NiCr–MgF₂ spectrally selective solar absorber with ultra-high solar absorptance and low thermal emittance

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A B S T R A C T

NiCr-MgF₂ spectrally selective solar absorber, which consists of the tandem films of Au, high-metal-volume-fraction (HMVF) NiCr-MgF₂, low-metal-volume-fraction (LMVF) NiCr-MgF₂ and MgF₂, is designed and fabricated for ultra-high solar absorptance and low thermal emittance. The performance of Au/NiCr-MgF₂ (HMVF)/NiCr-MgF₂ (LMVF)/MgF₂ is simulated using the effective medium theory and film matrix method, and the optimized NiCr-MgF₂ spectrally selective solar absorber has a normal solar absorptance (αₛₙ) of 0.981 and a normal thermal emittance (εₜₙ) of 0.042 at 25 °C. The tandem films of Au/NiCr-MgF₂ (HMVF)/NiCr-MgF₂(LMVF)/MgF₂ are fabricated by magnetron sputtering and measured by UV-VIS-IR spectrometer, and it has an ultra-high near normal solar absorptance of αₛₙ 0.976 and a low near normal thermal emittance of εₜₙ 0.045 at 25 °C, which approaches very closely to the simulated limit. Furthermore, NiCr-MgF₂ spectrally selective solar absorber allows a wide incident angle (θ) with its angular solar absorptance αₛ(θ) 0.957 and angular thermal emittance ε(θ) 0.054 if θ < 50°. Such spectrally selective solar absorber is an outstanding candidate for solar thermal applications.

1. Introduction

Spectrally selective solar absorber captures and converts sunlight into thermal energy [1], and they are applied to solar hot water systems [2], concentrated solar power (CSP) plants [3–9], solar thermoelectric generators [10] and solar thermophotovoltaics [11]. To maximize photo-thermal conversion efficiency, the solar absorber should have high solar absorptance (αₛ) in the solar spectrum range (0.3–2.5 μm) and low thermal emittance (ε) in the infrared (IR) range (λ > 2.5 μm) [12–18].

Thus far, various solar absorbers have been widely investigated, for example, (1) intrinsic absorbers [19], (2) semiconductor-metal tandems [20], (3) multilayer stacks [21], (4) metal-dielectric (cermet) composite absorbers [12], (5) textured surfaces [22], and (6) selectively solar-transmitting coatings on blackbody-like absorbers [21]. Among them, cermet based solar absorbers have been attracting the attention of researchers due to their excellent performance on the spectral selectivity, i.e. high αₛ and low ε [23–25]. When metal nanoparticles are imbedded in the dielectric matrix, the cermet layer strongly absorbs solar radiation due to interband transitions in metal together with small particle resonances and becomes relatively transparent in IR range. This enables a high spectral selectivity for the cermet based solar absorber [1, 12, 26, 27]. Using Cr₂O₃, Al₂O₃, AlN, SiO₂ and ZrO₂ based cermet as absorption layer, the solar absorbers have demonstrated outstanding optical properties [28–34]. For the experimentally optimized cermet based solar absorbers, the values of solar absorptance and thermal emittance are mostly 0.93–0.96 and 0.05–0.10 for temperatures from 25 to 100 °C, respectively [28, 30, 33]. To date, the Ni–NiO cermet based solar absorber [24] is known to show the best spectral selectivity (αₛ/ε) being 0.969/0.047. How to improve the spectral selectivity of the cermet based solar absorber further is still an urgent and severe challenge.

The purpose of our research work is to achieve solar absorber with superior spectral selectivity. For this target, an optimal coating structure, appropriate materials and optimization method for the developed solar absorber are prepared. Firstly, a double cermet layer structure,
providing an optimal spectral selectivity for the solar absorber, is adopted [35]. Secondly and crucially, optically optimal dielectric materials for the cermet absorption layer and antireflection layer are chosen. The dielectric materials with lower refractive index (n), can make the sunlight sufficiently permeate into the solar absorber, which is benefit for enhancing solar absorption. In addition, the antireflection layer with lower refractive index material brings a better anti-reflective effect for sunlight, improving solar absorption further [23]. Compared with the above dielectric material for cermet layers (n(AlN) 2.13, n(Cr2O3) 2.12, n(ZrO2) 2.12, n(AL2O3) 1.67, n(SiO2) 1.47 at λ 1 μm), the MgF2 (n(MgF2) 1.37 at λ 1 μm) has the lowest refractive index [36–41]. Hence, MgF2 is selected as the dielectric material for the cermet and the antireflection layers in order to maximize solar absorption. The alloy NiCr is chosen as the light absorbing metal component in the cermet layers. Compared with low cost metals, e.g. Al and Cu, Au film has higher reflectance in IR range and is adopted as the IR reflector in our absorber. Finally, a theoretically optimization process, based on the effective medium theory and film matrix method [23, 24, 42, 43], is carried out to acquire the optimal parameters for the NiCr–MgF2 cermet solar absorber before preparation.

