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The Use of Thermoelectric Power Measurements to Study Recovery, Recrystallization, and Phase Transformations in Cold Worked Zr-1%Nb and Zircaloy-4 Nuclear Fuel Sheathing

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Thermoelectric power (TEP) measurements are used to study recovery, recrystallization, and other microstructural changes during annealing of cold worked Zr-1wt.%Nb and Zircaloy-4 tubing at temperatures from 300 to 1100 °C. The measured value of thermoelectric power is very sensitive to microstructural evolution in zirconium alloys, and TEP measurements correlate well with both microstructural changes, as seen using optical microscopy, and microhardness measurements.

1 Introduction

THE properties of metals and alloys depend on their microstructures. The microstructure is determined not only by the alloy composition, but also by the thermal and mechanical treatments to which the alloy has been subjected. Many techniques are used to determine the microstructural state of a metallic alloy, with optical metallography, electron microscopy, and X-ray diffraction techniques probably being the most common. These techniques are complimentary, but sometimes inadequate. Other indirect methods that depend on measuring the variation of a property that is microstructure dependent, are also widely used. These include resistivity, dilatometry, and hardness measurement (micro and macro).

In recent years, the experimental technique of thermoelectric power (TEP) measurement has been developed. This technique, also known as the Seebeck effect, was being used in the late 1940s,[1,2] but has only been widely used in the last 10 years or so, principally by Borrelly and his co-workers.[3-11] The thermoelectric power measurement is characterized by its simplicity, its easy implementation, and its strong sensitivity to microstructural evolution. It has been used to examine changes brought about by precipitation,[5,7-9] alloying elements or impurities in solution,[3,5,10] short-range ordering,[6] creation of dislocations by cold working,[2] and texture changes.[11]

The aim of this article is to apply the TEP technique to the study of microstructural changes in zirconium alloys. Some initial results on the influence of alloying elements on the thermoelectric power of zirconium have already been published.[12] Zr-1wt.%Nb and Zircaloy-4 fuel sheathing alloys have been chosen for the investigation. These materials are often used in the cold worked condition, and it is of interest to study changes in these materials caused by exposure to higher temperatures such as those during reactor operation (~300 °C) or during postulated accident situations such as a loss-of-coolant accident (>1000 °C). The range of heating temperatures used span this temperature range. Microhardness measurements and optical metallography were performed on all samples, and the results were compared to the TEP measurements.

2 Experimental Details

2.1 *Materials*

The materials used in this study were as-fabricated Zr-1%Nb and Zircaloy-4 nuclear fuel sheathing. The tubing was in the tube-reduced (60% for Zr-1wt.%Nb and 80% for Zircaloy-4) and stress-relieved condition. The tubing size was 13.4-mm outside diameter and 0.4-mm wall thickness. The chemical analyses for both materials are given in Table 1. The TEP samples, 70-mm long and 3-mm wide, were machined from the tubing.

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Table 1 Chemical Analysis of Zr-1wt.%Nb and Zircaloy-4 Fuel Sheathing

	Composition, ppm											
Specimen	Nb	Sn	O	Fe	Cr	Ni	Ti	Ta	Hf	Al	Si	Zn
Zr-1wt.%Nb	1.025%	< 25	1155	540	110	< 35	< 25	< 25	79	25	29	< 50
Zircaloy-4	(a)	1.53%	890	2040	970	< 35	(a)	(a)	(a)	(a)	(a)	(a)

(a) Not given.

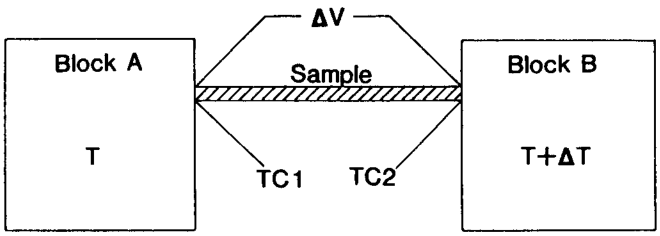

Fig. 1 Schematic diagram showing experimental setup for thermoelectric power measurements.

