

Effect of Oxidation on Transport Properties of Zirconium–1% Niobium Alloy

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The thermal conductivity and electrical resistivity of zirconium–1 wt% niobium samples were measured before and after the process of their oxidation in air. A special procedure was used to dissolve the gas and to smooth out its concentration in the alloy. The basic experiments were performed under high vacuum under steady-state temperature conditions. The temperature range was 300–1600 K for the pure alloy and 300–1100 K for the samples containing oxygen. It was found that the thermal conductivity—oxygen concentration relation reverses its sign from negative at low and middle temperatures to positive at temperatures above 900 K. The relation between the electrical resistivity and the oxygen content does not show this feature. The Lorenz function was found to have an anomalous temperature dependence.

KEY WORDS: electrical resistivity; high temperature; thermal conductivity; oxidation; zirconium.

1. INTRODUCTION

The system of Zr–O has been extensively studied for many years. Oxidation of a metal and dissolution of oxygen in its lattice produce marked changes in the physical properties and, respectively, the operating qualities of an equipment. The problem of the investigation of these changes for the zirconium is of prime importance in connection with the use of zirconium alloys as nuclear fuel jackets in nuclear reactors.

The subject matter of the present investigation was to study the effect of penetration of oxygen on the thermal conductivity of Zr–1% Nb reactor alloy. The possibility of perceptible changes of the thermal conductivity in

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the Zr–O systems is evident from the known data on electrical resistivity behavior. The latter has been appropriately studied by Gebhardt et al. [1] and Hörz et al. [2]. The values of the additional resistivity obtained by these authors, in both the α and the β phases of the system, may be used for the estimation of the possible change of the thermal conductivity using the Wiedemann–Franz law. However, in order to use this law it is necessary to know the value of Lorenz number and that the latter does not change with temperature and concentration of impurities.

It has been deduced from the above-mentioned works that the Matthiessen's rule does not hold for the Zr–O system. The additional resistivity appreciably decreases with temperature. This evidence indicates conclusively that the electronic structure of Zr is changed upon the penetration of oxygen into the metal. As a result of this, a change in Lorenz number may occur.

In this situation, any estimation of the thermal conductivity with the use of the unchanged Lorenz number $L_0 = 2.445 \times 10^{-8} \text{ V}^2 \cdot \text{K}^{-2}$ becomes not well grounded. These reasons have stimulated the performance of direct thermal conductivity measurements of the Zr–Nb–O system.

2. EXPERIMENTAL PROCEDURES AND RESULTS

Thermal conductivity experiments were performed by the longitudinal steady-state heat flow technique described previously in Ref. 3. The method allows one to obtain the thermal conductivity values for the chosen cross section of a cylindrical sample. It is particularly important for the investigation of properties of alloys, when the phase composition will be changed along the sample in accordance with the temperature distribution in it.

The samples for the investigation were in the form of a cylinder with a diameter of 5 mm and a length up to 30 mm. For oxidation the following procedure was used. The prepared samples were placed in a resistance furnace and were held in an air atmosphere at 1200–1300°C. The oxidation time was chosen based on the recommendation given in Ref. 4 so that the formed oxide film did not begin to crack and peel off. After that, the samples were annealed 8 h at temperatures of about 1500–1600 K and in a vacuum of 10^{-3} Pa. In the process of annealing, oxygen diffused from the film into the metal and oxygen concentration were equalized throughout the sample. During the oxidation and following vacuum annealing mass of the sample was continuously controlled with an electronic scale.

The samples were also weighed on an analytic scale for the subsidiary control after the high-temperature treatment. The assumption that there was enough time for homogenization of the samples during their annealing was checked in microhardness measurements after the thermal conductivity

Table I. Characteristics of the Samples

Sample No.	Mass before and after oxidation (g)	Geometry D/L (mm)	Impurities (at %)	$\rho(T)$ ($\mu\Omega \cdot \text{cm}$)
S0	—	12/60	0.1	47.8 (289 K)
S3	3.5413/3.5619	5/30	3.3	73.3 (298 K)
S6	3.5280/3.5680	5/30	6.3	103.5 (290 K)
S9	3.5920/3.6484	5/30	9.0	118.1 (298 K)

measurements. The data on kinetic properties presented in this work are related to the samples with an even microhardness distribution in cross section of the samples. Information on the studied samples is given in Table I.

