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Investigation of the Reaction Rates between Uranium and Liquid Aluminum

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EXECUTIVE SUMMARY

A limited study consisting of scoping experiments was carried out to determine if a uranium-niobium alloy was weakly or strongly resistant to penetration by liquid aluminum alloy 6061. Our investigation was limited to temperatures between 700° and 900° C and carried out using small cylindrical coupons of U-6wt.%Nb and unalloyed U in unsaturated molten aluminum and aluminum alloy 6061 baths. The results indicate that indeed, significant dissolution of uranium into molten aluminum occurs and in relatively short times. The diameters of U-6wt.% Nb test cylinders immersed in unsaturated Al-6061 decreased linearly with time at 700 °C, 800 °C, and 900 °C at rates of 1.14 mm/h, 3.0 mm/h, and 3.5 mm/h, respectively. However, we have found that the reaction rates were significantly reduced by the alloying elements niobium and magnesium. These results suggest that a more detailed investigation could lead to a predictive capability for control of these reaction rates. In unalloyed U, the rate of U dissolution increased by up to a factor of ten relative to that in U-6wt.% Nb. In both materials, the dissolution of the U core was found to occur by advance of a continuous intermetallic layer, which redissolves into the unsaturated liquid Al bath. The Nb additions resulted in the formation of a thick transition layer composed of intermetallic and U-saturated liquid. In unalloyed U, however, the transition layer was largely reduced in thickness, allowing unsaturated liquid adjacent to the continuous intermetallic layer. Another important variable identified was the influence of surface condition on interface reactivity. At 900 °C, liquid attack was completely absent over large regions of U-6wt.% Nb samples immersed in Al-6061. Surface analysis by EDX identified the presence of up to 24 at.% Mg in unattacked areas. The functionality of surface oxides such as MgO, which may have coated some specimens during immersion into the liquid bath, native oxides, and other surface treatments in inhibiting wetting and reaction with liquid Al requires further investigation.

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INTRODUCTION

A limited study consisting of scoping experiments was carried out to determine if uranium and its alloys were weakly or strongly resistant to dissolution by liquid aluminum or aluminum alloys such as 6061. Rapid dissolution of U was expected at temperatures in excess of the eutectic between Al and U at 646°C when the U concentration remained below its solubility limit in Al (approximately 2.0 at.% at 732°C). In such a case, the reaction rates could be relatively rapid, being limited by liquid phase diffusion rates. The formation of an intermediate phase at the solid/liquid interface, however, could largely reduce these dissolution rates. Such an intermediate phase would restrict the transport rate of Al to the U-alloy interface by requiring solid state diffusion through the intermediate phase. Three intermediate phases reported in the U-Al binary phase diagram (see Figure 1) are; $U_{0.9}Al_4$, with a solidus at 731°C, UAl_3 , with a solidus at 1350°C, and UAl_2 , which melts congruently at 1620°C. The precipitation of one or more of these phases is predicted if the concentration of U from the dissolving alloy exceeds the solubility limit within the liquid Al (e.g. 2.0 at.% U at 732°C for binary U-Al). In solid-state reactions between U and Al, one or more of these intermetallic phases have been reported to form by Al diffusion into the U, with the dominant phase dependent upon the reaction temperature [1, 2]. The type of intermetallic phase and its thickness is expected to largely influence the rate of U transport into the Al liquid. The experiments in this investigation focused upon the rate of U6Nb reaction in Al-6061 at temperatures between 700 °C and 900 °C. These alloys introduce the additional elements Nb, Si, and Mg into the system, the influence of which has been investigated by microchemical analysis of alloying element distributions in the reaction zones. Comparative evaluations of reaction rates between unalloyed U and U6Nb in a high-purity Al bath were also performed to assist in determining the influence of these minor alloying element additions.

The results of this investigation provide the temperature dependence of U6Nb dissolution rates in unsaturated Al-6061 liquid. Microstructural characterization provides some insight into the reaction mechanisms but extrapolation to other temperatures and other compositions will likely require an improved understanding of the phase equilibria, interdiffusion rates, and interface reaction rates in these systems.

EXPERIMENTAL PROCEDURE

Cylinders of U-6wt.% Nb and depleted U-238, 0.125" (3.18 mm) in diameter and 1.5" (38.1) in length were machined from bulk plate along the rolling plane. The U-6wt.% Nb plate, fabricated at Martin Marrietta's Y-12 Plant, varied between 5.91 and 6.39 wt.% Nb and 97 to 103 wt. ppm C. The depleted U-238 was 99.9 pct pure and the high purity Al was 99.999 pct pure. The Al-6061 material was nominally 97.9 Al- 0.6 Si- 1.0 Mg- 0.28 Mn- 0.20 Cr, all in wt. pct.

Heat treatments were performed in an argon-filled glovebox. An electrical resistance pot furnace was positioned within a recess in the glovebox floor and continuously purged with Ar. This environment was insufficient to prevent formation of an oxide dross at the top of the crucible with the Al-6061 bath, which reached a maximum thickness of approximately 0.15" (0.4 mm). No oxide dross was observed with the high-purity Al and a fiber-frax insulating blanket was placed over the crucible to compensate for the associated increase in heat losses. MgO crucibles, 2.25" (57.2 mm) in diameter and 5.0" (127 mm) deep were used to contain the molten Al with secondary containment provided by an outer 0.010" (0.25 mm) thick Ta crucible. New MgO crucibles and Al rods were used after each resolidification event to prevent reheat cracking of the Al-filled crucibles. A liquid volume of approximately 16 in³ (260 cc) was used, which would require complete dissolution of approximately 30 U specimens to surpass the equilibrium solubility of 2.0 at.% U in Al at 732 °C. Test temperatures were maintained at 700 °C, 800 °C, and 900 °C within 3 °C, monitored by a type-K thermocouple sheathed with Ta. The bath was unstirred although thermal gradients within the bath were measured as less than 1°C.