In this paper, a novel Au/NiCr–MgF2 (HMFV)/NiCr–MgF2 (LMVF)/MgF2 solar absorber with the double cermet layer structure, is theoretically optimized and fabricated by magnetron sputtering. The fabricated solar absorber is found to have an extremely high near normal solar absorptance of 0.976 and a low near normal thermal emittance of 0.045 at 25 C. To the best of our knowledge, this is the best spectral selectivity reported so far. Furthermore, the NiCr–MgF2 cermet based solar absorber allows a wide incident angle (θ) with its angular solar absorptance αs(θ) 0.957 and angular thermal emittance ε(θ) 0.054 if θ 50°.

2. Theoretical model

The spectral selectivity of a solar absorber is evaluated by the solar absorptance and thermal emittance. The angular solar absorptance αs(θ), angular thermal emittance ε(θ) and hemispherical thermal emittance εh are defined by Eqs. (1)–(3), respectively,

\[ \alpha_s(θ) = \frac{\int_{0.3\mu m}^{2.3\mu m} R \ \theta \ \lambda \ I_0 \ \lambda \ d\lambda}{\int_{0.3\mu m}^{2.3\mu m} I_0 \ \lambda \ d\lambda} \] (1)

\[ \varepsilon(θ) = \frac{\int_{2.5\mu m}^{100\mu m} R \ \theta \ \lambda \ I_0 \ \lambda \ T \ d\lambda}{\int_{2.5\mu m}^{100\mu m} I_0 \ \lambda \ T \ d\lambda} \] (2)

\[ \varepsilon_h = \int_0^{\pi/2} \int_{2.5\mu m}^{100\mu m} \sin \theta \ 1 \ R \ \theta \ \lambda \ I_0 \ \lambda \ T \ d\lambda \ d\theta \] (3)

where I0, λ, T and R from θ are respectively the solar radiation spectrum, blackbody radiation spectrum at 25 C and angular reflectance spectrum of the solar absorber [25, 44]. The normal solar absorptance and normal thermal emittance are marked as αsn and εtn respectively. The photo-thermal conversion efficiency η is introduced to characterize the compromise of normal solar absorptance and hemispherical thermal emittance as [25]:

\[ \eta = \frac{\varepsilon_h \theta T^4}{CT} \] (4)

where σ, T, C, and I are Stefan-Boltzmann constant, working temperature of solar absorber, concentration ratio and solar radiation, respectively. In our simulation, the conditions are as follows: T 25 C, C 2.3 and I 1000 Wm−2.

The double cermet layer structure of the NiCr–MgF2 cermet based solar absorber consists of four layers (Fig. 1) [35]: (1) An antireflection (AR) MgF2 layer that enhances the transmission of solar radiation by antireflection. (2) HMFV and LMVF cermet layers which absorb solar radiation by the combination of intrinsic and interference absorption. (3) An IR-reflective Au layer, which has high reflectance in IR region to reduces the thermal emittance. The thickness of the Au layer is ~100 nm, which is optically opaque in IR region. The HMFV and LMVF cermet layers are composed of many NiCr and MgF2 minilayers which are alternately deposited. The expected metal volume fraction is adjusted by the current and deposition times of the NiCr and MgF2 minilayers.

The optical constants (refractive index n and extinction coefficient k) of Au, Ni, Cr and MgF2 are obtained from Refs. [41, 45, 46]. The optical constants of alloy NiCr in the cermet layer are calculated by Eq. (5):

\[ \tilde{n}, \tilde{n}, k = \sqrt{\frac{4n^2 - \tilde{n}^2}{5}} \] (5)

where \( \tilde{n}, n, k \) is the complex refractive index [47]. The Bruggeman model based on the effective medium theory [23], is adopted to calculate the optical constants of the NiCr–MgF2 cermet layer. Having acquired the optical constants of the four layers, the reflectance spectra of this NiCr–MgF2 cermet based multilayer solar absorber are calculated using the film matrix approach [48]. Finally the values of solar absorptance, thermal emittance and photo-thermal conversion efficiency are calculated according to Eqs. (1)–(4).

