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**An In Situ Electron Microscopy Technique for the
Study of Thermally Activated Reactions In Multilayered Materials**

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AN *IN SITU* ELECTRON MICROSCOPY TECHNIQUE FOR THE STUDY OF THERMALLY ACTIVATED REACTIONS IN MULTILAYERED MATERIALS

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ABSTRACT

A novel *in situ* transmission electron microscopy technique for the observation of reaction processes in multilayered materials is reported. The technique involves constant heating rate experiments of multilayered materials in image and diffraction modes. Because the fine scale microstructure of multilayered materials is typically a small fraction of the TEM specimen thickness, realistic comparison of the microstructural evolution with that of similarly processed thick foil samples is possible. Such experiments, when well designed, can provide rapid characterization of phase transformations and stability of nano-structured materials. The results of these experiments can be recorded in both video and micrograph format. The results and limitations of this technique will be shown for the Al/Zr and Al/Monel multilayered systems.

INTRODUCTION

The success of transmission electron microscopy (TEM) as a characterization tool in providing the link between a materials microstructure and physical properties is due to its unparalleled spatial resolution. However, one limitation of conventional TEM is that most observations are only static or "post-mortem", allowing only indirect conclusions about the mechanisms of microstructural evolution. *In situ* HVEM techniques allow for the possibility of overcoming this limitation through direct observation of materials under dynamic conditions [1]. The development and success of *in situ* experiments hinge upon the proper use and development of instrumentation, specimen preparation and sample design.

Multilayer structures are synthetic, alternately layered, fine-structured materials and fall into a special class called nanostructures. These materials are not only of scientific interest but also are increasingly found to have direct technological applications. This interest is due to their enhanced physical properties. Characterization of the microstructure of these materials is the key to understanding and tailoring their properties. Because of the fine-scale microstructure produced during the synthesis of these materials, TEM is an ideal tool for characterization of these structures. With the fine structural scale of nanostructured materials being of a comparable length scale of the TEM specimen thickness, the ability to compare the dynamic reaction in a thin foil to bulk behavior becomes more realistic. The static characterization of multilayers and thin films has received considerable attention; [2-4] are recent examples. The majority of dynamic *in situ* TEM experiments performed on these types of materials has been related to heating of the microstructure in order to observe stability and phase transformations. Sinclair [5] reviews a number of successful *in situ* TEM heating experiments of thin films and multilayers; most of these notable experiments were for specimens viewed in cross-section. These cross-sectional experiments are very labor intensive; preparation of specimens and a heating experiments take many hours or days to perform.

The *in situ* technique which we describe here is considerably less labor and time intensive. A number of plan view specimens can be made in an hour and contain an order of magnitude more electron transparent area than cross-sectional specimens. An individual constant heating rate experiment may only take 5 to 30 minutes to complete. It will also be shown that results of these *in situ* experiments are equivalent to similarly processed thick samples.

MATERIALS AND METHODS

The sample materials are Al/Zr and Al/M(Monel-Ni 30at%Cu) multilayer foils. The bulk stoichiometry, multilayer period and total thickness for the Al/Zr and Al/M multilayers are: Al₃Zr, 42nm, 41μm and Al₁M₁, 70nm, 43μm respectively. The reactivity of Al with Monel is expected to be equivalent to the Al-Ni system. The multilayer foils were synthesized by planar magnetron sputter deposition on to glass substrates. *In situ* specimens were prepared by the conventional plan view techniques of electropolishing and ion milling. The *in situ* heating experiments were performed on a JEOL 200CX. A heating holder was fitted to a specially built controller with temperature feed back in order to control the heating rate. Experiments were recorded in both video and micrograph format.

EXPERIMENTAL

A. Sample design

In designing a multilayer for *in situ* TEM heating, several parameters were considered. Layering materials, repeat period and total film thickness were our critical parameters. The selection of Al with Zr and Monel is due to the interest in their highly reactive nature. The period of the multilayers was kept below 100nm so that several periods would be contained within the electron transparent region of the TEM specimens. The total thicknesses of the foils were increased considerably over most other traditional films to facilitate handling and use in other characterization instruments, such as a differential scanning calorimetry (DSC).

B. Specimen preparation

For our *in situ* experiments a combination of traditional preparation techniques were utilized. 3mm discs were extracted by spark cutting or disc punching from free standing multilayer foils. The discs were then electropolished to perforation using a solution of 90% Methanol, 9.5% Sulfuric acid and 0.5% Hydrofluoric acid. The electropolishing parameters used were -25°C and 25V. Specimens were then ion milled under low power conditions; 2-3kV, .1-2mA and a 10° angle of incidence. Ion milling removes any organic contamination, smooths out any etching effects from polishing and removes the thinnest regions which are typically bent and will continue to bend during heating.

