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Design and fabrication of heat resistant multilayers

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Abstract

Many promising applications of multilayer x-ray optical elements subject them to intense radiation. This paper discusses the selection of optimal pairs of materials to resist heat damage and presents simulations of multilayer performance under extreme heat loadings.

Introduction

Multilayers have been used in environments where x-rays or other radiation is sufficiently intense to degrade performance. Examples include such applications as synchrotron primary monochromators and end-mirrors for x-ray lasers. These two examples illustrate the range of environments and performance expectations. A multilayer in the synchrotron application will attain a moderately high steady-state temperature in a hard vacuum, and it will be expected to maintain a reliably constant thickness of its layers without warping or wrinkling. In the laser application, the multilayer is expected to normally reflect a predetermined wavelength, but only for a short period. The damage mechanisms (and therefore the designs and fabrications) are different for the pulsed and cw applications.

Damage mechanisms

Diffraction and reflection arises from regularly spaced, smooth layers with different refractive indexes. Damage mechanisms reduce smoothness, decrease the refractive index gradient at the interface, or cause irregularities in the layer thicknesses. Multilayers are typically made by condensation from low pressure gases (e.g., by evaporation, sputtering or chemical vapor deposition). Such methods seldom produce layers which are in chemical equilibrium with respect to crystallization, although microcrystals may be present. They may also be out of equilibrium with respect to chemical bond formation. For example, a multilayer composed of equal numbers of W and C atoms could presumably form a single, homogeneous layer of the compound WC. In addition, entropy of mixing may drive diffusion of the materials into one another. In most cases, the rate of crystallization, chemical reaction, and diffusion can be ignored at room temperature, but may become objectionable at some higher temperature.

Because the temperature is proportional to the rate of absorbed radiation, materials should be selected that minimize total multilayer absorption of all incident radiation (not just the wavelengths of interest). What is more, severe strain between layers can develop if their thermal expansion coefficients are not well matched. The residual stress resulting from fabrication or annealing could cause enhancement or relief, depending upon its direction. Low absorbance could help keep the temperature below that where mechanical failure of the layers occurs.

In cw applications, melting will distort the layer spacing, if not by flow under the influence of gravity, then by surface tension. In the anticipated pulsed applications, there is not enough time for liquid flow and so it appears that melting can be ignored, at least as a first approximation.

Direct vaporization of solid materials (sublimation) can completely remove an unprotected material exposed to a vacuum over a long period of time. The rate of mass removal depends on several factors, the most important of which is the vapor pressure of the material in question. Vapor pressure increases approximately exponentially with the Kelvin temperature, T . For example, the vapor pressure, P , (in Torr) of solid chromium is given by¹

$$\log_{10} P = 10750 - \frac{20120}{T}$$

MASTER (1).

Graphs of vapor pressure vs temperature² show the least volatile elements to be W, Ta, Re, and C. At 3000 K their vapor pressures range from 10^{-4} to 10^{-2} Torr (0.013 to 0.133 Pa). Vapor pressures are additive (Dalton's Law), so the vapor pressures of all of the materials in a multilayer could tend to delaminate the structure as temperature increases. Delamination is opposed by the cohesive forces in the structure, and for pulsed applications, by the inertia of the layers. The cohesiveness of the materials mentioned above is large compared to the vapor pressure (at least below the melting point). The ultimate strength of tungsten is 1500 MPa, and graphite is 7 MPa, but interfaces are not necessarily as cohesive as pure materials.

EAB

Rapid heating and the consequent expansion generates a shock wave which may cause spalling at multilayer surfaces. Inhomogeneous heating aggravates the problem. The refractory metals undergo a transition from brittle to ductile at some temperature depending upon the history of the test piece. The transition occurs between about 448 and 623 K for tungsten. Brittleness exacerbates spalling. A less serious consequence of rapid heating is compression and rarefaction of layers which results in detuning.

The x rays themselves have potential for direct damage. In most applications, the primary absorption mechanism is photoionization. The resulting electrons are not expected to do significant damage, but crystal imperfections (e.g. color centers) are created over long exposure periods. Radiation damage of this type has not been shown to degrade multilayer performance in the x-ray portion of the spectrum.

Continuous-use applications

To a first approximation, multilayers which are expected to perform for extended periods should have maximal difference in the refractive indexes of the two layer materials, should continue to operate at the highest possible temperature, should have minimal mass loss through sublimation, and should show minimal blurring of interfaces by diffusion.

