

## NITRIDE-FORMING BEHAVIOR IN LIQUID CADMIUM-URANIUM-LANTHANIDES ALLOYS

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### Abstract

The nitride formation reaction of liquid 2wt% U-1wt% Gd-1wt% Ce-Cd alloys has been studied over the temperature range of 773~873 K using graphite and molybdenum crucibles. The Cd-U alloys were contacted with nitrogen gas or  $\text{Li}_3\text{N}$ . Uranium in the liquid Cd alloy was preferentially nitrated to form  $\text{U}_2\text{N}_3$ , which were produced at nitrogen gas-liquid alloy interface. A little gadolinium precipitated as nitrides, GdN or (U,Gd)N phase. The rest of gadolinium and almost all of cerium remained in the Cd phase as  $\text{MCd}_{11}$  (M: Gd and Ce) intermetallic compounds. Resistance of Ce to nitridation is due to the lower activity coefficient in Cd-rich solution at the temperatures.

## 1. Introduction

The nitride-forming reaction in liquid alloys containing actinide and lanthanide elements is of interest for both technological and fundamental science. 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. The 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 other liquid-metal 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.  $\text{Li}_3\text{N}$  may be also used in the liquid Cd process as a nitriding agent, instead of nitrogen gas, because the nitrogen evolved during electrolyzing the nitrides in the salt is trapped by lithium to form  $\text{Li}_3\text{N}$ .

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 in closed quartz ampoules using nitrogen gas or  $\text{Li}_3\text{N}$ . Reaction temperatures used were 773 and/or 873 K. Graphite and/or 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-2wt%U-1wt%Gd-1wt%Ce alloys were prepared in an inert atmosphere. Uranium, gadolinium, cerium and cadmium metals of 99.9% 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.

Nitridings were performed in nitrogen gas of 99.995wt% purity. About 250 Torr nitrogen was contained in the quartz ampoule of 20~50cc 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 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 ampoules in water after nitriding and correcting the rest of nitrogen gas.

In the case of nitriding with  $\text{Li}_3\text{N}$ , the Cd-U alloy containing Gd and Ce was sealed with  $\text{Li}_3\text{N}$  under vacuum in a quartz ampoule using a graphite crucible and then heated to 773 K. The amount of  $\text{Li}_3\text{N}$  added was ~25mg, which was determined from a condition that an increase of inner pressure in the quartz ampoule due to decomposition of  $\text{Li}_3\text{N}$  to  $\text{N}_2$  is not in excess of 760 Torr at 773 K.

In addition, a simple technique was employed to measure the time dependences of the amount and pressure of nitrogen reacted with the Cd-U alloy. The Cd-U alloy containing Ce and Gd was held in a long glassy carbon crucible in order to prevent loss of Cd due to vaporization during nitriding. The crucible was then placed in a quartz tubing, which is connected with a pressure gauge for measuring the pressure in the system. The dead volume of the system was measured with pure helium. Nitriding of the alloy with nitrogen was performed at 873 K without stirring.

After nitriding, the samples were cut to 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  $\mu\text{m}$  in diameter, respectively. The X-ray intensities were converted into compositions using the pure

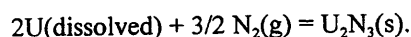
elements, UN and U<sub>2</sub>N<sub>3</sub> standards. The detection limits of the EPMA analysis are about 0.1, 0.1, 0.2, 0.2, 0.5 and 1.0 wt% for Cd, U, Gd, Ce, N and C, respectively.

### 3. Results

#### 3.1 Reaction with nitrogen gas

##### 3.1.1 Products for the graphite crucibles

Fig.1 shows the results when the Cd-2wt%U-1wt%Gd-1wt%Ce alloys were nitrided for 100 and 170 h at 873 and 773 K, respectively, in the graphite crucibles. The compositions of precipitates found in the alloy solidified from 873 K are summarized in table 1, where the concentration of nitrogen in stoichiometric U<sub>2</sub>N<sub>3</sub> 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<sub>2</sub>N<sub>3</sub> and U(C,N) phases. The U<sub>2</sub>N<sub>3</sub> 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 figs.1(a) and (d). This suggests that the U<sub>2</sub>N<sub>3</sub> 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<sub>2</sub>N<sub>3</sub> can be described by the equation,



