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Computer simulation of the optical properties of high-temperature cermet solar selective coatings

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Abstract

A computer simulation is developed to calculate the solar absorptance and thermal emittance of various configurations of cermet solar selective coatings. Special attention has been paid to those material combinations, which are commonly used in high-temperature solar thermal applications. Moreover, other material combinations such as two-, three- and four-cermet-layer structures as solar selective coatings have been theoretically analyzed by computer simulation using three distinct physical models of Ping Sheng, Maxwell–Garnett and Bruggeman. The novel case of two-cermet-layer structure with different cermet components has also been investigated. The results were optimized by allowing the program to manipulate the metal volume fraction and thickness of each layer and the results compared to choose the best possible configuration. The calculated results are within the range of 0.91–0.97 for solar absorptance and 0.02–0.07 for thermal emittance at room temperature.

Keywords: Solar selective absorber; Cermet; Simulation; Effective medium theory; Optical properties

1. Introduction

It is believed that improving the efficiency of solar thermal energy conversion systems strongly depends on the optical properties of solar selective materials used in their solar energy absorber surfaces. Solar selective absorbers must capture the largest possible amount of solar energy, and at the same time minimize the losses by thermal radiation emission. Ideally, these materials should be perfect absorbers over the solar spectrum and perfect reflectors in the thermal infrared (IR). The latter is in order to avoid heat losses due to the emission of radiation from the surface according to Kirchhoff's law.

Composite media, materials with a rough or porous surface, and multilayer films are the practical options for solar selective absorbers. Among the selective materials, cermets (ceramic-metal composites) are of special interest because of their high thermal stability, which makes them particularly suitable for high-temperature applications in photo-thermal solar energy conversion.

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Nomenclature

HMVF	high metal volume fraction
LMVF	low metal volume fraction
R	reflectance of multilayer
VF	volume fraction
ε_A	dielectric function of metal
ε_B	dielectric function of ceramic
t	amplitude of transmittance of thin film
r	amplitude of reflectance of thin film
f_A	filling factor
M	characteristic transfer matrix
n_0	refractive index of air
n_T	refractive index of substrate
n_1	refractive index of thin film
l	thickness of thin film (nm)
λ	wavelength (nm)
ε^{MG}, ε^{BR} and ε^{PS}	the average dielectric functions of a composite in Maxwell–Garnett (MG), Bruggeman (BR) and Ping Sheng (PS) approximations, respectively
v_1 and v_2	the relative probabilities of the occurrence for type-a and type-b in Ping Sheng model

Cermets for solar applications usually consist of nanometer-sized metal particles (~1–20 nm) embedded in a ceramic binder. This material is deposited over a metallic substrate and may be covered with an anti-reflection coating to enhance the solar absorptance. Also, it has been found that grading the concentration of the metal particles from a low metal particle density at the air/cermet interface to a high metal particle density at the cermet/substrate interface, improves the spectral selectivity of the coatings (Ritchie and Window, 1977). In particular, a system with two-cermet-layers with different metal concentrations provides the best optical results (Zhang and Mills, 1992a,b; Zhang, 1998; Zhang, 2001).

The selectivity of cermets is based on a tandem effect: the cermet itself absorbs radiation strongly in the region below the cut-off wavelength (between 2 and 3 μm) and is almost transparent to IR wavelengths. Meanwhile, the metallic substrate provides high IR reflectance and contributes a small portion of the absorption in the ultraviolet (UV) and visible regions.

In this work by computer simulation, the effect of increasing the number of cermet layers on the optical response of the selective absorber as compared to that of two-cermet-layers is investigated. Also the effect of using a two-cermet-layer structure, having different metallic or ceramic components, on the optical properties of a cermet selective absorber will be shown. In addition a survey on the choice of cermet components has been carried out based on their optical constants.

The optical response of cermets is usually modelled using the so-called effective medium theories. Based on these theories, we simulated the optical response of various structures of cermet selective absorber coatings. For better performance, it is considered that in all structures the cermet layers are sandwiched between an anti-reflection layer (such as Al_2O_3 or SiO_2) and an IR-Reflector layer (Cu). Also the metallic components of the cermets are chosen to be Stainless steel (SS), Au or Cu and the ceramic components are either alumina or silica.