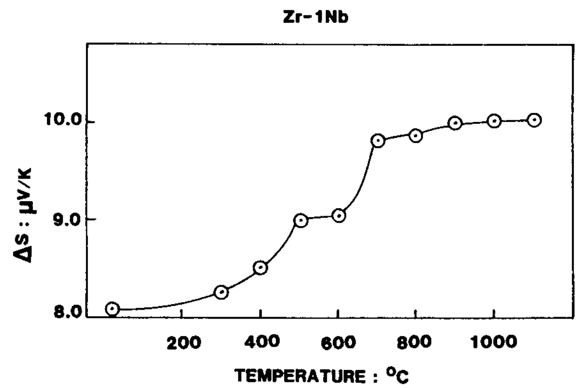

Fig. 2 Dependence of the thermoelectric power ΔS ($\mu V \cdot K^{-1}$) on the annealing temperature of cold worked Zr-1wt.%Nb fuel sheathing.

2.2 *Heat Treatment*

The samples were sealed in vacuum-evacuated quartz tubes for heat treatment. They were heated at temperatures from 300 to 1100 °C (at 100 °C intervals) for 10^4 sec and then cooled to room temperature for the TEP measurements.

2.3 *Thermoelectric Power Measurements*

The measurement system is shown schematically in Fig. 1. A voltage ΔV is generated by a thermocouple formed by the sample and the reference metal, which is an aluminum block. The hot and cold junctions of this thermocouple are placed at temperatures of T (Block A) and $T + \Delta T$ (Block B). The sample is pressed onto these blocks so as to ensure a good thermal and electrical contact. The relative thermoelectric power of the sample with respect to the reference aluminum at the mean temperature T is given by the equation:

$$\Delta S = \Delta V / \Delta T \qquad [1]$$

where ΔV is the voltage generated by the thermocouple and the two aluminum blocks.[13] The mean temperature was fixed at 20 °C and the temperature difference, ΔT, was set at 10 °C.

2.4 *Optical Metallography*

Specimens suitable for optical metallography were cut from the tubing using a slow speed diamond saw, mounted using a cold mount, and then ground and polished to 600 grit. The specimens were then swab etched using a $45HNO_3$:$45H_2O$:10HF solution and examined by optical metallography at 100 and 500× magnification.

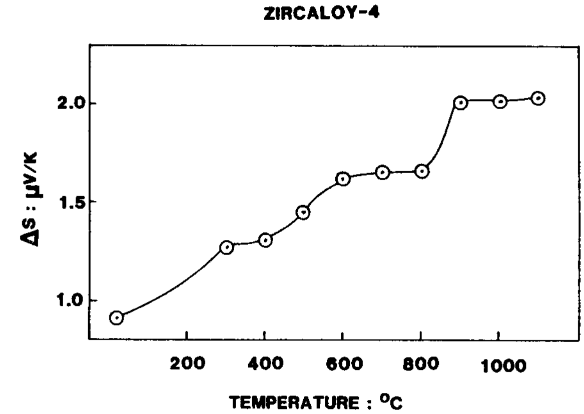

Fig. 3 Dependence of the thermoelectric power ΔS ($\mu V \cdot K^{-1}$) on the annealing temperature of cold worked Zircaloy-4 fuel sheathing.

2.5 *Microhardness Measurements*

The microhardness measurements were made using a 50-g load and a Knoop indentor. A Knoop rather than a "regular" indentor was used to obtain information on the anisotropy of microhardness. The Wheeler and Ireland[14] technique was used for the determination of the mechanical anisotropy. This technique involves making Knoop hardness impressions on the three orthogonal surfaces of the tube geometry and from these constructing a flow surface based on the Knoop hardness number (KHN). The Knoop hardness number is obtained by measuring the long diagonal of the Knoop impression and then using tables to obtain the Knoop hardness number.