Selection of materials

To maximize the refractive index difference, one must know the index of every candidate material at the wavelength of interest. In the past, this has been somewhat impractical, so a high-Z element and a low-Z element were selected. (Z is the atomic number.) The most popular low Z element has been carbon. Silicon provides an even larger difference in refractive index over much of the soft x-ray region, but it melts at a relatively low temperature and will not be considered further here. For preliminary screening of material pairs, it would be convenient to base the selection on data which is more accessible than refractive index. At a given wavelength (except near absorption edges) the refractive indexes of the elements are proportional to total electron density given by

$$\rho_e = \frac{ZN_o}{V_a} = \frac{ZN_oA}{\rho} \quad (2)$$

where Z is atomic number, N_o is Avogadro's number, V_a is the atomic volume, A is the gram atomic mass, and ρ is the physical density. This total electron density (not to be confused with conduction electron density) is a more reliable guide than Z and more readily available than measured or calculated refractive indexes.

The selection of optimal materials should also be based on their thermal properties. Figure 1 is a rough but useful guide to such selection. It shows melting points of some elements and refractory compounds plotted against total electron density. The position of carbon is somewhat arbitrary. Carbon does not melt, but its vapor pressure is 0.1 MPa at the plotted temperature of 4200 K. A carbon-containing multilayer may resist delamination at even higher temperatures if it is well bonded to the other material. The ultimate strength of graphite is approximately 7 MPa at room temperature.

Promising pairs of materials can be selected from Figure 1 by choosing those with large differences in electron density and with melting points high enough for the intended application. It is clear that TaC/C is the best and HfC/C is second best. For these two materials, melting will first occur at the interfaces and at the eutectic temperatures (3718 and 3453 K for crystals, lower for typical multilayers).

Vapor pressure is another important factor in the selection because of sublimation and possible delamination. The vapor pressures of the carbides are essentially the same as the constituent elements because under vacuum at high temperatures, the compounds are unstable with respect to decomposition and evaporation of one or both of the elements. Few materials have lower vapor pressures than these at elevated temperatures (tungsten is the major exception). Because C has the highest vapor pressure, the other material should cover all of the carbon. Note also that all of the materials mentioned here form volatile oxides when exposed to oxygen at high temperatures.

It is clear that there is a tradeoff between melting point and maximal difference in total electron density (i.e., W has the highest density but not the highest melting point). However, there are two mitigating factors: the carbides with high melting points are interstitial compounds (carbon atoms in interstices of the metal lattice), so the electron density is not much lower for the carbide than the metal; and the peak reflectance is not a linear function of the difference in refractive index. Table 1. compares the calculated performance of multilayers in order to show the amount of degradation that can be expected by using high-melting but lower density materials. The layer pair thickness is adjusted in each case to give maximum peak reflectance when the angle of incidence is 10° . Also, γ (the ratio of the dense layer thickness to bilayer thickness) is adjusted to maximize reflectance.

Table 1. Calculated reflectances of high-temperature multilayers

Materials	d=23.3			d=127.5		
	γ	Peak	Integrated	γ	Peak	Integrated
W/C	0.32	0.539	0.069	0.39	0.151	0.289
WC/C	0.30	0.525	0.057	0.40	0.133	0.252
HfC/C	0.37	0.352	0.030	0.42	0.105	0.196
TaC/C	0.33	0.452	0.044	0.41	0.117	0.224

Limiting diffusion

Solid state diffusion is rapid at the high temperatures of interest, but it will not occur if the diffusing material is insoluble in the material across the interface. A limited amount of solubility can be tolerated, depending on how much it changes the refractive index gradient across the interface. Published phase diagrams^{3,4} indicate solubilities at various temperatures as well as the compounds which have been observed for almost all pairs of solid chemical elements. Such phase diagrams can be consulted to eliminate pairs of materials which may lose interface sharpness through diffusion. Figure 2 is a portion of the Ta-C phase diagram redrawn from reference 5. The lower right portion indicates virtually no mutual solubility of TaC and C.

The conventional methods of fabrication usually produce layers which are unstable with respect to crystallization or chemical reaction, or both. Although changes are generally slow at room temperature, they become troublesome at elevated temperatures. For example, W/C multilayers have been observed to recrystallize between 923 and 1023 K with total loss of reflectivity due to W crystal penetration of the C layers and generation of roughness⁶. This is a much lower recrystallization range than is observed for bulk W⁷, but in all cases the temperatures depend strongly on impurities and the history of the specimen. At approximately 1100 K, a chemical reaction producing WC can be expected to begin propagating from the interfaces.

In summary, multilayers for continuous duty, high-temperature applications can be optimally designed by selecting pairs of materials which meet the following criteria: have maximum difference in refractive index, absorb a minimal amount of the incident radiation, remain solid at the temperature of the intended application, have no tendency to recrystallize disruptively, have similar thermal expansion coefficients (or compensating residual stress), and have limited solubility in one another. In addition, the chemical elements involved should have low vapor pressures or should be overcoated with a material that does (e.g. tungsten if its absorbance is low enough at the wavelength of interest). We suggest that TaC/C multilayers are an excellent choice where maximum working temperature is important and the x-ray wavelength is relatively short. However, it must be admitted that no single pair of materials is likely to be optimum for all applications because of differing environments.

