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BASIC COMPATIBILITY STUDIES OF ADVANCED FUELS WITH 3d TRANSITION METALS*

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Abstract

It is often observed in equilibrium compatibility studies that more than one type of compound forms in one overall fuel-transition metal reaction. In addition, compounds formed may contain elements in varying proportions. These observations have been formulated into a simple rule and examined by experimental studies and thermodynamic calculations. The results presented here deal mainly with the equilibrium compatibility of uranium carbides with (Cr-Fe-Ni) alloys.

Introduction

Previous investigators have found that the compatibility of uranium carbide fuels with (Cr-Fe-Ni) alloys is restricted at some temperatures by the formation of one or more of the following types of compounds.

1. Intermetallic compounds of uranium with the transition metals. These compounds will be Laves phases such as UFe_2 or UNi_5 (1,2).
2. Ternary compounds involving uranium, transition metals and carbon. With chromium, $UCrC_2$ may form (3), with iron $UFeC_2$ may form (3,4) and with nickel $UNiC_2$ or U_2NiC_3 may form (1).
3. Carbides of the transition metals, such as $Cr_{23}C_6$ and Cr_7C_3 (2,3).

In the present studies we have considered reactions involving sub-stoichiometric UC, (UC + U), and stoichiometric UC. The main emphasis of these experimental and theoretical studies has been on reactions which

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produce more than one product and on product: which contain more than one transition metal. The principle aim is an overall evaluation of the equilibrium compatibility of uranium carbides with (Cr-Fe-Ni) alloys. This is done by combining our results with those of previous investigators. In addition these studies enable us to propose a general rule which is applicable to all fuel-cladding compatibility studies.

Experimental

All materials were obtained from the Solid State Division of ORNL and had a purity of $> 99.9\%$.

Alloys of uranium and chromium with iron and/or nickel were prepared by arc melting mixtures of the respective elements and annealing in flowing argon for 66 hours at 800°C . X-ray diffraction films were obtained from a Debye-Scherrer camera using CuK_{α} radiation.

The uranium-carbon, (Cr-Fe-Ni) samples were prepared by arc melting mixtures of the elements and annealing in a vacuum furnace at 1000°C for one week. X-ray diffraction studies were made of these samples on a Siemens diffractometer using CuK_{α_1} radiation.

Thermodynamic data used in the calculations were obtained from the references listed in Table 1.

Results and Discussion

Laves Phases

Laves phases are AB_2 or AB_5 intermetallic compounds. The AB_2 compounds have one of three closely related crystal structures (12). Uranium occupies the A positions and transition metals occupy the B positions in these compounds.

Laves phases will form when uncombined uranium is present in either carbide or nitride fuels, or as a result of a reaction which gives another product in combination with a Laves phase.

Chromium does not form binary compounds with uranium (13). We have investigated the formation of AB_2 Laves phases containing uranium, chromium, and at least one other 3d transition metal. Since there were no thermodynamic or phase data, we first approached the problem using Pauling's description of metal bonds to help predict chromium compositions where these Laves phases form. This analysis is described in detail in reference 10. Since this is not a conventional procedure, we will briefly outline how it was done.

Pauling (14) expresses the relationship between interatomic distance and bond number as:

$$d = 2R(1) + 0.600 \text{ \AA} \log N, \quad (1)$$

where

d = interatomic distance,

$R(1)$ = the single bond radius (i.e., the radius that results when a single bond is formed),

N = bond number.

We have used other relationships given by Pauling (14) to determine minimum and maximum single bond radii for the 3d transition metals from chromium through nickel. A computer routine was developed to calculate bond numbers in Laves phases containing transition metals. With the bond numbers we were able to calculate limits to Laves phase formation based on limits to single bond radii. These calculations indicated that a significant amount of chromium could substitute for Mn, Fe, Co, and/or

Ni. Our experimental results confirmed this, and the experimentally determined limits of composition corresponded to those calculated. Chromium can substitute for up to 60 at % of the iron in a $U(Cr,Fe)_2$ Laves phase and for up to 54 at % of the nickel in $U(Cr,Ni)$ Laves phases.

UC Compatibility

Chromium and iron are separately compatible with uranium monocarbide. Nickel reacts with UC to form UNi_5 and $UNiC_2$ (1). The formation of more than one product greatly extends the composition range where UC is incompatible with (Cr-Fe-Ni) alloys.

In this discussion we first examine reactions involving UC-(Cr-Ni), UC-(Fe-Ni), and UC-(Cr-Fe). Then, additional thermodynamic calculations are combined with these results to evaluate compatibility of UC with (Cr-Fe-Ni) alloys.

If a chemical reaction is to occur, the overall Gibbs free energy of formation for the products must be more negative than the overall Gibbs free energy of formation for the reactants. One product alone may not have a Gibbs free energy of formation sufficiently negative for a reaction to occur. However, a number of products may have combined Gibbs free energies of formation which permit the reaction.

This is illustrated by our studies of reactions between UC and (Cr-Ni) alloys.