Ideally, these hardness tests should be made at temperature after a given heating period. However, producing hardness impressions on the thin wall of fuel sheathing required suitable mounting and metallographic polishing. Therefore, the microhardness tests, like TEP measurements, were performed at ambient temperature after cooling from the heat treatment temperature. The heat treated specimens for microhardness testing were cut into sections approximately 7 by 10 mm. Then each set of three sections (orientations) were mounted together (in cold mounting epoxy) to display all three surfaces (axial, radial, and tangential). They were wet polished and etched using similar procedures as for optical metallography. Hardness indentations for the six orientations on the three surfaces were made to prepare a flow surface diagram. Five or more hardness impressions were made for each section. The microhardness in the Z direction (axial) was determined from the flow surface diagram, and this value is reported and compared to the TEP measurements. A full description of the microhardness technique as applied to the anisotropy of Zircaloy-4 fuel sheathing can be found in Ref 15.

3 Experimental Results

3.1 *Thermoelectric Power*

As previously noted, the TEP measurements were made at 20 °C on specimens of Zr-1wt.%Nb and Zircaloy-4 that had been heated to temperatures up to 1100 °C and then cooled to room temperature. The TEP measurements were made on sam-

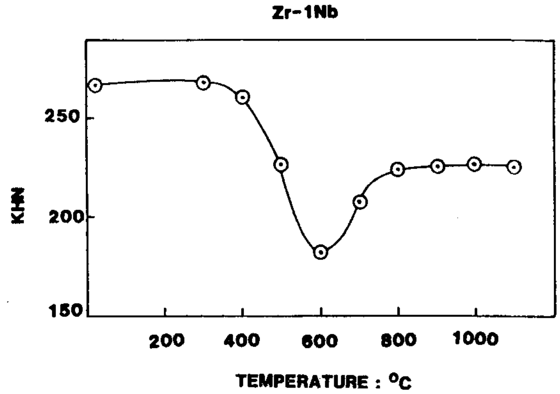

Fig. 4 Dependence of Knoop microhardness number on the annealing temperature of cold worked Zr-1wt.%Nb fuel sheathing.

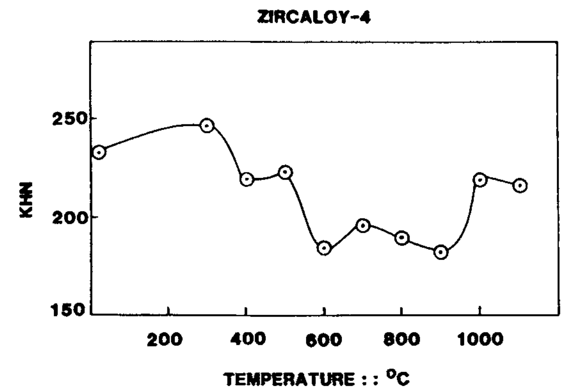

Fig. 5 Dependence of Knoop microhardness number on the annealing temperature of cold worked Zircaloy-4 fuel sheathing.

ples taken along the rolling direction of the tube. The results are summarized in Fig. 2 and 3.

For both alloys, the general trend is for the value of TEP, $\Delta S \mu V/K$, to increase with increasing heat treatment temperature. There are regions where changes in ΔS with temperature are fairly smooth, or ΔS remains approximately constant, and other regions where changes in ΔS with temperature are more abrupt. These abrupt changes in ΔS with temperature could indicate a phase change. These changes occur between 600 and 700 °C for Zr-1wt.%Nb and between 800 and 900 °C for Zircaloy-4.

