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SOLID STATE REACTION OF Al AND Zr IN Al/Zr MULTILAYERS: A CALORIMETRY STUDY

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ABSTRACT

The exothermic, solid state reaction of Al and Zr has been studied in thick Al/Zr multilayers using Differential Scanning Calorimetry and X-ray diffraction. The multilayer samples were magnetron sputter deposited into highly textured alternate layers of Al and Zr with nominal composition Al_3Zr. The samples used in this study were 47μm thick with a 427Å period. When samples were isochronally scanned from 25°C to 725°C, a large exotherm at ~350°C was followed by one or two smaller exotherms at ~650°C. The first exotherm is dominated by a diffusion based reaction of Al and Zr that produces two phases in isochronal scans: amorphous Al-Zr and cubic Al_3Zr, and two additional phases in isothermal anneals: Al_2Zr and tetragonal Al_3Zr. The exothermic heat from this multi-phase reaction is measured using isochronal scans and isothermal anneals, and the heat flow is analyzed using a 1-D diffusion based model. An average activation energy and a diffusion constant are determined. In the isothermal scans, the total exothermic heat increases linearly with $\sqrt{\text{time}}$, and layer thicknesses vary linearly with heat.

INTRODUCTION

Solid state reactions (SSRs) have been studied in a wide variety of multilayer materials [1-3]. The typical nano-scale dimensions of these layered materials make them ideally suited for thermodynamic and kinetic investigations. The small thicknesses of the individual layers provide short diffusion distances and high interface densities which in turn reduce the time and temperature needed to complete reactions in the solid state. SSRs can be thermally characterized in multilayer materials at relatively low temperatures using differential scanning calorimetry (DSC). The measurements are quantitative, and they are free of environmental contamination. Two types of DSC measurements are commonly used: isochronal scans and isothermal anneals. The data from these experiments can be used to determine the heats and the kinetics of the SSRs. Clevenger and coworkers [4] studied silicide formation in Ni/Si multilayer films, Highmore and coworkers [5] determined activation energies and pre-exponential factors for interdiffusion of Ni and Zr in amorphous NiZr, and Weihs, Barbee and Wall [6, 7] measured heats and activation energies for Cu/Zr multilayers.

This paper focuses on SSRs in the Al/Zr system, and it is part of a much larger project designed to investigate SSRs in a variety of binary and ternary transition metal systems using multilayer materials [8]. Here, differential scanning calorimetry and X-ray diffraction are used to characterize the heats, the rates, and the products of SSRs in Al-rich Al/Zr multilayers. Free-standing, Al/Zr multilayer foils with Al_3Zr stoichiometry were isochronally scanned to high temperatures (725°C) to determine the heats and temperatures of the exothermic reactions. The kinetics of the first and largest reaction were then studied using isothermal experiments and a 1-D diffusion model. Activation energies and diffusion constants were quantified, and they are compared to literature values obtained from bulk samples. The crystal structures of the foils were determined using symmetric X-ray diffraction (XRD) scans, and variations in crystal phases and layer thicknesses were characterized.

EXPERIMENTAL PROCEDURES

Multilayer foils were magnetron sputter deposited onto 27 inch diameter octagonal float glass substrates that were rotated above Al and Zr targets in a planetary fashion. The rate of rotation and the power applied to the sputtering guns determined the amount of material that was deposited in each rotation and therefore in each layer. The thickness of each layer (and the foil) varied with position on the substrate. The thickest part is a few inches from the center of the

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substrate and the thinnest section is on the outer edge of the substrate. All measurements reported here were performed on 47μm thick foils with a 427Å period. Based on a calibration of deposition rates and a wet chemical analysis of a similar Al/Zr multilayer sample, the composition of this sample was determined to be 25.4 atomic % Zr with an expected experimental error of 5% (±1.3 at %).

All thermal measurements were made with a Perkin-Elmer DSC7 system. Pieces of the foils were cut, weighed, and crimped in aluminum or copper pans, and then purged with Ar gas in the DSC sample chamber before heating. The isochronal scans were performed at a heating rate of 25° per minute with a maximum temperature of 725°C [9]. For the isothermal tests, samples were heated at 100° per minute to the hold temperature and then a constant temperature was maintained for 120 minutes. In both the isochronal and the isothermal tests, a baseline for subtraction was determined by repeating the temperature cycle with the same heating parameters.

