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Sputter deposition of Mo-alumina cermet solar selective coatings: Interrelation between residual oxygen incorporation, structure and optical properties

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Abstract

Mo/alumina cermet-based selective coatings are of great interest for concentrated solar-thermal power systems, in particular, parabolic trough collectors. We report on the sputter deposition of high-performance multilayer Mo/alumina cermet coatings on stainless steel with a solar absorptance of 94% and a thermal emittance of 8% (at 400 °C), and excellent thermal stability. The selective coatings were deposited in a 0.95 m³ sputtering chamber in order to correlate the deposition parameters, such as presence of residual gases, deposition power, and sputtering method (DC or RF), with the coating composition and the resulting optical properties. X-ray photoelectron spectroscopy, x-ray diffraction, and Raman spectroscopy have been applied to quantitatively describe the effect of residual oxygen on the distribution of oxidation states of Mo in the metallic infrared reflector layer, the high and low metallic volume fraction cermet layers, as well as the composition of the alumina top layer. The results provide strategies to obtain optimal selective coatings under conditions where residual oxygen cannot be avoided, which are essential for a successful transition from a laboratory to pre-industrial scale of vacuum deposition systems.

1. Introduction

Molybdenum and alumina are attractive materials for the fabrication of solar selective coatings related to their refractory and optical properties. The most commonly reported systems are Al₂O₃/Mo/Al₂O₃ (AMA) multilayers [1–4] and Al₂O₃/Mo cermets [5–8], deposited via sputtering techniques. These coatings have been reported to be thermally stable up to at least 400 °C (in vacuum) and have been successfully tested in commercial applications, in particular in parabolic trough solar collectors [9]. Further improvement of the thermal stability of these selective coatings is actively studied [7, 10–15], for example, by modifying the composition such as in MoSi₂-based selective coatings [10], or by including an inert Al₂O₃ top layer [11]. In the case of multilayer coatings (AMA), a certain degree of oxidation of the very thin intermediate Mo layer (about 10 nm) appears to be crucial for the correct adjustment of the refractive index [2, 6]. For the cermet-based coatings, control over the volume fraction of the Mo nanoparticles embedded in the alumina layer is extremely important for optimal spectral performance [13, 16–18].

For multilayer-based selective coatings, the combination of the refractive indices, \( n(\lambda) = n(\lambda) + jk(\lambda) \), of the individual layers determine the reflectance spectrum of the multilayer structure [2, 16, 19]. Ellipsometry is generally used to obtain \( n(\lambda) \) of individual films [20], however, in order to apply the Fresnel equations and transfer matrix model for multilayers, the values of \( n(\lambda) \) and \( k(\lambda) \) of each individual layer as well as the film thickness are needed [21]. Sputtered thin film layers of different materials may have very different optical properties than those reported for bulk materials and generally available in the literature [22, 23], which

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complicates the modelling of sputtered thin film multilayer selective coatings. The real optical properties of sputtered thin films depend on several factors; in particular, the level of impurities due to residual gases during the sputtering process appears to be critical \[24–26\], which becomes particularly important during scale-up of the technology.

In this work, we present a detailed study of the effect of the incorporation of residual oxygen during the sputter deposition of Mo-alumina cermet multilayer selective coatings on their optical properties. We use a large-scale sputtering chamber (0.95 m³), designed for the deposition of selective coatings on metallic tubes for solar receivers in parabolic trough collectors. We apply x-ray photoelectron spectroscopy (XPS) to study the oxidation states of Mo, x-ray diffraction (XRD) for the analysis of composition and crystallinity, Raman spectroscopy for the analysis of Mo-O bonds, and UV–vis–NIR reflectance spectroscopy for the characterization of the performance of the selective coatings. We demonstrate that even with higher partial pressure of residual gases, excellent selective coatings can be deposited onto a 1.5 m stainless steel tube.

2. Methodology

2.1. Mo-alumina cermet multilayer coating

The selective coatings studied in this work have a conventional cermet-based coating structure, as shown in figure 1. The multilayer coating prepared in this work is composed of 4 layers, with the following nominal film thicknesses: (i) a 300 nm thick Mo layer functioning as an infrared reflector; (ii) a 50 nm highly absorbing cermet layer with a high metallic volume fraction (HMVF); (iii) a second 50 nm cermet layer with a lower metallic volume fraction (LMVF); and (iv) a 50 nm anti-reflective alumina layer. The experimental nominal metal volume calculated using the deposition rate of each component as a function of magnetron power is 60% for HMVF cermet and 20% for LMVF cermet, respectively.