3.2 *Microhardness Measurements*

Microhardness measurements are summarized in Fig. 4 and 5 for Zr-1wt.%Nb and Zircaloy-4, respectively. The trends are somewhat more complex than for the TEP, because the Knoop hardness number first decreases and then increases. However, a few general observations can be made. For Zr-1wt.%Nb (Fig. 4), the Knoop hardness number decreases for all heating temperatures of 600 °C and less. The Knoop hardness number then increases again for temperatures greater than 600 °C, but remains fairly constant for temperatures of 800 to 1100 °C. For Zircaloy-4 (Fig. 5), the trends are not as obvious, but in general there is a decrease in Knoop hardness number for temperatures up to 600 °C. The Knoop hardness number then remains constant or slightly increases for temperatures of 600 to 900 °C before increasing again at temperatures greater than 900 °C.

3.3 *Optical Metallography*

Selected optical micrographs are given in Fig. 6 and 7. The main points to be noted are as follows.

Zr-1wt.%Nb. The as-received structure (Fig. 6a) consists of elongated αZr grains and some β phase. There is partial recrystallization at 500 °C (Fig. 6b), and this is complete by 600 °C (Fig. 6c). At temperatures of 700 to 900 °C (Fig. 6d and e), the alloy goes through a phase change at temperature, *i.e.*, from $\alpha + \beta_{Nb}$ to $\alpha + \beta_{Zr}$, and the β_{Zr} transforms to α' on cooling. There is an increasing amount of transformed β as the temperature increases. At 1000 °C, the alloy is completely in the single β_{Zr} phase region at temperature and on cooling transforms to a Widmanstätten basketweave α' structure.

Zircaloy-4. The as-received structure consists of elongated α grains (Fig. 7a). Heating at 500 °C produces partial recrystallization (Fig. 7b), and heating at 600 °C produces a fully recrystallized structure (Fig. 7c). The structure after heating at 800 °C (Fig. 7d) consists of equiaxed α grains. At 900 °C, the alloy enters the $\alpha + \beta$ phase region at temperature, and on cooling, the β phase transforms completely to an α' structure (Fig. 7f).

4 Discussion

The changes experienced by the Zr-1wt.%Nb and Zircaloy-4 fuel sheathing on heating at temperatures up to 1100 °C can be divided into two main categories, namely those associated with the removal of cold work (*i.e.*, recovery and recrystallization) and those associated with any phase changes. In general, the removal of cold work occurs at the lower temperatures, *i.e.*, ≤600 °C, for the heating period used in this study (10^4 sec) and phase changes do not occur until ≥600 °C for Zr-1wt.%Nb and ≥850 °C for Zircaloy-4 (see Fig. 8a and b) for phase diagrams of Zr-Nb and Zr-Sn systems.[16]

The changes due to recovery, which could not be seen by either optical metallography or microhardness measurements, were reflected in an increasing TEP value for both Zr-1wt.%Nb and Zircaloy-4 as the materials were heated to temperatures up to 500 °C. Recrystallization, which occurs between about 500 and 700 °C, produced a noticeable reduction in Knoop hardness number and was visible by optical metallography, but produced only a small change in TEP value. The phase changes that occur in Zr-1wt.%Nb at temperatures above 610 °C produce a further increase in TEP value and microhardness. Such increases are not evident in Zircaloy-4 where the phase changes to the β phase (and to a transformed β product on cooling to room temperature) do not occur until temperatures above about 850 °C. Once either material reaches a fully β structure at the elevated temperature, the microhardness and TEP value on cooling to room temperature remains approximately constant.