UC-(Cr-Ni)

X-ray diffraction and metallographic examination indicate that both UNi_5 and $Cr_{23}C_6$ are formed as products over a wide (Cr-Ni) composition range. A general reaction for this system may be written:

Using std. free energies of formation we calculate that this reaction is thermodynamically possible at 700-1000°C for chromium contents of $x_{\text{Cr}} = 0$ to $\approx .95$.

Thus, although chromium alone does not react with UC, the large negative std. free energy of formation for UNi_5 enables both products to be formed over this composition range.

UC-(Fe-Ni)

The reactions in this system are somewhat more complicated because a larger number of products may form. The general equation may be written:

The compound written as U(Fe,Ni)C_2 is a solid solution between the isomorphic compounds UFeC_2 and UNiC_2 . We have prepared the intermediate compound $\text{UFe}_{.5}\text{Ni}_{.5}\text{C}_2$, lattice constants for the tetragonal structure, $a = 4.952 \pm 0.001 \text{ \AA}$, $c = 7.362 \pm 0.002 \text{ \AA}$.

Our metallographic, electronic microprobe, and x-ray diffraction studies indicate that < 8 at % of the nickel in UNi_5 may be substituted by iron.

The product written as X/Y is actually two uranium-nickel compounds of unknown structure (1^c). These compounds appear in the uranium-nickel phase diagram at compositions of ~ 77 at % Ni and ~ 73 -79 at % Ni (15).

UC-(Cr-Fe)

In their studies of the UC-(Cr-Fe) system, Dutta and White (2) observed a reaction which produces more than one product. The general reaction may be written:

This reaction occurs for chromium compositions between $x_{\text{Cr}} = 0.08$ to 0.98 (2).

Based on lattice constants alone, our experimental results for this reaction indicate that iron may substitute for some of the chromium in Cr_{23}C_6 , but there is no chromium substitution for iron in UFe_2 .

UC-(Cr-Fe-Ni)

Figure 1 shows an equilibrium compatibility diagram for UC with (Cr-Fe-Ni) alloys. The white areas of the diagram indicate the (Cr-Fe-Ni) alloy compositions where some reaction takes place with UC. The black areas of the diagram are where UC is compatible with (Cr-Fe-Ni) alloy and lie very close to either the chromium or the iron corner of the diagram.

We have called Figure 1 an equilibrium compatibility diagram. It is important to distinguish this from a phase diagram. Figure 1 indicates areas of compatibility or incompatibility - it does not give phases or relations between phases. The outer boundaries for this diagram were obtained by combining our calculations for UC-(Cr-Ni) with those of Dutta and White (2) for UC-(Fe-Ni) and UC-(Cr-Fe) reactions. The inner portions of the diagram were calculated using std. free energies of formation obtained from references listed in Table 1. Since this is a compatibility diagram it was only necessary to calculate that some reaction could or could not occur.

Compatibility studies (2,4) and our thermodynamic calculations have found that all compositions of (Cr-Fe-Ni) alloys are incompatible with hyperstoichiometric uranium monocarbides, $\text{UC} + \text{U}_2\text{C}_3$, or UC_2 .

Summary

Figure 2 summarizes compatibility studies of uranium carbides with (Cr-Fe-Ni) alloys. The reactions are divided into three regions based on carbon content of the uranium carbide. We see that at equilibrium, (Cr-Fe-Ni) alloys are compatible only at compositions very close to 100 at % chromium or iron. Thus, the actual compatibility of uranium carbide fuels in a reactor system will be determined only by the transport of materials taking part in the various reactions.

This result does not necessarily limit the life of potential uranium carbide-(Cr-Fe-Ni) fuel cladding couples. Contact compatibility studies with and without sodium or helium bonding will show whether material transport is important relative to other cladding failure mechanisms.

The observations presented in the previous section lead to two statements which are applicable to any fuel-cladding compatibility study.

1. One element may substitute for another element in a product compound. The substitution of one element for another is illustrated by our studies of Laves phases.
2. More than one type of product may occur in one overall fuel-cladding reaction. Reactions of UC with (Cr-Fe-Ni) alloys are examples of the formation of more than one type of product.

Based on these statements, we propose a general rule of equilibrium compatibility: The compatibility of a given fuel with a number of different elements is not simply the sum of the compatibility behaviors for the individual elements.

A corollary of this rule can also be stated: If a given element reacts with the fuel in question, i.e., is incompatible, adding a second or third

element to reduce the activity of the element which is incompatible will not necessarily improve compatibility but may just change the products formed. Conversely, two or more elements which are separately compatible with a given fuel may not be compatible when reacted in combinations.

Table 1

References for Thermodynamic Data

Material	Reference
UC	5
U_2C_3	5
UFe_2	6
UNi_5	7
$UFeC_7$	8
$Cr_{23}C_6$	9
Cr_7C_3	9
Cr_3C_2	9
(Cr-Fe)	10
(Cr-Ni)	10
(Fe-Ni)	11
(Cr-Fe-Ni)	Assumed ideal for calculations

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Figure 1

**EQUILIBRIUM COMPATIBILITY DIAGRAM
FOR UC-(Cr, Fe, Ni)
700-1000 °C**

Figure 2

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EQUILIBRIUM COMPATIBILITY OF URANIUM CARBIDES WITH (Cr-Fe-Ni) ALLOYS (700-1000°C)