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Nitridation of uranium and rare-earth metals in liquid Cd

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Abstract

The nitride formation reaction of liquid 2 wt% U–1 wt% Gd–1 wt% Ce–Cd alloys has been studied over the temperature range of 773–873 K using graphite and molybdenum crucibles. Uranium was preferentially nitrided to form U_2N_3, which were produced at the nitrogen gas–liquid alloy interface. A little gadolinium was precipitated as nitrides, GdN or the (U, Gd)N phase. Almost all of the cerium and some gadolinium remained in the Cd phase as MCd_{11} intermetallic compounds. Resistance of Ce to nitridation is due to the lower activity coefficients in a Cd-rich solution at these temperatures. © 1997 Elsevier Science B.V.

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1. Introduction

The nitride-forming reactions in liquid alloys containing actinide and lanthanide elements have a potential for reprocessing spent fuels, in particular, metallic and nitride fuels. The actinide nitride has been extensively studied as a candidate fuel for actinide burning system. In the proposed pyrochemical processing [1], nitride fuels are recovered as metals or alloys by electrorefining in a LiCl–KCl eutectic salt. The recovered metallic fuels are then converted to the nitrides in liquid Cd–An (An: actinides) alloys. In this process, actinides can be separated from lanthanides as a result of activity coefficient differences between actinides and lanthanides. Further removal of lanthanides from actinides may be achieved if necessary [2]. The use of Cd–An alloys is superior in some points, such as high vapor pressure of Cd to any other processes, for example, the liquid tin process [3,4]. In the liquid tin process, it is difficult to remove Sn by distillation after nitriding because of its high boiling point.

The purpose of this study is to understand the basic behavior of nitriding in liquid Cd containing uranium and lanthanides and to determine if lanthanides could be separated by nitride precipitation techniques in Cd–U alloys.

2. Experimental

Nitriding of liquid Cd–U–Gd–Ce alloys was performed at a nearly constant nitrogen pressure in a closed quartz ampoule. The reaction temperatures used were 773 and 873 K. Graphite and molybdenum crucibles were used to contain the liquid Cd alloys and they were degassed in a high vacuum at 1023 K before alloying. Molybdenum is considered to be the best material as a container for liquid Cd alloys because the solubility of Mo in liquid Cd is very small at the present temperatures (about 10^{-7}–10^{-6} wt%) [5,6].

Approximately 7 g Cd–2 wt% U–1 wt% Gd–1 wt% Ce alloys were prepared in an inert atmosphere. Uranium, gadolinium, cerium and cadmium metals of 99.9 wt% purities were weighed and placed in quartz tubes together with graphite or molybdenum crucibles in an argon-atmosphered glove box. The samples in the quartz ampoules were sealed in high-purity helium gas and then melted for 20–50 h at 873 K to obtain the homogenized Cd–U–Gd–Ce alloys.

The nitriding was performed in nitrogen gas of 99.995 vol.% purity. About 250 Torr nitrogen was contained in the quartz ampoule of 20–50 cm^3 in volume at room temperature. The nitrogen pressure increased up to about 600–700 Torr at the reaction temperatures of 773 and 873 K, where nitriding times were 100–170 h. For the Mo crucibles, the liquid Cd alloys were often stirred during

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nitriding using Mo rods which were placed in the Mo crucible. To terminate the nitriding, the quartz ampoules were water-cooled. The amounts of nitrogen absorbed in the liquid alloys were measured by fracturing the quartz ampoule in water after nitriding and correcting the rest of the nitrogen gas.

After nitriding, the samples were cut in half together with the crucibles and products in the Cd alloys were examined. Electron-probe micro-analysis (EPMA) was used to identify phases in the Cd alloys, in particular, the stoichiometry of nitride precipitates of uranium or lanthanides. The acceleration voltage and beam size were 20 kV and ~ 1 μm in diameter, respectively. The X-ray intensities were converted into compositions using the pure elements, UN and U_2N_3 standards. The detection limits of the EPMA analysis were about 0.1, 0.1, 0.2, 0.2, 0.5 and 1.0 wt% for Cd, U, Gd, Ce, N and C, respectively.