The thermal conductivity of the sample designated as S0 (Zr-1% Nb alloy before oxidation) has been studied in the temperature range 400–1500 K, included the temperature range of the β phase. The temperature distribution was measured with chromel–alumel thermocouples and an optical pyrometer. Six independent series of measurements on the two samples were made. The measurements were performed both at a step-by-step rise of temperature and at its decrease. The experimental data are shown in Fig. 1. In the range of the α phase, the thermal conductivity of the alloy changed moderately. The thermal conductivity begins to increase as the temperature approaches the zone of the α - β phase transition. In the range of the β phase, it increases almost linearly with temperature. The

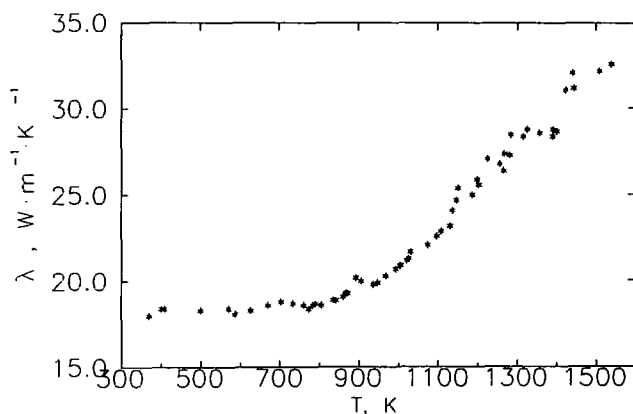


Fig. 1. Thermal conductivity of Zr+1% Nb alloy as a function of temperature.

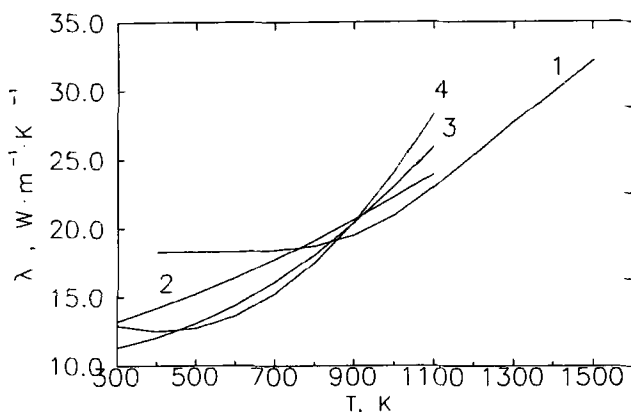


Fig. 2. Thermal conductivity of the samples with different concentrations of oxygen. (1) S0; (2) S3; (3) S6; (4) S9.

obtained data in the whole temperature range 450–1500 K was treated by the least-squares method yielding the following equation:

$$\lambda = 21.59 - 1.513 \times 10^{-2}T + 1.515 \times 10^{-5}T^2 \quad (1)$$

where λ is in $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and T is in K. The standard deviation is 0.67%.

In Fig. 2, the thermal conductivity of the initial alloy is compared with the conductivity of the oxidized samples. These samples were studied only in the range of the α phase. A decrease in the thermal conductivity was clearly revealed for the oxidized samples. However, it is worth noting that the oxygen effect on thermal conductivity depends on temperature. The curves $\lambda(T)$ with different oxygen contamination intersect in the vicinity of 900 K. So at high temperatures the oxygen concentration has the opposite influence on thermal conductivity compared with the low-temperature region.

The investigations of the thermal conductivity were accompanied by a study of temperature dependence of electrical resistivity of the same samples. The electrical resistivity was measured by the four probe direct current method. The samples were heated in the vacuum furnace. For the temperature control, a chromel–alumel thermocouple was used, which was welded to the sample surface. Two voltage probes were used to measure the potential drop on the central part of the sample. In addition, measurement of the voltage drop across a standard resistor permitted the measurement of the electrical current and thus calculation of the electrical resistivity. Possible experimental errors due to parasitic EMF were avoided by

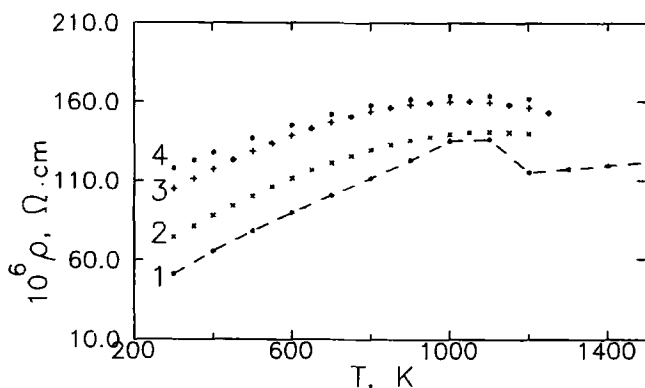


Fig. 3. Electrical resistivity of Zr + 1% Nb alloy with different concentrations of oxygen. (1) S0; (2) S3; (3) S6; (4) S9.

reversing direction of the current. The experimental data are shown in Fig. 3.