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<sub>2</sub>N<sub>3</sub> precipitates, they contained a little gadolinium and cadmium of 0.4 and 0.5 wt%, respectively. However it was not obvious whether the chemical form of Gd is nitride or metallic. As a result of the high density of U<sub>2</sub>N<sub>3</sub> compared with Cd, the U<sub>2</sub>N<sub>3</sub> precipitates formed at the alloy surface were expected to sink to the bottom of the graphite crucible. However the U<sub>2</sub>N<sub>3</sub> 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<sub>2</sub>N<sub>3</sub> layer at the alloy surface solidified from 773 K can be observed. The U<sub>2</sub>N<sub>3</sub> layer formed on the overall surface of the liquid alloy would depress further nitridation of uranium dissolved in the Cd alloy. In a deed, the amount of nitrogen absorbed in the liquid alloy nitrided for 170 h at 773 K was below about 1 ccSTP, which correspond to about 10% in conversion rate of U dissolved in the Cd alloy to U<sub>2</sub>N<sub>3</sub>.

By contrast, the U(C,N) phase concentrated at the near bottom of the 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. Therefore, formation of the 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. On the other hand, the concentration of U in the Cd phase nitrided at 873 K was below about 0.1wt% which corresponds to the detection limit of the EPMA analysis. However, 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 (Gd,Ce)Cd<sub>11</sub> phase, where the concentrations of Gd and Ce were a little scattered among the precipitates, as shown in table 1. The intermetallic compound MCd<sub>11</sub> 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, 6.3E-7 and 1.3E-8 at 773 K, respectively [6] and indicate that the Cd-Ce, Gd alloys are very stable and the much larger concentrations are necessary to equal the chemical activity of U.

##### 3.1.2 Products for the Mo crucibles

The appearance of nitride precipitates for the Mo crucible was significantly different from that for the graphite crucible. Table 2 indicates the compositions of precipitates found in the alloy nitrided for 100 h at 873 K. Fig.2 shows typical sections of the near bottom and near surface regions of the Cd alloys nitrided for 100 h at 873 and 773K, respectively. From the EPMA analysis, both the precipitates appear to consist of  $U_2N_3$  and U-N phases containing gadolinium. The formation of the nitride layer on the alloy surface found at 773 K is also very similar to those for the graphite crucible without stirring. The nitride precipitates found on the near bottom region are likely to have a very thin layer structure, suggesting that the precipitates were formed at the alloy surface. 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.

As shown in table 2, the EPMA analysis of the thin layered U-N precipitates found at 873 K, which contained a little gadolinium, showed that the precipitates have low nitrogen contents, 6.4~7.2 wt%, compared with that of  $U_2N_3$  phase (8.1 wt%), and 0.3~2.4 wt% Gd was present in the precipitates. 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 alloys during nitriding are summarized in table 3. For the nitriding at 873 K, the conversion of U to  $U_2N_3$  attained to about 92%. At this stage where the concentration of U in Cd is very low, the chemical activity of U would be greatly reduced to approximately that of Gd and Gd is likely to form the nitride, probably 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, as shown in fig.2(b) also contained 0.9 wt% Gd, 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 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 that at 873 K. This indicates that uranium in the Cd alloy would be not completely nitrided at 773 K.

### 3.1.3 Time dependence of nitriding reaction

Fig.3 shows the time dependences of nitrogen pressure in the quartz ampoule and conversion of uranium in the Cd-U alloy to  $U_2N_3$  during nitriding at 873 K. The conversion was calculated from the amount of nitrogen absorbed in the Cd alloy. The equilibrium amount of  $U_2N_3$  formed was about 45%. Therefore, the nitriding of uranium dissolved in the Cd alloy was not completed. The time dependence of conversion demonstrates that the reaction rate increases rapidly at early stage, attains the maximum at ~5 hours and then decreases gradually. This tendency means that  $U_2N_3$  layer formed at the alloy surface prevented further progress of nitriding reaction. From the EPMA analysis, the formation of  $U_2N_3$  layer at the alloy surface was also observed. As mentioned before, it is likely that mechanical stirring is an effective technique for enhancing or completing the conversion of uranium to nitride.

