International Journal of Thermophysics, Vol. 19, No. 2, 1998

Thermal Diffusion Through Multilayer Coatings: Theory and Experiment[1]

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Thermal diffusion through aluminum oxide/molybdenum multilayers (10, 20, and 40 bilayers on molybdenum substrates) was studied through thermal pulse experiments. In these experiments, a thermal pulse (< 50 ns) was delivered by a laser to the front surface of the specimen and the resulting temperature transient on the rear surface, typically several degrees, was recorded. An integral solution for the equations governing heat transfer was used to relate experimental results to the thermal resistance of the interfaces. Experimental studies were conducted at temperatures from 950 to 1150°C, relevant to thermal barrier applications. Significant densification of the oxide layers was observed during the experiments at all but the lowest temperature. As a result of these experiments, an upper bound has been placed on the interface thermal resistance.

KEY WORDS: aluminum oxide; laser pulse; molybdenum; multilayer; thermal barrier coatings; thermal diffusion; thermal diffusivity.

1. INTRODUCTION

Recent efforts with multilayer thermal barrier coatings (TBCs) are motivated by the possibility that these materials possess lower thermal conductivities than would be anticipated from the macro properties of the constituent layers. Indeed, the thermal transport properties of thin film coatings can be lower than the macro values [1, 2]. An issue, for multilayer TBCs in particular, is whether this decrease is due to an interface resistance associated with the interfaces between the layers, a "bulk" effect

[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22–27, 1997, Boulder, Colorado, U.S.A.

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0195-928X/98/0300-0525$15.00/0

due to, for example, a density less than the crystalline value ("substandard") within the layers, or a combination of the two.

Recent work on Fe/Cu multilayers [3] showed that multilayers of this particular metal/metal system possess thermal transport properties similar to those of macro materials. The effect of the interfaces on thermal transport was shown to be consistent with an interfacial thermal resistance no higher than $10^{-5}\,K \cdot cm^2 \cdot W^{-1}$. This value is consistent with results obtained for the thermal resistance associated with other metal/metal interfaces using a thermoreflectance technique at room temperature [1].

Thermal transport through multilayers of aluminum oxide/molybdenum (alumina/Mo) was studied in this work in order to include an oxide typically used in TBCs. The opaque Mo layers were used to reduce radiative heat transfer because an integral solution to the heat transfer problem, including interface resistance, is possible if radiative heat transfer can be neglected. Molybdenum and aluminum oxide are mutually insoluble and do not react under the conditions studied.

2. EXPERIMENTAL

2.1. Specimen Fabrication

Molybdenum substrates, 76 μm thick, were coated with multilayers of alumina/Mo using an electron beam deposition system. The coatings, of nominally identical total thickness, were divided into either 10, 20, or 40 bilayers; some results for the 10- and 40-bilayer samples have been published previously [4]. Studies of the coatings by cross sectional transmission electron microscopy indicated that while the Mo layers were approximately the desired thickness, the thickness of the alumina layers was approximately twice the desired value. Because thickness control was accomplished with a quartz crystal oscillator that utilized the density of the depositing material as an input, the doubled thickness of the alumina indicates that the density of the alumina layers is approximately 50% that of crystalline alumina. Because the substrates were not heated during deposition, this substandard density is not unusual.

2.2. Pulsed Heating System

Thermal transport through the multilayer alumina/Mo coatings was studied using a pulsed laser heating technique. Because the experimental system [5] and modifications [3] have been described previously, only a summary description of the experiments follows.

A Q-switched laser pulse ($<0.1\,\mu$s) was applied to the "front," uncoated surface of the substrate. The thermal transport properties of the coating/substrate were determined from the time constant associated with the resulting temperature increase (transient) in the "rear," coated surface. This temperature transient, typically several degrees Celsius, was obtained from the changing radiance of the rear surface using an InGaAs detector and amplification electronics; it was necessary to conduct experiments at temperatures higher than approximately 900°C, as there was insufficient signal from the detector below this temperature. The high ambient temperature prior to the laser pulse, used as the specimen temperature, was determined by a pyrometer viewing a blackbody cavity in the specimen holder. Reliability of the measurement system has already been demonstrated; the thermal diffusivity of Mo specimens obtained in the temperature range 1000 to 1600°C using the pulsed heating system was within the estimated experimental uncertainty ($\pm 6\%$) of the accepted values [3].