2. Theoretical simulation

If the refractive indices of the metal, ceramic and cermet materials are known, one can calculate the reflectance, then the solar absorptance, emittance and photo-thermal efficiency of the solar selective coatings (Granqvist, 1991). The refractive index of cermet materials can be calculated from the refractive indices of metal and ceramic components using a physical model. The most widely physical models used for the dielectric function of a composite have been proposed by (Bruggeman, 1935; Ping Sheng, 1980; Maxwell–Garnett, 1904). For identical spherical grains with size much less than the wavelength of light, the average dielectric function of a composite in the Bruggeman (BR), Maxwell–Garnett (MG) and Ping Sheng (PS) approximations, is given by the following formulae:

$$\varepsilon^{MG} = \varepsilon_B \frac{\varepsilon_A + 2\varepsilon_B + 2f_A(\varepsilon_A - \varepsilon_B)}{\varepsilon_A + 2\varepsilon_B - f_A(\varepsilon_A - \varepsilon_B)} \tag{1}$$

$$f_A \frac{\varepsilon_A - \bar{\varepsilon}^{BR}}{\varepsilon_A + 2\bar{\varepsilon}^{BR}} + (1 - f_A)\frac{\varepsilon_B - \bar{\varepsilon}^{BR}}{\varepsilon_B + 2\bar{\varepsilon}^{BR}} = 0 \tag{2}$$

ε^{MG} and ε^{BR} are the average dielectric functions of a composite in Maxwell–Garnett (MG) and Bruggeman (BR) approximations. Where ε_A and ε_B are the dielectric functions of metal (A) and ceramic (B), respectively. The filling factor f_A represents the volume fraction occupied by the metal spheres having ε_A.

Also Eq. (3), according to the Ping Sheng model that supposes composite film as a mixture of two types coated spheroidal units, dielectric-coated metal spheroids described as type-a units and metal-coated dielectric spheroids described as type-b units, estimates the average dielectric function of a cermet as follows:

$$v_2 \frac{\zeta_1 - \varepsilon^{PS}}{\zeta_1 + 2\varepsilon^{PS}} + (1 - v_2)\frac{\zeta_2 - \varepsilon^{PS}}{\zeta_2 + 2\varepsilon^{PS}} = 0 \tag{3}$$

While

$$\zeta_1 = \varepsilon_A \frac{(2\varepsilon_A + \varepsilon_B) - 2(1 - f_A)(\varepsilon_A - \varepsilon_B)}{(2\varepsilon_A + \varepsilon_B) + (1 - f_A)(\varepsilon_A - \varepsilon_B)}$$

$$\zeta_2 = \varepsilon_B \frac{(\varepsilon_A + 2\varepsilon_B) + 2f_A(\varepsilon_A - \varepsilon_B)}{(\varepsilon_A + 2\varepsilon_B) - f_A(\varepsilon_A - \varepsilon_B)} \tag{4}$$

$$v_1 = \frac{(1 - f_A^{1/3})^3}{(1 - f_A^{1/3})^3 + \left[1 - (1 - f_A)^{1/3}\right]^3} \tag{5}$$

$$v_2 = (1 - v_1) \tag{6}$$

where v_1 and v_2 are the relative probabilities of the occurrence for type-a and type-b units, respectively, at any metal volume fraction. ξ_1 and ξ_2 are defined for the purpose of simplification.