Prior to testing, the U and U-alloy specimens were acid cleaned in a 50% HNO₃/50% H₂O bath, forced-air dried, and stored in Drierite desiccant for no more than 24 h prior to testing. The threaded end of each test cylinder was suspended from matching stainless steel nuts attached coaxially to 0.065" (1.65 mm) stainless steel wires. Standard compression fittings were placed on each wire to control the effective wire length and fix the depth of specimen immersion at approximately 1.0" (25 mm) when moved between the upper and lower staging plates. The staging plates were fixed approximately 12" (300 mm) and 6" (150 mm) above the top of the crucible. Up to 4 specimens were immersed into the liquid bath simultaneously. Each specimen was removed from the bath individually after immersion times between 225 s and 7,200 s at 700°C, 56 s and 3600 s at 800°C, and 112 s and 1800 s at 900°C.

Each specimen was carefully sectioned transverse to the longitudinal axis at two locations, 0.25" (6.3 mm) and 0.5" (13 mm) from the immersed end, and mounted to maintain best perpendicularity with the plane of polish. On several of the specimens, the remaining ligaments were also cut longitudinally across the position of the liquid interface when immersed. Optical metallography was used to measure the diameter of the remaining U or U-alloy core, the thickness of any intermetallic layers, and the overall diameter after testing. Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) were used to characterize the composition of each distinct region of the reacted specimens and to identify the intermediate phase compositions. Vickers microhardness measurements, averaging five readings from each distinct reaction layer at a constant 100 g load, were also performed for selected U6Nb specimens exposed to 700 °C, 800 °C, and 900 °C Al-6061 baths.

RESULTS

Reaction Rates in Aluminum Alloy 6061.

Immersion of the U6Nb specimens in liquid Al-6061 resulted in a U6Nb core diameter which decreases linearly with time at 700 °C, 800 °C, and 900 °C, as summarized in Figure 2. The rate of decrease in specimen diameter is linear over the entire range of immersion times investigated, increasing from 0.00074 inch/min (0.019 mm/min) at 700 °C to 0.002 inch/min (0.050 mm/min) at 800 °C, and 0.0023 inch/min (0.058 mm/min) at 900 °C. For reference, the 0.125 inch (3.2 mm) diameter specimen was completely consumed in approximately 60 min at 800 °C. The temperature dependence of the reaction rates is complex, however, with rates increasing more rapidly between 700 °C and 800 °C, than between 800 °C and 900 °C.

At each test temperature, an intermetallic layer rapidly develops between the U6Nb core and the Al-6061 liquid. In Figure 3, the thickness of the intermetallic layer is seen to increase to approximately 0.004 inch (0.1 mm) within the shortest immersion times evaluated (224 s at 700 °C, 56 s at 800 °C, and 112 s at 900 °C). The layer thickness reaches a steady-state value of 0.005 inch (0.13 mm) within 60 min at 700 °C and within 1 min 800 °C, but continues to increase in thickness at 900 °C. A maximum thickness of approximately 0.010 inch (0.25 mm) was reached after 30 min at 900 °C.

At all three temperatures, the dissolution of the U6Nb core occurred uniformly, maintaining a roughly circular cross-section. No preferential penetration of liquid along grain boundaries or inclusion clusters was observed. The intermetallic layer adjacent to the U6Nb core was always single-phase in appearance and sufficiently brittle to contain cracks running through the thickness of the layer. The composition and morphology of the outer layers varied with test temperature.

For a test temperature of 700 °C, the progression of microstructural evolution with time is shown in Figure 4. Both the U6Nb core diameter and the adjacent intermetallic layer diameter decrease linearly with time. Meanwhile, the outer diameter of the specimens increase to approximately 0.2 inch (5 mm) within the first 30 min, as plotted in Figure 5. Similar results occur at 800 °C, as shown in the micrographs in Figure 6 and the plot in Figure 7. The rate of reaction at the two locations (0.2 inch and 0.5 inch from the specimen end) were indistinguishable and the values were averaged in the plotted data. This uniformity of reaction is consistent with the behavior observed in the longitudinal sections after 15 min at 700 °C and 800 °C, as shown in Figure 8. The extent of reaction is continuous for these specimens up close to the position of the liquid interface during immersion, with no undercutting at the position of the former liquid interface.