XRD characterizations were performed with a Scintag diffractometer and software. The machine was calibrated using a silicon powder standard. The widths of the silicon peaks were determined as a function of 2θ, and the full widths were attributed to machine broadening effects based on the size of the Si crystallites (30 μm). This calibration permitted the determination of layer thicknesses using Al and Zr peaks' widths and the Scherrer Equation [10]. To identify the products of the SSRs, samples were heated beyond an exotherm in the DSC and then quenched. Cross-sectional transmission electron microscopy (TEM) was also used to examine the structure and layering in the foils.

RESULTS

The as-deposited multilayer samples consist of highly textured, alternating layers of polycrystalline Al and Zr. Figure 1 shows a cross-sectional TEM micrograph of a 47 μm thick multilayer foil, and Figure 2 shows results from a symmetric XRD scan of the foil. The as-deposited sample (Figure 2) shows 4 main peaks: 34.8° (Zr (002)), 38.4° (Al (111)), 73.5° (Zr (004)), and 82.4° (Al (222)), verifying that the multilayers are textured with the FCC Al and HCP Zr close-packed planes lying in the plane of the foil. High resolution TEM verified that thin amorphous Al-Zr reaction layers form at the Al/Zr interfaces during deposition [11].

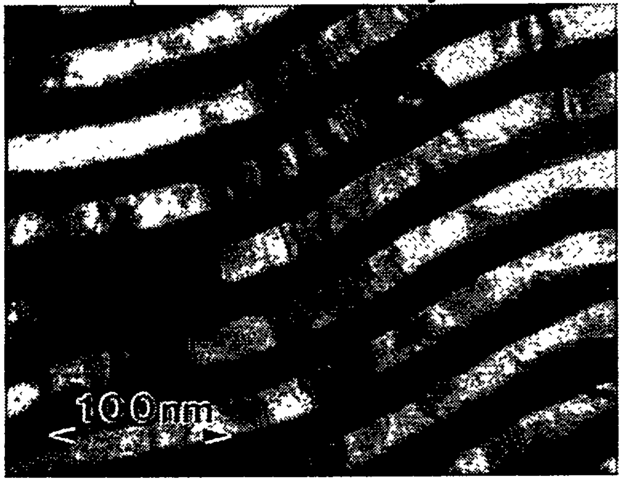

Figure 1: Cross-sectional TEM micrograph of an as-deposited Al/Zr multilayer sample

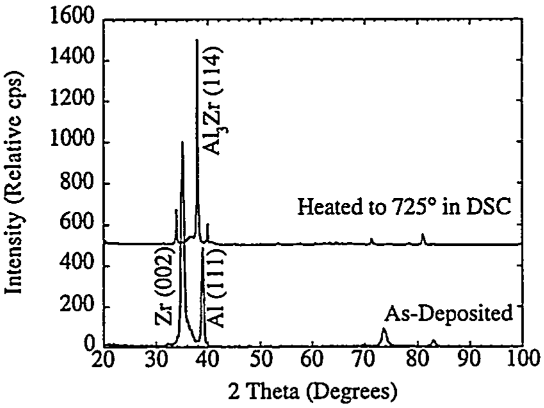

Figure 2: Data from symmetric XRD scans of as-deposited and heated (725°C) Al/Zr multilayer samples

Three different exothermic reactions were observed in the heat flow data when these samples were isochronally scanned to 725°C (Figure 3). The final products of the three reactions are predominantly tetragonal Al_3Zr with some hexagonal Al_2Zr, based on XRD scans and TEM analysis [11]. The heat for the first, large exotherm at 358°C was 777 J/g while the total heat of all three exotherms in Figure 3 was 1060 J/g. Samples were also isothermally annealed at 290°, 300°, and 310°C to study transformation kinetics of the first, large exotherm in Figure 3. The resulting heat flow data is shown in Figure 4. The heat flows were integrated and are plotted vs. √time in Figure 5.

