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INVESTIGATION INTO RECRYSTALLIZATION OF NIOBIUM  
AND ITS ALLOYS

[Issledovaniye Rekrystallizatsii Niobiya i ego  
Splavov]

BY: Ye. M. Savitskiy, V. V. Baron, K. N. Ivanova

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In this article results of experimental investigations of niobium recrystallization are analyzed as well as the effect of alloying with silicon, vanadium, titanium, chromium, zirconium, molybdenum, tantalum, tungsten, lanthanum on the temperature of its recrystallization. The effect of the aforementioned elements on hardness, ductility and the technological properties of niobium alloys are studied.

Niobium is a high-melting metal; according to the latest data its melting point is  $2460 \pm 10^{\circ}\text{C}$ . It has high corrosion resistance to many acids, and other valuable physico-chemical properties, analogous to those of tantalum. The main fields of industrial use of niobium (as well as of Ta) are at present the chemical industry, vacuum engineering and metallurgy (where niobium is used as an alloying addition and is being added to special steels in the form of ferro-niobium).

Owing to its lower specific gravity ( $8.57 \text{ g/cm}^3$ ) in comparison to the analogous tantalum ( $16.6 \text{ g/cm}^3$ ), niobium possesses an advantage from the economical point of view, particularly now, when it has been established that sources of its raw material were considerably larger than those of tantalum. Lately, in foreign literature there are a series of statements, considering niobium as a metal with greatest possibilities of using in atomic power engineering [1 - 5]; the low cross section of thermal neutron capture by niobium (lower than for other high-melting metals); resistance to the effect of uranium and liquid coolant metals (sodium and others), combined with its satisfactory properties at higher temperatures, make this metal a particularly suitable construction material for nuclear reactors (casings for uranium and plutonium heat-liberating elements). However, the application of niobium and its alloys was as yet not sufficiently developed. This was obviously due to the fact that sufficient amounts of pure niobium were not available and that its

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properties were not sufficiently studied. Properties of niobium alloys were even less investigated. Moreover, the few available data pertain mainly to metal ceramic materials, although arc smelting is the most efficient production method for large-size industrial structures of high-melting metals (such as Mo, Nb and others).

Recrystallization processes of niobium and its alloys were hardly investigated, as well as the effect of alloying on the temperature of recrystallization and the mechanical and technological properties of niobium.

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However, studies of recrystallization processes are indispensable for determining the maximum working temperature of heat-resistant materials and for establishing optimum technology of their treatment.

We undertook an investigation into niobium recrystallization and into the effect of alloying with boron, silicon, vanadium, titanium, chromium, zirconium, molybdenum, tantalum, tungsten, lanthanum and mix-metal on the temperature of its recrystallization.

The investigation dealt also with the effect of the enumerated elements on hardness, ductility and technological properties of niobium alloys in dependence on the conditions of mechanical and thermal treatment. The following initial materials were used: compact ceramic niobium of 99 - 99.2% Nb concentration, electrolytic chromium, iodides of titanium and zirconium, vanadium of 99.4% concentration, boron - 94%, silicon - 98.6%, molybdenum - 99.98%, tantalum - 99%, tungsten - 99.9%, lanthanum - 98.5%. Mix-metal contained 96.7% (La + Ce), and other rare-earth elements.

The enumerated elements were added to niobium in amount of from 0.2 to 5 per cent in weight. The selection of alloying elements was determined by the supposed possibility of raising the melting point and recrystallization temperature of niobium in its alloying with high-melting elements, which form large regions of substitution solid solutions on niobium base (Nb with W, Ta, Mo, Cr, Zr, V, Ti); and with elements sharply differing from niobium by atomic dimensions and forming narrow regions of interstitial solid solutions (B, Si) on its base and metallic compounds. Niobium alloying with lanthanum, mix-metal and such chemically active elements as zirconium, titanium, vanadium,

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was also aimed at increasing the ductility of the available, not sufficiently pure, hard niobium, containing a considerable amount of gaseous impurities and carbon. Portions of alloys weighing 70 - 80 g were cast in an arc furnace with unfusing electrodes on a copper water-cooled bottom.

