Optical properties of selectively absorbing Ni/Al$_2$O$_3$ composite films

H. G. Craighead and R. A. Buhrman

School of Applied and Engineering Physics and Materials Science Center, Cornell University, Ithaca, New York 14853

(Received 15 June 1977; accepted for publication 20 July 1977)

Composite films of Ni particles embedded in an Al$_2$O$_3$ matrix have been produced by controlled coevaporation. The optical properties of the Ni/Al$_2$O$_3$ composites measured over the range of the solar spectrum are in good accord with the predictions of Maxwell-Garnett theory provided the Ni volume fraction is $\leq 0.2$. The composite films have excellent spectral selectivity for the absorption of solar radiation, with a solar absorptivity of 0.94 obtained for a film produced with a composition gradient. Low-temperature emissivities of $\sim 0.1$ have been obtained with composite films evaporated on highly reflecting metal substrates.

PACS numbers: 84.60.Td, 78.65.-s, 81.20.Nd, 81.15.Ef

The efficiency of solar photothermal collectors is increased by the use of a spectrally selective absorber which has a high absorptivity over the range of the solar spectrum and low emissivity in the infrared. Such a collector absorbs much of the incident solar energy but loses little energy by reradiation. Composite films of small metal particles embedded in a dielectric, also known as cermet films, have optical properties appropriate for good selective solar absorbers. They absorb strongly in the visible due to interband transitions in the metal and the small particle resonance, while they are as transparent as the dielectric in the infrared.\textsuperscript{1} By depositing such a composite film on a reflecting (i.e., low emissivity) metal backing one obtains a selective absorber which is also a good thermal conductor.

Composite Ni/Al$_2$O$_3$ films were produced by simultaneous evaporation of the metal and dielectric. The materials were evaporated from two independently controlled electron-beam evaporators in an oil-free vacuum system with typical system pressures before evaporation of $3 \times 10^{-8}$ Torr. Thirty cm above the evaporation sources, the substrate was clamped to a copper block which could be heated to temperatures as high as 500 °C. During each deposition a thin composite film, a few tens of nanometers thick, was evaporated on a carbon-covered grid for transmission electron microscopy, while a thicker film was deposited for optical measurements. The substrates used for the optical samples were usually fused-quartz plates. Since the two evaporation sources are independently controlled, there is the possibility of varying the composition-depth profile of the films. This ability can be used to enhance the absorption without resorting to the use of interference layers.

The electron micrograph in Fig. 1 shows the typical microstructure of composite films. The Ni forms small nearly spherical particles embedded in the aluminum-oxide matrix. The size of the Ni particles is highly dependent on the substrate temperature during deposition. At a substrate temperature of 500 °C, the Ni particles have diameters as large as 50 nm. When evaporated on an unheated substrate, the Ni particle diameters are typically 5–10 nm. Electron-diffraction studies indicate the Ni particles are crystalline, while no crystalline diffraction peaks are observed from the aluminum-oxide.

The transmission and specular reflection of Ni/Al$_2$O$_3$ films with uniform composition, evaporated on fused quartz.
quartz, were measured in the wavelength range 0.3 - 2.5 μm. The solid line in Fig. 2 shows the measured reflection and transmission for a 190-nm-thick composite with Ni volume fraction 0.19 deposited on fused quartz. From the measured reflection, transmission, and thickness we calculate the extinction coefficient $K$ shown as the solid line in Fig. 3.

For comparison with the measured optical properties, we calculate the optical properties of a uniform composite film using the theory of Maxwell-Garnett. The expression for the effective dielectric constant $\epsilon$ of a composite material is

$$\epsilon = \epsilon_i [2\epsilon_m(1-F) + \epsilon_m(2F + 1)]/[\epsilon_i(F + 2) + \epsilon_m(1-F)].$$

Here $\epsilon_i$ is the dielectric constant of the insulating medium, which we take to be a constant value of 3.12 over this wavelength range, $\epsilon_m$ is the complex dielectric constant of Ni, which we take as the bulk measured values of Johnson and Christy, and $F$ is the Ni volume-filling fraction. The dashed curve in Fig. 3 shows the calculated imaginary part of the index of refraction when $F = 0.19$. The dashed curves in Fig. 2 show the Maxwell-Garnett calculations for the reflectivity and transmission of a 190-nm-thick composite on fused quartz with composite parameters matching the experiment.

Figures 2 and 3 show that there is significant agreement between the measured optical properties and the predictions of Maxwell-Garnett theory without using any adjustable parameters. We have observed good agreement of observed optical properties with Maxwell-Garnett predictions for Ni volume fractions up to ~0.2 regardless of the Ni particle diameter, within the 5- to 50-nm size range. In all measurements, however, we have not observed the predicted structure in the extinction coefficient around 0.4 μ which should appear due to an interband transition in Ni. The structure is presumably smoothed out, perhaps due to lattice distortion or surface effects in the Ni particles. Regardless, we see that the Ni/Al₂O₃ composite has the spectral absorption selectivity desired for a good solar absorber.