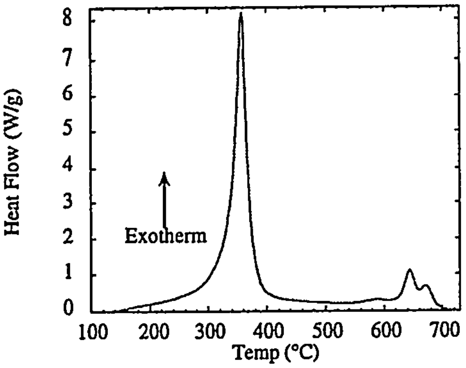

Figure 3: Isochronal scan at 25°/minute

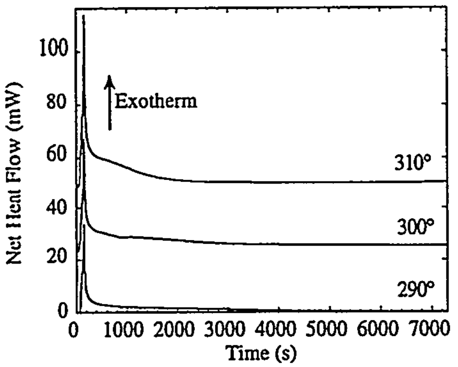

Figure 4: Isothermal scans at 290°, 300° and 310°C

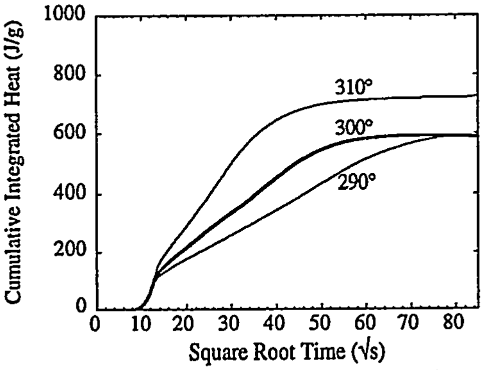

Figure 5: Cumulative integrated heat vs. √time

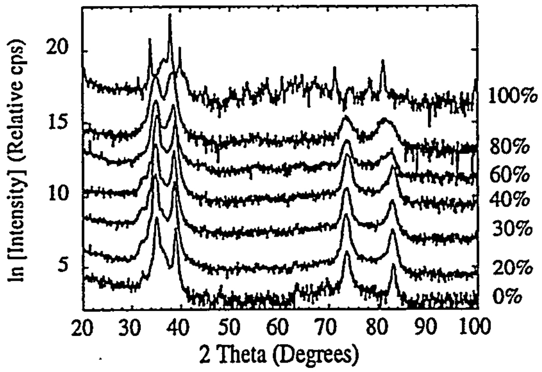

Figure 6: ln [intensity] vs. 2 theta for XRD. The percentages indicate the amount of reaction completed.

To identify the products of the isothermal anneals, samples were examined with symmetric XRD scans. After 4 hrs at 290°C, metastable, cubic Al_3Zr [12-16] and Zr are the only crystalline phases present. The width of the Al_3Zr (111) peak suggests that the thickness of the Al_3Zr layer is 87Å. The one, weak Zr peak indicates that very little of the original Zr is left in the foil. After 4 hrs at 300°C, the peaks for cubic Al_3Zr are sharper, the small Zr peak is gone, and peaks for hexagonal Al_2Zr appear. Thus, all Al and Zr has mixed and transformed. After 4 hrs at 310°C, a fourth phase, tetragonal Al_3Zr, also appears, and more heat is released compared to the lower temperature anneals. To identify the SSRs that occur toward the beginning of the isothermal tests, the products of shorter, partial anneals were examined with XRD and TEM [11].

TEM observations of annealed samples [11] clearly show that the amorphous Al-Zr present at Al/Zr interfaces in as-deposited samples grows in a planar, 1-D manner during low temperature (275°C) anneals. The interfacial amorphous layers grow to a thickness of 20-40Å after 2 hrs at 275°C, and no additional crystalline phases are observed [11]. These TEM observations agree with the XRD results for samples annealed for different times at 300°C. A series of samples was annealed at 300°C for times that were pre-determined to yield 20%, 30%, 40%, 60%, 80%, and 100% of the total heat for the 300°C isothermal anneal. These percentages were simply based on the total heat (592 J/g) released in the reaction and the heat released after various times at 300°C. The XRD scans of the partially annealed foils are shown in Figure 6. As the majority (> 60%) of the heat is released in the 300°C isothermal anneal in Figure 5, no new crystalline phases nucleate (Figure 6). The Al and Zr peaks, however, are shifting and broadening, and these changes are used to calculate variations in layer thicknesses as the reaction proceeds. The results are plotted in Figure 7. Note that the Al and Zr layer thicknesses are decreasing as the anneal proceeds and heat is released. After 80% of the heat has been released, the (111) peak for metastable cubic Al_3Zr peak appears and broadens the (111) Al peak (Figure 6). When 100% of the reaction has been completed, the XRD spectrum shows sharp peaks for cubic Al_3Zr and Al_2Zr. At this point, the predominant crystalline phase is cubic Al_3Zr with some Al_2Zr.

