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T. P. Weihs, T. W. Barbee, Jr., and M. A. Wall

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PHASE TRANSFORMATIONS IN Cu-Zr MULTILAYERS

T.P. Weihs, T.W. Barbee, Jr., and M.A. Wall, Lawrence Livermore National Laboratory, Livermore, CA 94550

ABSTRACT

A study of phase transformations is reported for Cu-rich, Cu-Zr multilayer foils that were synthesized using magnetron sputter deposition and annealed using a differential scanning calorimeter. The foils range in composition from 1.6 at% to 9.0 at% Zr and consist of alternate layers of polycrystalline Cu and Zr. Differential scanning calorimetry, X-ray analysis and electron microscopy were used to examine three distinct reactions in the foils: a mixing and an amorphization of the Cu and the Zr, a crystallization of this amorphous phase to the metastable intermetallic, $\text{Cu}_{51}\text{Zr}_{14}$, and a transformation of the $\text{Cu}_{51}\text{Zr}_{14}$ phase into the equilibrium phase, Cu_9Zr_2 . The as-deposited layering remained stable during the first two reactions and then broke down in the third reaction as large grains of Cu_9Zr_2 encompassed the smaller Cu grains. The heats of the reactions and the activation energies of these reactions are measured and are compared to values reported for bulk samples. The measured heats provide evidence that amorphous Cu-Zr alloys phase separate and that mixing and short range ordering produce 3.5 times more heat than long range ordering produces when Cu and Zr react and form $\text{Cu}_{51}\text{Zr}_{14}$.

INTRODUCTION

As applications of multilayered films extend into high temperature environments, the need to understand their structural stability increases. The transformation of phases and the break-down of layering are of prime importance. This paper examines both issues for magnetron sputter deposited Cu-Zr multilayers. While the Cu-Zr system offers few applications at elevated temperatures due to the rapid oxidation of Zr, it provides useful insights as a model system. It contains a large number of stable intermetallic compounds; [1] it amorphizes in the solid state; [2] it phase separates while amorphous; [3] and it deposits readily into a layered structure. [2] Here, we investigate both the evolution of phases and the stability of layers in Cu-Zr multilayered foils by varying the average compositions, the layer thicknesses and the thermal histories of the free-standing foils. The average compositions of the foils range from 1.6 at% Zr to 9.0 at% Zr and their individual layer thicknesses range from 12Å to 503Å. The results presented here for multilayers are compared with data reported in the literature for bulk alloys.

EXPERIMENTAL PROCEDURES

Cu and Zr were alternatively magnetron sputter deposited onto 3in and 6in (100) Si wafers at applied powers between 41W and 645W. The multilayers were approximately 26µm thick and were easily handled as free standing foils. This capability greatly facilitated thermal, structural and mechanical characterizations. The overall compositions of the samples, the layer thicknesses and the foil thicknesses were based on calibrated deposition parameters and are listed in Table 1. The particular thicknesses were chosen so that once the Zr reacted with the excess Cu, the remaining Cu layers would be approximately 350Å thick in all samples. This structural condition was designed for an accompanying mechanical study. [4]

Table 1: As-Deposited Layer and Film Thicknesses

Sample	% Zr	Cu (Å)	Zr (Å)	Film (µm)
A	1.65	368.8	12.3	25.5
B	3.09	387.3	24.5	25.7
C	5.52	424.9	49.2	26.5
D	7.38	467.4	73.9	27.1
E	9.00	502.5	98.5	27.4

Differential scanning calorimetry (DSC) was used to vary the thermal history of the multilayers while monitoring their heats of transformation. For each DSC run, up to five disks with 6mm diameters were punched from the multilayered foils and then crimped flat in Cu pans. The flat and uniform nature of the disks provide excellent thermal

conduction and enabled more than 15mg of sample to be included in each test. During the measurements, the DSC chambers were continuously purged with high purity Ar to minimize

oxidation. The heats of reactions (Q) were calculated from isochronal scans in which temperature was varied from 50°C to 725°C at 100°C/min. The crystalline phases formed during the exothermic reactions were confirmed using x-ray diffraction (XRD) of annealed disks. In some cases, samples were mounted in wax and ground into powder to avoid the effects of texturing. Cross-sectional transmission electron microscopy (TEM) and cross-sectional scanning electron microscopy (SEM) were used to confirm the presence and the uniformity of layering within particular samples. For the SEM analysis, the samples were first mechanically polished and then chemically etched to reveal the layered structures.

