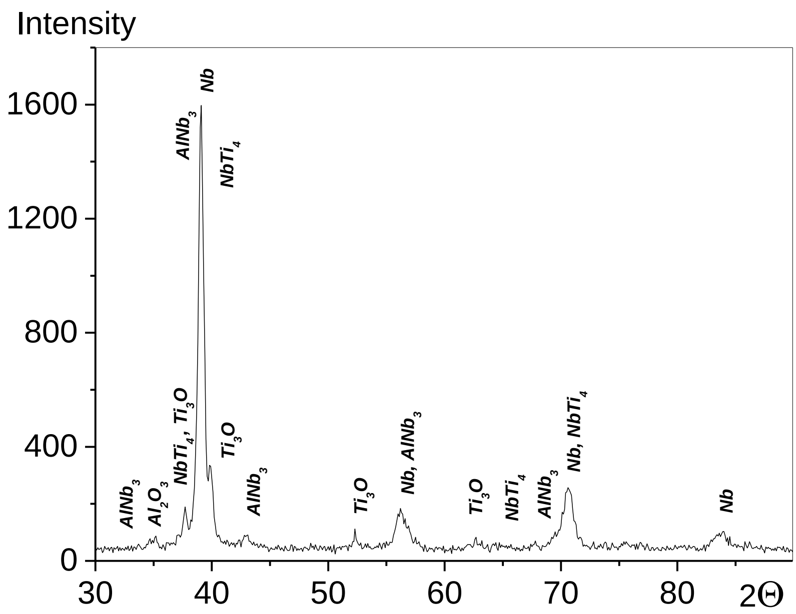

Fig. 6. X-ray diagram of phase composition of alloy on the basis of niobium sintered at 1375 ^{o}C during one hour

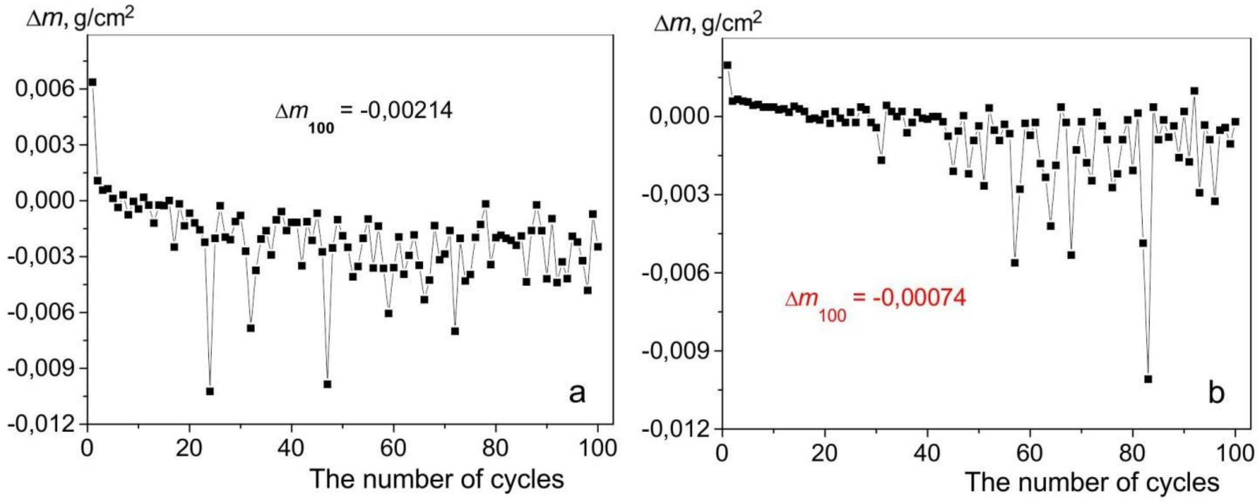

Fig. 7. Cyclic heat resistance of dispersion-strengthening niobium alloy developed with the application of reaction sintering with density ρ = 5.788 g/cm^3 (a) and ρ = 5.558 g/cm^3 (b) at a temperature 1200 °C

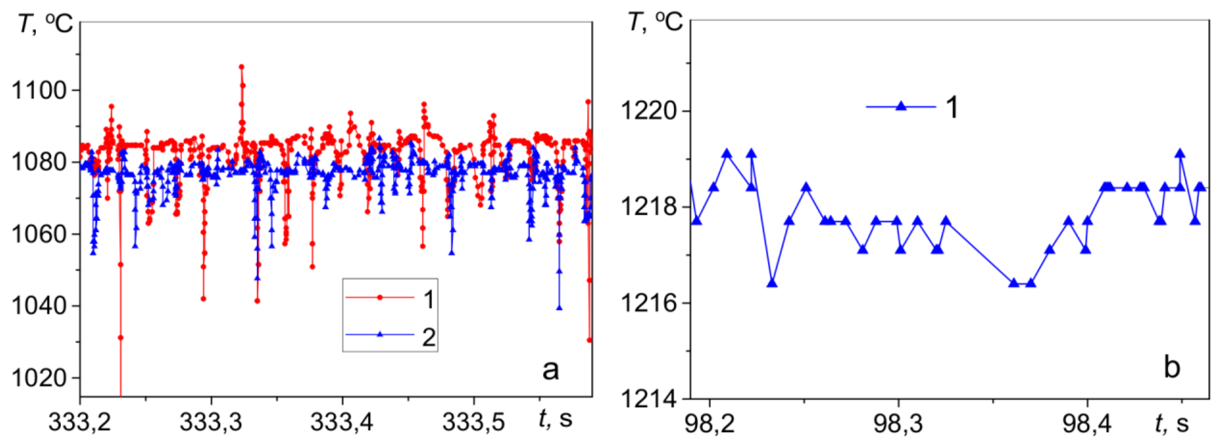

Fig. 8. Thermokinetics of niobium materials oxidation process: a – 37 % Ti, b – 45 % Ti; 1 and 2 - indicated value of thermoelements which are installed on the surface and 2 mm deeper, respectively

Table – Physical and mechanical properties of tailored composition developed alloy on the basis of niobium

Density, ρ	g/cm^3	5.558
Tensile strength, $\sigma_в^{20}$	MPa	900-1000
Tensile strength, $\sigma_в^{1100}$	MPa	80-110
Elongation at 20 °C, %	%	18-25
Tensile strength, $\sigma_в^{1200}$	Mpa	55-60