3. DATA ANALYSIS

Prediction of the rear surface temperature transient, determined by the heat transfer equations within the layers and the temperature and heat flux boundary conditions at the interfaces between the layers of the multilayer coating/substrate system, was accomplished using an integral solution developed to capitalize on the periodic nature of the coatings [3]. The integral solution gives the rear surface temperature transient for a multilayer/substrate specimen composed of a multilayer with an arbitrary number of bilayers, an interface resistance between every layer, and substrate under and a capping layer over the coating. The input parameters required to generate a solution are the thermal resistance at the interfaces and the thermal diffusivities, thermal conductivities, and thicknesses of the layers, substrate, and cap.

Figure 1 shows a typical temperature transient obtained from the radiance signal of the "rear," coated surface of the specimen after the laser pulse was applied at $t = 0\,\mu$s to the "front" substrate surface; the overlaid simulations are described in Section 4. The temperature transient was normalized utilizing the signal prior to the laser pulse for the baseline and the plateau after the laser pulse for the maximum. The time constant $t_{1/2}$, defined as the time required to reach one-half of the maximum temperature excursion, is used here to analyze the results of the pulsed heating experiments. The time $t_{1/2}$ is in fact a unique measure of the thermal diffusivity of homogeneous specimens [6]; such is not the case with nonhomogeneous specimens. However, if the specific heat and thermal conductivity of the substrate, Mo, are well characterized [7, 8], and the specific

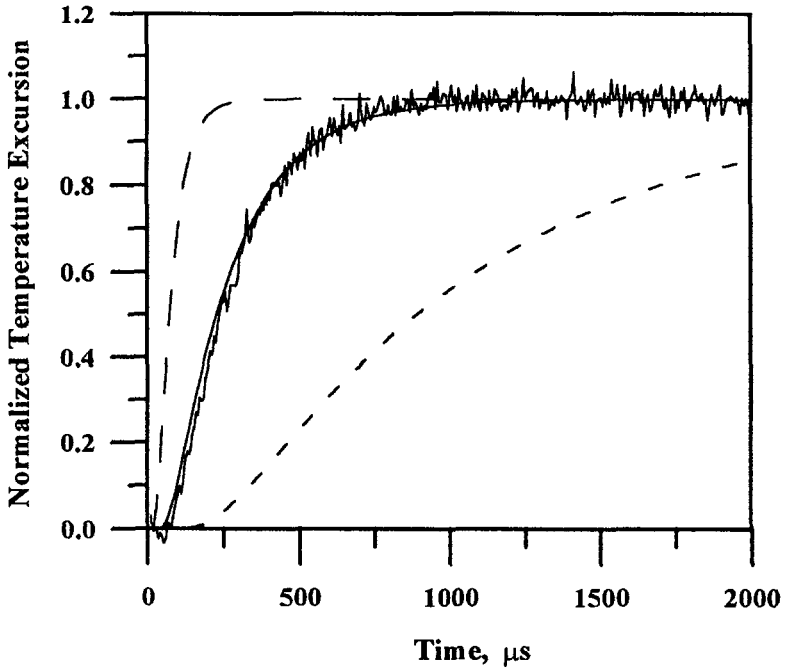

Fig. 1. A normalized temperature transient obtained from a 10-bilayer specimen of alumina/Mo. Curves obtained from the integral solution for macro properties with an interface resistance of 2×10^{-5} K · cm^2 · W^{-1} (long dashes), indistinguishable from the solution with no interface resistance, and an interface resistance of 2×10^{-2} K · cm^2 · W^{-1} (short dashes), as well as for 50% dense alumina with no interface resistance (solid line) [4].

heat of the coating is known, the $t_{1/2}$ value and results from the integral solution do determine the average thermal conductivity of the coating (including both interface and bulk contributions). Bulk values of these properties, as well as layer dimensions obtained by scanning electron microscopy (SEM), are presented in Table I.