At 900 °C, the extent of reaction is uniform within large regions but is virtually absent from adjacent areas. The appearance of typical specimens after removal from the liquid bath at 700 °C, 800 °C, and 900 °C are compared in Figure 9. The build-up of Al-rich material on the outside of the specimens is

significantly greater for the tests at 700 °C and 800 °C than at 900 °C. In addition, large regions remained unaffected by immersion times of up to 30 min, maintaining the original specimen contour with no indications of liquid reaction. These "unwet" regions maintained the luster of the original specimen surfaces prior to immersion. In regions that were "wet" by the liquid, reaction rates appear uniform, and the data plotted was measured from these regions shown in Figure 10. In Figure 11, the U6Nb core, intermetallic layer, and outside diameters all decrease with immersion time at 900 °C, although the thickness of the intermetallic layer increased with time. Metallographic cross-sections of the "unwet" regions showed no indications of any reaction when viewed by optical microscopy but surface composition analysis by EDX revealed modification of the surface chemistry. The surface, as viewed in the SEM, consisted of microroughened patches scattered within a smooth matrix, as shown in Figure 12. Magnesium concentrations were highly elevated in both areas, while no other elements contained in the Al-6061 were present. The composition of the smooth region was measured as U-4.8 at.%Nb-13.3 at.%Mg, and the microroughened area as U-4.8 at.% Nb-24 at.% Mg. It is unclear whether the Mg was present as an oxide and whether the Mg is present as a thin layer of greater Mg concentration (e.g. thinner than the approximate 1 μ m thickness sampled by EDX).

Reaction Rates in High Purity Aluminum.

The behavior of U6Nb in high-purity Al liquid at 700 °C was evaluated for immersion times of 30 min and 60 min. The U6Nb core diameter decreased linearly with time at a rate slightly lower than that measured in Al-6061, as shown in Figure 13. The shape of the U6Nb core and the surrounding intermetallic layer remained uniformly circular in cross-section as shown in the optical micrographs in Figure 14. The intermetallic layer adjacent to the U6Nb core grew in thickness from 0.01 inch (0.25 mm) after 30 min to 0.018 inch (0.45 mm) after 60 min immersion, unlike the behavior in Al-6061 liquid at 700 °C in which the intermetallic layer thickness did not exceed 0.005 inch (0.13 mm). A single test at 800 °C for 30 min resulted in no remaining material below the immersion level. Note that a similar test in Al-6061 resulted in a residual U6Nb core diameter of 0.075 inch (1.9 mm).

The behavior of 99.9 wt.% depleted U-238 in high-purity Al was evaluated at 700 °C and 800 °C. Reductions in the core diameter at 700 °C occurred at rates 5 to 10 times faster in the unalloyed U than in U6Nb. The thickness of the intermetallic layer and the diameter of the residual U core varied from location to location resulting in irregular wavy/oval shaped cross sections as shown in the optical micrographs in Figure 15. Localized areas were unaffected for times up to 7.5 min at 700 °C, maintaining their original surface contour. Little to no Al-rich deposits were present outside of the intermetallic layer and the outside diameter, equal to the U core plus adjacent intermetallic layer only, continuously decreased with increasing immersion times. The intermetallic layer thickness' are greater than those for U6Nb in Al-6061 but similar to those for U6Nb in high-

purity Al. Minimum and maximum residual core diameters and intermetallic layer thickness' are plotted for each cross section in Figure 16. Considering the minimum residual core diameters, the rate of core diameter reduction decreases with increasing immersion time between 1 min and 15 min. A roughly linear fit to these values is achieved when plotting core diameter versus $(1/\sqrt{t})$. Specimens immersed for 30 min at 700 °C had no material remaining below the immersion level. At 800 °C, specimens with immersion times of 450 s, 225 s, 112 s, and 56 s had no material remaining below the immersion level. A single specimen immersed for 28 s visibly necked at the immersion level upon removal and dropped into the bath indicating a contribution of strength loss to specimen loss in the unalloyed U.

Microstructures of U-6 wt.%Nb in Al-6061 Liquid.

Exposure of U6Nb specimens to liquid Al-6061 rapidly resulted in the formation of an intermetallic layer adjacent to the U6Nb core. The interface between the intermetallic layer and the U6Nb core is macroscopically uniform but contains fingers of the core material extending approximately 10 μm beyond the advancing intermetallic interface, as shown for a 700 °C specimen after 30 min in Figure 17. Beyond this interface region, a single-phase, continuous intermetallic layer is present for all immersion times. At 700 °C and 800 °C, the outer diameter of the withdrawn specimens increased with increasing immersion time while the intermetallic layer thickness remained roughly constant. The constant thickness of the continuous intermetallic layer, and the decreasing U core diameter, require that the intermetallic break down along its outer diameter into Al-rich reaction products. Three distinct layers are observed outside of the continuous intermetallic region in Figure 17. The innermost of these layers consists of interconnected intermetallic (light phase) with a cellular/dendritic morphology within a two-phase matrix consisting of an intermediate phase (grey) and finely dispersed resolidified liquid (dark phase). The second layer consists of discontinuous intermetallic islands within a similar two-phase matrix with increased volume fraction of liquid. The outermost layer consists of clusters of intermetallic particles scattered within an Al-rich liquid. These layers remain roughly uniform in thickness for times of up to 15 min at 700 °C, but then break down by the macroscopic intrusion of Al-rich liquid at periodic locations around the perimeter. The Al-rich liquid extends into the first of the layers outside the continuous intermetallic layer and grows laterally to consume additional intermetallic within the two outer layers. The resulting cross-sections have an appearance resembling flowers with multiple petals which separate regions of liquid intrusion and extend in length with increased immersion time. This instability occurred only for times beyond 15 min at 700 °C and was not observed in the 800 °C or 900 °C tests.