RESULTS AND DISCUSSION

The following presentation of results begins with a description of the particular phases and structures that developed when the Cu-Zr multilayers were scanned in temperature up to 725°C. Then, the heats of reactions and the activation energies of reactions are reported. Lastly, the implications of these results for amorphous phase separation and the formation of $\text{Cu}_{51}\text{Zr}_{14}$ will be discussed.

The as-deposited layered structure of Sample B (3.1% Zr) is shown in a cross-sectional TEM micrograph in Figure 1(a). Polycrystalline Cu layers alternate with thin layers of Zr. At higher magnifications, the onset of solid state amorphization (SSA) is seen within the Zr layers.

Figure 1: TEM images of (a) as-deposited polycrystalline Cu layered with Zr (Sample B) and (b) Cu grains imbedded in Cu_9Zr_2 after heating to 725°C at 100°C/min (Sample E).

Figure 2: Isochronal DSC scans of 4 Samples that are listed in Table 1. The heating rate was 100°C/min.

Three significant exotherms were observed (Figure 2) when these multilayers were scanned from 50°C to 725°C at 100°C/min. The broad, initial exotherm is due to the remaining SSA of the Zr layer; the second exotherm is due to the formation of the crystalline phase, $\text{Cu}_{51}\text{Zr}_{14}$, and the third exotherm is due to grain growth in the Cu-Zr phase as the layering breaks down and $\text{Cu}_{51}\text{Zr}_{14}$ transforms to Cu_9Zr_2 . The same three reactions, labeled Rx 1, Rx 2 and Rx 3, were observed for all 5 samples.

For XRD, SEM and TEM analysis, three specimens of Sample E were isochronally scanned 20°C beyond each exotherm in Figure 2 and then quenched. XRD traces for the three specimens that were scanned to 400°C, 525°C and 725°C at 100°C/min are shown in Figure 3. An XRD trace of an as-deposited specimen is also included. For Sample E, which has the thickest layers of Zr as-deposited, the (111) and (222) Cu reflections and the (002) Zr reflection dominate the measurement. These diffraction peaks demonstrate that the Cu and Zr layers are predominantly crystalline and textured. The Cu reflections in the other traces show the Cu remains crystalline and textured after heating to 725°C. The Zr reflection disappears as all of the Zr and some of the Cu react and sequentially form (a) an amorphous layer by 400°C, (b) the hexagonal phase $\text{Cu}_{51}\text{Zr}_{14}$ by 525°C[1] and (c) the stable crystalline phase, Cu_9Zr_2 , by 725°C.[2,5] The major XRD reflections of the two intermetallic phases, $\text{Cu}_{51}\text{Zr}_{14}$ and Cu_9Zr_2 ,

can be observed in Figure 3 near 2θ values of 40° and 36°, respectively. For these XRD traces, the specimens were crushed into powders to reduce the strong (111) and (222) Cu peaks. XRD pole figures confirm that the Cu grains remain crystalline and highly textured up to 725°C.

Figure 3: Symmetric Θ - 2Θ XRD traces of DSC specimens from Sample E that were scanned at 100°C/min. The maximum DSC temperatures are marked.