4. COMPARISON OF 10-, 20-, AND 40-BILAYER SPECIMENS

Experimental transient times $t_{1/2}$ are compared with the values predicted using macro properties in Table II. Transient times $t_{1/2}$ neglecting heat losses (note the flatness of the plateau in Fig. 1) were obtained from the integral solution [3] based on macro properties for the substrate, coating, and cap with different values of interface resistance; they are overlaid on an experimental transient in Fig. 1. The smallest value of interface resistance

Table I. Macro Transport Properties of Alumina/Mo Multilayer Constituent Materials at 1200 K and Layer Thicknesses

Material	Thermal diffusivity ($cm^2 \cdot s^{-1}$) [7]	Thermal conductivity ($W \cdot cm^{-1} \cdot K^{-1}$) [8]	Average layer(s) thickness (μm)		
			Bilayers		
Alumina/Mo			10	20	40
Mo (layers)	0.339 (±6%)	1.05 (±4–10%)	0.18 (±5%)	0.10 (±10%)	0.045 (±10%)
Substrate				76 (±2%)	
Capping layer				0.2 (±5%)	
Alumina					
100% dense	0.0138 (±4–10%)	0.0655 (±6–10%)	1.14 (±3%)	0.55 (±3%)	0.26 (±3%)
50% dense[a]	0.0030 (±8%)	0.0071 (±9%)			
			Intended thickness[b]		
			0.50	0.25	0.125

[a] Properties estimated from a compilation of experimental data [7, 8].
[b] Intended thicknesses of alumina layers are provided only so the reader may judge the densities.

Table II. Comparison of $t_{1/2}$ (μs) Values from Theory[a] and Experiment for Alumina/Mo Multilayer Coatings

	Bilayers		
Method: experiment/computation	10	20	40
Experiment (from fit at 1200 K)[b]	210 ± 10	190 ± 8	152 ± 7[c]
Integral solution			
$\rho = 0\ K \cdot cm^2 \cdot W^{-1}$	73.3	71.1	66.9
$\rho = 2 \times 10^{-5}\ K \cdot cm^2 \cdot W^{-1}$	74.1	72.7	70.1
$\rho = 2 \times 10^{-2}\ K \cdot cm^2 \cdot W^{-1}$	887	1665	3081
$\rho = 0\ K \cdot cm^2 \cdot W^{-1}$; alumina, 50% dense	228	218	197

[a] Values of transient time $t_{1/2}$ (μs) determined using macro physical properties given in Table I.
[b] Uncertainty is the root mean square deviation of data.
[c] This value is lower than the value originally published in Ref. 4 because the authors were unaware of the initial increase in $t_{1/2}$ at temperatures of interest (see Fig. 2).

modeled comes from metal/metal multilayer results [1, 3]; the largest value was proposed from the results of a variety of techniques utilizing oxide films of varying thicknesses [2]. Transient times $t_{1/2}$ obtained from the integral solution using the different interface resistances are presented in Table II, as are values obtained using the properties of 50% dense alumina (with zero interface resistance).

From Table II, it is evident that the alumina/Mo coatings possess thermal transport properties that differ substantially from macro properties, i.e., those for fully dense coatings with zero interface resistance. Furthermore, it is unambiguously clear that the interface resistance $2 \times 10^{-2}\,\mathrm{K \cdot cm^{-2} \cdot W^{-1}}$ is incompatible with the experimental results (Table II); the experimental $t_{1/2}$ values are significantly smaller than the predicted values (Table II) for all three types of coatings, and other effects, e.g., decreased density, would further increase the predicted $t_{1/2}$ value. In fact, the observed decrease in $t_{1/2}$ as the number (density) of bilayers increases from 10 to 40 is inconsistent with a purely interfacial effect. However, this trend is consistent with the trend (if not the actual values) caused by the unequal total thicknesses of the 10-, 20-, and 40-bilayer coatings for macro properties with a low interface resistance ($\leqslant 2 \times 10^{-5}\,\mathrm{K \cdot cm^2 \cdot W^{-1}}$). This implies that an effect associated with the bulk of the layers (i.e., substandard density) is responsible for some portion of the decrease in thermal transport properties. The much better match of the experimental $t_{1/2}$ values and those predicted using macro properties of 50% dense alumina (Table II) appears to confirm the above.

