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Letter to the Editors

Comments on the paper ‘Phase diagram calculations of the U–Pu–N system with carbon and oxygen impurities’, by D.D. Sood, R. Agarwal, V. Venugopal [Journal of Nuclear Materials 247 (1997) 293]

G.C. Jain

Radiometallurgy Division, Bhabha Atomic Research Centre, Mumbai 400085, India

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Abstract

We published a paper entitled ‘Experimental evaluation of oxygen solubility in UN, PuN and (U,Pu)N’ authored by G.C. Jain and C. Ganguly in the Journal of Nuclear Materials 202 (1993) 245. Oxygen solubility limits were experimentally determined from lattice parameter and composition of the phases. The lattice parameter was determined from X-ray diffraction measurement and the composition was evaluated from chemical analysis results. Sood et al. have made some comments on a part of our data on the UNCO and PuNCO systems in the last two paragraphs in the chapter of Results and discussion on p. 299 of their above cited paper. In this context, the following comments are offered.

1. UNCO System

Sood et al. have considered the first three out of the eight values presented in Table 2 of our paper. In this table the variation in the lattice parameter of U(N,C,O) phase with the change in its UC/(UC + UN) mole ratio has been shown. On the basis of their calculations they have inferred that our samples were a phase mixture of SS + $UN_{1.5}$ + C or SS + C rather than SS + UO_2 phase mixture as reported by us [the term SS is used here for solid solution U(N,C) or U(N,C,O)]. Accordingly, Sood et al. have suggested the presence of higher nitride of uranium, $UN_{1.5}$, and free carbon in our samples.

1.1. Presence of $UN_{1.5}$

Our experimental measurement by XRD did not reveal the presence of any $UN_{1.5}$. It may be present at a concentration level too small to be detected by XRD. However, if one examines the method for preparation of the samples used in our work (see Experimental), possibility of the presence of even trace quantity of $UN_{1.5}$ can be ruled out. In synthesising the nitride, during cooling below 1623 K the atmosphere of the furnace was changed to a strongly reducing one (Ar + 8v/o H_2). After the synthesis, samples were sintered at 1923 K for 4 h in the same reducing atmosphere to obtain homogeneous and near equilibrium product. During synthesis as well as sintering, the material was treated at temperatures above 1423 K for 14–17 h in reducing atmosphere. Being a highly unstable compound, under these conditions of preparation, the $UN_{1.5}$ phase cannot be present even in trace quantity in our samples [1,2].

1.2. Presence of free carbon

Sood et al. have analysed our data and predicted, as shown in Table 2 of their paper, that the UNCO phase contains very little carbon (as combined carbon) and most of the carbon is present as free carbon. They further state that all the oxygen is present in UNCO phase as (UO), which could be as high as 7.5 mol%. This is contrary to our finding that UN has no oxygen solubility or limited solubility up to a maximum of 3 mol% of (UO). Since UO_2 has been detected to be present in our samples (by XRD), the free carbon cannot coexist with UO_2, particularly under the experimental conditions used for preparation of these samples.

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Our observation, in Section 3.1.1 of our paper, of no oxygen solubility or limited solubility up to a maximum of 3 mol% of (UO) in UN is based on the fact that the lattice parameter of UN (0.4888 nm) remains unaffected even in the presence of oxide phase. Hence the steady increase in the lattice parameter of U(N,C) solid solution, in the presence of oxide phase, noted with UC/(UC + UN) mole ratio in the last column of Table 2 of our paper is only due to the increase of UC content in U(N,C) solid solution and there is no possibility of the presence of free carbon. This increase in the lattice parameter is in good agreement with the results reported by other workers [3–5].

1.3. Absence of UO_2

In their calculation Sood et al. have indicated the absence of oxide phase. However, our XRD results clearly indicate the presence of oxide phase and there is no reason to doubt this experimental fact.

The difference in our experimentally determined data and the results predicted by Sood et al. on the basis of their phase diagram calculations can be attributed to the uncertainty in the thermodynamic data used and the various assumptions made by them during the course of the calculations.

2. PuNCO system

Sood et al. have stated that the value of 13 ± 3 mol% (PuO) obtained by us for the solubility of (PuO) in PuN, though in agreement with 14 mol% of (PuO) reported by Lorenzelli et al. [6], could not be rationalised. They stated this on the basis of the discussion of the mass balance in no. 9 sample of Table 4 of our paper. In our paper, the mass balance of various data reported in Tables 1–5 has not been explicitly mentioned and the results of chemical analysis and XRD have been reported as such. Considering the various uncertainties in the values of the chemical analysis and XRD method (see Experimental), there is a good mass balance in almost all the values reported in our work. However, the no. 9 value of Table 4 is an exception where the mass balance is not achieved. This value has not been used for determination of oxygen solubility in PuN. It has been used along with the other 11 values of Table 4 to determine the lattice parameter of carbon-free Pu(N,O) solid solution in presence of oxide phase and to derive the Eq. (2) as well as to generate the plot in Fig. 4. The oxygen solubility value in Pu(N,O) solid solution has been obtained in our paper from the data of Table 3. Eq. (1) of our paper has been derived on the basis of these data and the variation of the lattice parameter is shown in Fig. 3 (as × marks). In the same figure the first four values (1–4) from Table 4 have also been shown (as ○ marks). These four values of Table 4 have been chosen because of their low PuC content ($\leqslant 1.5$ mol%) comparable with the data in Table 3. Results of Table 4 indicate the variation in the lattice parameter of Pu(N,C,O) solid solution with the change of its PuC/PuN mole ratio as shown in the last column of the same table.

In Table 4 of our paper, sample no. 9 is unique in a sense that while its carbon content of 0.048 w/o is comparable to those of the first four samples (0.038–0.053 w/o), as shown in column 3, its lattice parameter (0.4915 nm) is relatively larger (0.4912–4913 nm). This large value of lattice parameter is due to a high PuC/(PuC + PuN) mole ratio (0.042) of no. 9 sample (as shown in the last column of the same table) compared to the first four samples (0.010–0.015). Hence this value has been included to show such a variation.

In the same volume of the Journal of Nuclear Materials where the work of Sood et al. has been published, another paper by Ogawa et al. [7] shows a similar calculation for the Pu–N–O system. In the latter paper, a phase diagram is derived with the use of the published thermodynamic data giving a maximum oxygen solubility of ~12–13 mol% of (PuO) in Pu(N,O) phase. This solubility is in good agreement with our value and these authors have referred to our work.

The calculations reported by Sood et al. for predicting the phase diagrams are for the temperatures of 1000 and 1500 K as mentioned in the second paragraph of their Results and discussion. Our experimental data have been obtained for samples sintered at 1923 K. Hence the comparison of their findings with our results is not justified. Ogawa et al. [7] have carried out the calculation for a temperature of 1923 K and their finding is in good agreement with our results. The results reported in our work are based on well characterised materials and sufficiently large number of data covering a wide range of concentrations. There are few findings reported in the literature on oxygen solubility in the UNCO and PuNCO systems where such a large number of data have been reported and analysed. Our findings are definitely useful in the refinement and better understanding of these systems.

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