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STUDY OF SOLID STATE REACTIONS IN Nb/Al MULTILAYER THIN FILMS

Differential scanning calorimetry

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Abstract

Solid state reactions of sputter-deposited Nb/Al multilayer thin films, with periodicities in the range 10–333 nm, have been studied by differential scanning calorimetry. The first phase to form upon annealing the films in $NbAl_3$. Constant-heating-rate calorimetric measurements show the presence of two peaks for the formation of this phase, while isothermal scans reveal that the first peak is associated with a nucleation and growth type transformation. The formation of $NbAl_3$ is thus interpreted as a two-stage process of nucleation and growth to coalescence (first peak) followed by growth until the consumption of one or both reactants (second peak).

Keywords: calorimetry, intermetallic phases, Nb/Al, solid state reactions, thin films

Introduction

The Nb–Al system contains three intermetallic phases: $NbAl_3$, sigma Nb_2Al and A15 Nb_3Al. Both the sigma and the A15 phases have extended stoichiometry ranges. Various studies show that when Nb/Al multilayer thin films are annealed, the trialuminide, $NbAl_3$, is the first phase to form [1, 2]. For films with Nb in excess of the trialuminide stoichiometry, the reaction continues with the formation of the sigma and the A15. The final phases in the films depend on the overall composition and, in certain cases, on the multilayer periodicity [1].

In this paper we focus on the formation of the first phase in the reaction of sputter-deposited Nb/Al multilayer thin films studied by both heat-flux and power – compensated differential scanning calorimetry (DSC). The results of the present work will be compared and contrasted with those for evaporated Nb/Al films [1, 2], where DSC had also proved to be a powerful method in the investigation of the kinetics of formation of intermetallic phases.

Experimental

Multilayer thin films of Nb/Al with bilayer thicknesses, Λ, in the range 10–333 nm and a total thickness of 1 μm were sputter-deposited on $(1\bar{1}02)$ sap-

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phire, Si wafers and glass slides. The wafers and slides were precoated with a 200 nm-thick Cu layer. This layer was dissolved in a solution of equal volumes of distilled water and 65% nitric acid to yield free-standing films for calorimetric measurements. The calorimetric measurements were performed in two different types of calorimeters, one a TA Instruments (formerly DuPont) heat-flux 910-DSC, and the other a Perkin Elmer DSC-2C. The 910-DSC is a differential thermal analyzer that we have calibrated so as to obtain quantitative heat flow data. This instrument has lower sensitivity, but a larger temperature range of operation compared with the DSC-2C. The 910-DSC was modified to allow it to be evacuated and then operated under a controlled atmosphere in order to avoid oxidation and/or contamination of the thin multilayer films. The runs were carried out under 1 sccm of flowing 99.9999% purity Ar. In order to load the free standing films into the sample crucible of the 910-DSC they were enclosed in a 1x1 cm Pt foil that weighed approximately 100 mg. The mass of the thin films ranged from 9–21 mg but was typically around 20 mg. The sample assembly was then placed in a Pt crucible in the DSC furnace. An empty Pt foil, with a weight equal to weight of the Pt foil plus film assembly, was folded and placed into the reference crucible in order to match the heat capacities of the two crucibles as closely as possible. In addition, appropriate amounts of alumina powder were added to both crucibles to insure uniform thermal contact to the thermocouple junctions and to make the heat capacities of both crucibles equal. In order to run the standard materials under similar experimental conditions to those for the thin films, the standards were also enclosed in Pt foils except in cases where they would react with the foil. The thin-film samples were heated at a given rate to the desired temperature, cooled and heated and cooled again without disturbing the sample or the furnace. Since the Nb/Al reactions of interest are irreversible, the second heating cycle allowed the calorimetric baseline to be determined.

The raw data from the heat-flux 910-DSC are triplets of time, t, temperature, T, and temperature difference between the sample and the reference crucibles, ΔT. In order to convert the raw data into heat flow rate we have followed the method of Coffey *et al.* [2] and determined the cell constants through a series of calibration runs at two different heating rates using In, Sn, $KClO_4$, Ag_2SO_4, K_2SO_4, Al, K_2CrO_4, Au and Cu with purities >99.99% as standards. These constants are the cell thermal conductivity, K, and the cell heat capacity, C, and are shown as a function of temperature in Figs 1a and b, respectively.