C. In situ heating

Specimens were mounted in a single tilt heating holder between Cu washers. The Cu washers facilitate the heat transfer from the furnace to the thin regions of the specimen. The heating rates can be varied from 1 to 100°C/min while heating to 700°C using a process temperature controller. These rates are similar to the heating rates used during DSC studies. The experiments performed were viewed in bright field (BF) and selected area diffraction (SAD) mode. Experiments were recorded using a TV rate CCD camera connected to a Hi-8 format recorder. TEM was performed on the as-deposited and the *in situ* heated structures. When intermediate transformations were observed additional heating experiments were performed under similar conditions but the heating was ended near or just beyond the reaction temperature. TEM characterization could then be performed on these intermediate reactions. To validate the *in situ* results 3mm diameter multilayer foil samples of Al/Zr and Al/M were *in situ* TEM heated under similar conditions. The specimens were then thinned for TEM observation and compared to the *in situ* thin foil specimens.

RESULTS

ALUMINUM/ZIRCONIUM

Plan view TEM specimens from an Al/Zr multilayer sample were heated *in situ* at a constant heating rate of 50°C/min. from room temperature to 725°C. Separate heating experiments were performed under identical conditions; one in bright field and another in SAD mode. Simultaneous

playback of these two experiments showed a correlation between morphological changes in the image mode and crystal structure changes in the diffraction mode. The first transformation started at $\approx 360^\circ\text{C}$ and was completed by $\approx 420^\circ\text{C}$. A second transformation started at $\approx 660^\circ\text{C}$ and was completed by $\approx 710^\circ\text{C}$. A second set of BF and SAD mode *in situ* heating experiments were performed at a $50^\circ\text{C}/\text{min.}$ to 375°C , just beyond the start of the first transformation.

TEM characterization of the BF and SAD mode heating experiments is as follows. The plan view as-deposited structure consists of a bimodal grain size. The larger grains ($\approx 50\text{nm}$ diam.) are the pure Al FCC phase and the finer grains ($\approx 10\text{nm}$ diam.) are the pure Zr HCP phase, Fig. 1a. Upon heating through the first reaction a uniform, fine grain size ($\approx 20\text{nm}$), metastable Al_3Zr cubic phase has appeared, Fig. 1b. Continued heating through the second transformation resulted in the nucleation and growth of a larger grain size ($\approx 200\text{nm}$), stable, Al_3Zr tetragonal phase and a minor amounts of Al_2Zr , Fig. 1c.

Fig. 1, BF and SAD results of *in situ* heating of Al/Zr thin foil specimens, A) Elemental Al and Zr, B) Cubic Al_3Zr at $50^\circ\text{C}/\text{min.}$ to 360°C , C) Tetragonal Al_3Zr at $50^\circ\text{C}/\text{min.}$ to 600°C . All BF micrographs are at the same magnification.

ALUMINUM/MONEL

In similar fashion as the Al/Zr, plan view TEM specimens from an Al/M multilayer sample were heated *in situ* at a constant rate of $50^\circ\text{C}/\text{min.}$ to a temperature of 700°C in both BF and SAD TEM modes. Again, simultaneous playback of the recorded experiments showed a direct correspondence between microstructural and diffraction pattern changes. Two low temperature transformations were observed at $\approx 250^\circ\text{C}$ and $\approx 350^\circ\text{C}$ with the end of the first transformation overlapping considerably with the beginning of the second. A third higher temperature transformation occurred at $\approx 500^\circ\text{C}$. Two additional BF and SAD mode constant heating rate *in situ* experiments were then performed; one to the first reaction at 250°C , a second to 400°C .

TEM characterization of the BF and SAD mode heating experiments is as follows. The as-deposited structure consists of a bimodal grain size distribution of pure FCC Al ($\approx 20\text{nm}$ diam.) and FCC Monel ($\approx 10\text{nm}$), Fig. 2a. Upon heating to the first reaction FCC Al is no longer present and a number of new Al rich phases have appeared; Al_3M , Al_2M and small amount of Al_3M_2 ; Monel is still present, Fig. 2b. Heating through the second transformation resulted in the formation of Al_3M_2 with some Monel remaining, Fig. 2c. Heating through the final transformation temperature resulted in the formation of Al_1M_1 , identical to the Al_1Ni_1 B2 compound, Fig. 2d.

THICK SAMPLE HEATING

Prior to preparation for TEM observation, thick foil multilayer samples of Al/Zr and Al/M

were constant-rate heated *in situ* in the TEM to temperatures closely corresponding to the different reaction temperatures seen in the previous *in situ* thin foil specimen experiments. Figures 3 and 4 show the results of the TEM characterization of these thick foil heating experiments. For both the Al/Zr and Al/Monel systems there is a close correspondence of morphology and product phase formation to the *in situ* thin foil specimen heating.

To compare our *in situ* results to conventional characterization techniques, thick multilayer foil samples were constant rate heated in a Differential Scanning Calorimeter to obtain exothermic reaction temperatures. After initial DSC reactions were observed additional samples were DSC heated to intermediate reaction temperatures then cooled back down to room temperature. X-ray diffraction was then performed on the DSC heated foils to determine the phases that were present after each reaction temperature. A detailed report of the DSC and X-ray diffraction study on the reactivity and phase formation in these multilayer systems is reported by [6-7]. There is very good agreement between the reported DSC/X-ray results and this TEM data.

