FORMATION OF PU AMORPHOUS ALLOYS OR
METASTABLE STRUCTURES IN PU-FE, PU-TA, PU-SI ALLOYS*

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SUMMARY

Sputter deposition technique was used to study the possible formation of amorphous structures in Pu-Fe, Pu-Ta, and Pu-Si systems. A triode sputtering system, employing a split target configuration of pure alpha Pu and a selected solute element, was used to prepare sputtered coatings: 13 to 59 atomic percent (a/o) Fe, 10 to 50 a/o Si, and 15 to 65 a/o Ta. The compositions were determined by Energy Dispersive Spectroscopy (EDS) and microprobe measurements. The structure of the coatings was determined by x-ray diffraction techniques. The temperature stability of the obtained structures was determined by Differential Scanning Calorimetry (DSC) measurements. The Pu-Fe and Pu-Si binary systems showed strong evidence for the formation of amorphous phases in the sputtered coatings. In addition, the x-ray analyses indicated the presence of Pu₆Fe in the 13 to 20 a/o Fe range of Pu-Fe alloys and no apparent crystalline phases over the entire 10 to 50 a/o Si range of Pu-Si alloys. In the Pu-Ta system, the DSC data obtained for compositions below 50 a/o Ta did not show typical crystallization exotherms. At compositions above 50 a/o Ta, a metastable bcc alpha Ta structure was observed with an expanded lattice parameter. The calculated volume expansion (2.9%) corresponds to 29 a/o of Pu in solid solution if the lattice parameter is assumed to follow Vegards Law. After storage in a nitrogen glovebox atmosphere for over two years, the Pu-Si and Pu-Ta coatings have maintained a metallic luster and have shown no visible evidence of surface oxidation.

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INTRODUCTION

Sputter deposition is an attractive technique that is being used increasingly for preparing wide ranges of both stable and metastable alloys in the form of coatings. The "triode," when used for this purpose, allows fabrication of thick deposits (0.1-5 mm). In addition, a range of continuously changing compositions across the surface can be deposited if a composite target is used. This approach therefore greatly facilitates studies of metastable alloys, particularly in highly reactive systems such as those based on Pu, because it eases the problems associated with the handling and characterization.

Metastable and amorphous alloys of Pu with the elements Mn, Fe, Co, Ni, Cu, and Ru have been prepared previously by liquid quenching (LQ) technique. An amorphous Pu 0.625 Ga 0.375 alloy was also produced by a large dose neutron irradiation. Earlier investigators have reported the occurrences of metastable structures in several alloys of Pu with Ti, Ga, and Ce following liquid quenching, and in Pu with Ga, Ta, Ag, and Co following high-rate sputtering.

In the present paper we report on the application of high-rate sputtering technique for alloys of Pu in the Fe, Ta, and Si. Samples of thickness between 0.05 and 0.2 mm were obtained in the form of deposits with slowly varying composition across the surface and covering a range of several atomic percent in each system. The ranges of amorphous phase formation in Pu-Fe alloys were found to be more extensive than those reported previously following the LQ technique. In addition, we report here new wide ranges of amorphous or metastable phase formation in the systems Pu-Si and Pu-Ta.

EXPERIMENTAL TECHNIQUES

Sputtered deposits of gradually changing composition were prepared by high-rate triode sputtering from a split-target of plutonium (Pu) and a selected solute element. Two different triode sputtering systems were used to prepare deposits for this study. The first triode system was a commercial Plasmax Model 130 (L.M. Simard Inc.) that was subsequently replaced with a system designed at the Pacific Northwest Laboratory. The latter system is
described here in more detail because all the prepared deposits were made with both systems. The split sputtering targets were made from rectangular bars, of dimensions 28.6-by-1.3-by-6.4-mm thick or from 47-mm-diameter half disk pieces of elemental Pu and the selected solute element. The two pieces were clamped side-by-side in a Cu water cooled target holder. The elemental Pu pieces were cast and machined into the appropriate shape. The purity of the Pu used was at least "three nines," with typical analyses between 99.95 and 99.97 (major impurities being 200 Ni, 90 Mg, 50 C, 40 Fe, 30 Al, and 10 ppm Si by weight). The solute elements used for the other half of each target were also at least 99.9 wt% pure.