The least-squares method was used in order to approximate the data by the following equations. Sample S0 (350–1050 K),

$$\rho = 5.703 + 0.1552T - 2.79 \times 10^{-8}T^3 \quad (2)$$

Sample S3 (273–1250 K),

$$\rho = 31.041 + 0.1493T - 4.055 \times 10^{-8}T^3 \quad (3)$$

Sample S6 (273–1250 K),

$$\rho = 64.348 + 0.1402T - 4.406 \times 10^{-8}T^3 \quad (4)$$

Sample S9 (273–1250 K),

$$\rho = 85.368 + 0.1121T - 3.339 \times 10^{-8}T^3 \quad (5)$$

where ρ is $\mu\Omega \cdot \text{cm}$ and T is in K .

3. DISCUSSION

According to the phase diagram of the Zr–O system, the compositions studied in this work belong to the range of solid solutions with the hexagonal close packed lattice in the temperature range of our measurements. Probably, the presence of niobium atoms in the lattice does not make a major change in the structure of the solution.

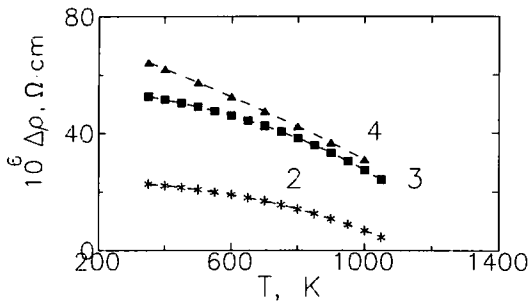


Fig. 4. The resistivity increment in Zr+1% Nb alloy. (2) S3; (3) S6; (4) S9.

For the simple metals, the little quantities of impurities usually do not markedly affect the temperature dependence of the kinetic properties at high temperatures. It is embodied in the validity of the Matthiessen's rule and in the small influence of such impurities on the Lorenz function $L(T) = \lambda \rho T^{-1}$.

In the present case the results were different. Figure 4 shows the resistivity increment (or the impurity resistivity) of the alloy that resulted by the penetration of oxygen. In this case, the Matthiessen's rule was not satisfied. For the Zr-O system this fact was noticed earlier in Refs. 1 and 2.

The temperature dependence of the Lorenz function $L(T)$ is illustrated in Fig. 5; it can be seen that it is highly sensitive to the oxygen content. An increase in the oxygen concentration tends to increase the value of the Lorenz function on one side and to a more strongly marked anomaly in its temperature dependence on the other side. This anomaly is expressed in the

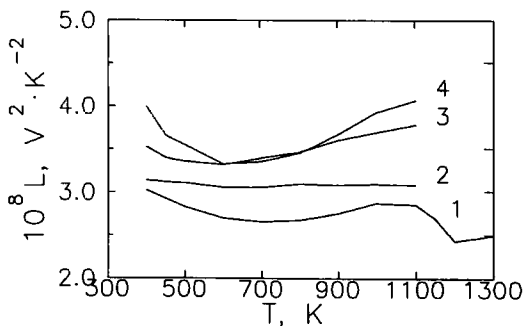


Fig. 5. The Lorenz function of the samples: (1) S0; (2) S3; (3) S6; (4) S9.

form of a minimum in the Lorenz function and in its increase with temperature as the range of the phase transformation is approached.

The cause of the above marked anomalies should be searched for in the electronic structure of the investigated samples. In zirconium, there are energy bands the tops (or bottoms) of which lie in the nearest vicinity of the Fermi energy [6]. Electrons of these bands are involved in heat and charge transfer processes in accordance with increases in temperature. These are accompanied with a change in the typical temperature dependence form for the thermal conductivity, the electrical resistivity, and the Lorenz ratio.

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