The first Mo layer (300 nm) must provide a high reflectance in the infrared spectral region, while the HMVF cermet layer provides high absorption in the UV-visible spectral region. The LMVF cermet layer provides a good optical match between the absorbing and the alumina antireflective layer, providing additional absorption. In addition, interference between layers improves the optical absorption of the coating \[20\]. In order to obtain the best spectral performance, the properties of each individual layer and the optical match at the interfaces must be optimized.

2.2. Film deposition

The antireflective (Al₂O₃), cermet (Mo-Al₂O₃) and metallic layer (Mo) were deposited by sputtering using two planar, rectangular magnetron sputtering guns (Gencoa SW50200), each of them capable of being operated in the DC or RF mode, using an Advanced Energy MDX-1K and Advanced Energy Cesar RF Power Generator with a power output of about 1 kW. The Mo and Al₂O₃ targets (rectangular 5 cm × 20 cm) have a purity of 99.95% and 99.99%, respectively. The substrates (glass or steel) are mounted on a cylindrical holder that rotates with an adjustable circular rotation speed. This configuration allows control over the thickness of sequentially deposited films in the case of co-sputtering. For the rotation speeds and sputtering power used in this work, the thickness of sequential films is about 0.15 nm, thus providing a very small amount of material during each pass of the substrate.
The growth rates of the layers were separately measured as a function of the power applied to the targets using an Inficon SQM-160 rate/thickness monitor and verified with a KLA Tencor D-120 profilometer. The nominal cermet filling factor \( f \) was estimated from the separately measured growth rates of the two components. The actual value of \( f \) was experimentally corroborated for several cermet samples using quantitative XPS. The metallic Mo IR reflector was deposited on a borosilicate glass substrate without intentional heating. The sputtering power density and the pressure in the chamber strongly affected the structure of the film; hence, the process parameters were adjusted in order to achieve metallic films with optimal reflectivity in the infrared region. The optimized parameters for the deposition of the IR reflector were found to correspond to an RF power density applied to the target of 6 W cm\(^{-2}\) and argon pressure in the chamber of 0.3 Pa. Individual cermet layers were deposited in sequential co-sputtering mode on glass, in order to determine the thickness, structure and optical parameters. The very short residence time of the substrate while passing in front of the targets resulted in the effective incorporation of metallic nanoparticles dispersed in the ceramic matrix. After a thorough cleaning process of all components (motion system, magnetron guns, and inner surfaces) of the chamber, an initial base vacuum of around \( 10^{-3} \) Pa was normally achieved within about two hours. The argon pressure in the chamber during the deposition of the cermet layers was 0.93 Pa. For the HMVF and LMVF films, the amount of molybdenum deposited was controlled by regulating the DC output power applied to the Mo magnetron gun, while the alumina matrix was obtained at a fixed RF power density (5.6 W cm\(^{-2}\)).

The internal volume of the chamber of 0.95 m\(^3\) is very large in comparison with most sputtering systems used for research purposes, which means that the level of residual gases is expected to be larger than usually found. In order to estimate the amount of residual gases in the system, the changes in the chamber pressure were studied once the vacuum pumps were isolated (valve fully closed). This study was performed for two different situations: (i) with the valve fully closed and no intentional intake of any gas, such that pressure changes are only due to system leaks and internal de-gassing; and (ii) with the valve fully closed and an intentional intake of argon at 20 Sscm. From this study we found that the amount of residual gases (impurities) corresponds to about 1% of all gases present; this percentage of residual gases does not necessarily all correspond to oxygen as other substances, such as CO\(_2\), H\(_2\)O, N\(_2\), as well as carbonaceous compounds, may also be present; for smaller, research chambers the level of residual gases is usually up to about 0.3% [27]. Before each deposition experiment, the chamber was flushed with argon and evacuated [28]. Oxygen was not supplied to the chamber intentionally during any of the deposition processes.

### 2.3. Characterization

The properties of isolated films and complete coatings were studied using x-ray diffraction (XRD) (Bruker D8-Advance), Raman spectroscopy (WITec Alpha 300), and x-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific K-Alpha Surface Analysis). Reflectance spectra were obtained in the range of 0.3 to 2.7 \( \mu \)m using UV/Vis and NIR spectrophotometers (Avantes, model AVA4048; model AvaSpec-NIR256–2.5) equipped with an integrating sphere (Avantes, model 50-LS-HAL). The reflectance spectra in the range of 2.5 to 15 \( \mu \)m were obtained with an FTIR spectrometer (Perkin Elmer, model Frontier NIR/MIR) also equipped with an integrating sphere (PICO, model IntegratIR). The solar absorptance was determined by weighting the reflectance spectrum against the solar radiation spectrum. For the determination of the thermal emittance, the reflectance spectrum was weighted against the black body radiation function at different temperatures. In the case of transparent or semi-transparent samples on glass substrates, the transmission spectra were measured in the UV/Vis region with the same spectrophotometer (Avantes, model AVA4048).