For deposition, Al substrates circular in shape (50.8 and 57.2 mm in diameter) were situated parallel to the target at a distance of 25.4 mm. They were directly water cooled and the temperature at the back surface of each substrate was monitored with a thermocouple. It ranged from 15 to 18°C during sputtering. The sputtering chamber was evacuated to \(4 \times 10^{-6}\) Torr with a turbopump, backfilled with purified research grade krypton (Kr) gas, and then continuously pumped through an automatically controlled leak valve to maintain a Kr gas pressure between \(2-3 \times 10^{-3}\) Torr. The Al substrates were initially sputter etched for 10 minutes at 100 volts before the target was sputtered at 600 volts. Current densities on the target were typically 11 mA/cm\(^2\) but were varied between 6 and 14 mA/cm\(^2\). All the power supplies had current limiting controllers placed in their electrical circuits to reduce the possibility of arc formation. The substrate was electrically isolated from the system, and it acquired a negative potential between 25 and 30 volts during sputtering. Seven deposits (for the three systems studied) were made at deposition rates between 2000 and 4000 A/min.; their final thickness ranged between 0.05 and 0.20 mm. All sputtered samples were produced by continuous deposition which typically lasted between 4 and 8 hours.

**SAMPLE CHARACTERIZATION**

Initial characterization of the sputtered deposits involved x-ray diffraction of the sputtered surface at the center and at the Pu rich and solute rich edges of each sample. X-ray patterns were obtained with a commercial Philips x-ray diffractometer adapted for automated use at LLNL.
and using a graphite monochromatized CuK radiation. The varying compositions of the coated substrate surfaces were measured using a Kevex Model 0800 x-ray Energy Dispersive Spectrometer (EDS) system. Compositions were measured on a 2.5-to-5.0-mm grid over the entire surface of each coated substrate. A 5-mm section in the center of the substrate sample (between the Pu rich and the solute rich edges) was removed for metallography and microprobe analysis to confirm independently the compositional profile and to verify that there was no compositional gradient across the thickness of the deposits.

Thermal analysis of selected deposits was performed using a Perkin Elmer Differential Scanning Calorimeter (DSC). In some cases, samples were sealed in Al capsules to prevent oxidation. Scans were obtained in purified helium in the range between 30 and 400°C at a heating rate of 40°C/min. Second and third scans obtained after cooling back to 25°C confirmed that crystallization (and endothermic recovery) had occurred during the first scan. Appropriate Pu metallography methods were used to prepare samples for the electron microprobe measurements.

COMPOSITION OF SAMPLES

The compositional profiles of Pu and respective solute element being co-sputtered can be estimated from the individual element sputtering yields and assuming a Knudsen cosine law for deposition. A calculated profile for a Pu-Ta deposit and the actual chemical composition of Ta as measured by the x-ray EDS analysis are shown in Fig. 1. In the calculated profile derivation it was assumed that the ejected sputtered atoms followed a \( \cos \theta \) distribution and that the effective sputtering yields were \( S = 1.49 \) atoms/ion for Pu and \( S = 0.77 \) for the solute element Ta.

A more accurate prediction of the deposition profiles than that shown in Fig. 1 would necessitate an accurate knowledge of the true angular distribution of the sputtered atoms which is known to change with target voltage and with atomic mass. It would also be necessary to account for "cross contamination" between half targets, which could significantly affect
the sputtering yields. This effect is illustrated in Fig. 2 for another Pu-Ta sputtering experiment. Part of the Pu target, adjacent Ta half piece target, was found to contain Ta (EDS).