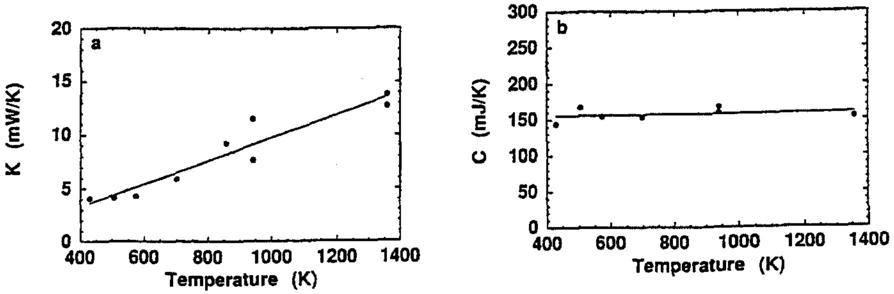

Fig. 1 Cell calibration parameters (a) K and C as a function of temperature (b)

The DSC-2C was calibrated including thermal-lag corrections at various heating rates. The free-standing films were loaded into Cu pans which was placed in the DSC-2C sample cell, with an empty Cu pan placed in the reference cell. Before each run this DSC-2C cell was pumped and flushed with 99.9999% Ar several times in order to avoid sample contamination during heating. The films were annealed in flowing Ar, with heating rates ranging from 10–160 K min^{-1}. Typically a 1–10 mg sample was used for each measurement, which consisted of heating at the desired rate to completion of the reaction, cooling to room temperature at the maximum possible rate, and repeating the heating and cooling cycles. As mentioned before, because of the irreversibility of the reactions, the second heating cycle allows the calorimetric baseline to be determined without disturbance to the sample. Isothermal DSC measurements were performed by heating the calorimeter at 20 K min^{-1} to the hold temperature. Again, a second measurement was carried out under identical conditions in order to establish the baseline. For all types of measurement, the reported calorimetry traces are the difference in the power signal between the first and the second heating cycles.

Results

Figure 2 shows the power *vs.* temperature for a 1Nb/1Al (50 at.% Al) multilayer films with $\Lambda = 143$ nm and Al layer thickness, $t_{Al} = 69$ nm, annealed at a constant heating rate of 20 K min^{-1} in the 910-DSC. Three exothermic peaks are present in this trace, marked as A, B and C. X-ray and electron diffraction and transmission electron microscopy [3] show that both peaks A and B are associated with the formation of the same product phase, $NbAl_3$. Peak C arises from the formation of A15 Nb_3Al and sigma Nb_2Al phases and is only seen in films with overall Al concentrations lower than 75 at.% [1].

Figure 3 presents the heat-flux calorimetry traces for a series of Nb/Al multilayer films, including the film in Fig. 2, that were annealed at a heating rate of

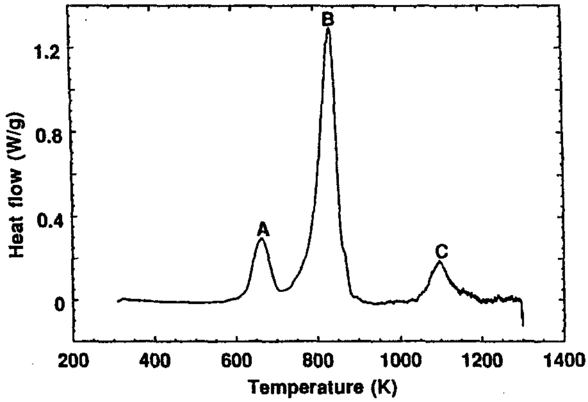

Fig. 2 Heat-flux calorimetry trace for a 1Nb/1Al multilayer film with a $\Lambda = 143$ nm, and $t_{Al} = 69$ nm annealed at 20 K min^{-1}

20 K min^{-1}. Since the focus of the present paper is the formation of the first phase, $NbAl_3$, the calorimetric traces in Fig. 3 have been limited to a maximum temperature of 1000 K. For comparison with these traces, DSC-2C plots for a heating rate of 40 K min^{-1} are shown in Fig. 4. These traces, except that for the film with $\Lambda = 10$ nm, also clearly show two peaks, A and B, for the formation of $NbAl_3$. Peak C is not accessible in the DSC-2C, because the maximum operating temperature is limited to 1000 K. Thus all the films in Fig. 4 had been selected to have an overall composition of 1Nb/3Al so that they would be fully reacted by 1000 K.