### 3. Results and discussion

#### 3.1. Effect of residual oxygen on Mo IR reflective layer

For a high-quality selective coating, the reflectance in the infrared region of the solar spectrum is high and, given that the absorber film should be transparent to IR, should be defined by the metallic under-layer, in this case Mo. It is known that Mo thin films grown by sputtering techniques, even without the intentional inclusion of oxygen during the deposition process, may contain a certain amount of oxygen, which may affect the infrared reflectance [23, 29, 30].

Figure 2(a) shows the XRD patterns of Mo thin films deposited by RF and DC-sputtering at the same power output of 300 W. The diffraction pattern of the RF-sputtered film shows peaks at 40.6° and 70.7°, corresponding to the (110) and (211) planes, respectively. The DC-sputtered thin film pattern shows lower intensities and wider peaks. In addition, while only two peaks are observed for the RF-sputtered film, the DC-sputtered films are differently textured and the Mo(200) peak at 58.8° is also observed.

DC sputtering is performed at higher Ar pressure (2.3 Pa), which results in a decrease of the Mo film deposition rate, which is an important factor in the texturing of the film as well as the level of possible
contamination of Mo with residual gases. The DC-sputtered film shows an additional broad band around 22°, which may be associated with Mo-O bonds [31]. We believe that the higher intensity observed for the RF sputtered films is related to larger crystal growth and difference in texturization. In addition, DC sputtering at high output powers proved to be unstable in our experimental setup, especially during long deposition processes.

Figure 2(b) shows Raman spectra of two Mo films deposited by RF sputtering at different power: for the film prepared at 150 W, corresponding to a lower deposition rate, a host of Mo-O peaks is observed, that are absent for the 300 W film. Hence, relatively high presence of residual gases, common in large chambers, leads to oxygen incorporation.

The effect of deposition rate and residual oxygen incorporation is found to strongly influence the optical properties of the metallic Mo film. Figure 2(c) shows the reflectance spectra of the two RF-sputtered Mo thin films deposited at different power outputs, and the spectrum for pure, bulk Mo is shown as a reference. The spectrum of the film deposited at 300 W is very similar to the reference in the visible spectral area, while acceptable similarity is observed in the infrared region. The lower reflectance in the NIR and IR regions has been related to oxygen contamination [32], and correlates with the Raman spectra. The correlation between power output and the quality of the optical and electrical properties is in accordance with several reports in the literature [23, 29–35]. We can conclude that RF sputtering at high deposition rates is the preferred method for the deposition of the Mo infrared reflector layer; hence, we used RF-sputtering at 300 W for the optimized selective coatings. The lattice parameter, calculated using the NRST (Nelson-Riley-Sinclair-Taylor) method, for the Mo film was found to be 3.154 Å versus 3.148 Å, which is commonly reported for bcc molybdenum [36]. The presence of interstitial oxygen atoms may explain this difference, indicating that oxygen is still present in the 300 W RF-sputtered film, which is confirmed by XPS. This could also explain the lower reflectance values of the sputtered films, especially in the N1R region, compared to the spectral performance of a bulk Mo film as shown in figure 2(c). These results show very good correlation with FDTD simulations [37].

3.2. Sputter deposition of alumina and cermet layers

The alumina and cermet layers have been deposited by DC sputtering; this is more economical, and for the cermet film, some additional incorporation of residual oxygen is not expected to significantly affect the properties. Figure 3 shows the XRD patterns for alumina on glass, the HMVF cermet on glass, and for the glass substrate. The broad band observed at around 23° corresponds to the amorphous glass substrate. A small shoulder is observed for the cermet film at around 40°, which may be associated with nanostructured metallic Mo. A similar, low intensity and broad XRD peak has been reported for Ni-Cr cermets, where the peak shape was attributed to nanostructuring of Ni metallic particles [38]. The aluminium oxide matrix is found to be amorphous, and deficient of oxygen, which is often observed during RF-sputtering in an Ar atmosphere [39].