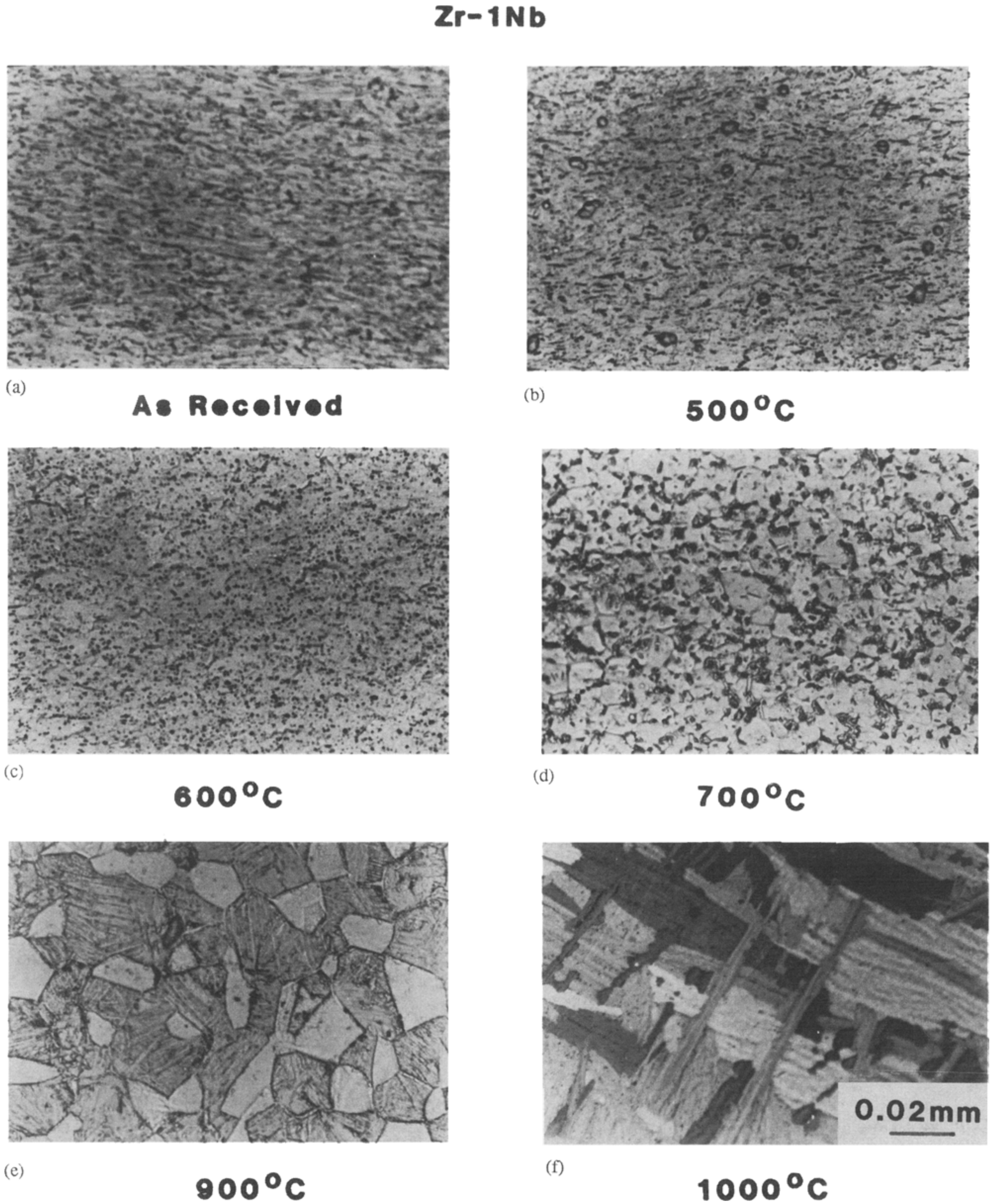

Fig. 6 Optical micrographs showing the microstructures of Zr-1wt.%Nb after heating for 10^4 sec at temperatures from 500 to 1000 °C and cooling to room temperature. (**a**) As received. (**b**) 500 °C. (**c**) 600 °C. (**d**) 700 °C. (**e**) 900 °C. (**f**) 1000 °C.