Single-pulse applications

For certain x-ray laser and plasma diagnostic experiments, the objective is to maintain reflectance for as long as possible (tens of nanoseconds) before the heat load destroys the multilayer. In such cases, the important properties are much different than for continuous use applications. For these short periods, melting can be tolerated (if interfaces do not become optically rough), and vapor pressure is of no consequence until it causes delamination. We expect the tolerable vapor pressure to be very high because it must overcome both cohesion and inertia on a nanosecond time scale. Diffusion and shock are problems in this time regime, but can be minimized by selecting mutually insoluble materials and materials which have low absorbance. The ultimate criterion is the maximum radiation fluence (J/cm^2) the multilayer can be exposed to before it fails. Without knowing the energy spectrum for the intended application, we restate the criterion as the maximum deposited energy per unit volume of multilayer. This assumes the same amount of energy is deposited in each layer pair, which is unlikely to be the case, but without knowing the characteristics of the incoming radiation, we cannot improve on this assumption. Note that comparisons based on energy per unit volume can be significantly different from those using energy per unit mass, a measure which is commonly seen in similar evaluations. It should also be noted that the thermodynamic equilibrium arguments which follow can be considered worst case situations. That is, there may not be time to achieve equilibrium (e.g. melting or vaporization), and diffusion can cause mixing up to but not beyond the equilibrium solubility limit.

Selection of materials

There are two components to the amount of heat a material will absorb for a given increase in temperature: the heat capacity multiplied by the temperature change, and the latent heat of any phase changes which might occur. In pulsed applications, the constant volume version of each is closer to reality, but constant pressure data are more readily available and have very nearly the same values so long as vaporization is not involved. Constant pressure values (enthalpy and heat capacity at constant

pressure) have been used to construct Figure 3., which is useful in materials selection for pulsed applications in the same way as Figure 1. is for continuous-use applications. That is, the highest peak reflectances are available from pairs of materials that are widely separated along the abscissa, and good thermal properties are indicated by high placement on the ordinate.

It is not clear from experiments what the phase criteria are for multilayer stability and reflectance. If all the layers vaporize, they will mix rapidly and reflectivity will be lost. (There are a few known cases of immiscible gases, but none at high temperatures or even with materials that are solid at room temperature.) However, it may be possible for a set of entirely melted layers to reflect until forces disrupted their positions. Alternating layers of liquid and gas would also presumably reflect if smoothness and regular spacing persisted. And there is no obvious reason why stiff, solid layers separated by liquid or gas would not reflect well. The method of using Figure 3. depends on which of these situations one expects to occur. The most revealing illustration is the case where one material remains a solid.

As an example, take a TaC/C multilayer with $\gamma = 0.333$. If the densities of TaC and C are taken as 13.9 and 2.0, the overall composition of the multilayer is 29.8 atom percent Ta and 70.2 atom percent C. As the temperature of such a multilayer rises, the phase situation is represented on Figure 2. by a point directly above 70.2 atom percent C and at the temperature of interest (assuming equilibrium is achieved and the layers are pure, crystalline materials). It can be seen that below 3718 K pure TaC and pure C coexist as solids. At this eutectic temperature, a small amount of material melts. The liquid has the composition of the eutectic mixture (61% C). This third type of layer with an intermediate total electron density will degrade, but not destroy the reflectance of the multilayer. As the temperature increases, its thickness will grow and its composition will change in accordance with the solidus line. This line is the locus of solid-liquid equilibrium points for systems with $C \geq 61\%$. It is dashed in this diagram because it is estimated rather than being based on experimental points. Using tie lines and the lever rule, one can calculate the amount of TaC, C, and liquid mixture at any temperature. In this example, TaC solid will remain until its melting point (4258 K) is reached. After absorbing 7.5KJ/cm³ heat of fusion, it will be completely melted between the remaining carbon layers. As the temperature rises, the state point finally reaches the dashed equilibrium line and the remaining small amount of carbon dissolves in the liquid. This will occur at higher temperatures the larger the percent carbon (the smaller γ).

If the objective is getting to the highest possible temperature before the last solid carbon disappears, then one should select materials which have the solidus line displaced to lower percentages of carbon. Ir-C is probably such a phase diagram, although the solidus is estimated rather than having been observed.

Similar reasoning reveals the phases and the temperature changes for other pairs of materials. Based on this information, the heat absorbed to reach any temperature (and its corresponding phases) can be calculated by standard thermodynamic methods. However, the data needed are often questionable at these high temperatures, and it is very unlikely that the process will remain near thermodynamic equilibrium. Solids may superheat before melting, and large gradients in concentration may exist in the liquid between solid layers. These effects help maintain reflectance, but lateral gradients within layers would degrade it. Lateral gradients could arise from random nucleation of melting.