Chemical compositions of each distinct layer or microstructural constituent, shown in Figure 17, are listed in Table I for a U6Nb specimen immersed 30 min at 700 °C. The U6Nb core contained only U and 12.5 at.% Nb (5.30 wt.% Nb). The adjacent single-phase intermetallic layer was approximately

75 at.% Al with 22 at.% U and 3.4 at.% Nb, which closely corresponds to $(\text{U})\text{Al}_3$ intermetallic present in the U-Al binary phase diagram (Fig. 1). The Al content in the continuous intermetallic increased at its outer diameter to approximately 80 at.%, which corresponds to the $(\text{U})\text{Al}_4$ phase. The Al content of the blocky white intermetallic present in the adjacent multiphase layer was also approximately 80 at.%. The second and third multiphase reaction layers had increasing overall Al concentrations and elevated concentrations of Si, which partitioned into the blocky white intermetallic phase. The grey phase consistently contained approximately 3 at.% U with elevated ratios of Nb/U (relative to the U6Nb core value of 0.14), increasing from 0.7 in the first multiphase layer to 1.0 in outer layer. The outermost region contained no detectable U in the resolidified liquid.

The individual reaction layers in a U6Nb specimen immersed 15 min at 800 °C are shown in Figure 18 and the chemical compositions are listed in Table II. The U6Nb core composition remained unaffected by the treatments. The adjacent intermetallic was enriched in Al relative to that formed at 700 °C, and constant at approximately 82 to 83 at.% Al through the thickness of the continuous intermetallic layer and extending into the outer multiphase layers. The composition fits within the solubility range postulated for $\text{U}_{0.9}\text{Al}_4$ (UAl_4) but is not predicted to exist above 732 °C (Fig. 1). The first multiphase layer consisted of interconnected intermetallic with a cellular/dendritic morphology and a two-phase dark/grey Al-rich matrix. Nb partitioning occurred within this layer with Nb/U ratios decreasing to 0.08 within the white intermetallic phase. As at 700 °C, the Nb/U ratios within the grey phase increased with increasing distance from the U6Nb core to as high as 1.2 in the outer layer. The second outer layer was multiphase with an average of 91 at.% Al. Blocky white particles of approximately 3 μm diameter were uniformly dispersed within this layer with a composition close to that present in the inner layers. The matrix consisted of either dark single-phase regions or two-phase regions containing dispersed grey precipitate. The uniformly dark matrix contained little-to-no U (measured as 0.1 at.% U) and was primarily Al (99.3 at.% Al). The two-phase matrix region contained 3.5 at.% U, which exceeds the solubility limit predicted in the U-Al system at 800°C (Fig. 1). The outermost region of this specimen consisted of 15 μm to 30 μm Al-rich cells (99.5 at.% Al-0.5 at.% Mg) separated by at least three distinct intercellular precipitates. Blocky white particles enriched in Si, and blocky grey particles with a high Nb/U ratio of 1.2 and containing 1.6 at.% Cr were approximately 5 μm in diameter, and a finely dispersed two-phase intercellular region contained an average composition of 94.8 at.% Al-0.8 at.% Mg-1.8 at.% U-1.8 at.% Nb-0.7 at.% Cr.

Microstructures and compositions of a U6Nb specimen immersed at 900°C for 7.5 min are shown in Figure 19 and in Table III, respectively. Outside of the U6Nb core was a thick intermetallic layer bordering a thin transition layer and an Al-rich matrix containing discontinuous particles. The thick intermetallic layer adjacent to the U6Nb core again contains a relatively high Al concentration of 82.0 at.%. A two-phase region at the outer diameter of the intermetallic layer, consisting of the interconnected intermetallic (white) penetrated by an Al-rich

phase (dark), is just 20 μm in thickness. It contains a high concentration of Si with an overall composition of 70.5 at.% Al-9.5 at.% Si-17.8 at.% U-2.3 at.% Nb. Bordering this transition layer is an Al-rich matrix containing discontinuous particles of a blocky grey phase and a blocky white phase. The grey phase again contains a high Nb/U ratio of 1.3 and approximately 1.6 at.% Cr, and the white phase contains a high Si content of 15.3 at.% and undetectable levels of Nb. The dark matrix was measured as 99.4 at.% Al- 0.6 at.% Mg.

Microstructures of U-6 wt.%Nb and Unalloyed-U in High-Purity Al Liquid.

Microstructures and compositions of a U6Nb specimen immersed in high-purity Al at 700 °C for 60 min are shown in Figure 20 and Table IV, respectively. The interface between the U6Nb core and the intermetallic layer is similar to that observed in Al-6061. The composition of the continuous intermetallic layer increases from 76.5 at.% at the interface to 82.0 at.% at the center of the layer and to 86 at.% at its outer diameter. Similar results were observed after only 30 min at 700 °C. The microstructure contained evidence of being multiphase with alternating elongated uniform white regions and grey regions containing a widely scattered dark precipitate near the outer diameter. Adjacent to this intermetallic layer, the Al is unsaturated with a U concentration of only 1.7 at.%. With increasing diameter, the Al concentration further increased and the U and Nb concentrations further decreased.