Thus, the three techniques—TEP, microhardness, and optical metallography—are complementary and provide information on all the microstructural changes occurring as a result of the heating. The TEP technique is really the only one of the three

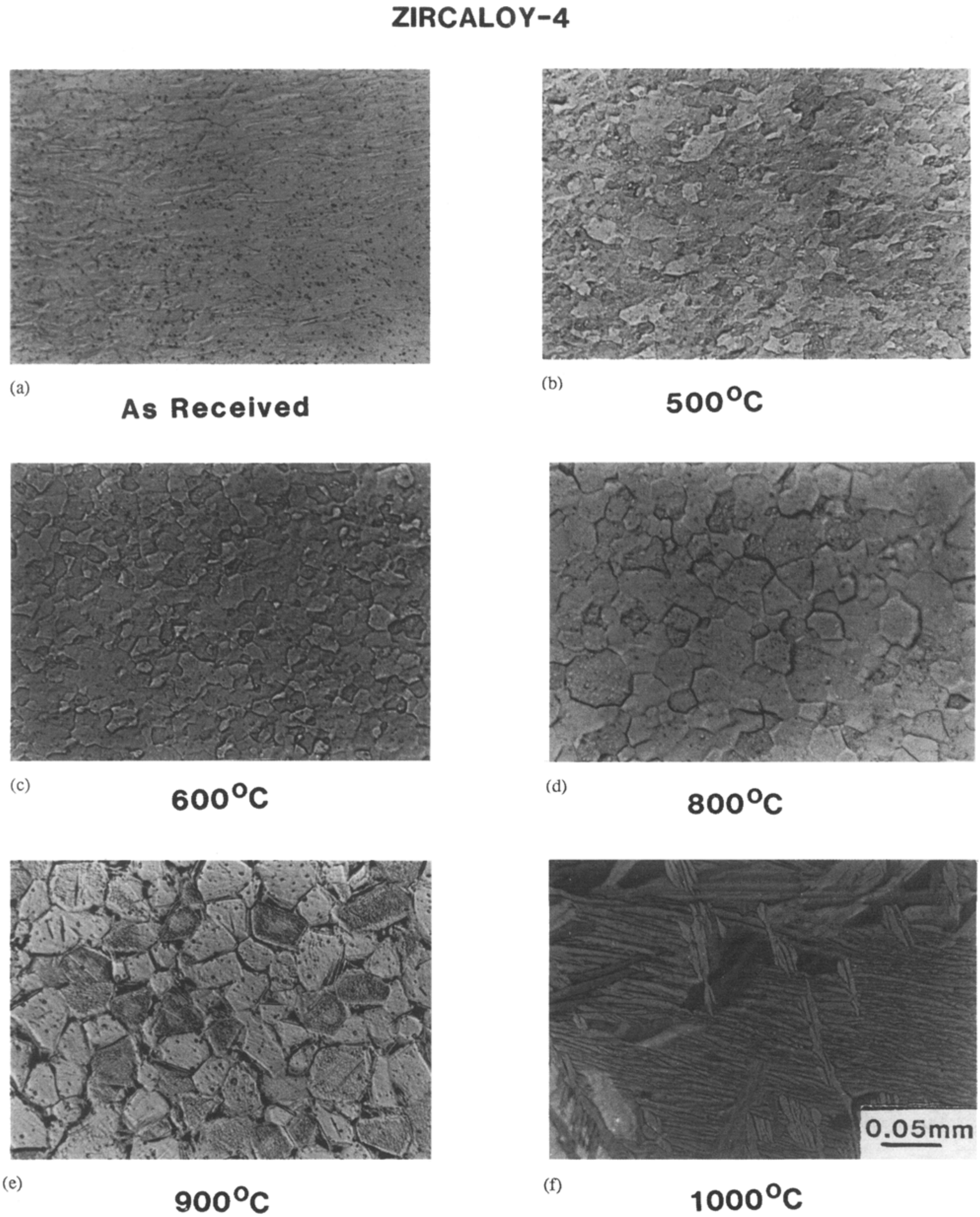

Fig. 7 Optical micrographs showing the microstructures of Zircaloy-4 after heating for 10^4 sec at temperatures from 500 to 1000 °C and cooling to room temperature. **(a)** As received. **(b)** 500 °C. **(c)** 600 °C. **(d)** 800 °C. **(e)** 900 °C. **(f)** 1000 °C.