3. Results and discussion

3.1. Products for the graphite crucibles

Fig. 1 shows the results when the Cd–2 wt% U–1 wt% Gd–1 wt% Ce alloys were nitrided for 100 h at 873 and 170 h at 773 K, respectively, in the graphite crucibles. The composition of precipitates found in the alloys solidified from 773 and 873 K are summarized in Table 1, where the concentration of nitrogen in stoichiometric U_2N_3 is about 8.1 wt%. The EPMA analysis of the Cd alloys solidified from 773 and 873 K clearly indicated that uranium precipitates in the Cd alloys were mainly U_2N_3 and U(C, N) phases. The U_2N_3 phase was found only at the surface of the Cd alloy, that is, the interface between the liquid alloy and nitrogen gas, as shown in Fig. 1(a) and (d). This suggests that the U_2N_3 phase was formed by a direct reaction between the dissolved uranium in the Cd melt and nitrogen gas in atmosphere. The formation reaction of the U_2N_3 can be described by the equation

$$2\underline{U}(\text{dissolved}) + 3/2N_2(g) = U_2N_3(s).$$

The reaction appears to be rapid at 873 K, producing porous reaction layers, accompanied by considerable amounts of spalled fragments. From the EPMA analysis of the U_2N_3 precipitates, they contained a little gadolinium and cadmium, as shown in Table 1. However it was not obvious whether the chemical form of Gd is nitride or metallic. As a result of the high density of U_2N_3 compared with Cd, the U_2N_3 precipitates formed at the alloy surface were expected to sink to the bottom of the graphite cru-

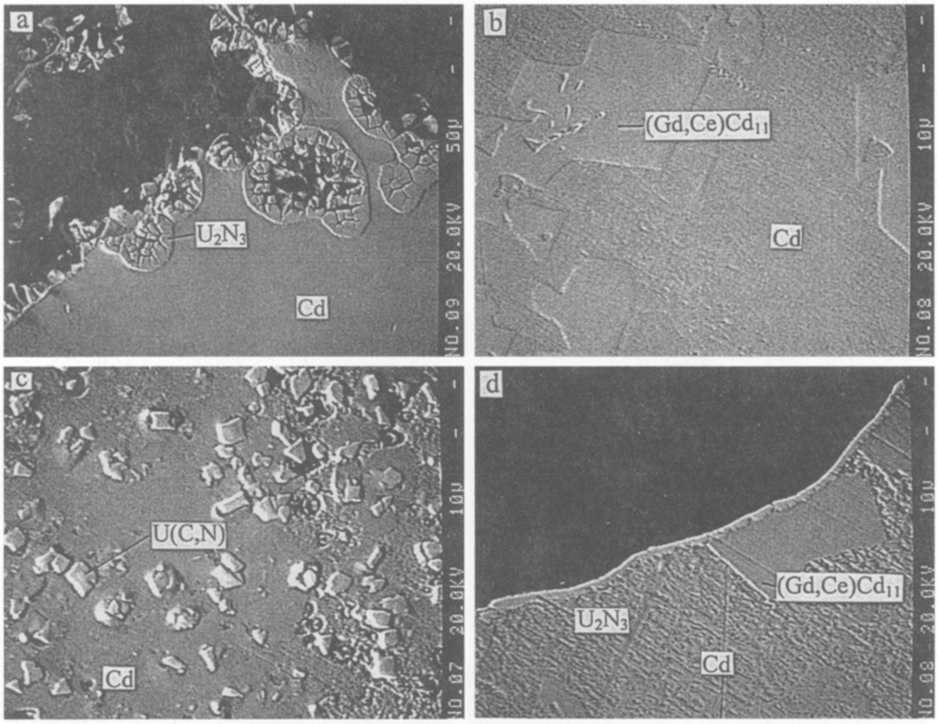

Fig. 1. Backscattered electron micrographs of the Cd alloys in graphite crucibles: Micrographs (a), (b) and (c) were taken at the near surface, center and near bottom regions of the alloy solidified from 873 K, respectively. Micrograph (d) was taken at the near surface region of the alloy solidified from 773 K.

Table 1
The compositions of products in the Cd alloys nitrided at 773 and 873 K for the graphite crucibles

Phases	Temp. (K)	Concentrations (wt%)					
		Cd	U	Gd	Ce	N	C
Cd matrix	773	99.9	< 0.1	< 0.2	< 0.2	< 0.5	
	873	99.9	< 0.1	< 0.2	< 0.2	< 0.5	
U_2N_3	773	0.7	91.6	0.3	< 0.2	7.4	
	873	0.5	91.0	0.4	< 0.2	8.2	
(Gd, Ce)Cd_{11}	773	87.0–87.5	3.5–3.3	6.8–1.4	2.7–7.7	< 0.5	
	873	88.1–88.3	< 0.1	7.7–5.5	4.2–6.2	< 0.5	
U(C, N)	773	0.2	94.9	< 0.2	< 0.2	2.4	2.4
	873	< 0.1	95.8	< 0.2	< 0.2	2.3	1.9

cible. However the U_2N_3 did not sink and increased its thickness at the alloy surface through nitriding. This is mainly due to formation of the layered nitride at the liquid alloy surface as a result of static nitriding reaction without stirring, as clearly shown in Fig. 1(d), where formation and growth of very thin adherent U_2N_3 layer at the alloy surface solidified from 773 K can be observed. The U_2N_3 layer formed on the overall surface of the liquid alloy would depress further nitridation of uranium dissolved in the Cd alloy. In deed, the amount of nitrogen absorbed in the liquid alloy nitrided for 170 h at 773 K was below about 1 cm^3 STP, which corresponds to about 10% in the conversion rate of U dissolved in the Cd alloy to U_2N_3.