Cast alloys were subjected to annealing in a vacuum at 1,400°C for 50 hrs; to chemical analysis, to investigations into their microstructure and to hardness measurements. As a result of the chemical analysis it turned out that changes in the alloy composition compared to that of the charge were observed in alloys containing La and mix-metal (loss in burning amounted to 1 - 2%). A reduced amount of loss (tenths of a per cent) occurred in alloys with chromium, vanadium, silicon and boron.

Rough coarse-grained structure was observed in cast niobium and in the majority of alloys in cast and annealed state, in contrast to the initial compact ceramic material, having a finer grained structure. A certain reduction of grain size in comparison with cast niobium was noticed in alloys with considerable content of boron, silicon, zirconium, lanthanum and mix-metal. The effect of alloying additions on the hardness of cast niobium is shown in Figure 1.

The indicated graph shows that additions to niobium of silicon, boron, vanadium (up to 1%) and chromium (up to 5%) cause a strong increase of hardness. Titanium has a lesser effect on the hardness. There is almost no increase in hardness by adding tungsten, tantalum, molybdenum and zirconium in amounts of 3 and 5%. Addition of these metals amounting to ~5% even reduces hardness. This can be caused by a deoxidation process. A content of over 0.2% lanthanum and mix-metal reduces niobium hardness. Comparison of atomic dimensions of the enumerated elements with those of niobium permits the following remarks: Elements increasing the hardness of niobium, have considerably smaller atomic dimensions than niobium (silicon, boron, chromium, vanadium). Elements whose atomic dimensions approach or exceed those of niobium, have only a slight effect on its hardness, or even reduce it.

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In order to investigate recrystallization processes all specimens were subjected to deformation. Since cold deformation proved unapplicable to

niobium and particularly to some of its alloys in cast and annealed state (specimens broke even at a low degree of deformation), niobium and its alloys were treated at higher temperatures. In order to prevent oxidation, vacuum rolling at 1,450 - 1,350°C was carried out under the supervision of S.P. Kovtun, a scientific worker.

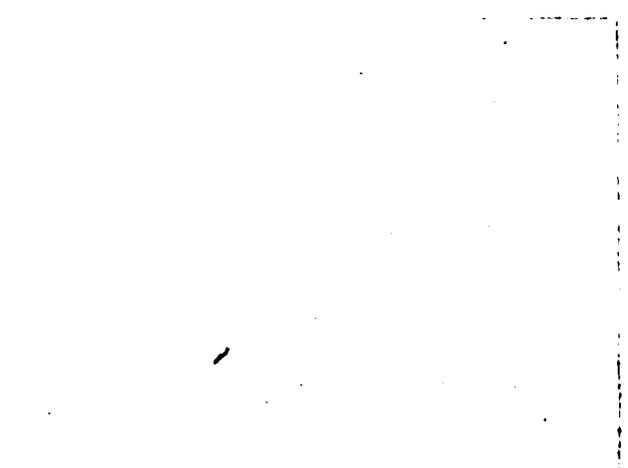


Fig. 1. The effect of alloying additions n (%) on hardness

Hk  $\left( \frac{\text{kg}}{\text{mm}^2} \right)$  of niobium.

On the whole 60 alloys were rolled. Alloys with 3 and 5% Cr 1.2; \*) 1.6% mix-metal and with 1% Si were of a poor quality when treated under the chosen conditions. The general degree of deformation in rolling was 50%. Rolling was performed with shrinkage not over 0.2 - 0.5 mm per operation, with intermediate annealing at the temperature of rolling. As a result, reducing of the cast coarse grain sizes in niobium and its alloys was not observed and cold hardening after the last pass did not exceed 12 - 15%. In order to obtain finer and more uniform initial structure, all rolled specimens were subjected to recrystallization annealing. The coarse-grain structure and the low deformation of hot-rolled niobium and its alloys entailed high temperatures of their recrystallization. The temperature of beginning recrystallization of hot-rolled niobium was 1,550°C. This is explained by the strong effect of the degree of deformation on the temperature of recrystallization. It is considerably higher in low than in high degrees of deformation. Moreover, the size of initial grains has a likewise strong effect on the

rate of formation of crystallization-centers; new recrystallized grains arise more rapidly in spots where the crystalline lattice is more deformed, mainly at the grain boundaries. The presence of coarse initial grains reduces the rate of recrystallization process. Figure 2 shows microphotos of niobium, illustrating the coarse-grained structure of niobium in cast, annealed and hot-rolled state (Figure 2, a, b). Annealing of hot-rolled niobium at  $1,560^{\circ}\text{C}$  and holding for 1 hour causes the formation of new grains, mainly at the boundaries of the old grains. Only after raising annealing temperature up to  $1,730^{\circ}\text{C}$  and extended holding up to 2 hours 40 minutes, new recrystallization grains were forming all over the volume of the niobium specimen (Figure 2, v, g).

