CONCLUSIONS

1. Large lamellar precipitates of Nb₂C and complex alloyed (Nb, Zr)C or (Nb, Hf)C are formed in Nb – Zr(Hf) – C alloys during cooling of ingots.

2. Annealing of Nb – Zr(Hf) – C alloys at 1900° produces an even dispersed structure with primary precipitates of (Nb, Zr)C or (Nb, Hf)C more highly alloyed with zirconium or hafnium than in the cast alloy.

3. Dispersed zirconium (hafnium) nitrides and Nb₂N are observed in cast Nb – Zr(Hf) – N alloys.

4. Annealing of Nb – Zr(Hf) – N alloys at 1800° leads to more complete decomposition of the solid solution than in the cast condition and the formation of dispersed ZrN (HfN) and also Nb₂N.

LITERATURE CITED


PHASE COMPOSITION OF Nb–M–C ALLOYS

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One of the principal methods of increasing the heat resistance of niobium alloys is alloying of the solid solution with refractory metals (Mo, Ta, W), which raises the recrystallization temperature [1]. Additional hardening is obtained by the formation of dispersed refractory compounds (carbides, oxides, nitrides).

We investigated the effect of alloying elements on the phase composition and properties of niobium alloys (see Table 1) after different heat treatments.

Nb – C Alloys. The solubility of carbon in niobium is relatively high at eutectic temperature but decreases rapidly with decreasing temperature [2]. Holding niobium alloyed with ~ 0.1% C by weight (0.77 at. %) at temperatures above 1800°C and rapid cooling may lead to a homogeneous solid solution, although inclusions of second phase are rarely observed in the microstructure of quenched niobium alloyed with carbon. Powder patterns of the quenched alloy showed that the second phase is hexagonal niobium carbide — Nb₂C (a = 3.12 Å, c = 4.99 Å).

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Composition, wt. %</th>
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<tbody>
<tr>
<td></td>
<td>Mo</td>
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<tr>
<td>1</td>
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<td>-</td>
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<tr>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>14.9</td>
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</tbody>
</table>

Notes. All alloys contained ≤ 0.004% O; ≤ 0.006% N; alloy 6 contained ≤ 0.02% O and ≤ 0.02% N.

Translated from Metallovedenie i Termicheskaya Obrabotka Metallov, No. 4, pp. 32-34, April, 1978.
The structure of the quenched alloy is unstable and during subsequent heating to 1100-1400°C the supersaturated solid solution of carbon in niobium undergoes intensive decomposition. Increasing the holding time at aging temperatures (1100-1400°C) leads to coalescence of the Nb2C previously formed.

**Nb – Mo – C Alloys.** The addition of up to 15% Mo by weight to the niobium alloy with carbon does not lead to formation of independent second phases based on molybdenum, although the total quantity of carbides in the quenched alloy is larger than in the Nb – C alloy. This is explained by the substantial reduction of the solubility of carbon in niobium with the addition of molybdenum. For example, the addition of 5 at.% Mo lowers the solubility of carbon in niobium to 0.08-0.1 at.% at 2000°C[3]. The activity of molybdenum with respect to carbon is substantially lower than with respect to niobium, and as noted above no independent molybdenum carbide is formed, although chemical analysis of Nb2C precipitated from the alloys after quenching and aging showed that niobium carbides are alloyed with a small amount of molybdenum.

Raising the carbon content to 0.24% by weight leads to formation in the quenched alloy of acicular precipitates of second phase along with precipitates of spheroidal shape, which is characteristic of Nb2C. The acicular phase was identified by x-ray analysis as Nb2C2 (a =11.48 Å, c =18.30 Å) with a hcp lattice. Holding at 1100-1400°C leads to disappearance of acicular precipitates, and only Nb2C is observed at these temperatures.

**Nb – Ti – C Alloys.** Microstructural analysis of quenched and aged samples showed that titanium is fairly evenly distributed in niobium. The atomic dimensions of titanium (1.46 Å) and niobium (1.45 Å) are almost identical, so that no size factor affects the solution of titanium in niobium, and no substantial accumulation of titanium is observed. It would seem that carbon, which is distributed both in the grains and in the boundaries, should combine with titanium as the more thermodynamically active element and not with niobium, but Nb2C slightly alloyed with titanium is formed due to the concentration factor. However, as was reported earlier [4], with the addition of quadrivalent titanium to pentavalent niobium the charge in the respective corners of the crystal lattice and a stress field is created, which has a considerable effect on the fine structure of the alloy.

**Nb – Zr – C Alloys.** The second phase precipitated from quenched alloy 5 is hexagonal carbide Nb2C. In alloy 6, with an elevated oxygen concentration, still another phase was identified – ZrO2. Microprobe data indicate that the zirconium in the alloy is distributed quite evenly. A particularly high concentration of zirconium is observed in the grain boundaries. This distribution of zirconium is favored by its large atomic size (1.60 Å) and high chemical activity with respect to interstitial elements (C, O, N) as compared with niobium. Consequently, the most favorable sections in the Nb – Zr system for concentration of zirconium are the grain boundaries, where the interstitial impurities are also found.

Holding at 1100-1400°C leads to disappearance of large Nb2C particles characteristic of the quenched structure and numerous finely dispersed precipitates evenly distributed in the grains.

The x-ray diffraction analysis showed that the finely dispersed precipitates are (Zr, Nb)C with a fcc lattice. The extent to which this carbide is alloyed with zirconium depends on the holding time at aging temperature. The lattice constant changes from a =4.48 Å (corresponding to ~5 mole % Zr in carbide) after holding at 1300°C for 1 h to a =4.50 Å (~20 mole % Zr) after holding 5 h at this same temperature.

The distribution curves of the alloying elements in aged samples obtained by microprobe analysis showed an elevated concentration of zirconium around large particles of Nb2C, which is explained by the presence of stress fields around the precipitated carbides. Because of the concentration of zirconium in places with different defects of the crystal structure, conditions are created in which the hexagonal Nb2C in a given microvolume becomes thermodynamically unstable and goes into solution, while (Zr, Nb)C is formed in sections where zirconium and carbon accumulate.

**Nb – Mo – Ti – Zr – C Alloys.** Alloys of this system are typical representatives of multicomponent niobium alloys in which high heat resistance is due to combined hardening (alloying of the solid solution + precipitation hardening).