3. Experimental section

The stainless steel (SS)/Au/NiCr–MgF2 (HMFV)/NiCr–MgF2

![Fig. 1. (a) Schematic diagram and (b) cross-sectional TEM micrograph of the Au/NiCr–MgF2 (HMFV)/NiCr–MgF2 (LMVF)/MgF2 solar absorber.](image-url)
The reflectance spectra in 0.3–2.5 μm and 2.5–24 μm are measured using Cary 5000 UV–Vis–NIR and Bruker Vertex 80 FT-IR spectrometers, respectively. The near normal reflectance spectra in 0.3–2.5 μm and 2.5–24 μm are measured using an integrating sphere accessory with incident angle of 3° 40′ and an A519 VW mirror reflectance accessory with incident angle of 12°, respectively. The angular reflectance spectra in 0.3–2.5 μm and 2.5–24 μm are measured by a UMA angular reflectance accessory (6°–80°) and an A513/Q angular reflectance accessory (15°–80°), respectively. The reflectance values in 25–100 μm are extrapolated referring to standard EN 673 [27]. The cross-sectional image of the solar absorber deposited on Si substrate are measured using FEI Tecnai TF-20 transmission electron microscopy (TEM). The thickness of the absorber is determined from the cross-sectional micrograph [49]. The reflectance and transmittance spectra in 0.3–2.5 μm of the NiCr–MgF2 cermet layers deposited on quartz substrate are measured by Cary 5000 UV–Vis–NIR spectrometer. The optical constants of the NiCr–MgF2 cermet layers are fitted by the matrix formulation approach [48,50] based on the reflectance, transmittance and thickness.

4. Results and discussion

4.1. Theoretical optimization of solar absorber

4.1.1. Effect of metal volume fractions

The refractive index (n(λ)) and absorption coefficient (α(λ) = 4πk(λ)/n(λ)) of the NiCr–MgF2 cermet layers with different metal volume fractions (f) on the wavelength are calculated by effective medium theory (Fig. 2 (a) and (b)). The measured n(λ) and α(λ) of the deposited NiCr–MgF2 cermet layers with f = 0.13 and 0.25 agree well with the calculated values (Fig. 2 (c) and (d)). The n(λ) of MgF2 and α(λ) of NiCr are also plotted in Fig. 2 (a) and (b), respectively, for the designed tandem films. According to Kirchoff’s law, an ideal cermet layer of solar absorber needs to have high α(λ) in solar spectrum range (λ ∈[0.3, 2.5] μm) and zero α(λ) in thermal emission range (λ > 2.5 μm). It is observed that in reality NiCr–MgF2 cermet does not exhibit ideal spectral selectivity features. As shown in Fig. 2 (b), NiCr–MgF2 cermet with f = 0.4 has a certain degree of spectral selectivity, i.e., greater α(λ) in λ ∈[0.3, 2.5] μm than that in λ > 2.5 μm, and under consideration of cermet to selectively absorb solar radiation. However, the solar absorption coefficient and spectral selectivity of cermet are contradictory. The cermet with higher metal volume fraction has greater α(λ), which is helpful to absorb solar radiation under the condition of effective anti-reflection. The cermet with higher metal volume fraction is found to exhibit less difference in the absorption coefficient between solar spectrum range and thermal emission range of the solar absorber. Therefore, metal volume fractions in both LMVF and HMVF NiCr–MgF2 need to be chosen carefully to compromise solar absorption and spectrally selectivity. Moreover, individual layers with different metal volume fractions have different n(λ) and k(λ), which lead to reflection at interfaces. Such reflection is not good for absorbing solar radiation, but is helpful to suppress the thermal radiation by reflecting the incident infrared radiation. Therefore, the combination of thicknesses of individual layers also need to be optimized to minimize the reflection in solar spectrum range and maximize the reflection in IR range. These contribute to effective absorption of solar radiation and suppression of IR radiation.

Metal volume fractions of LMVF (fL) and HMVF (fH) NiCr–MgF2 are chosen in the range of 0.1–0.2 and 0.2–0.4, respectively. NiCr–MgF2 with metal volume fraction of fH has good spectral selectivity and the counterpart with fL absorbs solar radiation effectively. Combination of fL and fH is also for the effective reflection in IR radiation due to the big differences of n and k of individual layers in IR region.