Microstructures and compositions of a 99.9 at.% U specimen immersed in high-purity Al at 700 °C for 15 min are shown in Figure 21 and Table V, respectively. A thin transition layer, 5 μm to 7 μm in thickness, was present between the pure U core and a thick intermetallic layer, and appears as a distinct phase. The composition of this transition layer was 78.7 at.% Al-21.3 at.% U. The thick intermetallic layer appeared continuous with a composition slightly richer in Al at 82 at.% Al-18 at.% U which is similar in composition to that formed in U6Nb in an Al- 6061 bath at 800 °C. Outside of the intermetallic layer, a thin region of Al-rich composition was present, measured as 98.9 at.% Al- 1.1 at.% U. Despite the low U concentration, some coring is evident, with solidification cells darker in contrast than the intercellular regions.

Microhardness Measurements.

The microhardness of distinct reaction layers were measured for U6Nb specimens immersed in Al-6061 at 700 °C, 800 °C, and 900 °C, and the results are presented in Table VI. The hardness of the U6Nb core showed a mild dependence upon heat treatment, increasing from 700 °C (151 HV) to 800 °C (188 HV) but decreasing to an intermediate hardness for 900 °C treatments (178 HV). The intermetallic layers adjacent to each core had extremely high hardness. The intermetallic formed at 700°C was the softest at 642 HV, increasing to 668 HV at 800 °C, and 698 HV at 900 °C. The outer region of the 900 °C intermetallic layer showed evidence of partial decomposition and the hardness decreased to 620 HV.

The two-phase region in the 700 °C specimen had a hardness of 488 HV decreasing to 177 HV in the outermost material. The 800 °C specimen also decreased in hardness with increasing diameter, decreasing to 542 HV in the inner multiphase region, to 213 HV in the outer multiphase region, and to 188 HV in the outermost material. The 900 °C specimen did not have a pronounced multiphase region containing a high-Al phase. The thin layer at the outside diameter had the lowest measured hardness at 92 HV, corresponding to the highest Al concentration of any area measured.

DISCUSSION

The rate of U6Nb dissolution in Al-6061 increased with increasing temperature, as expected by increased diffusion rates. However, the increase in dissolution rate between 700 °C and 800 °C was larger than between 800 °C and 900 °C. From Figure 3, it can be seen that at 900 °C the thickness of the intermetallic layer increases to approximately double the thickness at 700 °C and 800 °C. A thicker intermetallic layer is expected to decrease the rate of U and Al transport through the layer and slow the rate of U core dissolution. Thus the temperature dependence of the reaction rates is complex and cannot be readily extrapolated to higher temperatures without additional mechanistic understanding.

The rate of U6Nb core dissolution is also expected to be sensitive to the nature of the intermetallic phase which forms adjacent to the core, which influences solubility ranges and rates of diffusive transport. At 700 °C, a measured Al concentration of 75 at.% closely fits the stoichiometry of the UAl_3 phase present in the U-Al binary system (see Fig. 1). At 800 °C and 900 °C, the intermetallic adjacent to the U6Nb core contains approximately 82 at.% Al which is within the postulated solubility range for $U_{0.9}Al_4$ but which should be unstable below 732 °C according to the binary U-Al phase diagram. Thus either the phase diagram is in error, the phase equilibria are significantly modified by the alloying elements, or the intermetallic layer exists as two-phase liquid plus intermetallic at 800 °C and 900 °C. The uniformity of the intermetallic layer and the limited time for diffusive transformation and homogenization during cooling discount the possibility of a two-phase layer containing UAl_3 plus Al liquid adjacent to the U6Nb core. More likely is either an increased solubility range for UAl_3 relative to line compound predicted by the phase diagram, or the existence of an intermetallic of higher-Al content above 732 °C. Kiessling [2] reported the existence of a UAl_4 phase with an extended solubility range between $UAl_{4.5}$ and $UAl_{4.9}$, but which melts at 730 °C. The existence of a UAl_5 phase is in dispute, being listed as present in the phase diagram of Kassner et. al. [3] but of unknown composition and range of thermal stability. Positive identification of this and other reaction products could be determined by microdiffraction measurements using transmission electron microscopy, but was beyond the scope of this study.

The composition of the U was determined to be significant with respect to the reaction kinetics in liquid Al. The rate of U6Nb dissolution was similar, however, in high-purity Al and in Al-6061 at 700 °C. Therefore, the high rates of dissolution in unalloyed U relative to that of U6Nb can be attributed to the influence of Nb versus differences in the composition of the Al liquid. While the mechanism by which Nb reduces the rate of U alloy dissolution has not been modeled, it appears to be related to a change in the ability of the intermetallic layer to redissolve into the Al liquid. The net rate of U or U-alloy dissolution is dependent on intermetallic formation at the core/intermetallic interface and dissolution of the intermetallic into the liquid. The principal difference in the evolution of high-purity U in liquid Al at 700 °C is the nearly complete absence of a multiphase zone between the continuous intermetallic layer and the liquid Al bath. In U6Nb specimens, the intermetallic layer is bordered by a relatively thick multiphase region which typically consists of an intermetallic phase of similar Al concentration, an Al-rich grey phase enriched in Nb and exceeding the solubility of U in liquid Al, and a dispersed Al-rich liquid. Conversely, in the high-purity U, the continuous intermetallic layer is bordered by Al-rich liquid with a concentration of 98.9 at.% Al (see Table VI). It thus appears that the limited solubility of Nb in liquid Al reduces the rate of intermetallic dissolution into the liquid, resulting in thick multiphase regions bridging the liquid from the continuous intermetallic layer and the U6Nb core. The finely dispersed liquid within these regions is expected to reduce the rate of U transport and reduce the rates of core thinning.