The compositional ranges for each of the three systems studied are shown in Fig. 3 below the corresponding phase diagrams. These compositions were determined by EDS and microprobe measurements. In the present work, XRD and DCS experiments were performed on samples (i.e. portions of a continuous deposit) which varied in composition. Therefore individual composition values refer to mean compositions of approximately 2-3 a/o.

RESULTS AND DISCUSSION

X-RAY DIFFRACTION

Pu-Fe System

X-ray diffraction (XRD) patterns exhibit rather broad, low intensity peaks characteristic of an amorphous structure. XRD patterns for a specific deposit (Exp 34) are shown in Fig. 4. The first peak at 2θ = 28.6 can be shown to correspond to the (111) peak of the fcc PuO₂ oxide present on the surface of the deposit. The additional relatively sharp peaks in the x-ray pattern from the 22 atomic percent (a/o) Fe composition correspond to the Pu₆Fe phase. The presence of the crystalline Pu₆Fe phase, with an amorphous phase, was noted at compositions between 13 and 25 a/o Fe but no crystalline phases were observed in sputtered deposits between 25 and 59 a/o Fe.

Calculation of an "effective particle size," using the Scherrer equation for the first broad maximum in the diffraction patterns, yielded a value between 12-15 Å. We conclude from this that the material may be regarded as amorphous.

The first diffuse maximum and its Bragg angle position can also be used to estimate the nearest neighbor distances (NND), using the Ehrenfest formula. The calculated NND for the Pu-Fe alloys decreased from 3.14 Å to 3.00 Å for compositions between 22 and 50 a/o Fe. Earlier work¹ by LQ technique produced amorphous phases in the eutectic region (15-20 a/o Fe). Here by the use of vapor quenching (VQ) technique, we are not limited to eutectic compositions and can extend the range for amorphous compositions over compound regions. In fact the maximum, Fe rich, composition that can be produced by sputtering has yet to be determined.
Pu-Si System

XRD patterns for two Pu-Si deposits (18 and 35 a/o Si) are shown in Fig. 5. Similar patterns were obtained for compositions between 18 and 48 a/o Si and they confirm that these deposits also are amorphous. These coatings were found to be very oxidation resistant as evidenced by the lack of a broad Pu oxide peak normally observed at $2\theta = 28.6$ degrees. The NND results (for compositions between 18 and 43 a/o Si) indicate an increase from 3.18 to 3.30 Å.

Pu-Ta System

XRD patterns for two Pu-Ta deposits (21 and 36 a/o Ta) are shown in Fig. 6. These deposits also appear to be amorphous although the width of the first maximum in each case is somewhat narrower than the two other systems studied and the calculated "effective particle size" is between 16 and 20 Å. The diffraction lines appearing in the 50 a/o Ta deposit (Fig. 7) correspond to an expanded bcc alpha Ta lattice. The calculated lattice expansion of 2.9% for the metastable bcc phase corresponds to approximately 30 a/o Pu in solid solution, assuming that Vegards law can be applied. The calculated NND values indicate only a little change from 3.13 to 3.05 Å for compositions between 24 and 50 a/o Ta.

Earlier work\(^1\) by sputtering indicated that a Pu-8 a/o Ta deposit had an expanded lattice corresponding to 0.85% and that heat treatment at 700°C was required to get the lattice parameter to collapse. For Pu-5 and 10 a/o Ta sputtered deposits\(^5\) a metastable strained β was reported that remained stable up to 300°C (10 a/o Ta) in DTA experiments.