It is plausible that the Mo particles present in cermets obtained at lower DC power level are considerably oxidized, however, it is difficult to be sure of this. In the experimental configuration of the sputtering system, the cermet deposition process is achieved in a sequential manner, and the quantity of material deposited by each substrate pass corresponds to only a 0.15 nm uniform film, which is on the order of a typical lattice parameter. The microstructure is determined by surface diffusion and grain nucleation and growth [39], thus forming the cermet composite. During cermet deposition the Al2O3 magnetron gun is also working, which could produce a gettering effect.
3.3. XPS analysis of the Mo-alumina cermet layers

Figure 4 shows the XPS depth profile of a typical cermet-based selective coating prepared under the conditions described previously. The graph has been divided in seven clearly identifiable different zones in order to simplify the discussion, and to clarify the structure and the chemical composition of the coating. Zone 1 corresponds to the last layer of the coating, the antireflective alumina layer. Zones 2, 3 and 4 correspond to the LMVF cermet layer. Zone 5 corresponds to the HMVF cermet film, while zone 6 includes the transition area between the HMVF cermet and the Mo infrared reflective layer. Zone 7 corresponds to the metallic Mo film.

Zones 2, 4, and 6 represent transition areas between the different layers of the selective coating. This progressive change in composition has been reported previously in the case of W/WAlN/WAlON/Al₂O₃-based coatings with important consequences for the optical properties related to the gradation of the refraction indices [40]. The progressive change with depth is more pronounced in the case of the LMVF cermet. This could be
related to the higher Mo deposition rate in the case of the HMVF cermet, which helps to stabilize the cermet composition; at low Mo flux, diffusion during the growth process may explain the spatial variation observed.

The interdiffusion of species for similar coatings has been reported previously [11–14]. In particular, a very broad transition region between the cermet and Mo infrared reflector layers has been reported previously [7].

In table 1, the composition of the layers in each region as obtained from the XPS analysis is summarized; the composition of the LMVF cermet has been taken at the centre of zone 3. It can be observed that x (where $x = O/Al$) for the case of the alumina antireflective layer is lower than the value of $x = 1.5$ that corresponds to $Al_2O_3$.

Hence, the alumina layer has an oxygen deficiency, could be due to preferential evaporation of the alumina target species ($Al, O$) related to the argon atmosphere [41]. Oxygen-deficient sputtered alumina has been reported previously [42–45].

Interestingly, the value for $x$ seems to increase in the case of the cermet, which could indicate a stoichiometry change for the alumina in the presence of Mo. However, the value of $x = 2$ found for the HMVF layer is not reasonable for an aluminum oxide, hence we need to consider the presence of oxygen associated with the molybdenum atoms. In fact, the metallic molybdenum infrared reflector used in this coating appears to have around 10% of oxygen impurities as can be seen in table 1 and figure 4.

A simple calculation can be performed in order to test the hypothesis of constant stoichiometry of alumina in all layers with $x = 1.28$. For the LMVF layer, the difference between $x$ values is 1.5–1.28 = 0.22, and for the HMVF, 1.94–1.28 = 0.66. If this oxygen excess in each cermet is related to Mo, then the quotient of both $x$ differences, 0.66/0.22 = 3, must be equal to the ratio of the atomic percentage of molybdenum in both cerments, 44.7/15.3 = 2.9. As can be seen, the values of these coefficients are very close, in agreement with the hypothesis that the stoichiometry of alumina remains constant and that a certain quantity of oxygen is bound to Mo. If we consider that $x = 1.28$ for both cerments, using table 1, we can calculate that the $O/Mo$ quotients are 0.45 and 0.27, respectively, for LMVF and HMVF cerments. In the case of the Mo infrared reflector, the $O/Mo$ quotient is approximately 0.1. Note how the oxygen content in Mo decreases with the increase of sputtering power during Mo deposition. If we consider that the oxygen atoms associated with Mo are present as $MoO_3$, the $O/Mo$ quotients can be used to calculate that we have 22.5% and 13.5%, respectively, of this oxide in the LMVF and HMVF cerments, i.e., about 77.5% and 86.5% of metallic Mo, respectively.

In order to address the effect of oxygen in the cerments in detail, and to corroborate the hypothesis of the constant composition of alumina, high-resolution XPS spectra of Mo, Al and O were measured at different removal sputtering time, i.e., different depths into the coating.