Fig. 2, BF and SAD results of *in situ* heating Al/Monel thin foil specimens, A) Elemental Al and Monel, B) Al_3M , Al_2M , Al_3M and Monel at $50^\circ\text{C}/\text{min.}$ to 250°C , C) Al_3M_2 and Monel at $50^\circ\text{C}/\text{min.}$ to 400°C , D) Al_1M_1 at $50^\circ\text{C}/\text{min.}$ to 600°C . All BF micrographs are at the same magnification.

DISCUSSION

The Al/Zr and the Al/M systems are highly reactive systems. The multiple compound formation and large heats of formation for these compounds are a good measure of the reactivity. The DSC/X-ray and *in situ* TEM thin and thick foil results shows the reaction path for phase formation from sequentially layered pure elements to the final high temperature stable compounds: $\text{Al} + \text{Zr} \Rightarrow \text{Al}_3\text{Zr}$ (cubic) $\Rightarrow \text{Al}_3\text{Zr}$ (tetragonal) + Al_2Zr (Hexagonal) and $\text{Al} + \text{M} \Rightarrow \text{Al}_3\text{M} + \text{Al}_2\text{M} + \text{Monel} \Rightarrow \text{Al}_3\text{M}_2 + \text{Monel} \Rightarrow \text{Al}_1\text{M}_1$. Cross-sectional TEM revealed a thin amorphous reaction layer at the Al/Zr interfaces [7]. The intensity of diffraction pattern from this small volume is too weak to be observed in the plan view TEM specimens.

The success of our *in situ* TEM constant heating rate experiments in obtaining results comparable to bulk foil *in situ* heating and conventional DSC heating is due to several factors. First, by orientating the multilayer specimens in plan view the interfaces between the pure elemental layers

Fig. 3, BF and SAD results of heating thick foil Al/Monel samples, A) $\text{Al}_3\text{M} + \text{Al}_2\text{M} + \text{Monel}$ at $50^\circ\text{C}/\text{min.}$ to 275°C , B) $\text{Al}_3\text{M}_2 + \text{Al}_3\text{M} + \text{Monel}$ at $50^\circ\text{C}/\text{min.}$ to 450°C , C) Al_1M_1 at $50^\circ\text{C}/\text{min.}$ to 600°C .

Fig. 4, BF and SAD results of heating thick foil Al/Zr samples, A) Cubic Al_3Zr at $50^\circ\text{C}/\text{min.}$ to 375°C , B) Tetragonal Al_3Zr at $50^\circ\text{C}/\text{min.}$ to 720°C . All micrographs are at the same magnification.

Fig. 5, BF micrograph showing larger grains in the thicker region and small grains in the thinner regions. Al/Mat 725°C .

are contained within the electron transparent region. DSC studies [7] indicate that diffusion in these systems is primarily one dimensional, perpendicular to the interfaces. If the multilayer specimens are oriented in cross-section then the multilayer interfaces contained in the foil are small in area and are short circuited to the surfaces of the specimen. Vacancies, which are necessary to support the diffusion process, may be lost by boundary diffusion to the surface of the specimen foil in cross-sectioned specimens. This will slow or impede any reaction. Secondly, plan view specimens typically have many times more electron transparent area as do cross-sectional specimens, thus increasing significantly the statistical sampling of the diffraction data. Finally, plan view specimens are also easier and faster to prepare for TEM observation than cross-sectional specimens: many experiments can be run in a short period of time, thus increasing the confidence level of the data. *In situ* cross-sectional experiments do have the advantage of observing the location at which new phases nucleate and grow with respect to the interfaces.

Performing these experiments with multilayer samples having small periods (<100nm) insures that several layers and interfaces will be contained within the electron transparent area. With larger periods, the possibility of not having one complete period in the specimen exists. It is also possible that for larger period samples or thin specimens that a non-integral number of periods (ie; 3.5, 6.5....) will be contained in the specimen. With smaller periods and thicker specimens the local compositional error from an extra one-half layer becomes increasingly small. A final limitation of these *in situ* experiments is that the specimen thickness may limit the final grain size of the reaction product phases, Fig. 5. This becomes more pronounced at higher temperatures where grain growth occurs. After viewing a number of experiments, it was observed that the reaction temperatures in the TEM were sometimes higher than expected from the DSC results. There is always the concern of the conduction of heat through a thin specimen foil to achieve a temperature in the electron transparent region that is similar to that of the thermocouple contact point on the furnace.

CONCLUSION

We have described a technique for the dynamic observation of the microstructural evolution in reactive multilayer systems: Al/Zr and Al/Monel. The results of this technique were validated by the similar heating of thick foil samples and then observing in TEM. This TEM data is also comparable to DSC and X-ray characterization studies performed on these same two alloy systems. This technique is relatively fast and simple to perform. However, the thin foil may limit the final grain size at high temperatures and the heat flow through a thin sample sometimes is slowed. When applied to fine scale structures these *in situ* experiments can yield rapid TEM results comparable and complementary to the combination of DSC and X-ray diffraction.

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