The decreased quality of the fit obtained assuming 50% dense alumina for the 20- and 40-bilayer specimens is consistent with the normalized alumina densities of the coatings (determined from the intended alumina layer thickness divided by the actual layer thickness; see Table I). The normalized densities of 0.44, 0.45, and 0.48 for the 10-, 20-, and 40-bilayer coatings, respectively, predict faster thermal transport in the 40-bilayer samples, i.e., a decreased $t_{1/2}$, and slower thermal transport in the 10 bilayer sample, i.e., an increased $t_{1/2}$. This trend is consistent with the experimental trend of $t_{1/2}$ values: the 40-bilayer value being the most below the prediction and the 10-bilayer value being the least below the prediction. The difference between the experimental and the predicted $t_{1/2}$ values for the 40-bilayer specimens, closest to 50% dense, may reflect inaccurate determination of specimen densities or the properties of 50% dense alumina.

The highest value of interface resistance compatible with the experimental results is the highest value for which the integral solution predicts $t_{1/2}$ values less than the experimental $t_{1/2}$ values. This condition is most stringent with the 40-bilayer specimens, as they have the highest

interface densities, yielding an upper bound for the interface resistance of $6 \times 10^{-4}\ \mathrm{K \cdot cm^2 \cdot W^{-1}}$. To determine the interface resistance more accurately requires separate knowledge of the fraction of the reduction of transport properties that is due to effects within the layers (i.e., substandard density). The effect of annealing on the thermal transport properties of 10-bilayer specimens, results of which are presented in Section 5, yields the answer.

5. STUDIES OF THE ANNEALING BEHAVIOR OF 10-BILAYER SPECIMENS

Under the assumption that substandard density was reducing the thermal transport through the alumina/Mo multilayer coatings, annealing studies were conducted in the temperature range 1030 to 1150°C. To ensure uniformity of the coatings, specimens [6.4 mm (0.25 in.) in diameter as well as larger pieces] were cut from a single strip of 76-μm (0.003-in.)-thick Mo that had been coated with 10 bilayers of alumina/Mo and a Mo cap (Table I). Specimens were annealed in the furnace of the pulsed heating system so that transport property measurements could be conducted without interruption of the annealing process.

Pulsed heating measurements were conducted on each specimen near 950°C immediately before and after annealing to assess specimen uniformity at the start of the anneals and to allow specimen comparison after the anneals. Preanneal values were between 200 and 219 μs for $t_{1/2}$, differing significantly from the 73-μs prediction of the integral solution [3] based on macro properties and layer dimensions (Table II). Note that the Mo substrate alone would exhibit a $t_{1/2} = 24\ \mu$s using a specimen thickness $L = 76\ \mu$m and thermal diffusivity $\alpha = 0.335\ \mathrm{cm^2 \cdot s^{-1}}$ [7] in Parker's formula, $t_{1/2} = 1.37L^2/(\pi^2\alpha)$, for homogeneous materials [6].

Figure 2 summarizes the dependence of the transient time $t_{1/2}$ on the time spent at the annealing temperature T_A. Aside from an initial decrease in thermal transport properties (increased $t_{1/2}$) in specimens at lower annealing temperatures, the thermal transport properties of all specimens increased during the course of the anneals (decreased $t_{1/2}$). The higher the annealing temperature, the more rapidly this occurred. Assuming that the rate of the underlying physical process (densification) has an Arrhenian dependence on the annealing temperature, $\exp(-Q/kT_A)$, yields a best-fit value $Q/k = (5 \pm 1) \times 10^4\ \mathrm{K}$ ($Q = 4 \pm 1$ eV per atom) for the activation energy. The $t_{1/2}$ values obtained during each anneal, normalized by the preanneal value, are plotted in Fig. 3 against the anneal time multiplied by $\mathrm{C} \cdot \exp(-5 \times 10^4/T_A)$, where T_A is in K and C is an arbitrary constant. Aside from the data at 1030°C, the curves overlay reasonably well, though