Having obtained the optical constants of the cermet material, the optical properties of the solar selective absorber coatings can be calculated according to the following matrix formulation.

$$\begin{bmatrix} 1 \\ n_0 \end{bmatrix} + \begin{bmatrix} 1 \\ -n_0 \end{bmatrix} r = M \begin{bmatrix} 1 \\ n_T \end{bmatrix} t \tag{7}$$

where n_0 and n_T represent the refractive index of air and substrate, respectively and M denotes the characteristic transfer matrix. Also, r and t are amplitude of reflectance and transmittance of one layer thin film sandwiched between air and substrate.

$$M = \begin{bmatrix} \cos kl & -\frac{i}{n_1} \sin kl \\ -in_1 \sin kl & \cos kl \end{bmatrix} \tag{8}$$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi n_1}{\lambda_0} \tag{9}$$

where l and n_1 are the thickness and refractive index of the thin film, respectively. If there is a multilayer, the characteristic matrix and reflectance amplitude are calculated as follows:

$$M = M_1 M_2 M_3 \ldots M_N = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \tag{10}$$

$$r = \frac{An_0 + Bn_T n_0 - C - Dn_T}{An_0 + Bn_T n_0 + C + Dn_T} \tag{11}$$

$$R = \mid r^2 \mid \tag{12}$$

where R is the reflectance of the multilayer.

To have a near ideal solar selective absorber coating, one should optimize the optical response of the absorber so that the reflectance of the multilayer is minimized in the solar region of the spectrum and maximized in the IR region. To achieve this goal, we used a non-linear optimization program in the simulation.

3. Results and discussion

3.1. Comparison of linear- and sequence-graded cermet structures

It has been reported that two-layer cermets with different metal contents (one with low metal volume fraction (LMVF) and the other with high metal volume fraction (HMVF)) lead to the best optical response of the solar selective absorber coatings in comparison with metal integral graded cermet selective absorbers (Zhang and Mills, 1992a,b; Zhang, 1998; Zhang, 2001). The schematic diagram of the layers used in this double-cermet structure is shown in Fig. 1.

In this work, by computer simulation we investigated the effect of increasing the number of cermets in sequence-graded structures on the optical properties of selective absorber. The resultant optical properties are summarized in Table 1. In Fig. 2, the optimized thickness and metal volume fraction of each of the cermets constituting the assumed structures is shown.

Solar absorptance and emittance values extracted from simulation are shown to 3 significant figures. Accurate measurement to such precision is unrealistic. With comparison on the basis of 2 significant figures, it is evident that increasing the number of cermets does not improve the optical response of the selective coatings and that there is no strong dependence of cermet structure on the final optical properties. It can be concluded that the two-cermet-layer structure, because of ease of fabrication, is the most suitable for a cermet solar selective absorber. The thickness and metal content of cermets derived by optimization are almost coincident with those of the two-cermet-layer structure.

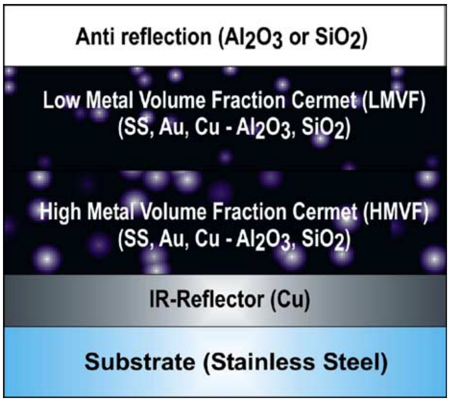

Fig. 1. Schematic diagram of a double-cermet structure solar absorber.

Table 1
The optical properties of sequence-graded (having 2, 3, ... cermet layers) and linear-graded structure as solar selective absorber coatings with the structure of Al_2O_3 (anti-reflection layer)/SS–Al_2O_3 (LMVF cermet)/SS–Al_2O_3 (HMVF cermet)/IR reflector (Cu)/substrate (SS) (use of 3 significant figures for comparative purposes only)

	2 Cermets	3 Cermets	4 Cermets	5 Cermets	6 Cermets	7 Cermets	7 Cermets linear graded
Solar absorptance	0.914	0.915	0.915	0.915	0.915	0.914	0.908
Emittance	0.028	0.028	0.028	0.028	0.028	0.028	0.032