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Grains thus obtained were much finer than those of cast structures and permitted already the application of cold deformation with considerable degrees of shrinkage to niobium and its alloys. Investigations into temperatures of beginning recrystallization of niobium and its alloys were only performed after obtaining relatively fine-grained initial structures of the specimens ( $d_{av}$  of grain =  $70\mu$ ), followed by their cold deformation with shrinkage by 70% (compression on a hydraulic press) and recrystallization annealing at different temperatures for one hour, in order to determine the beginning of recrystallization.

The temperature of beginning recrystallization was determined by methods of roentgenographic and microstructural analyses and by the hardness method.

Fig. 2. Microstructure of cast and hot-rolled niobium, x 100:  
a - cast and annealed at  $1,400^{\circ}\text{C}$ ; b - hot-rolled at  $1,450^{\circ}\text{C}$ ;  
v - hot-rolled and annealed at  $1,560^{\circ}\text{C}$ ; g - hot-rolled and  
annealed at  $1,730^{\circ}\text{C}$ .

Roentgenograms were obtained with molybdenum radiation and exposure for 1 hour. Etching of sections for microscopic examination was carried out with a mixture of hydrofluoric and nitric acids. Hardness was measured

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after penetration of a pobedite cone (Pobeditovyy konus) with a tapered angle of  $90^\circ$  under a load of 100 kg.

Figure 3 shows microstructures and roentgenograms of niobium after cold deformation and annealing. In Figure 3 formation of a new recrystallization grain after annealing at  $1,125^\circ\text{C}$  is visible on a background of cold deformation texture (Figure 3, a, b). The subsequent growth of this grain at annealing temperatures raised up to  $1,200^\circ\text{C}$  is shown. On roentgenograms of the same specimens the appearance of spots on compact Debye rings can as well be observed, which is characteristic of the initial stage of the recrystallization process (Figure 3, g, d). Figure 3, e shows the subsequent increase of their number at higher annealing temperatures. The hardness of cold-deformed niobium is  $240 \text{ kg/mm}^2$  and is reduced after annealing at  $1,100^\circ - 1,125^\circ\text{C}$  to  $208 \text{ kg/mm}^2$ , that is to say, at a temperature corresponding to beginning niobium recrystallization, and then remains unchanged up to high-temperature annealing at  $1,560^\circ\text{C}$ , due to the slow growth of niobium grains at higher annealing temperatures.

Besides determining the temperature of niobium recrystallization after cold deformation by 70%, the effect of the degree of deformation on the temperature of recrystallization was investigated. As a result it was established that with a lower degree of deformation up to 12 - 13%, the temperature of beginning recrystallization of niobium increased up to  $1,300^\circ\text{C}$  in contrast to deformations of 50 - 70% corresponding to temperatures of  $1,150$  and  $1,125^\circ\text{C}$ .

In order to clear up the effect of the aforementioned alloying additions on recrystallization temperature of niobium, analogous thermal treatment of all hot-rolled alloys was carried out to obtain a finer-grained initial structure than that of the cast state. The only difference was that optimum annealing temperatures of these alloys differed from each other and were selected for each alloy according to the results of a series of annealing. Alloys thus treated as well as niobium were subjected to cold deformation by 70% and to annealing, and temperatures of their beginning recrystallization were determined.

In all cases the beginning of recrystallization was clearly discerned by the roentgenographic and microscopic methods, as described above. Changes in hardness after annealing at a temperature corresponding to the beginning of recrystallization, were likewise distinctly revealed on the curves of "annealing temperature versus hardness" in the form of a sharp decrease of hardness values. Moreover, it can be noted, that this reduction of hardness, corresponding to the beginning of the recrystallization process, occurred in niobium and its alloys somewhat earlier than that defined by the methods of roentgenographic and microstructural analyses.