4.1.2. Effect of layer thicknesses

Thicknesses of MgF2 (dMgF2), LMVF NiCr–MgF2 (dLMVF) and HMVF NiCr–MgF2 (dHMVF) are optimized with the optical opaque Au (100 nm) on the substrate for constructive interference absorption to solar radiation and keeping high reflectance in IR region by transfer matrix. Fig. 3 shows the simulated normal solar absorptance and normal thermal emittance of NiCr–MgF2 solar absorber as a function of thicknesses of MgF2. LMVF and HMVF NiCr–MgF2, where dAR, dAR(LMVF) and dAR(HMVF) are in the range of 0–200 nm and metal volume fractions of LMVF and HMVF NiCr–MgF2 are 0.17 and 0.32, respectively. As shown in Fig. 3 (a), the normal solar absorptance is mainly determined by LMVF and HMVF NiCr–MgF2, whose critical thicknesses are about 50–100 nm for effective absorption of solar radiation. Fig. 3 (b) shows the set of dots of [dAR, dAR(LMVF), dAR(HMVF)] whose corresponding normal solar absorptance are not less than 0.970, and the maximum normal solar absorptance is 0.983 at [dAR, dAR(LMVF), dAR(HMVF)] [86, 82, 174] nm. These dots form a relatively big volume in the space of [dAR, dAR(LMVF), dAR(HMVF)]. It indicates a wide process window of high-solar-absorption for NiCr–MgF2 solar absorber arising out of low n and k of MgF2 in UV-VIS-IR range. As shown in Fig. 3 (c), the normal thermal emittance of NiCr–MgF2 absorber is mainly determined by HMVF NiCr–MgF2, and the thicker HMVF NiCr–MgF2 results in higher normal thermal emittance. It can be observed that in the IR range (λ > 2.5 μm), the MgF2 and LMVF NiCr–MgF2 have extremely low absorption coefficients, resulting negligible effect of the thickness dAR and dAR(LMVF) on the normal thermal emittance. Fig. 3 (d) shows the set of sets of dots [dAR, dAR(LMVF), dAR(HMVF)] whose corresponding εn = 0.050. Fig. 3 (e) shows the set of dots of [dAR, dAR(LMVF), dAR(HMVF)] whose corresponding εn = 0.970 and εn = 0.050. As marked in Fig. 3 (e) and listed in Table 2, the maximal εn = 0.971 at [dAR, dAR(LMVF), dAR(HMVF)] [84, 77, 137] nm and fAR = 0.17, 0.32, and the corresponding normal solar absorptance and normal thermal emittance are 0.981 and 0.042, respectively.

4.1.3. Effect of incident angles

Spectral reflectance at near normal incidence is usually measured to characterize optical property of solar absorber. Actually, the solar absorptance is strongly dependent on the incident angle of sunlight on the absorber surface due to the varied position of the sun with time. Therefore it is valuable for solar absorber to have high absorptance at wide incident angle range for both CSP and non-CSP applications [32, 43, 51–54]. Fig. 4 shows the simulated absorption spectra of the optimized solar absorber at different incident angles from 0° to 90°. The optimized solar absorber shows an excellent spectral selectivity over a wide angular range from 0° up to 90°. As the condition of constructive interference absorption is not valid at big incident angles, the absorptance in solar spectrum range decreases significantly and thus the solar absorptance deteriorates if incident angle is greater than 50°. While the
4.2. Experimental deposited solar absorber