From the EPMA analysis, no contamination with carbon was detected in the Cd alloys, but the U(C, N) phase concentrated at the near bottom of the graphite crucible, as shown in Fig. 1(c). Precipitates of uranium carbide, probably, UC, were also observed around the bottom of the Cd alloy homogenized in a helium atmosphere at 873 K before nitriding. This means that the UC precipitates were produced by a reaction between uranium and free carbon in the liquid Cd. The formation of U(C, N) precipitates in the nitrided alloy was due to nitridation of the UC precipitates formed during alloying with atomic nitrogen dissolved in the Cd melt, suggesting that the uranium carbide would be unstable with respect to the uranium nitride. On the other hand, the concentrations of U in the Cd phases after nitriding was very low, but a small fragment of pure uranium was found at the near bottom of the Cd alloy nitrided at 773 K, suggesting that 2 wt% U may be in excess of the solubility of U in the Cd alloy at 773 K. From the U–Cd binary phase diagram [5], the solubilities of U in Cd are 2.35 and 2.14 wt% at 773 and 873 K, respectively.

The lanthanides, in particular, cerium, were quite different in their precipitation behavior from uranium. Cerium nitride, probably CeN, or Ce-contained U–N phases cannot be found in the Cd alloys nitrided at 773 and 873 K. Almost all the lanthanide elements precipitated in the Cd alloy as a M(M:Gd, Ce)–Cd intermetallic compound. From the EPMA analysis, the M–Cd intermetallic compound was estimated to be the (Gd, Ce)Cd_{11} phase, where the concentrations of Gd and Ce were significantly scattered among the precipitates, as shown in Table 1. The inter-

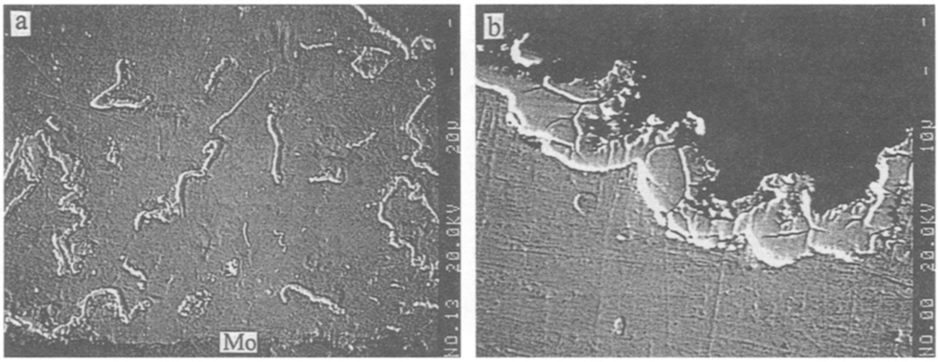

Fig. 2. Backscattered electron micrographs of the Cd alloys in Mo crucibles: Micrographs (a) and (b) were taken at the near bottom and the near surface regions of the alloys solidified from 873 and 773 K, respectively. Both the precipitates are U_2N_3 containing GdN or (U, Gd)N.

Table 2
The compositions of products in the Cd alloys nitrided at 773 and 873 K for the Mo crucibles

Phases	Temp. (K)	Concentrations (wt%)				
		Cd	U	Gd	Ce	N
Cd matrix	773	100	< 0.1	< 0.2	< 0.2	< 0.5
	873	100	< 0.1	< 0.2	< 0.2	< 0.5
U_2N_3	773	1.3	90.0	0.9	< 0.2	7.8
	873	< 0.1	91.9	< 0.2	< 0.2	8.1
U–N–Gd	873	1–0.9	89.4–92.4	2.4–0.3	< 0.2	7.2–6.4
(Gd, Ce)Cd_{11}	773	92.6–87.5	< 0.1–1.5	5.4–1.2	3.2–9.8	< 0.5
	873	89.2–88.4	< 0.1	2.6–7.5	8.2–4.2	< 0.5

metallic compound MCd_{11} formed on water-cooling after nitriding and remained in suspension in the Cd melt. The result that unlike U, the lanthanides, in particular, cerium, did not form the nitrides can be explained by the very low activity coefficients of lanthanides in cadmium, compared with that of uranium. The activity coefficients of U, Gd and Ce in Cd are 75, 6.3×10^{-7} and 1.3×10^{-8} at 773 K, respectively [6] and indicates that the Cd–Ce, Gd alloys are very stable and the much larger concentrations are necessary to equal the chemical activity of U.