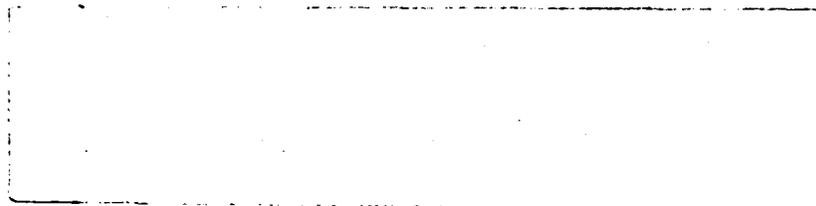


Figure 3. Microstructure (x 100) and roentgenograms of niobium after cold deformation and annealing: a - deformed by 70%; b - deformed and annealed at 1,125°C; v - deformed and annealed at 1,200°C; g - deformed by 70%; d - deformed and annealed at 1,125°C; e - deformed and annealed at 1,160°C.

Further increase in annealing temperature of alloys (up to 1,560°C), as in the case of niobium, did not entail substantial changes in hardness and in the grain size. As a result of the investigations performed the temperature of beginning recrystallization for niobium was determined. The effect of addition of boron, silicon, chromium, zirconium, vanadium, titanium, molybdenum, tantalum, tungsten, lanthanum and mix-metal (from 0.2 to 5 per cent in weight) on the temperature was established as well.

Data obtained are given in Figure 4. They show that, according to this viewpoint, alloying elements can be divided into two groups: elements which raise the temperature of niobium recrystallization and elements which reduce it. Tungsten, tantalum, molybdenum, vanadium, zirconium, and titanium belong to the first group. Some of these metals (V, Zr, Ti) raise temperatures only in case of their low content, and have no effect or even reduce the temperature if their content is higher. Others (Mo, W, Ta) entail a raise of temperature in both cases. Elements which reduce recrystallization temperatures over the whole investigated

range of concentrations (B, Cr, La) belong to the second group. Addition of mix-metal also reduces the temperature of niobium recrystallization. The amounts of silicon applied did not affect the temperature of niobium recrystallization.

It is interesting to observe that the first group includes most high-melting metals, whose atomic dimensions approach those of niobium (the difference in the dimensions of atom radii in % does, on the average, not exceed 4 - 5).

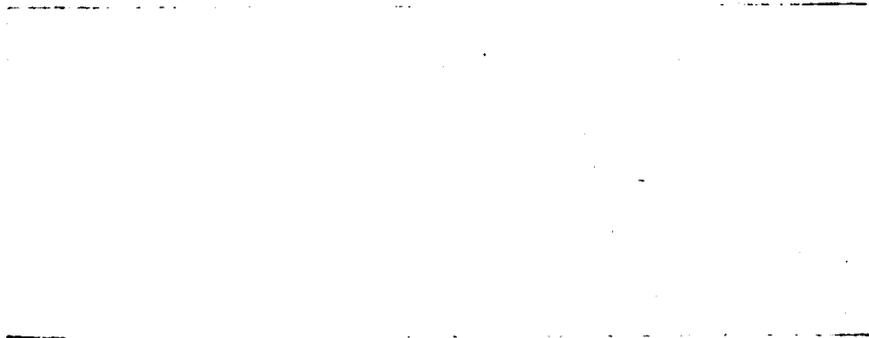


Fig. 4. The effect of alloying additions  $n$  (%) on the temperature  $t$  ( $^{\circ}\text{C}$ ) of recrystallization of niobium and its alloys.

The second group includes less high-melting elements, whose atomic dimensions differ from niobium atom dimensions by 20 - 25% to either side. In all cases the relatively slight effect of such alloying elements with very different physico-chemical and mechanical properties, on recrystallization temperature of niobium should be noted, as well as the high recrystallization temperature of niobium itself, which even at a 70% deformation is 0.51 of  $T_s$ . Probably, the high temperature of recrystallization and the low effect of the enumerated alloying additions is explained by the very considerable amount of oxygen, nitrogen and carbon impurities in the niobium used. These impurities cause a sharp raise of its recrystallization temperature and complicate the effect of the alloying elements on recrystallization processes.