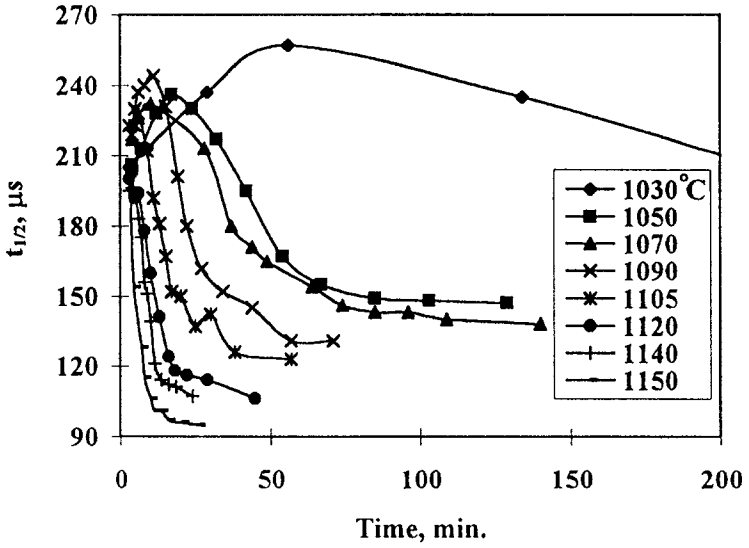

Fig. 2. The characteristic time $t_{1/2}$ of the thermal transient as a function of the time at various annealing temperatures for 10-bilayer alumina/Mo specimens.

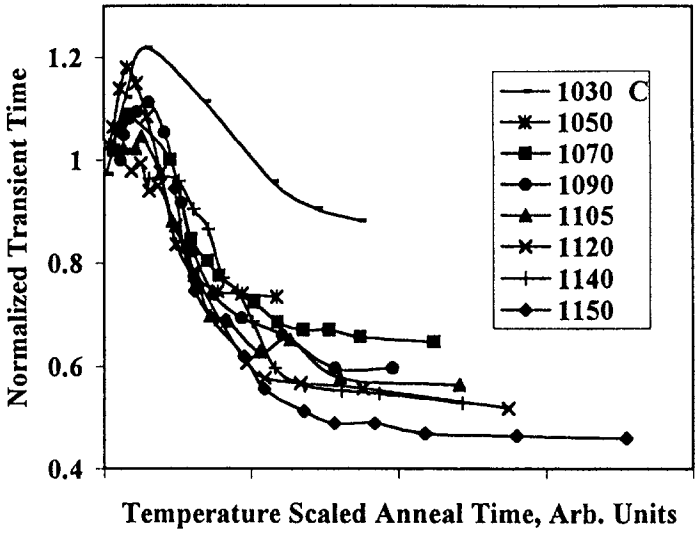

Fig. 3. The characteristic time $t_{1/2}$ of each 10-bilayer alumina/Mo specimen normalized by the value prior to annealing as a function of the temperature-scaled anneal time.

it appears that $t_{1/2}$ stabilizes (densification slows) at a value that depends on the annealing temperature.

The large uncertainty associated with the activation energy, as well as the poor fit of the lowest temperature data in Fig. 3, is possibly due to the initial increase in $t_{1/2}$ at the lower anneal temperatures (Fig. 2). Because densification cannot give rise to this initial behavior, a different phenomenon must be its source. One possible explanation (unexamined) is microcracking in the coating caused by stresses developed during specimen heating.

