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

K. Barmak, C. Michaelsen1 and F. Ma

Department of Materials Science and Engineering, Lehigh University, Bethlehem PA 18015, USA
1Institute of Materials Research, GKSS Research Center, 21502 Geesthacht, Germany

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 NbAl3. 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 NbAl3 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: NbAl3, sigma Nb2Al and A15 Nb3Al. 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, NbAl3, 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, A, in the range 10–333 nm and a total thickness of 1 μm were sputter-deposited on (1102) sap-
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 reactions of interest 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, $\Delta T$. 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, KCIO$_4$, Ag$_2$SO$_4$, K$_2$SO$_4$, Al, K$_2$CrO$_4$, 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.

![Graph](image1.png)

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