THERMAL STABILITY

Differential scanning calorimeter (DSC) data were taken for Pu-Fe, Pu-Si and Pu-Ta alloys. The XRD pattern for the 25 a/o Fe sample (Exp 34) and the resulting DSC scans (from the same sample) are shown in Fig. 8. On heating the glass transition endotherm at approximately 107°C is followed by the crystallization exotherm with a peak temperature of 125°C. For a second sputtered deposit (Exp 32), crystallization temperatures (Tc) between 230 and 250°C were observed for compositions between 20 and 40 a/o Fe. XRD patterns
taken after DSC scans showed the presence of Pu$_6$Fe, PuFe$_2$, and Pu oxides. The XRD pattern for the Pu-18 a/o Si sample and the resulting DSC scans, showed a clear crystallization peak at 208°C (Fig. 9). An XRD pattern after DSC showed the presence of delta phase Pu and Pu$_5$Si$_3$. The DSC data for the 25 to 63 a/o Ta compositions did not show sharp crystallization exotherms. An example for the 25 a/o Ta composition is shown in Fig. 11. The broad exotherm could represent the relaxation of the amorphous phase prior to crystallization; some processes related to solute partitioning; or the release of energy from a highly strained material. The DSC scan for the 63 a/o Ta composition most likely shows precipitation of Ta from supersaturated Pu-Ta solid solution over a relatively broad range.

The XRD peak intensities for the Ta-Pu samples after DSC were weak, except for the 63 a/o Ta deposit. For this Ta rich composition, it was possible to calculate the expanded Ta lattice which had decreased from 3.40 to 3.36 Å. The second DSC scans on reheating show no evidence for the transformations of alpha or beta Pu at temperatures up to 320°C where small endotherms were observed. Based on thermal stability results for the Pu-5 to 10 a/o Ta and Pu-92 a/o Ta compositions it appears likely that the maximum temperature of the DSC scans (427°C) was insufficient to reveal crystallization.

OXIDATION

The Pu-Si and Pu-Ta coatings were stored in nitrogen filled gloveboxes and have been exposed many times to an air environment over the past two years. The surfaces showed no visible evidence of oxidation and have retained their silver metallic luster. By contrast, the Pu-Fe coatings formed thin adherent oxide films that displayed different shades of brown depending upon the compositions. The oxide film, noted in XRD patterns (Pu-Fe alloys) as a relatively-broad diffraction peak at 28.6 degree 2θ (see Fig. 4), appears to be protective since a pure alpha Pu coating obtained for comparison was found to become completely oxidized in the same environment. Exposure of selected compositions from these three systems to one Torr water vapor at 90°C for 270 hours did not result in any oxidation of the coatings.
CONCLUSIONS

The results of this study clearly illustrate that sputtering can be used to prepare thick deposits of amorphous Pu alloys over extended compositional ranges compared to conventional liquid quench techniques. Limited characterization of these new amorphous alloys indicate improved corrosion behavior similar to other conventional amorphous metal alloys. In addition, we have formed a crystalline, metastable Pu-Ta solid solution containing up to 30 a/o Pu.

REFERENCES


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Figure 1. Calculated composition and measured Ta content (atomic percent by x-ray EDS and microprobe techniques) as a function of position on the substrate.

Figure 2. Scanning electron micrographs of Pu target surface that was poisoned with Ta from adjacent Ta split target.
Figure 3. Composition ranges investigated with split target and phases found in sputtered deposits shown below constitutional diagrams of Pu systems studies.
Figure 4. XRD patterns for sputtered deposits (varying between 22 and 50 a/o Fe) prepared from a split alpha Pu-Fe sputtering target (Exp 34).
Figure 5. XRD patterns for sputtered deposits (18 and 35 a/o Si) from a split alpha Pu-Si sputtering target.

Figure 6. XRD patterns for sputtered deposits (24 and 36 a/o Ta) from a split alpha Pu-Ta sputtering target.
Figure 7. XRD pattern for Pu-50 a/o Ta sputtered deposit which compares 2θ values for alpha-Ta (labeled with "l's") with diffraction peaks for expanded alpha-Ta (2.9%) from Pu solubility in Ta.
Figure 8. XRD pattern for a 25 a/o Fe sample and resulting DSC scans.
Figure 9. XRD pattern for an 18 a/o Si sample and resulting DSC scans.
Figure 10. DSC scans for Pu-25 a/o Ta and Pu-63 a/o Ta compositions heated from 50 to 427°C.

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