Figure 5 shows the XPS spectra of Mo, Al and O at the centre of the different regions shown in figure 4: $AlO_x$ (region 1), LMVF (region 3), HMVF (region 5) and Mo infrared reflector (region 7). In the case of Mo (figure 5(a)), we can see that the typical metallic Mo XPS spectra are slightly shifted to lower binding energy for all films. In the case of cerments, this shift is a somewhat larger. We can attribute this additional shift observed for the cermet layers to the nanostructuring of the film [46]. In the case of the Mo infrared reflector, the shift could be related to oxygen impurities that reduce the electron binding energy in Mo atoms through Mo lattice distortion due to Mo–O bonds. We can observe that in the case of cerments, the $3d5/2$ and $3d3/2$ peak intensity ratio decreases from 1.58 (~3/2) for the Mo infrared reflector to 1.29 in the case of the LMVF layer. In the case of alumina, the peak is shifted to lower binding energies in comparison to reported XPS of alumina. This observation could be related to the oxygen deficiency of the amorphous sputtered alumina material. In the case of the cerments, figure 5(b) illustrates that the oxygen peak has the tendency to shift towards the O peak of the Mo infrared film, which is well-associated with the position of this peak for the oxides $MoO_2$ and $MoO_3$. This is a good demonstration that in cerments, there is certain degree of oxygen incorporation bound to Mo atoms. The lack of any apparent structure in the O 1s XPS peaks can be related to the amorphous character of $AlO_x$ and $MoO_2$, which results in broad peaks.

Figure 5(c) shows the XPS spectra of Al. The observed peak shift to lower energies with respect to $Al_2O_3$ is also related with oxygen deficiency in the alumina film. An interesting observation is that, with respect to the peak in the $AlO_x$ reflective film, the Al peak of the LMVF cermet is shifted towards the Al 2p peak characteristic

| Element | Atom% in $Al_2O_3$ | Atom% in LMVF | Atom% in HMVF | Atom% in Mo |
|---------|-------------------|---------------|---------------|-------------|
| Mo      | 0                 | 15.3          | 44.7          | 91.6        |
| Al      | 43.7              | 33.9          | 18.9          | —           |
| O       | 55.9              | 51.0          | 36.7          | 8.40        |
| O/Al = x| 1.28              | 1.50          | 1.94          | —           |
| Mo/Al   | —                 | 0.45          | 2.30          | —           |
of Al$_2$O$_3$ while the peak of the HMVF cermet is shifted in the opposite direction. The presence of Mo nanoparticles clearly affects the position of the Al 2p peak: the increase of the metal volume fraction from the LMVF cermet to HMVF cermet implies a decrease in the distance between Mo nanoparticles, which can influence the local ordering of Al atoms and, hence, the core Al 2p binding energy. If for the HMVF cermet $f$ is about 50% and the Mo nanoparticles are about 2 nm, then the thickness of AlO$_x$ material between Mo nanoparticles should be about 2 nm as well, which represents only about 10 atomic layers.

Figure 6(a) shows the XPS spectra of figure 5(a), but normalized to the Mo 3d5/2 peak. In figure 6(b) we show simulated XPS spectra, adding the MoO$_2$ doublet reported in reference [47] in order to improve the fit. In this simulation we have intentionally exaggerated the intensity of the MoO$_2$ doublet, with the objective to visualize its effect on the XPS spectra (18% and 35% for LMVF and HMVF cermets, respectively). For the cermets, we observe an increase of the 3d3/2 peak intensity as well as peak broadening, in agreement with the experimental results. Very similar results have been reported for the first steps of Mo oxidation [46], where a strong chemical shift generally obtained for the MoO$_3$ oxide is not observed.

In figure 5(c) we can see the same simulation using the experimentally estimated MoO$_2$ contents from table 1 (22.5% and 13.5%, respectively, in LMVF and HMVF cermets). Figure 5(d) shows a zoom of the 3d3/2 Mo peak showing that the differences between LMVF and HMVF cermets is small, as also seen in the experimental spectra. The quantitative differences observed are related with the fact that the XPS spectrum of MoO$_2$ is much more complex than the one used in reference [48]. However, the other XPS peaks of MoO$_2$ are much smaller, which could explain the good qualitative capability of the simulation. We conclude that the simulation provides a good demonstration of the association of oxygen with Mo present in the cermets. An important aspect related to the presence of Mo-O bonds (MoO$_3$) in cermets films is the real microstructure of cermets, which may be determined using a detailed TEM analysis. Figure S3 in the Supplementary Materials shows a TEM image of an isolated Mn oxide particles that agrees best with MoO$_2$: the interplanar distance of 0.57 nm shows very good correspondence with the lattice constant of MoO$_2$ [48]. Note that a complete analysis of the particle size and distribution was not performed.