### 3.2 Reaction with $Li_3N$

Fig.4 shows typical cross sections of surface regions for the  $Li_3N$  contained Cd alloy annealed at 773 K. From the EPMA analysis, it was found that the reaction of the liquid Cd-U alloy with  $Li_3N$  yields the uranium sesquinitride,  $U_2N_3$ . The formation of  $U_2N_3$  occurred at both the surface of the liquid Cd alloy and the interface between Cd-Li phase and the liquid Cd alloys. The  $U_2N_3$  precipitates contained a little Gd. U(C,N) phase also precipitated at the near bottom of the alloy. Lanthanides, Ce and Gd, concentrated in the  $MCd_{11}$  intermetallic phase. The nitriding behavior of Cd-U-lanthanides alloy with  $Li_3N$  appears to be very similar to those with nitrogen gas. On the other hand, the Cd-Li precipitates floated to the alloy surface, suggesting that the reaction between Cd and  $Li_3N$  yields a low density Cd-Li intermetallic compound. The composition of the Cd-Li alloy lies in the range of  $CdLi_2$ ~ $CdLi_{3.5}$ ; the phase diagram of Cd-Li system suggests the product to be  $CdLi_3$  [5].

About 7 cc nitrogen remained in the quartz ampoule after nitriding. The amount of nitrogen evolved by complete decomposition of  $\text{Li}_3\text{N}$  is estimated to be ~8 cc. This suggests that almost all of  $\text{Li}_3\text{N}$  was decomposed by the reaction with Cd to evolve nitrogen gas and ~1 cc of the evolved nitrogen contributed the nitriding of uranium in the Cd alloy. The conversion of uranium to  $\text{U}_2\text{N}_3$  was no more than ~ 10%. This conversion rate is significantly lower than those for the nitriding with stirring.

The results of the present experiment described above indicate that the nitride precipitation technique using liquid Cd alloy could be a useful technique in separating lanthanides, in particular, light elements such as La ~ Nd from actinides. The  $\text{Li}_3\text{N}$  can be also used as a nitriding agent in this process, instead of nitrogen.

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**Table 1**

The composition of products in the Cd alloy at 873 K for the graphite crucible

Phases	Concentrations (wt%)					
	Cd	U	Gd	Ce	N	C
Cd matrix	99.9	<0.1	<0.2	<0.2	<0.5	
U <sub>2</sub> N <sub>3</sub>	0.5	91.0	0.4	<0.2	8.2	
(Gd,Ce)Cd <sub>11</sub>	88.1~88.3	<0.1	7.7~5.5	4.2~6.2	<0.5	
U(C,N)	<0.1	95.8	<0.2	<0.2	2.3	1.9

**Table 2**

The composition of products in the Cd alloy at 873 K for the Mo crucible

Phases	Concentrations (wt%)					
	Cd	U	Gd	Ce	N	C
Cd matrix	100	<0.1	<0.2	<0.2	<0.5	
U <sub>2</sub> N <sub>3</sub>	<0.1	91.9	<0.2	<0.2	8.1	
(Gd,Ce)Cd <sub>11</sub>	89.12~88.4	<0.1	2.6~7.5	8.2~4.2	<0.5	
U-N-Gd	1~0.9	89.4~92.4	2.4~0.3	<0.2	7.2~6.4	

**Table 3**

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

Temp. (K)	Time (h)	Initial volume (cc at STP/g U)	Absorbed volume (cc at STP/g U)	Conversion to U <sub>2</sub> N <sub>3</sub> (%)
773	100	100.2	55.3	78.3
873	100	89.8	64.6	91.5