Lacking information on these kinetic effects, the equilibrium data appear to be the best guide to materials selection. Note that boron absorbs more energy per unit volume than any of the other elements, but its vapor pressure is nearly 4 orders of magnitude higher than carbon at a given temperature. It may be an interesting candidate for the low-density material in certain applications. In spite of this, TaC/C appears to be the best general purpose multilayer for high temperatures.

Simulations

Once a material combination has been chosen which meets the requirements of the application and the multilayer parameters have been optimized it is desirable to obtain some indication of how the multilayer can be expected to perform. In order to facilitate the gathering of such information we are developing a code which will simulate the behavior of a multilayer in a high flux environment. The code performs three basic functions. First the amount of energy absorbed by the multilayer is calculated then the damage to the materials and the structure caused by the energy is assessed. Finally the reflectivity of the multilayer is computed. We will now describe in more detail the codes employed and their operation.

Energy deposition in our simulations is calculated by BUCKL. BUCKL is an analytic X-ray deposition code developed at Sandia Laboratories⁸. It includes important phenomena such as fluorescence and blackbody radiation making it more accurate than exponential codes and has the added features of being relatively fast and providing output files which are readable directly by CHARTD.

Given the energy deposition profiles by BUCKL, CHARTD assesses the damage done to the multilayer. CHARTD is a one-dimensional radiation hydrodynamic code also developed at Sandia⁹. It tracks the thermodynamic state of the materials in the multilayer as well as the positions and velocities of the material interfaces. CHARTD is especially useful in damage study because it estimates the pressure in the layers which will lead to delamination and also provides detailed treatment of phase

changes. One damage mechanism which is not treated, however, is diffusion at the interfaces. This should present no great problem though because the material temperatures are known and phase diagrams can be consulted to determine if the diffusion is significant.

The reflectivity of the damaged multilayer is calculated by LSMLAYERS, a code developed at BYU¹⁰. The code is based on Parrat's formula and includes roughness and diffusion. Recursive codes such as LSMLAYERS have been shown to be mathematically equivalent to analytic codes such as LSMEXACT^{10,11} but have the necessary features to allow the nonuniform layer thicknesses encountered in damaged multilayers.

Using these codes we have been able to simulate the performance of various multilayers. The results of these simulations will be described below. In order to facilitate these simulations the codes are being modified to make them more appropriate for multilayer calculations and they are being integrated into a single unit to improve the interfaces between the codes themselves and the codes and the user. These improvements will also widen the range of problems handled by the codes. For instance the number of material layers allowed will be increased so that up to a thousand layers may be considered.

Simulation Results

As stated above for many applications the TaC/C multilayer appears to be the best choice. To provide a means for comparison we have simulated the behavior of a W/C and a WC/C multilayer and compared the results to those of the TaC/C simulation (all of the samples had the same geometry). As a first estimate energy was absorbed uniformly throughout the multilayer. Our initial simulation showed that the TaC/C combination has a much greater melt resistance than either W/C or WC/C while the melt resistance of WC/C is only marginally better than that of W/C. Attempts to refine this information through further simulations have been hampered by an intermittent bug in the code which appears to be VAX dependent, therefore these results should be considered preliminary. We did, however, observe large (75%) losses of reflectivity for absorbed energy of approximately .5J/cm². This is in reasonable agreement with measurements made by Kohler, et.al¹². Delamination was also observed in each case and appears to be the mechanism which eventually destroys each sample.

Fabrication and Testing

One restriction on material combinations which was not discussed above but which for the present time may be the ultimate restriction is the difficulty in fabricating a multilayer out of a given combination of materials. Indeed in our search for the optimal combination some materials were found which would make excellent robust multilayers but present extreme difficulties given current fabrication technology. For example a B/C multilayer would have some advantages but boron is extremely difficult to sputter. Other combinations presented occupational hazards. We have fabricated a TaC/C multilayer (using a Balzers triode sputtering system) which shows six orders of reflectivity with peak reflectivity of approximately 22% at 2.54Å. Our fabrication facilities are currently undergoing refinements which should result in significant improvements in the quality and performance of the multilayers we produce.

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Figure 1. Melting point vs total electron density. Carbon sublimates so the plotted point is at the temperature where its vapor pressure reaches 0.1 MPa.

Figure 2. A portion of the Ta-C phase diagram redrawn from reference 5.

Figure 3. Absorbed energy vs. total electron density of selected materials. Squares indicate energy absorbed by solid in going from 300 K to the melting point of the pure material. Circles show the additional energy required for complete melting. The triangle shows the energy absorbed in taking solid boron from 300 K to liquid boron at its boiling point.

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