One possibility would be to have both pure Mo and MoO$_2$ nanoparticles present in the film; another option is that core–shell nanoparticles with a Mo core and MoO$_2$ shell are formed. In both cases the calculation of the Mo volume fraction is more complex due to the presence of Mo–O bonds. We have deposited cermet films with different expected metal volume fraction as separate layers on a variety of substrate, and found that the intimate relationship between sputtering conditions and cermet composition and properties complicate the comparison of results on individual films to those in the cermets. In addition, the analysis of individual films was complicated by charging issues, especially for lower MVF films. Based on these results, which are in accordance with reports in the literature, we decided to focus the analysis of the HMVF and LMVF cermet films as present in the complete selective coating. It is important to emphasize that in most publications related to cermets for selective solar absorbers, it is usually assumed that all sputtered metal is incorporated into the cermet as pure metal [7]. In this work, and based on the experimental results, we have developed a simple method to quantitatively consider the incorporation of oxygen by calculating the metal volume fraction of cermets ($f$) (see Supplementary Information for details). The results are as follows:

$$f = 51\% \text{ for the HMVF and } f = 18\% \text{ for the LMVF.}$$

Note that the real metal volume fractions are somewhat below the nominal values of 60% and 20%, respectively. These results show that the real $f$ value of the cermets is affected by Mo oxidation during the
sputtering process, related to specific characteristics of the vacuum chamber, in particular due to residual oxygen. In the case of small-volume sputtering research vacuum chambers, this effect is expected to be less important. However, the presence of MoO2 either as nanoparticles or as a shell of metallic Mo nanoparticles does not necessarily have a deleterious effect on the optical properties of the cermet. This issue will be addressed in future research.

### 3.4. Optical properties and stability of selective coatings

The optical properties of the Mo/Al2O3 cermet-based selective coatings are mainly determined by the size and distribution of Mo nanoparticles in the oxide host. In a separate paper, we reported on the optical properties of sputtered Mo using FDTD (Finite-Difference Time Domain) simulations, comparing experimental with simulated results using different size distributions of the Mo particles, as well as different optical constants. Using optical constants specifically determined for sputtered Mo in an atmosphere where partial oxidation may occur, broad fluctuations in calculated spectra were completely eliminated for both random and bcc particle distributions. It is worth emphasizing that the differences between bcc and random simulations are minimal when optical properties for sputtered Mo are used in the simulations. Based on these simulations, the Mo particle size is estimated to be around 2 nm [37].

In Figure S1 (available online at stacks.iop.org/MRX/8/105506/mmedia) in the Supplementary Materials, the transmittance spectra of a semi-transparent Mo film and a HMVF cermet film are shown, and includes an estimation of the extinction coefficient k using Beer–Lambert law. The horizontal lines represent the reported average values of k [16], using the Maxwell–Garnet model for pure Mo and two cermets with a Mo volume fraction \( f = 20\% \) and \( f = 50\% \), respectively [16]. The experimental results show that the extinction coefficient of the cermet films is lower than that of pure Mo in good correspondence with the values reported in the...
The value of \( k \) obtained for the HMVF cermet film is lower than the value reported for a 50% cermet, which could be related to the incorporation of residual oxygen. The effect of the reduction of the extinction coefficient of Mo with a soft, intentional introduction of oxygen during sputtering deposition has been reported for alumina/Mo/alumina selective multilayer coatings [12], claiming a corresponding improvement of the coating characteristics. Also, a lower than expected volume fraction of Mo in cermet films has been explained by a lower Mo deposition rate in cermet films as compared to the rate obtained when only Mo is deposited [7]. Our molybdenum films exhibit very good quality compared with reported sputtered films, and also compared with other deposition methods for Mo films, such as laser, and pulsed-laser deposition methods [50, 51]. Detailed studies show on oxygen-deficient MoO3-δ films prepared by PLD show that the deficiency parameter \( \delta \) is intimately related to the deposition parameters [52].

Figure 7 shows the reflectance spectrum of the cermet-based (Mo-Al2O3) selective coating deposited under the optimal conditions for each layer; the solar spectrum (air mass 1.5) and the black body radiation spectrum calculated for \( T = 300 \) °C are also included. In table 2 we show the calculated values for thermal emittance, \( \varepsilon \), and solar absorptance, \( \alpha \), which are defined by the following equations:

\[
\alpha = \frac{\int_{2.5}^{\infty} (1 - R(\lambda)) P(\lambda) d\lambda}{\int_{2.5}^{\infty} P(\lambda) d\lambda}
\]

\[
\varepsilon = \frac{\int_{16}^{\infty} (1 - R(\lambda)) P_B(\lambda)d\lambda}{\int_{16}^{\infty} P_B(\lambda)d\lambda}
\]

Where \( P(\lambda) \) is the air mass 1.5 solar energy distribution spectrum, \( P_B(\lambda) \) is the black body thermal emissivity spectrum, and \( R(\lambda) \) corresponds to the reflectance of the selective coating. Note that AM 1.5 is used instead of the more commonly applied AM 1.5G spectrum, because the high-temperature selective coatings investigated in this work are generally applied in concentrated solar power systems. In these systems, only the direct part of the
solar irradiation spectrum is effectively focused onto the collector by the concentrator mirror, and the diffuse part is not taken advantage of. The cermet-based selective coating presents the expected optical properties including interferential behaviour in the visible region related to the multilayer character of the coating [5–8, 12–15].