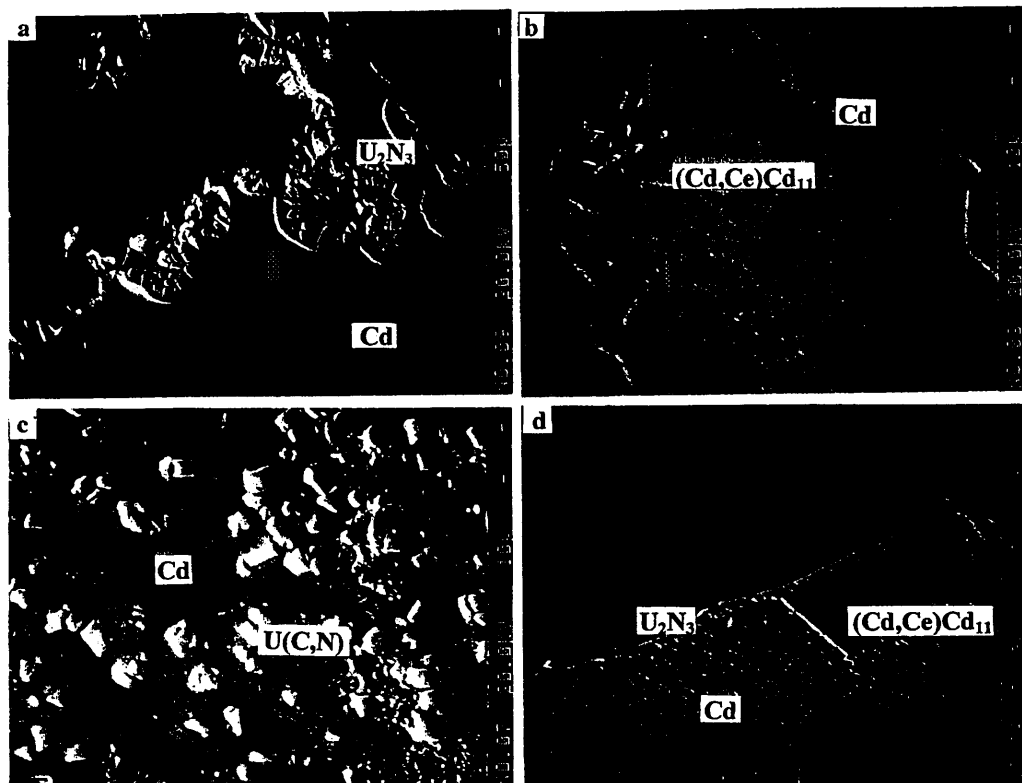


Figure 1 Backscattered electron micrographs of the Cd alloys in graphite crucibles : Micrographs a), b) and c) were taken of the near surface, center and near bottom regions of the alloy solidified from 873 K, respectively. Micrograph d) was taken of the near surface region of the alloy solidified from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

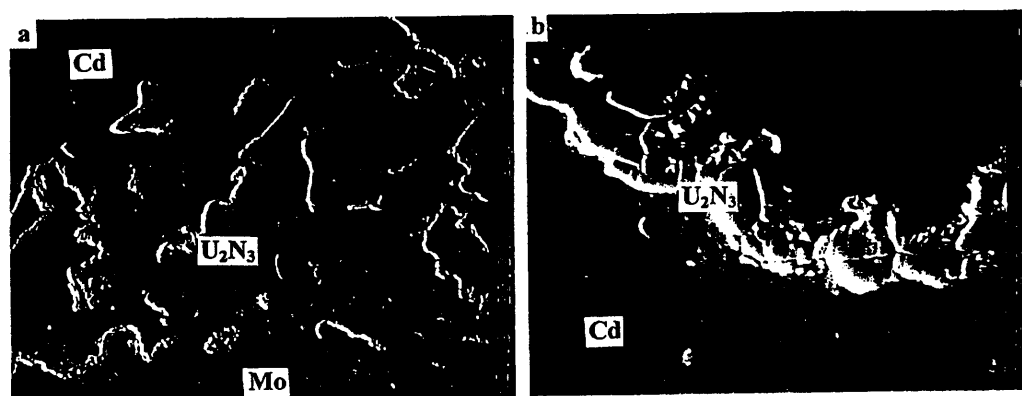


Figure 2 Backscattered electron micrographs of the Cd alloys in Mo crucibles: Micrographs a) and b) were taken of the near bottom and the near surface regions of the alloys solidified from 873 and 773 K, respectively. Both the precipitates are  $U_2N_3$ , containing GdN or (U,Gd)N.