6. DISCUSSION

Figure 4 shows micrographs of a 10-bilayer alumina/Mo coating in the as-deposited state and the specimen that was annealed at 1120°C. The change in coating thickness is evidence of the densification (approximately 25%) of the alumina layers; SEM studies confirm that negligible mixing has occurred. The specimens's postanneal $t_{1/2} = 99\,\mu$s [obtained at 950°C after a 45-min anneal at 1120°C (Fig. 2)] is much closer than its preanneal $t_{1/2} = 206\,\mu$s to the $73\,\mu$s predicted by the integral solution using macro properties (Table II). The postanneal $t_{1/2}$ for the 40-bilayer samples was less than $80\,\mu$s after 1 h at 1170°C. Using the approximate alumina layer thickness of $0.037\,\mu$m, the value in Table I reduced by the approximate 20% densification observed in the specimen, the $t_{1/2}$ of $80\,\mu$s corresponds, with macro properties and Mo thicknesses unchanged, to an upper bound for the interface resistance (see Section 4) of $9 \times 10^{-5}\,\mathrm{K \cdot cm^2 \cdot W^{-1}}$. Because the alumina density is still expected to be significantly below the crystalline value (see Table I), the interface resistance is likely to be considerably lower than the upper bound just obtained. Evidently, the thermal transport is reduced, in most part, by the substandard material density within the alumina layers rather than the thermal resistance of the interfaces between the layers.

This determination of the source of the decreased thermal transport properties is important. An effect associated with a modification within the bulk of the layers is not enhanced by the use of thinner layers. Furthermore, the benefits of substandard density disappear as the material densifies at elevated application temperatures. A true interfacial effect is enhanced through the use of thinner layers to obtain more interfaces in a coating of fixed thickness (though the stability of such layers can also become an issue at elevated temperatures [9]).

In conclusion, though the thermal conductivities of all of the as-deposited coatings were much lower than macro values, results of annealing studies indicate that this is associated mainly with the reduced density of

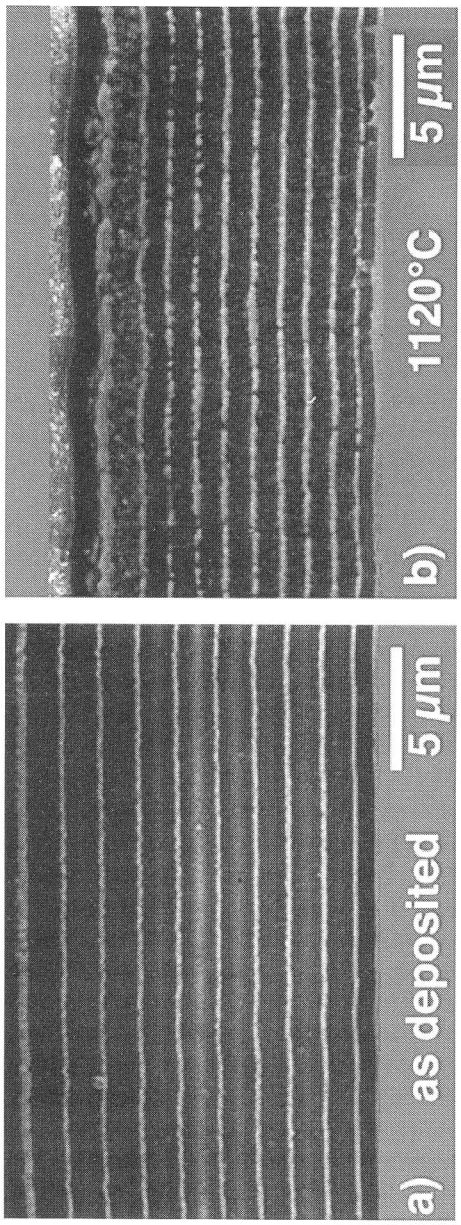

Fig. 4. Micrographs of the 10-bilayer alumina/Mo specimen both as-deposited and after being annealed at 1120°C for 45 min.

the alumina layers. Furthermore, the interface resistance associated with the interfaces within this material was found to be no higher than $9 \times 10^{-5} \cdot \text{cm}^2 \cdot \text{W}^{-1}$, consistent with values obtained for metal/metal multilayers [1, 3].

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