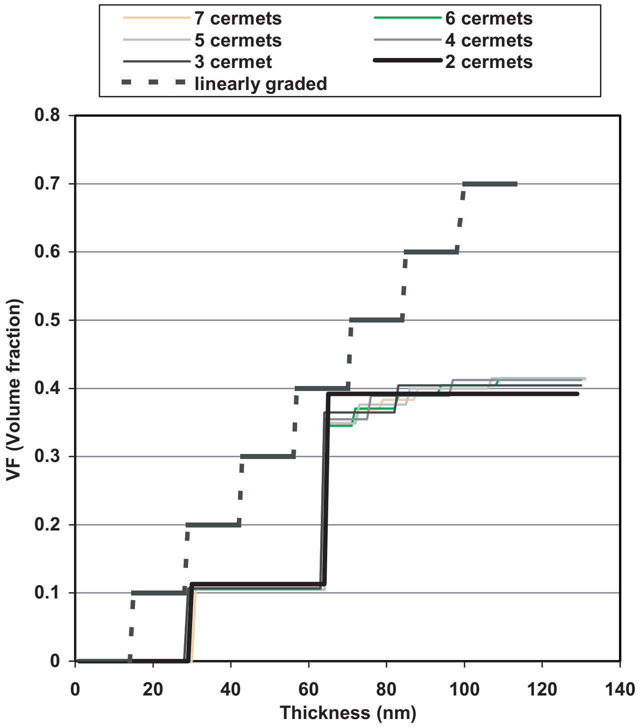

Fig. 2. Comparing thickness and VF of optimized sequence (in 2 and more cermet layers) and linear graded cermet structure.

3.2. Criteria for selection of cermet components

The choice of material for improving the selectivity of solar absorber coatings was investigated on the basis of their optical constants. It has been shown that higher refractive index composites lead to better selectivity (Farooq and Hutchins, 2002a,b). In addition, to achieve better optical properties, the optical constants of metallic component of the cermet should be close to those of ceramic component. We investigated cermet composites with a metallic component of Au, Cu or SS and a ceramic component of either Al_2O_3 or SiO_2.

For selecting the best configuration using the above materials, the Ping Sheng theory and the two-cermet structure schematically shown in Fig. 1, were assumed. Different configurations and conditions were tried. For example, simulations were performed with and without an anti-reflection coating for cermet layers having metal content of 70%, thickness 110 nm and metal content 42%, thickness 118 nm.

All the above assumptions led to the following optical preferences:

SS–SiO_2 > Au–SiO_2 > Cu–SiO_2
SS–Al_2O_3 > Au–Al_2O_3 > Cu–Al_2O_3

"The symbol (>) indicates that the composite in the left side has higher solar absorptance and lower thermal emittance than the composite in the right side".

It has been shown that a material with higher extinction coefficient may lead to higher solar absorptance (Farooq and Hutchins, 2002a,b). As the extinction coefficient of Al_2O_3 and SiO_2 in the solar spectrum is near to zero, then the solar absorptance can only depend on the extinction coefficient of the metal component of the cermet. In the wavelength range 450–550 nm, k_{Au}, k_{Cu} and k_{SS} are almost the same (Fig. 3) and higher solar absorptance will depend on higher refractive index of both ceramic and metallic components of the cermet and also on how close the refractive indexes of ceramic and metallic parts of composites are.

In our case, the n_{SS} (refractive index of Stainless steel) in the peak solar region as shown in Fig. 4, lies between the $n_{Al_2O_3}$ and n_{SiO_2}. Therefore, one can predict an improved optical response for SS–Al_2O_3 and SS–SiO_2 cermets compared to the other combinations.

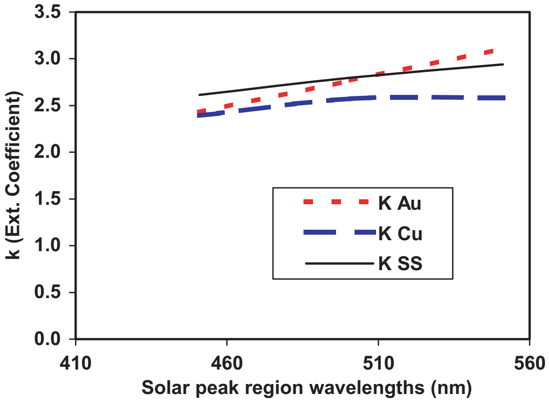

Fig. 3. Comparison of the spectral extinction coefficient (K) of Au, Cu and Stainless steel (SS).