While high-performance selective surfaces clearly can be produced using uniform Ni/Al₂O₃ composite films, it is straightforward to show that still greater efficiencies can be obtained with graded composite films in which the metal volume fraction gradually vanishes with distance to the front surface, thereby minimizing front surface reflection losses. We have constructed solar selective surfaces using graded Ni/Al₂O₃ composites. For example, such a composite was evaporated onto a low-emissivity silver layer on a fused-quartz substrate. Figure 4 shows the measured reflectivity for this sample. From the measured wavelength-dependent reflectivity $R(\lambda)$, we calculate the solar absorptivity $\alpha$, defined as

$$\alpha = \int [1 - R(\lambda)] s(\lambda) d\lambda / \int s(\lambda) d\lambda,$$

where $s(\lambda)$ is the solar energy spectrum. For this sample we obtain $\alpha = 0.94$. The emissivity of the films should be determined essentially by the reflectivity of the metal backing. Thus, for a silver or other highly

![Figure 2](image1.png)

**FIG. 2.** Reflection and transmission of a Ni/Al₂O₃ composite with 0.19 volume fraction Ni and thickness 190 nm deposited on fused quartz. The solid curves are measured, and the dashed curves are calculated from Maxwell-Garnett theory with no adjustable parameters.

![Figure 3](image2.png)

**FIG. 3.** The solid curve is the extinction coefficient computed from the measured optical data in Fig. 2. The dashed curve is the extinction coefficient calculated from Maxwell-Garnett theory.

![Figure 4](image3.png)

**FIG. 4.** Wavelength dependence of the reflectivity of a Ni/Al₂O₃ composite with a composition gradient deposited on an Ag layer.
reflecting metal backing, the low-temperature emissivity should be much less than 0.1.

The Ni/Al$_2$O$_3$ composites are completely stable in air at temperatures of a few hundred degrees Celsius, while composites with a thin protective surface layer of Al$_2$O$_3$ are stable at even higher temperatures. Ni/Al$_2$O$_3$ composites evaporated on fused quartz showed only very slight change in transmission after 100 h in air at 500 °C. Composite films having a protective layer of about 100 nm of Al$_2$O$_3$ showed negligible change in transmission after 115 h at 500 °C. Composite films having a protective layer of about 100 nm of Al$_2$O$_3$ showed negligible change in transmission after 115 h at 500 °C. At a temperature of 700 °C in air, the unprotected composites decomposed, apparently by oxidation. While the composite with the Al$_2$O$_3$ surface layer detached from the substrate at 700 °C it did not show rapid oxidation. Since our selectively absorbing Ni/Al$_2$O$_3$ film with a composition gradient has 100% Al$_2$O$_3$ on the front surface, such films can be expected to be oxidation resistant at quite high temperatures. When deposited on a polished copper substrate, the composite/metal system was stable in air up to 400 °C. Above 400 °C the selective absorber system deteriorated rapidly. It is expected that if a more stable metal surface, i.e., Mo, is used, the high-temperature stability of the complete selective absorber will approach that of the composite film alone.

There are other metals which when used in metal-insulator composites should, on the basis of Maxwell-Garnett predictions, show solar selectivity equal to or better than Ni. Two such metals are Cr and V. We have evaporated composite films of Cr and V with Al$_2$O$_3$ and SiO$_2$. The measured optical properties did not agree with Maxwell-Garnett predictions, the evaporated films being in general more transparent than expected. Electron microscopy showed the composites have a very finely divided structure with grain sizes on the order of 1 nm or less. Electron diffraction did not show any distinct crystal structure. We are continuing study of the properties and production of such composites.

In summary, we have produced Ni/Al$_2$O$_3$ composite films by dual-electron-beam evaporation and have shown that they have predictably good solar absorption characteristics. The composite films consist of nearly-spherical crystalline Ni particles with diameters on the order of 10 nm embedded in an aluminum-oxide matrix. The observed optical properties of uniform composite films show good agreement with the predictions of Maxwell-Garnett theory. By evaporating the film with a composition gradient the solar absorptivity is enhanced. The graded composition profile also increases the oxidation resistance of the film due to the protective surface layer of alumina, resulting in composite stability to quite high temperatures in air. The measured solar absorptivity is as high as 0.94 at air mass 2, which compares favorably with other cermet films, but we have not resorted to the use of any interference effects which could enhance $\alpha$ still further. The low-temperature emissivity for this high-absorptivity film should be <0.1.

The authors wish to thank Professor A. J. Sievers for initiating our interest in this subject and for many useful discussions, and thank Professor J. Silcox for the use of his electron microscope.

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