The calorimetry peak temperature data for different heating rates was used to determine the activation energy for each peak using well-established methods [4, 5]. The activation energies thus determined from the heat-flux calorimetry traces for our sputter-deposited Nb/Al films are $Q_A = 164.0 \pm 19.3$ kJ mol^{-1} and $Q_B = 241.2 \pm 57.9$ kJ mol^{-1} for peaks A and B, respectively. These values are in good agreement with the values of $Q_A = 164.0 \pm 28.9$ kJ mol^{-1} and $Q_B = 241.2 \pm 9.6$ kJ mol^{-1} obtained from the power-compensated DSC scans. For comparison, Coffey *et al.* [2] obtained 144.7± 19.3 kJ mol^{-1} for peak A and 135.1±28.9 kJ mol^{-1} for peak B for evaporated Nb/Al multilayers. Thus peak A shows a slight and peak B exhibits a large increase in activation energy for the sputtered *vs.* evaporated films. In addition, a comparison of peak temperatures at a given heating rate and Al layer-thickness shows that the sputtered films have consistently higher values than evaporated films.

The kinetics of transformation associated with peak A was studied isothermally for the film with a composition 1Nb/3Al (75 at.% Al) and a periodicity of 10 nm. The isothermal trace for this film at 570 K, shown in Fig. 5, is 'bell shaped' and,

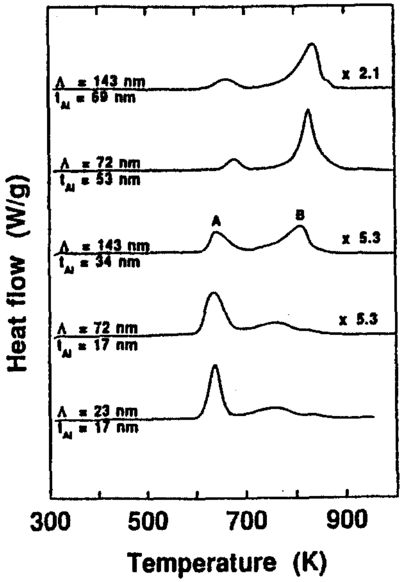

Fig. 3 Heat-flux DSC traces, limited to a maximum temperature of 1000 K, for a series of Nb/Al multilayer films annealed at 20 K min^{-1}. The multiplication factors on the curves account for unreacted Nb remaining at the end of peak B. The top trace in this figure is for the film in Fig. 2

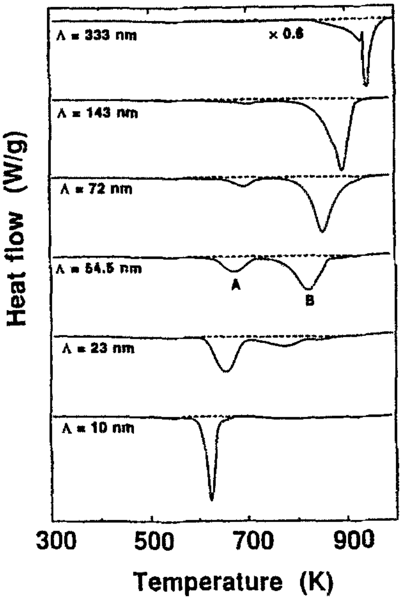

Fig. 4 Power compensated DSC traces for a series of 1Nb/3Al multilayer films annealed at 40 K min^{-1}

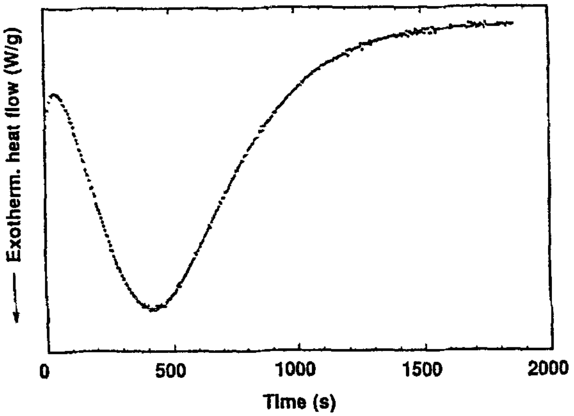

Fig. 5 Isothermal DSC trace at 570 K for a 1Nb/3Al multilayer film with Λ = 10 nm

therefore, characteristic of a nucleation and growth type transformation [6]. Similar traces were observed for the multilayers with larger periodicities.