In Figs. 5 and 6 the optical responses of various cermet combinations for the above materials have been shown. Although the refractive index of Cu in the solar peak region is greater than that of Au, at wavelengths greater than 550 nm its refractive index is lower than Au. Therefore, the Al_2O_3 or SiO_2 based cermets with metallic component of Au has better optical properties in comparison with Cu.

3.3. Two cermets structure with different material for cermet components

Usually, in the design of double-cermet-layer structures, the only difference between the two-cermet layers is in their thickness and metal content. In this study in addition to these parameters, the effect of using different materials for the components of the two cermets on the optical properties of the absorber was investigated.

Six distinct configurations, shown in Fig. 7, were considered. In all configurations, thickness and metal volume fraction of each cermet layer have been optimized to obtain the highest solar absorptance and lowest thermal emittance. The simulated optical results are shown in Table 2 and sorted by the optical preference.

In two of the configurations (numbered 2 and 6), the low and high metal volume fraction cermets are of conventional design having the same material components.

As stated in Section 3.1, comparison of the optical results should be done with the numbers rounded to 2 significant figures. In this case, there is some difference in

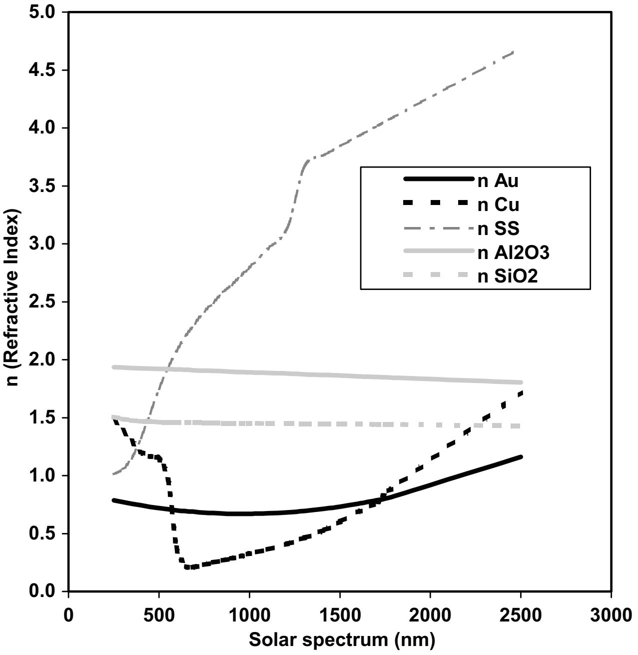

Fig. 4. Comparison of the spectral refractive index (n) of Au, Cu and Stainless steel (SS).

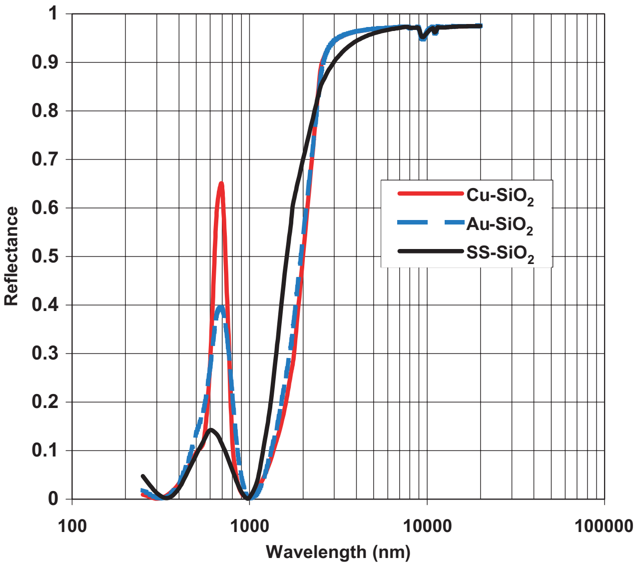

Fig. 5. Spectral reflectance for 3 combinations of SiO_2 based cermets, 118 nm thick with VF of 0.42.