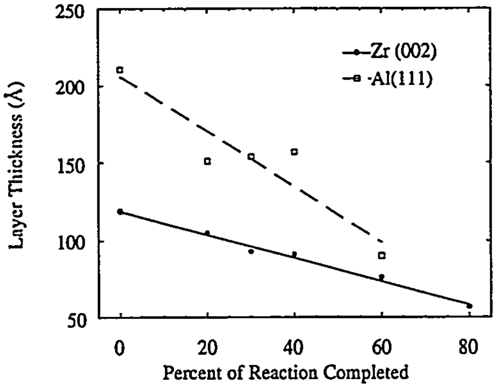

Figure 7: Layer thickness vs. percent of reaction completed for sample isothermally annealed at 300°C

DISCUSSION

Before analyzing the kinetics of the solid state reactions in the Al/Zr multilayers, the phases in the reactions are identified and discussed. In the as-deposited state, the multilayer foils consist of alternating layers of polycrystalline Al and Zr and thin, interfacial layers of amorphous Al-Zr [11]. The amorphous layers grow into the Al and Zr layers in a planar fashion during the majority of the first exothermic reaction [11], and the thicknesses of the Al and Zr layers decrease as shown in Figure 7. XRD and TEM [11] indicate that no crystalline phases are forming during the first 60% of the 290°C and 300°C anneals; only the amorphous alloy forms. After 60% of the heat has been released in these anneals, the metastable, cubic phase Al_3Zr nucleates and grows.

Toward the very end of the 300°C and 310°C isothermal anneals, additional phases appear: hexagonal Al_2Zr and tetragonal Al_3Zr. It is important to note that these additional phases do not form when the samples are isochronally scanned through the first exothermic reaction in Figure 3. The products of the isochronal scans differ from the products of the isothermal anneals for the same reaction. Thus, the paths and the products of the exothermic reactions depend on the time/temperature history of the reaction. Time/temperature/transformation diagrams that identify the reaction paths for various heating rates could be developed with additional investigations.

Given the above reaction paths for the isothermal anneals, the following kinetics analysis involves one or two elements diffusing through a multi-phase reaction layer. The reaction layer contains only amorphous Al-Zr during the first 60% of the reaction, and both amorphous Al-Zr and cubic Al_3Zr during the last 40% of the reaction. The two additional phases, Al_2Zr and tetragonal Al_3Zr, will not affect the measured kinetics because these phases only appear in the final, nonlinear portions of the Q vs. $\sqrt{t}$ curves in Figure 6. These nonlinear portions are not analyzed. Thus, it is the diffusion through amorphous Al-Zr and cubic Al_3Zr and the diffusion into the surrounding Al or Zr that is quantified. Two factors suggest that Zr is the dominant diffusing species in the SSRs. First, Zr diffuses faster in Al than Al diffuses in Zr (see Table 1 below). If the diffusion of one element into the other is rate limiting in the SSRs, then the much larger diffusion of the Zr will dominate. Second, the thickness of the Al layer decreases more rapidly than the Zr layer in Figure 7. This indicates that Zr diffuses and reacts more rapidly with Al than Al diffuses and reacts with Zr.

The kinetics of the "multi-phase" SSR described above can be studied using a one-dimensional (1-D) diffusion model that has been applied with success to other multilayer systems [6, 7, 17]. The 1-D, diffusion model can be applied to both isothermal and isochronal DSC experiments, but here, we concentrate on its application to the isothermal experiments. The model assumes exothermic, planar, diffusion-controlled growth of a reaction layer [7]. If the concentrations of the reactants at their interfaces with the unreacted layers are constant, and if the concentration profile across the reacted layer is linear, then the rate of growth of the reaction layer can be estimated using the following equation:

$$\frac{dw}{dt} = \frac{f}{w}\frac{D}{x(1-x)} \tag{1}$$

In Equation (1), w is the thickness of the reacted layer, D is the average interdiffusion coefficient in the reacted layer ($D = xD_{Zr} + (1-x)D_{Al}$), f is the concentration range over which the binary phase exists, and x is the composition of the multilayer in atomic percent. Rearranging and integrating Equation (1) gives

$$w = \sqrt{\frac{2fD}{x(1-x)}}\sqrt{t} \qquad (2)$$

Thus, at a given temperature, the thickness of the reaction zone grows linearly with √time. The thickness can also be related linearly to the heat that is produced by the exothermic reaction [6]. If ΔH_f is the enthalpy of formation for a given reaction (J/m^3), S is the total projected area of the reacted zone, and Q is the heat evolved, then Q will vary with √time as follows:

$$Q = S\Delta H f\sqrt{\frac{2fD}{x(1-x)}}\sqrt{t} \qquad (3)$$

For an isothermal experiment, S, ΔH_f, f, x, and D ($D = D_o \exp(-E/RT)$, where R is the gas constant and T is the temperature) are all constant, so Q varies linearly with √time. Furthermore, if S, ΔH_f, f, and x are known, D can be obtained from the slope of Q vs. √t. An average activation energy (E) for the SSRs can be determined using the slope of Q vs. √t and the following relation:

$$\ln(slope) = \ln\left(S\Delta H_f\sqrt{\frac{2f}{x(1-x)}}\right) + \frac{1}{2}\ln D_o - \frac{E}{2RT} \qquad (4)$$

A plot of ln(*slope*) vs. 1/T is shown in Figure 8.