In the SEM analysis, the prepared surfaces of specimens scanned to 525°C revealed a layered structure with the smallest period being approximately 500Å. All signs of layering were gone and a 2µm equiaxed structure appeared in samples scanned to 725°C. This indicates that the layered structure is lost when Cu_9Zr_2 forms during the third exotherm in Figure

2. The microstructure of Sample E after heating to 725°C is revealed in the TEM micrograph in Figure 1(b). Individual Cu grains are distributed throughout a highly faulted Cu_9Zr_2 phase. Electron diffraction patterns and dark field images show that the second phase is ordered, polycrystalline Cu_9Zr_2 [5] with an average grain diameter of 2µm. This grain size agrees with the equiaxed structure seen in the SEM cross-sections. The tremendous growth of the Cu-Zr grains from approximately 200Å in the layered Cu/ $\text{Cu}_{51}\text{Zr}_{14}$ structure to 20,000Å in the equiaxed Cu& Cu_9Zr_2 structure is not surprising since 700°C is 78% of the Cu-Cu Zr_2 eutectic temperature. In contrast to the Cu-Zr grains, the Cu grains are stable. Most of the Cu grains seen in Figure 1(b) are similar in size to the as-deposited grains in Figure 1(a) and their orientation within the foils does not change. Remnants of the initial layering can be observed in Figure 1(b) as small stacks of Cu grains.

Referring to Figure 2, we now consider the total heats evolved during these reactions. The integrated heats for the reactions are labeled as Q_1 , Q_2 and Q_3 . Q_1 is the heat of the solid state amorphization, Q_2 is the heat of the crystallization to $\text{Cu}_{51}\text{Zr}_{14}$ and Q_3 is the heat of the transformation from small-grained $\text{Cu}_{51}\text{Zr}_{14}$ to large-grained Cu_9Zr_2 . Because the first broad exotherm overlaps the second, more distinct exotherm, we report a combined heat for these first two reactions, Q_1+Q_2 , and a separate heat for the third reaction, Q_3 . All heats are plotted per mole of sample in Figure 4. The heat evolved during the first two reactions is expected to increase linearly with the at% Zr since Rx 1 and Rx 2 mark the formation of $\text{Cu}_{51}\text{Zr}_{14}$ from crystalline Cu and crystalline Zr. If the composition of one of the multilayers was increased to 21.5 at% Zr, then all of that foil would transform to $\text{Cu}_{51}\text{Zr}_{14}$, and Q_1+Q_2 should equal the enthalpy of formation for $\text{Cu}_{51}\text{Zr}_{14}$. In Figure 4, the sum of Q_1 and Q_2 does vary linearly with the at% Zr, as expected. For Samples A and B, though, a significant fraction of the total solid

state amorphization occurs during deposition. Consequently, the measured value of Q_1 is reduced and the sum, Q_1+Q_2 , falls below the linear fit. Extrapolating the linear fit in Figure 4 to 21.5 at% Zr, Q_1+Q_2 equals 13.6kJ/mol. Kleppa and Wanatabe[6] measured 14.07kJ/mol for the enthalpy of formation of $\text{Cu}_{51}\text{Zr}_{14}$ using bulk samples and drop calorimetry. The excellent agreement of these two values for the heat of formation verifies that the compositions of the multilayered foils do vary according to the predictions listed in Table 1.

Figure 4: The integrated heats of Reactions 1, 2 and 3 in Figure 2 are plotted as Q_1+Q_2 and Q_3 . All heats are calculated per mole of sample.

In contrast to the heat for the first two reactions, the heat for the third reaction is relatively constant in Figure 4. The fact that Q_3 does not scale linearly with the at% Zr suggests that the phase transformation from $\text{Cu}_{51}\text{Zr}_{14}$ to Cu_9Zr_2 produces only a small fraction of the reaction's heat. The main source of heat is believed to be a loss of interfacial and grain boundary energy as the layers break-down and the Cu_9Zr_2 grains grow. Although a careful analysis of the energetics of this break-down and grain growth process requires one to distinguish between Cu/Cu, Cu-Zr/Cu-Zr and Cu/Cu-Zr interfaces, we take a simpler approach here and consider only an average grain boundary

energy for the Cu-Zr grains that grow from approximately 200Å to 20,000Å in diameter. The average energy of the Cu boundaries is ignored as the Cu grains remain relatively stable in size throughout Rx 3. Q_3 can then be expressed as

$$Q_3 = \Delta H^{\text{tr}}_{\text{CuZr}} + \Delta H^{\text{gg}}_{\text{CuZr}} \quad (1)$$