The diameter of the U6Nb core was seen to decrease linearly with liquid immersion time, as shown in Figures 2 and 12. Mechanistically, a simple diffusion-controlled reaction is expected to result in a decrease in core diameter which is proportional to the square root of the immersion time [4,5]. The linear dependence observed indicates that the rate of transformation is interface controlled instead of diffusion controlled. Typically, interface-controlled growth rates are observed only where interfaces are coherent or semi-coherent. Another possibility is that the growth of U-Al intermetallics are restricted by their low solubility ranges, and by their related limitations on favorable interface compositions related to their ordered structures.

Despite the formation of a continuous intermetallic layer adjacent to the (U) core, the rates of (U) dissolution can be relatively aggressive. Therefore, it is especially noteworthy that, at 900 °C, much of the specimen surface contour remained unaltered. The fact that, after immersion for up to 30 min at 900 °C, the surface composition in these areas remained absent of any detectable aluminum indicates that surface treatments may be effective in protecting U alloys. Surface composition analysis of the protected areas revealed the presence of abnormally high Mg concentrations of up to 24 at.%. Coupled with this finding was a depletion of Mg in the Al-rich liquid attached to the outer diameter of the attacked regions supported by a reduction in hardness typical of higher-purity Al. It is likely that the Mg concentrated within the slag formed at the liquid surface by preferential oxidation due to its high vapor pressure and affinity for oxygen. Specimens inserted through this Mg-rich zone could have become

coated with Mg vapor or Mg oxide and provided a surface which is not "wet" by liquid Al. It is well known that MgO is resistant to attack by liquid Al, which makes it a common selection as a crucible material for liquid Al containment. The effectiveness of surface coatings including native oxides in improving the resistance to liquid attack was not evaluated here and would require additional testing.

CONCLUSIONS

Immersion tests of U-6wt.% Nb (U6Nb) in unsaturated Al-alloy 6061 liquid at 700 °C, 800 °C and 900 °C provide the data necessary to assess the integrity of U6Nb components subjected to such environments. The influence of minor alloying element additions have been elucidated through microchemical analysis of reaction products and through comparative tests of unalloyed U and U6Nb in high-purity Al liquid. Specific conclusions are listed below:

- 1). The diameter of U6Nb test cylinders immersed in unsaturated Al-6061 decrease linearly with time at 700 °C, 800 °C, and 900 °C at rates of 0.019 mm/min, 0.050 mm/min, and 0.058 mm/min, respectively.
- 2). Immersion of U or U6Nb in an unsaturated liquid Al bath results in the formation of a continuous intermetallic layer bridging the U core and the Al-rich liquid. At 700 °C, the composition of the intermetallic layer closely matches the stoichiometry of UAl_3 , while at 800 °C and 900 °C, the composition of the intermetallic layer closely matches that of UAl , the existence of which has not been verified in published phase diagrams.
- 3). The dissolution of the U6Nb core occurs by advance of the intermetallic by solid state diffusion, while the intermetallic layer redissolves into the liquid Al within a transition layer containing dispersed Al liquid. The thickness of the continuous intermetallic layer reaches a steady state value of 0.13 mm at 700 °C and 800 °C, but continues to thicken at 900 °C, reaching a thickness of 0.25 mm after an immersion time of 30 min.
- 4) In high-purity Al at 700 °C, the rate of U-6wt% Nb reaction is similar to its behavior in Al-6061, while unalloyed U thins at rates up to 10 times that of U-6wt.% Nb.
- 5) The influence of Nb in reducing the rate of U core thinning appears related to the formation of a thick transition layer composed of the adjacent intermetallic layer constituent, a Nb-enriched phase, and a dispersed U-saturated Al liquid. This transition layer is absent in unalloyed U and results in unsaturated Al liquid adjacent to the intermetallic layer, which is expected to speed the transport of U out of the intermetallic layer.

6) U6Nb reaction with liquid Al-6061 was completely suppressed at 900 °C in large regions of the specimen surfaces by an absence of liquid "wetting" of these surfaces which contain highly elevated Mg levels.

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Table I. Chemical Composition of Reaction Products for U6Nb Immersed in Liquid Al-6061 at 700 °C for 30 min.

Region	Chemical Composition, At.% (by EDS spectroscopy)					
	U	Nb	Al	Mg	Si	Other
core	87.5	12.5	-	-	-	-
continuous intermetallic (IM) layer, average	21.9	3.4	74.7	-	-	-
IM layer ID	22.0	4.3	73.8	-	-	-
IM layer center	20.5	2.9	76.6	-	-	-
IM layer OD	17.7	2.7	79.6	-	-	-
average of 1st outer layer	9.2	1.4	89.4	-	-	-
blocky white phase	20.9	-	79.1	-	-	-
two-phase dark/grey matrix	2.7	1.9	94.6	0.8	-	-
dark matrix	-	-	99.6	0.4	-	-
average of 2nd outer layer	4.1	1.0	92.2	-	2.7	-
large white blocky particle	22.0	-	65.7	-	12.3	-
grey matrix	3.1	2.8	92.8	0.9	-	0.4 Fe
dark area	-	-	99.5	0.4	-	-
average of 3rd outer layer	0.9	0.4	96.2	0.8	1.2	0.2 Cr, 0.2 Fe
white intercellular elongated particle	7.0	-	81.1	-	11.9	-
blocky grey phase	3.0	3.1	90.9	1.1	-	1.8 Cr
dark matrix	-	-	99.1	0.9	-	-

Table II. Chemical Composition of Reaction Products for U6Nb Immersed in Liquid Al-6061 at 800 °C for 15 min.

