SHORT NOTE

Electrical Properties of Uranium Carbonitride

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UC and UN are mutually soluble, and their solid solution compounds (UC\(_{1-x}N_x\)) promise good properties as nuclear fuel. A number of studies have been reported on the physical properties of UC and UN. It should nevertheless be very useful to study some properties of UC\(_{1-x}N_x\) whose electronic structure would vary systematically with the anion ratio. This report concerns measurements of the electrical resistivity and the Seebeck coefficient of UC\(_{1-x}N_x\) over the range from 80 K to about 1,000 K.

Sintered specimens of UC\(_{1-x}N_x\) of about 75~80% T.D. were prepared by the reaction UN + (1-x)C = UC\(_{1-x}N_x\) + (1-x)N\(_2\). X-ray diffraction on these specimens revealed diffraction patterns solely of single phase UC\(_{1-x}N_x\), whose lattice constants roughly agreed with values expected from the reaction process set forth above. The oxygen content of these specimens was determined by chemical analysis to be in the range 480~770 ppm. A high density sintered UN (96% T.D.) and an arc cast UC were also prepared for measurement. All the samples were 2x2x10 mm\(^3\) in size; measurements were made by conventional method.

Figure 1 presents the room temperature resistivity as function of composition in the UC-UN system. The resistivity is seen to decrease smoothly with increasing carbon content. In the range of x smaller than 0.2 in UC\(_{1-x}N_x\), this behavior does not always apply: Pascard\(^{10}\) has found that with a composition in the vicinity of UC, any excess C+N against U, however small, would be expelled from the system in the form of free nitrogen, accompanied by precipitation of the secondary phases of either U\(_2\)C\(_3\) or UC\(_2\). Such species, present in the form of impurities could be considered responsible for the increase of the resistivity in the range x<0.2, even though in the present case such a phase could not be clearly detected.

The temperature dependence of the electrical resistivity of UC, UN and UC\(_{1-x}N_x\) is shown in Fig. 2. The plotted values are normalized to 100% theoretical density.

Fig. 1 Room temperature resistivity vs. composition in UC-UN system

Fig. 2 Resistivity as function of temperature for UC, UN and UC-UN solid solutions

To discuss the conduction process of UN, we must bear in mind that UN has an antiferro-paramagnetic transition at approximately
50°K. This means that, beside the term related to phonon scattering, we must consider an antiferromagnetic spin-disorder term which would increase with temperature and reach a constant value above the transition temperature. The saturation value $\rho_m$ is in practice determined by extrapolation to 0°K of the curve of resistivity against temperature at a higher temperature range, if the residual resistivity is neglected. For UN, $\rho_m$ is approximately 95 $\mu $cm, while it is 0 $\mu $cm for UC. In the case of the UC-UN system, the replacement in UN of N atoms by C atoms will induce disorganization of the antiferromagnetic arrangement of the U ions, and may be expected to bring about a decrease of $\rho_m$. And such a trend is actually observed in practice.

The Seebeck coefficient was found positive for both of UN and UC$_{1-x}$N$_x$, and at lower temperatures it increased with temperature. The coefficient reached a maximum at approximately 600°K in the case of UN, which is in agreement with the trend indicated by Didchenko. This behavior was observed in the range $x > 0.7$. The values of the coefficient at room temperature were in the range of 50–60 $\mu $V/K for both UN and UC$_{1-x}$N$_x$($0.3 < x < 1$). A cross over from $n$- to $p$-type occurred at about 140°K in the case of UC, whose Seebeck coefficient was found to be on the whole lower than in UN and solid solutions, 25 $\mu $V/K at room temperature.

The authors agree with Kruger & Moser in believing that the conduction process of actinide compounds having a NaCl type crystal structure is governed by carrier transport in the $s+p$ band and by the scattering responsible for $s+p \rightarrow f$ transition. The Fermi level of UC is situated near the bottom of the $f$-band, which, according to some authors, is apparently modified in shape to some extent by a rather broader $d$-band. On the other hand, that of UN coincides precisely with a narrow $f$-band. In the case of UC$_{1-x}$N$_x$, increasing $x$ diminishes the contribution from the $d$-band, until the Fermi level finally falls on the $f$-band.

While the antiferromagnetic property of UN can hardly be clearly interpreted by such a simple model, high population of the state density in the $f$-band should quite conceivably be related in some manner to antiferromagnetism in UN. Based on this premise, the relation between resistivity and composition could be qualitatively explained in terms of spin-disorder, as discussed above. Furthermore, the energy derivative of the state density of UC at the Fermi level would consequently be smaller than that of UC$_{1-x}$N$_x$. Since thermoelectric power depends sharply on this derivative, UC would then naturally have a smaller Seebeck coefficient than either UN or UC$_{1-x}$N$_x$.

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**References**