Lattice Constants of Nb and NbO at Elevated Temperatures

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As part of attempts to determine phase diagrams of niobium alloys or compounds with germanium and aluminium we determined the lattice constants of pure niobium and of niobium alloys at various temperatures. In the majority of the cases NbO was formed as a thin surface layer, and therefore the lattice constant of this compound was inadvertently determined as well.

Experimental. A Philips high temperature attachment was mounted on a standard powder goniometer. Sample holders of tantalum were used in all runs. As niobium is very reactive at high temperatures, it was not possible to use an internal standard for calibration purposes in the high temperature region. Therefore a calibration valid at room temperature was used at high temperatures too. The ambient atmosphere was a problem. Niobium reacted with residual oxygen even in highly purified helium to form NbO and in some cases also NbO_2, and these oxides were formed at elevated temperatures also in a vacuum of about 10^{-4} mmHg. In a few cases, however, we were successful in obtaining a vacuum ($\sim 10^{-5}$ mmHg) which was good enough to prevent the formation of niobium oxides during the experiments. Niobium and germanium react slowly to form Nb_5Ge_3 and an A15 phase at temperatures from 500 °C and onwards. The germanium lines disappear first, whereas the niobium lines persist until the lines of the compounds dominate. NbO was formed too in several of these experiments. Niobium and aluminium reacted qualitatively similarly to niobium and germanium, but in the cases when aluminium was present together with niobium no NbO lines were found. Further information on the formation of niobium-germanium compounds is given separately.[1]

Niobium of nominal purity 99.8 % was purchased from Alpha-Inorganics. An analysis by X-ray fluorescence showed no foreign elements heavier than titanium. The lattice constant of niobium was determined at 23 °C, using either germanium or silicon as standard for calibration ($a_{Ge} = 5.6576$ Å, $a_{Si} = 5.43054$ Å, Cu$K\alpha_1 = 1.54051$ Å, Cu$K\alpha_2 = 1.54433$ Å). The mean value of a_{Nb} from seven different runs is $a_{Nb} = 3.3044$, $\sigma = 0.0008$ Å. Temperatures were measured using a W/W,Re thermocouple.

Discussion. NbO is assumed to have a narrow composition range, and the value of the lattice constant at room temperature found here (a = 4.210 Å) is in agreement with values reported by Brauer[2] (a = 4.2103 Å), and by Anderson and Magnéli[3] (a = 4.210 Å). NbO appears to be stable in the presence of Nb at 1735 K and at a pressure of 0.5×10^{-4} mmHg. When Ge is present too, NbO appears to be stable up to a temperature of about 1600 K. Al on the other hand appears to act as a better "getter" for oxygen than Nb, and no NbO lines were observed in experiments when Al was added to Nb. The temperature dependence of the lattice constant of NbO is shown in Fig. 1.

Fig. 2 shows the dependence of the lattice constant of Nb on temperature. Earlier data by Edwards, Speiser and Johnston[4] are shown on the graph as well. These data, obtained by photographic methods, look more accurate than the diffractometer data reported here. The following conclusions may be drawn from the combined available material:

The lattice constant of Nb, at 293 K, is 0.5 % larger in a mixture of Nb and NbO than in a pure Nb sample. Probably the difference is caused by dissolution of oxygen in niobium. The difference in lattice constant between "pure" and oxygen-contaminated Nb decreases with temperature, and extrapolation of the results indicates that the difference disappears at 2400 K. At this temperature oxygen probably does not dissolve in Nb. The graph also shows that the niobium lattice apparently expands less rapidly with temperature when germanium or aluminium is present with niobium. In these cases, however, reactions between niobium and the other elements were taking place slowly and these values do not represent equilibrium values.

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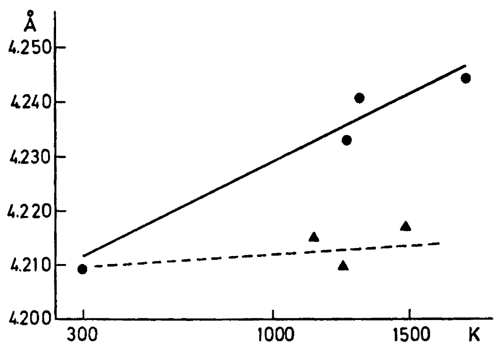

Fig. 1. Dependence of the lattice constant of NbO on temperature. ●, NbO from pure Nb; ▲, NbO in presence of Nb and Ge.

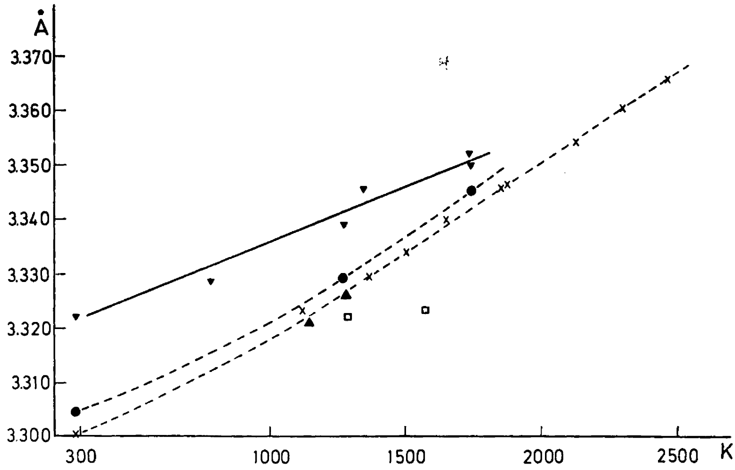

Fig. 2. Dependence of lattice constant of Nb on temperature. ▼, Nb contaminated with oxygen; ●, Nb without oxygen contamination, this paper; ×, Nb according to Ref. 4; ▲, Nb in the presence of Ge; □, Nb in the presence of Al.

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