The solar absorptance and thermal emittance values are adequate for application in solar-to-thermal energy conversion systems, and related to the universality of the importance of these properties this also applies to concentrated as well as other types of solar power conversion systems [53–55]. Hence, if properly taken into account in the design of the sputtering conditions, residual oxygen incorporation does not significantly affect the desired properties of the coating; hence, a large sputtering chamber with higher residual oxygen can be used for the scaled-up fabrication of solar collectors. Figure S2 in the Supplementary Materials shows a 1 m stainless steel tube for solar collectors coated with the selective coating using the results presented in this work, indicating the scalability of the process.

In addition to the optical properties, the thermal stability of a selective coating in air is an important factor for its applicability. Figure 8 shows the effect of a 2-hour thermal treatment in air at 450 °C and 500 °C, indicating that significant deterioration of the optical properties of the selective performance is not observed until 500 °C. The aim of this simple study was to see if oxidation of Mo in the cermet would decrease the thermal stability of this type of coating, since it is known that the degradation effect is linked to the interdiffusion of the layers in regions 2, 4, and 6, and the oxidation of Mo. It can be observed that the stability is not compromised, however, indicating the robustness of the selective coating to scale-up of the deposition process.

The effects of the thermal treatment are in good agreement with previously reported results for Mo/Al2O3 cermet coatings under vacuum conditions [15], illustrating the excellent thermal stability in air of the coatings presented in this work.

4. Conclusions

The development and optimization of large-scale vacuum and sputtering chambers present a great technological challenge for many reasons, most importantly, the presence of a significant amount of residual gases. One way to reduce the influence of residual gases is to increase the deposition rate of the sputtered species, which can be achieved by increasing the magnetron power. Oxygen contamination in Mo is found to increase from IR reflector to the LMVF cermet, which has been demonstrated by a detailed XPS analysis. This is related with the lower sputtering power used for the deposition of cermets. Despite significant oxygen incorporation in the Mo phase in all coating layers, good selective properties have been obtained. There is clear evidence that a considerable fraction of molybdenum is present in the metallic state, indicating that cermet materials are deposited. We have obtained high-performance multilayer Mo/alumina cermet coatings on stainless steel with a solar absorptance of 94% and a thermal emittance of 8% (at 400 °C), and excellent thermal stability. The thermal
stability of the coatings prepared in the large chamber is equal or better than the values reported in the literature for similar coatings.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