where $\Delta H^{\text{tr}}_{\text{CuZr}}$ is the enthalpy change due to the transformation of the Cu-Zr phase and $\Delta H^{\text{gg}}_{\text{CuZr}}$ is the enthalpy change due to grain growth in the Cu-Zr phase. To further simplify the analysis, Q_3 , $\Delta H^{\text{tr}}_{\text{CuZr}}$ and $\Delta H^{\text{gg}}_{\text{CuZr}}$ are all calculated per mole of Cu_9Zr_2 . The grain boundary enthalpy in both the $\text{Cu}_{51}\text{Zr}_{14}$ and Cu_9Zr_2 phases can be approximated using Chen and Spaepen's[7] equation,

$$H = g\gamma V/r \quad (2)$$

where the molar volume of the system is V , the average grain radius is r , the grain boundary energy is γ , and g is a numerical factor near unity. Considering Equation (2), the grain boundary enthalpy in the $\text{Cu}_{51}\text{Zr}_{14}$ phase should be approximately 100 times larger than the grain boundary enthalpy in the Cu_9Zr_2 phase because of the difference in average grain size. Thus, in calculating $\Delta H^{\text{gg}}_{\text{CuZr}}$, the enthalpy of the grain boundaries in the large-grained Cu_9Zr_2 phase can be ignored. Assuming that the grain size of the $\text{Cu}_{51}\text{Zr}_{14}$ phase scales with its layer thickness, t_{CuZr} , Q_3 can now be written as

$$Q_3 = \Delta H^{\text{tr}}_{\text{CuZr}} + g^*\gamma V/(t_{\text{CuZr}}) \quad (3)$$

where g^* is a modified constant. To test the validity of Equation (3), Q_3 is plotted in Figure 5 versus the reciprocal of the $\text{Cu}_{51}\text{Zr}_{14}$ layer thickness. While the data show some scatter, Q_3 does increase linearly as the layer thickness decreases. Using the slope of the line in Figure 5, the molar volume of $\text{Cu}_{51}\text{Zr}_{14}$ and the assumption that $g^* = 1.3$, [7] the grain boundary energy in the $\text{Cu}_{51}\text{Zr}_{14}$ phase was calculated to be 1.20N/m. While this number is a rough estimate, it is a reasonable increase over the grain boundary energy in pure Cu, which is 0.623N/m. [9] The

large-period superstructure of the $\text{Cu}_{51}\text{Zr}_{14}$ phase should produce grain boundaries with higher energies than those found in fcc Cu.

The intercept with the ordinate axis in Figure 5 yields a heat of 0.895 kJ/mol for the transformation from large grained $\text{Cu}_{51}\text{Zr}_{14}$ to large grained Cu_9Zr_2 . Remembering that the

Figure 5: The integrated heat of Reaction 3 in Figure 2 is replotted versus the reciprocal of the $\text{Cu}_{51}\text{Zr}_{14}$ thickness. The heats are given per mole of Cu_9Zr_2 .

Figure 6: A Kissinger plot of the three reactions for Sample E during isochronal scans to 725°C. The heating rates were varied from 100°C/min to 6.3°C/min.

amorphous Cu-Zr phase separates.[3] To examine this possibility using calorimetry, Q_1 was calculated for each sample by subtracting an estimate of Q_2 from the heat that could be measured accurately, $Q_1 + Q_2$. Q_2 was estimated by integrating from the inflection point between Rx 1 and Rx 2 to the end of Rx 2. While the resulting values for Q_1 are only approximate, they do vary linearly with at% Zr. The linearity of the variation implies that an amorphous Cu-Zr phase, with a particular heat of formation, is produced during Rx 1. This, in turn, supports Barbee's observation of phase separation in the amorphous Cu-Zr system.[3]

enthalpy of formation of $\text{Cu}_{51}\text{Zr}_{14}$ is approximately 14kJ/mol, little additional energy is produced when $\text{Cu}_{51}\text{Zr}_{14}$ transforms into Cu_9Zr_2 . Thus, the enthalpies of formation for both compounds are very similar in magnitude, as expected.[8]