4.2.1. Near normal solar absorptance and thermal emittance

Fig. 5 shows the measured reflectance spectrum of the deposited NiCr–MgF2 solar absorber with optimized metal volume fractions and thicknesses, which matches the simulated counterpart very well. The near normal solar absorptance is high up to 0.976 and the near normal thermal emittance at 25 °C are as low as 0.045, which is the best result as far as we know and very close to the limit of simulation. The high normal solar absorptance comes from three near-zero interference minimums which are located in 400–500 nm, 700–800 nm, and 1700–2000 nm, originating from interferences between MgF2, LMVF and HMVF NiCr–MgF2, and Au layers. The first interference minimum located at 400–500 nm results from λ/4 antirefection of MgF2 as \( n_{\text{MgF2}}(\lambda) \) 400–500 nm 1.38 and 4(\( n_{\text{MgF2}}d_{\text{MgF2}} \) 4 1.38 84 nm 464 nm. Meanwhile, the third interference minimum located at 1700–2000 nm is due to λ/4 antirefection of LMVF and HMVF NiCr–MgF2, because \( n_{\text{LMVF}} \) and \( n_{\text{HMVF}} \) at such wavelength range are about 2.00 and 2.46 and 4(\( n_{\text{HMVF}}d_{\text{HMVF}} \) \( n_{\text{HMVF}}d_{\text{HMVF}} \)) 4 (2.00 77 nm 2.46 137 nm) 1964 nm. The second interference minimum located from 700–800 nm is originated from 3λ/4 antirefection of MgF2, LMVF and HMVF NiCr–MgF2 as 4(\( n_{\text{HMVF}}d_{\text{HMVF}} \)) 4 (2.00 77 nm 2.46 137 nm) 1964 nm. The low normal thermal emittance comes from the low absorptance to IR radiation and the sharp step response from high absorptance to low absorptance at transition wavelength range, which is due to the moderate thickness of HMVF NiCr–MgF2 and high interface reflectance to IR radiation. The minor difference between the experimental and simulated normal solar absorptance results from the deviations between measured and simulated reflectance at 400–600 nm and 1000–1200 nm. Such deviations probably come from the difference of optical constants of Ni, Cr and MgF2 between thin films deposited by magnetron sputtering and counterparts in the database. The extremely small difference between the experimental and simulated normal thermal emittance is due to the deviation between measured and simulated reflectance at λ 15 µm and such deviation is in tolerance of measurement error of IR spectrometer.

4.2.2. Angular solar absorptance and thermal emittance

Fig. 6 shows the measured solar absorptance and thermal emittance values as a function of incident angle, which matches the simulated values very well. The experimental angular solar absorptance maintains very high values of 0.976–0.957 over a wide angular range from 0° up to 50°. When the incident angle increases from 60° to 80°, the experimental angular solar absorptance value decreases rapidly from 0.922 to 0.609. However, such angular dependence is a common shortcoming of interferometric solar absorber, and 50° is a fairly good result thanks to the low refractive index of MgF2. Moreover, the reflectance in λ 2.5 µm
has slight dependence on incident angle as it is mainly determined by differences of optical constants of all individual, and thus the thermal emittance is almost independent of incident angle. Therefore, the angular thermal emittance has low values of 0.045–0.054 from 0 to 50°.

5. Conclusions

An Au/NiCr–MgF₂(HMVF)/NiCr–MgF₂(LMVF)/MgF₂ spectrally selective solar absorber is designed and fabricated for ultra-high solar absorptance and low thermal emittance. The performance of NiCr–MgF₂ solar absorber is simulated using the effective medium theory and film matrix method, and the theoretically optimized NiCr–MgF₂ solar
Table 2
The theoretically optimized parameters for the Au/NiCr–MgF2 (HMVF)/NiCr–MgF2 (LMVF)/MgF2 solar absorber.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material</th>
<th>Metal Volume fraction</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR</td>
<td>MgF2</td>
<td>0</td>
<td>84</td>
</tr>
<tr>
<td>LMVF</td>
<td>NiCr–MgF2</td>
<td>0.17</td>
<td>77</td>
</tr>
<tr>
<td>HMVF</td>
<td>NiCr–MgF2</td>
<td>0.32</td>
<td>137</td>
</tr>
<tr>
<td>IR-reflector</td>
<td>Au</td>
<td>1</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 4. Simulated absorptance spectra of the optimized solar absorber at different incident angles from 0° to 90°.

Fig. 5. Experimental reflectance spectrum of the deposited solar absorber compared with the simulated one.

The absorber has a normal solar absorptance ($\alpha_n$) of 0.981 and a normal thermal emittance ($\varepsilon_n$) of 0.042 at 25°C. The tandem films of NiCr–MgF2 solar absorber is fabricated by magnetron sputtering and it has an ultrahigh near normal solar absorptance of $\alpha_n$ ~0.976 and a low near normal thermal emittance of $\varepsilon_n$ ~0.045 at 25°C, which is very close to the simulated limit. Furthermore, the deposited NiCr–MgF2 solar absorber allows a wide incident angle of 50° with $\alpha(\theta)$ ~0.957 and $\varepsilon(\theta)$ ~0.054. Such spectrally selective solar absorber is an outstanding candidate for solar thermal applications.

Fig. 6. Experimental solar absorptance and thermal emittance values of the deposited solar absorber as a function of incident angle compared with the simulated ones.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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