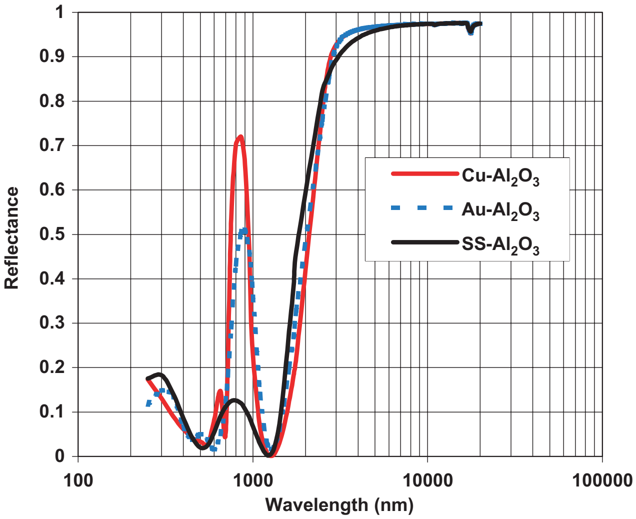

Fig. 6. Spectral reflectance for 3 combinations of Al_2O_3 based cermets, 118 nm thick with VF of 0.42.

solar absorptance, but the emittance dependence is not significant. Although the dependence is not very strong, it can be concluded that using different material components in the fabrication of double-cermet-layer absorbers, may lead to some small improvement in the optical characteristics when compared to double-cermet structures having identical material components.

Though, the number of possible configurations in design of double-cermet absorbers with different material components is numerous, choosing the best configurations is not really a difficult task, considering the fact that cermet layers with higher refractive index should be placed nearer the substrate and those with lower refractive index should be placed just adjacent to the anti-reflection coating. Also, the anti-reflection layer should have a refractive index between that of air and the underlying cermet layer. Obviously, an anti-reflection layer with a refractive index close to that of air reduces the surface reflection of the air–absorber interface.

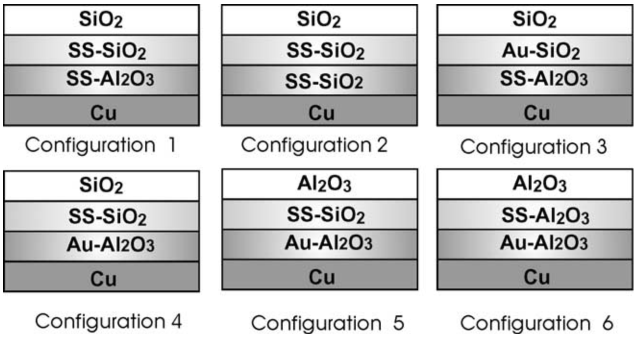

Fig. 7. Schematic representation of double-cermet structure employing different materials for the respective cermet components.

Table 2
Absorptance and emittance of 6 different configurations of double-cermet-layer structure absorbers (use of 3 significant figures for comparative purposes only)

Configuration	Solar absorptance	Emittance
1	0.963	0.037
2	0.954	0.041
3	0.952	0.038
4	0.942	0.037
5	0.931	0.039
6	0.928	0.034

It should be noted that the criteria mentioned in Section 3.2 would be a useful guideline in choosing materials as cermet components in the design of double-cermet absorbers with different cermet materials.

4. Conclusions

Through a computer simulation of the optical response of cermet based selective absorbers, different cermet structures were investigated and the following conclusions obtained:

- Increasing the number of cermets does not improve the optical properties of the selective coatings but it can be concluded that the two-cermet-layer structure, because of the ease of preparation, is the most suitable structure for fabrication of cermet based solar selective absorbers.
- Higher solar absorptance will depend on higher extinction coefficient and higher refractive index of both ceramic and metallic components of the cermet and also on how close the respective refractive indices of the ceramic and metallic parts are.
- Using different material components in the fabrication of double-cermet-layer absorbers, may lead to some small improvement in the optical characteristics when compared to double-cermet structures having identical material components.

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