3.2. Products for the Mo crucibles

The appearance of nitride precipitates for the Mo crucible was different from that for the graphite crucible without mechanical stirring. Fig. 2 shows typical sections of the near bottom and near surface regions of the Cd alloys nitrided for 100 h at 773 and 873 K, respectively. The formation of the nitride layer on the alloy surface found at 773 K is also very similar to that for the graphite crucible without stirring. The nitride precipitates found at the near bottom region are likely to have a very thin layer structure, suggesting that the precipitates were formed at the alloy surface and then sank to the bottom of crucible. Sinking of the nitride precipitates to the bottom can be explained by fragmentation of the nitride layer formed at the surface due to mechanical stirring during nitriding and density difference between the uranium nitride and the Cd alloy. For the graphite crucible, carbon contamination was observed in the uranium carbide phase. By contrast, for the Mo crucible, the EPMA analysis gave no indication that Mo was present in the uranium nitride and Cd alloy phases.

As shown in Table 2, the EPMA analysis of the thin layered U–N precipitates found at 873 K showed that the precipitates have lower nitrogen contents of 6.4–7.2 wt%, compared with that of U_2N_3 phase (8.1 wt%), and, in addition, contain 0.3–2.4 wt% Gd. This result suggests the product to be the mixture phase of uranium and gadolinium nitrides. The formation of U_2N_3 occurs initially and a decrease in concentration of U in the liquid Cd promotes formation of gadolinium nitride, GdN or (U, Gd)N. The amounts of nitrogen absorbed in the liquid Cd alloys during nitriding are summarized in Table 3. For the nitriding at 873 K, the conversion of U to U_2N_3 attained about 92%, where the concentration of U in Cd would be very low. At that time the chemical activity of U would be greatly reduced to approximately that of Gd and Gd is likely to form the nitride, probably such as GdN or (U, Gd)N, because the activity coefficient of Gd in Cd is higher than that of Ce. The formation of (U, Gd)N at the alloy surface means coprecipitation of U and Gd. Moreover, decomposition of U_2N_3 to UN in the liquid Cd could occur, because the solubility of nitrogen in liquid Cd is expected to be very low. The nitride layer formed on the alloy surface at 773 K also contained 0.9 wt% Gd, as shown in Table 2, suggesting that both U_2N_3 and GdN or (U, Gd)N could be formed simultaneously.

On the other hand, all of Ce precipitated in MCd_{11} intermetallic phases together with Gd in the Cd alloys solidified from both 773 and 873 K. As mentioned before, the strong resistance of Ce to nitride forming, compared

Table 3
The amounts of nitrogen absorbed into the Cd alloys in the Mo crucibles

Temperature (K)	Time (h)	Initial volume (cm^3 at STP/ g U)	Absorbed volume (cm^3 at STP/g U)	Conversion to U_2N_3 (%)
773	100	100.2	55.3	78.3
873	100	89.8	64.6	91.5

with U and Gd, can be explained by its lower activity coefficient in Cd, that is, its greater stability of Cd–Ce alloys. The composition of the MCd_{11} seems to be scattered among the precipitates, as shown in Table 2. This tendency was very similar to that for the graphite crucible. Some of the MCd_{11} precipitates found in the alloy nitrided at 773 K contained a little uranium and the conversion of U to U_2N_3 was low, compared with those at 873 K. This indicates that uranium in the Cd alloy would not be completely nitrided at 773 K.

4. Conclusions

The nitriding behavior of liquid Cd alloy contained uranium and lanthanides has been studied at the temperatures of 773 and 873 K. Uranium was preferentially nitrided in the Cd alloy to form the stoichiometric U_2N_3. Gadolinium nitride precipitated when the chemical activity of U would be reduced to that of Gd. Cerium remained in the Cd phase as MCd_{11} intermetallic compounds. The Mo crucible can be successfully used to hold the Cd alloy without Mo contamination, but the use of graphite crucible resulted in the formation of uranium carbide. It is also apparent that the nitriding behavior was significantly affected by some parameters such as mechanical stirring, temperature, probably, nitrogen pressure, etc. In particular, the stirring would be necessary for enhancing the nitriding reaction of uranium.

This procedure for reprocessing the alloy fuels, that is, the nitride precipitation in liquid Cd alloy, could be a useful technique in separating fission products, in particular, light elements such as La–Nd from actinides. The complete separation would be effected by controlling the nitrogen pressure.

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