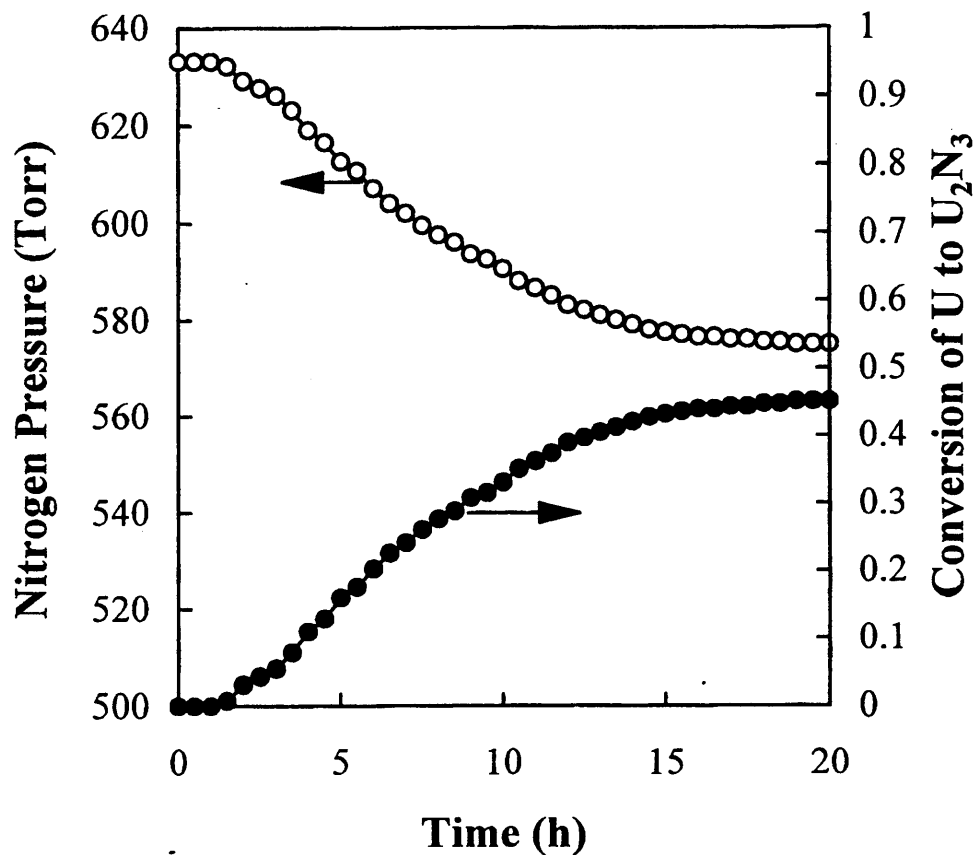


Figure 3 Time dependences of nitrogen pressure and conversion of uranium to  $U_2N_3$  for the Cd-U alloy nitrided at 873 K.

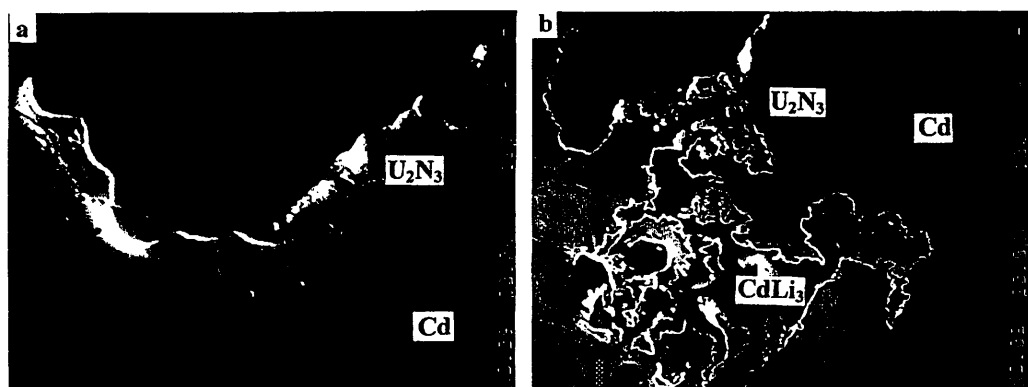


Figure 4 Backscattered electron micrographs of the Cd alloy nitrided with  $Li_3N$ : Micrographs a) and b) were taken of the near surface regions of the alloy solidified from 773 K. Gd-contained  $U_2N_3$  precipitates were found at the alloy surface and the interface between the Cd-Li intermetallic compound ( $CdLi_3$ ) and the Cd alloy