To characterize the kinetics of phase transformations in the Cu-rich multilayers, Sample E was isochronally scanned from 50°C to 725°C at 5 different rates. The three peak temperatures for each scan are plotted in a typical Kissinger analysis format[10] in Figure 6. The following activation energies were calculated from the linear fits: Rx 1 - $1.97 \pm 0.06 \text{ eV}$, Rx 2 - $2.47 \pm 0.03 \text{ eV}$ and Rx 3 - $2.69 \pm 0.10 \text{ eV}$. The last two activation energies, for the formation of $\text{Cu}_{51}\text{Zr}_{14}$ and Cu_9Zr_2 , bracket the value of 2.58eV reported by Buschow for the crystallization of a Cu-10%Zr amorphous alloy.[11] Thus, we find good agreement with measurements on bulk alloys.

Returning now to the heats of Rx 1 and Rx 2, amorphous phase separation and the enthalpy of formation of $\text{Cu}_{51}\text{Zr}_{14}$ are discussed. The solid state amorphization that occurs in these multilayered foils was expected to produce an alloy with approximately 25 at% Zr, based on the observation by Barbee and coworkers that

Cu₅₁Zr₁₄ is formed from crystalline Cu and crystalline Zr during the exothermic reactions, Rx 1 and Rx 2. The heat of Rx 1 is attributed to the mixing of the Cu and Zr which involves an increase in bond energies and a short range ordering in the amorphous Cu-Zr alloy. The heat in Rx 2 is attributed to the crystallization or long range ordering of the amorphous phase. By performing the following thermodynamic thought experiment, one can compare the magnitudes of these two sources. The formation of crystalline Cu₅₁Zr₁₄ is broken down into 3 separate steps. The first step is the amorphization of the polycrystalline Cu and polycrystalline Zr phases. This reaction is endothermic. The second step is the mixing of the amorphous Cu and the amorphous Zr. The third step is the crystallization of the amorphous Cu-Zr alloy. Since the first two steps occur during Reaction 1,

$$Q_1 = \Delta H_{\text{amorph}} + \Delta H_{\text{mix}} \quad (4)$$

where ΔH_{amorph} is the heat required to amorphize the Cu and the Zr and ΔH_{mix} is the heat produced from mixing these amorphous elements. ΔH_{amorph} is estimated to be -13.5kJ/mol for a 21.5 at% Zr sample based on an average heat of fusion.[6] Q_1 was determined to be 7.5kJ/mol for the same sample by deconvolving the DSC scans in Figure 2 and extrapolating to 21.5 at% Zr. Using these numbers, the heat of mixing is calculated to be 21.0kJ/mol. The heat of crystallization is simply equal to Q_2 which is $Q_1 + Q_2 - Q_1$ or 6.5kJ/mol. The ratio of 21.0 to 6.5 suggests that the mixing and the formation of short range order produce roughly 3.5 times as much heat as the formation of long range order in Cu-21.5 at% Zr alloys.

CONCLUSIONS

Phase transformations in Cu-rich, Cu-Zr multilayers have been examined using differential scanning calorimetry. Initially crystalline layers of Cu and Zr reacted to form 3 different Cu-Zr alloys as temperature was scanned from 50°C to 725°C. While a significant fraction of the Cu remained stable, some of the Cu and all of the Zr amorphized into a Cu-Zr alloy, then formed the crystalline intermetallic, Cu₅₁Zr₁₄, and finally transformed into the stable intermetallic, Cu₉Zr₂. The films remained layered until ~ 650°C, at which point Cu₉Zr₂ grains nucleated and grew significantly to encompass the stable Cu grains. The heats of the first two reactions varied linearly with at% Zr and provide evidence that amorphous Cu-Zr phase separates. The heat of mixing in Rx 1 is estimated to be 3.5 times larger than the heat of crystallization in Rx 2. The sum of the heats for the two reactions, $Q_1 + Q_2$, is in good agreement with the enthalpy of formation reported for Cu₅₁Zr₁₄. The heat for the final reaction is attributed to a loss of Cu-Zr grain boundary energy and scales inversely with the Cu-Zr layer thickness. The systematic variation of all the calorimetric data demonstrates that multilayered foils can be deposited in a controlled manner.

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