Actually, subsequent investigation of considerably purer iodide niobium, obtained at the laboratory of metallurgy of rare metals, proved that the recrystallization temperature of this niobium was reduced to  $940^{\circ}\text{C}$  at the same degree of deformation.

As already mentioned, niobium and its alloys were subjected to annealing in a vacuum at temperatures up to 1,560°C after cold deformation. Subsequently to annealing at different temperatures, their microstructure was examined; hardness and ductility under compression on a Gagarin press with a constant load (5 t) were measured.

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The investigation into the microstructure of niobium and its alloys, annealed at 1,200°C, showed that the grain size in all cases was a very small one ( $d_{av} \approx 5 - 10 \mu$ ) having in some alloys even a texture of deformation (alloys with 3 and 5% Mo).

A raise of annealing temperature up to 1,400°C entailed a very slight grain growth and only at 1,560°C the texture disappeared in all alloys, and in alloys with chromium a considerable growth of grains was observed. Hardness measurements of niobium and its alloys in different states, initial state and after cold deformation and annealing, showed its certain reduction after annealing at 1,200°C. As a result, considerable changes of the grain took place. A stronger effect of the grain change was discovered in measuring ductility of alloys (Figure 5). Coarse-grained cast alloys and niobium did not endure, in the majority of cases, even low degrees of deformation at room temperature, and broke. On the other hand, comparatively finer-grained "initial" specimens of niobium and its alloys possessed already a certain ductility (particularly niobium alloyed with lanthanum and zirconium). Cold deformation and subsequent annealing at 1,200°C increased still more ductility of niobium itself and of all its alloys. The ductility of niobium increased in this case from 7 - 8 to 60% and reached 70% in some alloys. Increase of ductility at finer grain size can probably be explained by the fact that the length of boundaries extends many times in comparison with coarse-grained materials; this entails a sharply reduced concentration of additions which are located along the grain boundaries and have a negative effect on ductility. As a result, ductile deformation is facilitated.

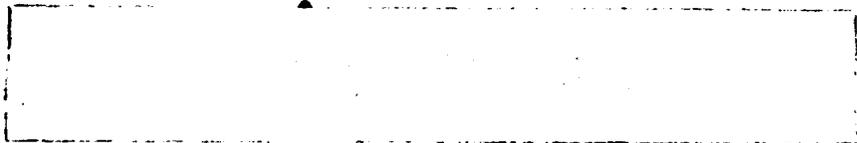


Fig. 5. Effect of alloying additions n (%) on ductility  $\Sigma$  (%) of niobium and its alloys in the initial state and in annealing at 1,200°C.

As a result of the developed method of mechanical and thermal treatment, which considerably increases the ductility of niobium and its alloys, it was possible to subject the majority of specimens to cold working (rolling) with an extremely high degree of shrinkage, without intermediate annealing. Niobium alloyed with zirconium and lanthanum showed best technological properties: the specimens were rolled into foils of 0.09 - 0.07 mm thickness with a degree of shrinkage up to 95 - 97%.

Niobium proved suitable for rolling, as well as alloys with mix-metal, tungsten (up to 2.2% W), vanadium (up to 0.2% V); Mo (up to 6% Mo), alloys with 0.5 - 0.6% Ta and with 0.3% B. In alloys with chromium and silicon and with a high content of boron, crack formation in rolling process occurred.

SUMMARY (Transcribed from the original English text)

Work by X-ray and microstructure analysis methods and by the hardness method has established the temperature at which recrystallization begins and its dependence on degree of deformation of niobium produced by the arc fusion method from compact ceramic material. The effect is explained of 11 alloying elements when their content forms from 0.2 to 5% by weight of niobium on the temperature of recrystallization (Figure 4).

The temperature of recrystallization of the purer iodide type of niobium is determined and the very strong effect of impurities on the temperature of recrystallization of niobium is brought to light. It is established that the size of the grain has little effect on the hardness of niobium and its alloys but has considerable influence on its plasticity. A method is worked out of mechanical and thermal processing of sheet niobium and its alloys, ensuring considerable improvement of their mechanical and technological properties.

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\* Translator remark:

There is an obvious misprint in the original: (page 40)  
There should be read: "3 and 5% Cr; 1.2 to  
1.6% mix metal".