Region	Chemical Composition, At.% (by EDS spectroscopy)					
	U	Nb	Al	Mg	Si	Other
core	87.7	12.3	-	-	-	-
continuous intermetallic (IM) layer	15.4	2.7	81.9	-	-	-
IM layer, ID	15.6	2.5	81.9	-	-	-
IM layer, center	15.3	2.6	82.1	-	-	-
IM layer, OD	15.3	2.5	82.2	-	-	-
1st outer layer, blocky white phase	16.3	0.5	83.2	-	-	-
1st outer layer, two-phase interparticle area	7.2	2.7	90.1	-	-	-
average of 2nd outer layer	5.8	1.2	91.1	-	1.8	-
blocky white phase	16.8	0.9	82.3	-	-	-
blocky grey particle	5.0	3.6	86.7	-	-	2.7 Cr
dark interparticle matrix	1.8	0.4	97.8	-	-	-
two-phase interparticle matrix	3.5	0.5	95.9	-	-	-
average of 3rd outer layer	1.4	1.2	96.8	-	-	0.5 Cr
blocky grey particle	4.9	6.2	87.3	-	-	1.6 Cr
two-phase interparticle matrix	1.8	1.9	94.8	0.8	-	0.7 Cr
dark interparticle matrix	-	-	99.5	0.5	-	-

Table III. Chemical Composition of Reaction Products for U6Nb Immersed in Liquid Al-6061 at 900 °C for 7.5 min.

Region	Chemical Composition, At.% (by EDS spectroscopy)					
	U	Nb	Al	Mg	Si	Other
continuous intermetallic (IM) layer	15.8	2.8	79.8	-	1.6	-
IM layer, ID	15.8	2.7	81.5	-	-	-
IM layer, center	15.2	2.8	82.0	-	-	-
IM layer, OD	12.4	2.7	76.8	-	8.0	-
average of 20 μ m thick two-phase layer	17.8	2.3	70.5	-	9.5	-
outer layer average	2.4	2.5	93.7	-	1.1	-
blocky white particle in outside layer	16.3	-	68.3	-	15.3	-
grey phase in outside layer	3.1	4.1	91.1	-	-	1.6 Cr
dark matrix in outside layer	-	-	99.4	0.6	-	-

Table IV. Chemical Composition of Reaction Products for U6Nb Immersed in High-Purity Liquid Al at 700 °C for 60 min (30 min data included).

Region	Chemical Composition, At.% (by EDS spectroscopy)					
	U	Nb	Al	Mg	Si	Other
core	86.2	13.8	-	-	-	-
continuous intermetallic layer	15.1	3.1	81.8	-	-	-
IM layer, ID	21.2	2.3	76.5	-	-	-
IM layer, center	15.0	2.6	82.3	-	-	-
IM layer, OD	11.9	2.3	85.8	-	-	-
IM layer, ID (700°C/30min)	(15.0)	(2.6)	(82.4)	-	-	-
IM layer, center (700°C/30min)	(15.0)	(2.6)	(82.3)	-	-	-
IM layer, OD (700°C/30min)	(12.4)	(2.1)	(85.5)	-	-	-
average of 1st two-phase layer	1.7	1.4	96.8	-	-	-
outside region	0.9	0.8	98.3	-	-	-

Table V. Chemical Composition of Reaction Products for Unalloyed U Immersed in High-Purity Liquid Al at 700 °C for 15 min.

Region	Chemical Composition, At.% (by EDS spectroscopy)					
	U	Nb	Al	Mg	Si	Other
core	100	-	-	-	-	-
5 μm thick intermetallic layer	21.3	-	78.7	-	-	-
intermetallic layer	18.0	-	82.0	-	-	-
outside region	1.2	-	98.8	-	-	-

Table VI. Microhardness of U6Nb After Immersion in Liquid Al-6061.

Treatment	Vickers Diamond Pyramid Microhardness (100 g load)			
	core	intermetallic layer	two-phase region(s)	outside region (Al-rich)
700 °C/15 min	151	642	488	177
800 °C/15 min	188	668	542 / 213	188
900 °C/15 min	178	698 / 620	-	92

Figure 1. U-Al binary phase diagram [3].

Figure 2. U6Nb core diameter vs. time of exposure to liquid Al-6061.

Figure 3. Thickness of the single-phase intermetallic layer formed adjacent to the U6Nb core vs. time.

(a)

(b)

Figure 4. Cross-section of U6Nb cylinders after exposure to Al-6061 at 700 °C for: (a) 3.75 min, (b) 7.5 min, (c) 15 min, (d) 30 min, (e) 60 min, (f) 120 min. (20X)

(c)

(d)

Figure 4. Cross-section of U6Nb cylinders after exposure to Al-6061 at 700 °C for: (a) 3.75 min, (b) 7.5 min, (c) 15 min, (d) 30 min, (e) 60 min, (f) 120 min. (20X)

(e)

(f)

Figure 4. Cross-section of U6Nb cylinders after exposure to Al-6061 at 700 °C for: (a) 3.75 min, (b) 7.5 min, (c) 15 min, (d) 30 min, (e) 60 min, (f) 120 min. (20X)

Figure 5. U6Nb core and reaction layer diameters vs. time of exposure to Al-6061 at 700°C.