Discussion

Constant-heating rate scans (Figs 3 and 4) in both the heat-flux and the power-compensated calorimeters show the presence of two peaks for the formation of the single products phase, $NbAl_3$. These figures also show that the relative size of the peaks A and B were a strong function of the initial Al layer thickness. For example, for the film with $\Lambda=333$ nm ($t_{Al}=245$ nm) peak A was barely visible and peak B dominated the trace, whereas for the film with $\Lambda=10$ nm ($t_{Al}=7.5$ nm) peak A was the dominant feature and peak B was absent. Furthermore, peak B in the film with $\Lambda=333$ nm occurred after an endothermic peak due to the melting of the not-yet-consumed Al. The absence of this endothermic peak in the traces for films with thinner Al layers is simple evidence of full consumption of Al in the formation of the trialuminide for all the films.

Double-peaked calorimetry traces for the formation of niobium trialuminide, with a systematic variation of peak heights with Al layer thickness similar to that seen in the present films, were also observed by Coffey *et al.* [2] in evaporated Nb/Al multilayers. These researchers argued that if the growth of the trialuminide were to occur in the direction perpendicular to the multilayer from the very beginning of the reaction, it would not be possible to observe two peaks. Therefore, they interpreted the presence of the two peaks as a two-stage process of phase formation in which the first stage (peak A) was the nucleation and lateral growth of the product grains to coalescence and the second stage (peak B) was the normal growth of this layer until the consumption of one or both reactants. Coffey *et al.* [2], however, did not provide direct evidence for the nucleation of one or both reactants. Coffey *et al.* [2], however, did not provide direct evidence for the nucleation and growth type transformation associated with peak A. Here, we provide this evidence through isothermal calorimetry scans, an example of which was shown in Fig. 5. The interpretation of our constant-heating-rate scans then follows that given by Coffey *et al.* [2]. This interpretation also explains the systematic variation in peak heights so that in films with small reactant layer thicknesses, such as for our film with $\Lambda=10$ nm, full consumption of Al occurs in stage one resulting in the absence of stage two. Conversely, for films with larger Al layer thicknesses stage one becomes a smaller fraction of the overall transformation and stage two, with growth normal to the film, dominates the calorimetry trace.

Although the formation of $NbAl_3$ in the present sputter-deposited films is qualitatively similar to that in the evaporated films, the peak temperatures – at given heating rates and Al layer thicknesses – and the peak activation energies are found to be higher, at times by significant amounts. A small increase in activation energy for the second calorimetry peak for $NiAl_3$ formation in sputter-deposited *vs.* evaporated Ni/Al multilayers has also been reported recently [7]. The higher values of the activation energies and peak temperatures in sputter-deposited Nb/Al films indicate that the $NbAl_3$ formation reaction is slower in the former compared with the latter. The reasons for these differences are not clear, but are expected to be related to the effect of the deposition process on the structure of the films.

Conclusions

Heat-flux and power compensated calorimetry traces showed that the formation of the first phase, $NbAl_3$, in the reaction of sputter-deposited Nb/Al multilayer thin films was a two-stage process. Isothermal calorimetry demonstrated that stage one was a nucleation and growth type transformation. In agreement with previous studies, the two stages were thus interpreted as nucleation and growth to coalescence of the first layer of grains of the product phase (stage one) followed by normal growth to full consumption of Al (stage two). This interpretation was also found to be consistent with the systematic variation of stage one and two peak heights.

Although the present sputter-deposited films showed many similarities in their calorimetric behaviour to evaporated films studied previously, it was found that the former showed higher reaction activation energies and peak temperatures. The reasons for these differences are believed to be related to the differences in the structure of the film resulting from the different deposition methods.

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