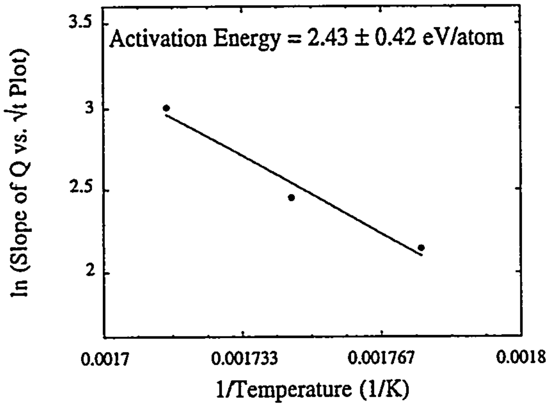

Figure 8: ln Slopes vs. 1/T. The slope of this line is related to the activation energy for the reaction (2.43 ± 0.42 eV).

Before applying Equations (3) & (4) to the data in Figure 5, it is informative to qualitatively compare the predictions of the model with the DSC data. First, note the striking linearity of the Q vs. √t plot in Figure 5. This linearity supports the assumption that the exothermic reaction is diffusion-controlled. Next, note that Al and Zr layer thicknesses decrease linearly with the % of reaction completed in Figure 7. These two sets of linear curves support the assumption that the heat produced varies linearly with the thickness of the reacted layer. Finally, consider the first peak in the isochronal scan in Figure 3. With a constant heating rate and a 1-D, diffusion controlled reaction, the rate of the reaction and the corresponding heat flow should increase with temperature until one layer is consumed [17]. Then, the reaction rate and heat flow should drop abruptly to zero. This asymmetric behavior is seen in Figure 3. Heat flow increases with temperature and drops abruptly on the high temperature side of the exotherm. Thus, both the isochronal and isothermal data qualitatively support the application of a 1-D diffusion controlled model to this Al/Zr multilayer system.

D, D_o, and E were calculated for the Al-Zr multilayers using ΔH_f = 592 J/g, f = 0.2, T = 300°C, and the data in Figure 5 and Figure 8. These values, as well as literature values for D, D_o and E [18] are shown in Table I. D_o was measured to be 218 m^2/s. This value is unusually high and may result from the production of stresses in the multilayers. Large stresses can be generated by the density increases associated with compound formation. The average interdiffusion coefficient (*D*) and the average activation energy for the Al/Zr multilayers were calculated to be 9.05 x 10^{-20} m^2/s and 2.43 ± 0.42 eV/atom, respectively, at 300°C. The corresponding values for Zr diffusing in Al at 300°C are 6.17 x 10^{-24} m^2/s and 2.51 eV/atom (Table I). The agreement between these measured values and the literature values for Zr diffusing in Al are close given the large extrapolation of the bulk data to lower temperatures. The activation energies are particularly close, well within the scatter of the value measured here. The agreement with literature supports the original argument that Zr is the dominant diffusing species.

Table I: Diffusion Data

Matrix	**Diffusing Species**	**D_o (m^2/s)**	**Temperature Range for D**	**Activation Energy (eV)**	**D (m^2/s) (at 300°C)**
Zr	Al	17 x 10^{-4}	600 - 800°C	2.91	4.9 x 10^{-29}
Al	Zr	728 x 10^{-4}	531 - 640°C	2.51	6.17 x 10^{-24}
Al/Al-Zr (This Study)	Zr	218	290 - 310°C	2.43 ± 0.42	9.05 x 10^{-20}

CONCLUSION

Al/Zr multilayer foils were characterized structurally and thermally using XRD, TEM and DSC. When the Al/Zr multilayers were heated, the Al and Zr mixed and transformed into compounds through a series of solid state reactions. The first alloys and compounds to form in these reactions are amorphous Al-Zr and cubic Al_3Zr. The kinetics of the SSRs that lead to their formation were analyzed using a 1-D, diffusion controlled model and the exothermic heat flows from isothermal anneals. The average interdiffusion coefficient and the average activation energy for the Al/Zr multilayers were calculated to be 9.05 x 10^{-20} m^2/s and 2.43 ± 0.42 eV/atom, respectively, at 300°C. Zr is thought to be the dominant diffusing species.

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