(a)

(b)

Figure 6. Cross-section of U6Nb cylinders after exposure to Al-6061 at 800 °C for: (a) 56 sec, (b) 3.75 min, (c) 15 min, (d) 30 min. (20X)

(c)

(d)

Figure 6. Cross-section of U6Nb cylinders after exposure to Al-6061 at 800 °C for: (a) 56 sec, (b) 3.75 min, (c) 15 min, (d) 30 min. (20X)

Figure 7. U6Nb core and reaction layer diameters vs. time of exposure to Al-6061 at 800°C.

Figure 8. Longitudinal sections of the U6Nb specimens bridging the position of the Al-6061 liquid immersion level: (a) 700 °C/15 min, (b) 800 °C/15 min. (20X)

(b)

(a)

Figure 9. Macrophotograph of the specimens as-removed from the liquid bath; left to right: 700 °C/120 min, 800 °C/30 min, 900 °C/3.75 min, 900 °C/7.5 min, 900 °C/30 min.

(a)

(b)

Figure 10. Cross-section of U6Nb cylinders after exposure to Al-6061 at 900 °C for: (a) 112 sec, (b) 3.75 min, (c) 7.5 min, (d) 30 min. (20X)

(c)

(d)

Figure 10. Cross-section of U6Nb cylinders after exposure to Al-6061 at 900 °C for: (a) 112 sec, (b) 3.75 min, (c) 7.5 min, (d) 30 min. (20X)

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(a)

(b)

Figure 14. Cross-section of U6Nb cylinders after exposure to high-purity Al at 700 °C for: (a) 30 min, (b) 60 min. (25X)

(a)

(b)

Figure 15. Cross-section of unalloyed U cylinders after exposure to high-purity Al at 700 °C for: (a) 112 sec, (b) 3.75 min, (c) 7.5 min, (d) 15 min. (25X)

(c)

(d)

Figure 15. Cross-section of unalloyed U cylinders after exposure to high-purity Al at 700 °C for: (a) 112 sec, (b) 3.75 min, (c) 7.5 min, (d) 15 min. (25X)

Figure 16. Unalloyed U core and reaction layer diameters vs. time of exposure to high-purity Al at 700 °C.

(a)

(b)

Figure 17. Cross section of U6Nb exposed to Al-6061 at 700 °C for 30 minutes (secondary electron images). Regions selected for chemical composition analysis are shown: (a) composite image showing U6Nb core (bottom), continuous intermetallic layer (area 4), first (area 3), second (area 2), and third (area 1) outer layers; (b) left-to-right are the U6Nb core, continuous intermetallic layer, and first outer layer.

(c)

(d)

Figure 17. Cross section of U6Nb exposed to Al-6061 at 700 °C for 30 minutes (secondary electron images); (c) left to right are the first outer layer and second outer layer, (d) first outer layer

(e)

(f)

Figure 17. Cross section of U6Nb exposed to Al-6061 at 700 °C for 30 minutes (secondary electron images); (e) second outer layer, (f) third outer layer (Al matrix with intermetallic particle clusters).

(a)

(b)

Figure 18. Cross section of U6Nb exposed to Al-6061 at 800 °C for 15 minutes (secondary electron images). Regions from individual reaction layers selected for chemical composition analysis are shown (18 a-f); (a) left to right are the U6Nb core, continuous intermetallic layer, first and second outer layers, (b) U6Nb core and carbide inclusion.

(c)

(d)

Figure 18. Cross section of U6Nb exposed to Al-6061 at 800 °C for 15 minutes (secondary electron images), (c) continuous intermetallic layer, (d) first outer layer.

(e)

(f)

Figure 18. Cross section of U6Nb exposed to Al-6061 at 800 °C for 15 minutes (secondary electron images), (e) second outer layer, (f) third outer layer.

(a)

(b)

Figure 19. Cross section of U6Nb exposed to Al-6061 at 900 °C for 7.5 minutes (secondary electron images). Regions from individual reaction layers selected for chemical composition analysis are shown (19 a-c), (a) right to left are U6Nb core, continuous intermetallic layer, thin two-phase layer, and outer layer, (b) two-phase layer (center).

(c)

Figure 19. Cross section of U6Nb exposed to Al-6061 at 900 °C for 7.5 minutes (secondary electron images), (c) outer layer.

(a)

Figure 20. Cross section of U6Nb exposed to high-purity Al at 700 °C for 30 minutes (secondary electron images). Regions from individual reaction layers selected for chemical composition analysis are shown (20 a-c), (a) U6Nb core, continuous intermetallic layer, and multiphase layer.

(b)

(c)

Figure 20. Cross section of U6Nb exposed to high-purity Al at 700 °C for 30 minutes (secondary electron images), (b) continuous intermetallic layer, (c) multiphase layer.

(a)

(b)

Figure 21. Cross section of unalloyed U exposed to high-purity Al at 700 °C for 15 minutes (secondary electron images). Regions from individual reaction layers selected for chemical composition analysis are shown (21 a-d), (a) U core, intermetallic layer, and outer region, (b) U core.

(c)

(d)

Figure 21. Cross section of unalloyed U exposed to high-purity Al at 700 °C for 15 minutes (secondary electron images), (c) thin intermetallic layer, (d) continuous intermetallic layer.