techniques that is able to monitor the changes occurring during recovery. Changes due to recrystallization are best monitored using microhardness measurements or optical metallography. Changes in TEP during recrystallization are quite small, which

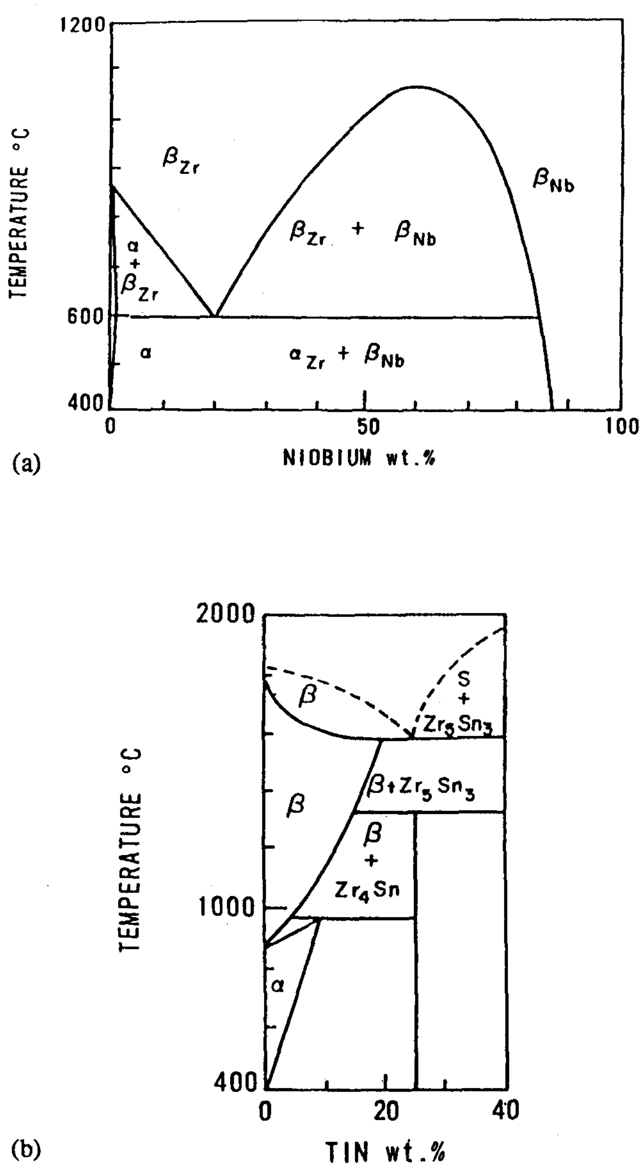

Fig. 8 Phase equilibrium diagrams for the Zr-Nb (**a**) and Zr-Sn (**b**) binary systems. From Ref 16.

is in agreement with previous studies of Merle and Borrelly in Zircaloy.[11] The phase changes can be adequately followed by either TEP, microhardness, or optical metallography.

5 Conclusion

The changes occurring in cold worked Zr-1wt.%Nb and Zircaloy-4 fuel sheathing due to heating for 10^4 sec at temperatures from 300 to 1100 °C (and cooling to room temperature) have been monitored using Knoop microhardness measurements, optical metallography, and thermoelectric power measurements. Changes in microstructure due to recovery, recrystallization, and phase changes were observed as changes in the value of TEP. The TEP technique is particularly useful in monitoring recovery effects that could not be detected using microhardness tests or optical metallography. Thermoelectric power is not particularly sensitive to recrystallization, which is better monitored by microhardness and optical metallography.

Acknowledgment

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