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References

[1] Schmidt R N and Park K C 1965 High-temperature space-stable selective solar absorber coatings Appl. Opt. 4 917–25
[2] Thornton J A, Penfold A S and Lamb J L 1980 Sputter-deposited Al2O3/Mo or Mo/Al2O3 selective absorber coatings Thin Solid Films 72 101–10
[3] Nuru Z Y, Arendse C J, Khamlich S and Maaza M 2012 Optimization of Al2O3/PT/Al2O3 multilayer spectrally selective coatings for solar–thermal applications Vacuum 86 2129–35
[4] Yangwei W, Weifeng Z, Limei L, Yan Q and Fachun L 2013 Colored solar selective absorbing coatings with metal Ti and dielectric AlN multilayer structure Sol. Energ. Mater. Sol. C. 115 145–50
[5] Laxnner M and Elgat Z 1990 Solar selective absorber coating for high service temperatures produced by plasma sputtering Optical Materials Technology for Energy Efficiency and Solar Energy Conversion IX 1272 240–9
[6] Du X K, Wang C, Wang T M, Chen B L, Zhou L and Ru N 2007 Magnetron sputtering high temperature Mo–Al2O3 cermet solar selective coatings Mater. Sci. Forum 546–549 1773–6
[7] Esposito S, Antonia A, Addonizio M L and Aprea S 2009 Fabrication and optimization of highly efficient cermet-based spectrally selective coatings for high operating temperature Thin Solid Films 517 6000–6
[8] Barshilia H C, Kumar P, Rajam K S and Biswas A 2011 Structure and optical properties of Ag–Al2O3 nanocermet solar selective coatings prepared using unbalanced magnetron sputtering Sol. Energ. Mater. Sol. C. 95 1707–15
[9] Peterson R E and Ramsey J W 1975 Thin film coatings in solar—thermal power systems J. Vac. Sci. Technol. 12 174–81
[10] Hernández-Pinilla D, Rodríguez-Palomo A, Álvarez-Fraga L, Céspedes E, Prieto J E, Muñoz-Martín A and Prieto C 2016 MoSi2–Si3N4 absorber for high temperature solar selective coating Sol. Energ. Mater. Sol. C. 152 141–5
[11] Céspedes E et al 2018 Role of Al2O3 antireflective layer on the exceptional durability of Mo–Si–N—based spectrally selective coatings in air at high temperature ACS Appl. Energy Mater. 1 6152–60
[12] Thornton J A and Lamb J L 1928 Thermal stability studies of sputter-deposited multilayer selective absorber coatings Thin Solid Films 96 175–83
[13] Du X, Wang C, Wang T, Zhou L, Chen B and Ru N 2008 Microstructure and spectral selectivity of Mo–Al2O3 solar selective absorbing coatings after annealing Thin Solid Films 516 9971–7
[14] Zhang K, Hao L, Du M, M J, Wang J N and Meng J P 2017 A review on thermal stability and high temperature induced ageing mechanisms of solar absorber coatings Renew. Sust. Energ. Rev. 67 1288–99
[15] Cheng J, Wang C, Wang W, Du X, Liu Y, Xue Y, Wang T and Chen B 2013 Improvement of thermal stability in the solar selective absorbing Mo–Al2O3 coating Sol. Energ. Mater. Sol. C. 109 204–8
[16] Li J F and Guo L Z 2011 Computer simulation on Mo/Al2O3 solar energy selective absorbing coating, advanced materials research Adv. Mater. Res. 189–193 66–9
[17] Yin Y and Collins E 1995 Optimization and analysis of solar selective surfaces with continuous and multilayer profiles J. Appl. Phys. 77 6485–91
[18] Zhang Q, C, Yin Y and Mills D R 1996 High efficiency Mo–Al2O3 cermet selective surfaces for high-temperature application Sol. Energ. Mater. Sol. C. 40 43–53
[19] Nejati M, Fathollahi V and Khaliabi M A 2005 Computer simulation of the optical properties of high-temperature cermet solar selective coatings Sol. Energ. 78 235–41
[20] Kats M A, Blanchard R, Genevet P and Capasso F 2013 Nanometre optical coatings based on strong interference effects in highly absorbing media Nat. Mater. 12 20–4
[21] Knittel Z 1976 Optics of Thin Films (New York, NY: Wiley)
[22] Barshilia H C, Selvakumar N, Vignesh G, Rajam K S and Biswas A 2009 Sol. Energ. Mater. Sol. C. 93 315–23
[23] Jankowski A F and Schrawyer L R 1990 Reactive sputtering of molybdenum Thin Solid Films 193 194–61–71
[24] Jiang H, Zhu J, Huang Q, Xu J, Wang X, Wang Z, Pflaumt S and Mette A 2011 The influence of residual gas on boron carbide thin films prepared by magnetron sputtering Appl. Surf. Sci. 257 9946–52
[25] Kobayashi S, Suzuki K and Katsube T 1988 Changes of residual gas species in a vacuum chamber during electron bombardment Appl. Surf. Sci. 33–34 370–8
[26] Rafaja D, Köstenbauer H, Mühlle U, Löffler C, Schreiber G, Kathrein M and Winkler J 2013 Effect of the deposition process and substrate temperature on the microstructure defects and electrical conductivity of molybdenum thin films Thin Solid Films 528 42–8
El-Hady K A, Soliman H, Abou G H, Poussy A I and Fathy M 2011 Preparation and characterization of DC sputtered molybdenum thin films Thin Solid Films 156 243–9

Bardin T T, Pronkoz J G, Budhani R, Lim J S and Bunshah R 1988 The effects of oxygen concentration in sputter-deposited molybdenum thin films Thin Solid Films 153 246–51

Dan A, Biswas A, Sarkar P, Kashyap S, Chattopadhyay K, Barshilia H C and Basu B 2018 Enhancing spectrally selective response of W AlN solar absorber cermets IEEE J. Photovolt. 9 105507–14

Choi J G and Thomson L T 1996 XPS study of as-prepared and reduced molybdenum oxides Surf. Coat. Technol. 288 27–31

García-Valenzuela J, Rivera R, Morales A B, Gerling L, Caballero A, Asensi I, Voz C, Bertomeu J and Andreau J 2016 Main properties of Al2O3 thin films deposited by magnetron sputtering of an Al2O3 ceramic target at different radio-frequency power and argon pressure and their passivation effect on p-type c-Si wafers Thin Solid Films 619 288–96

Vuoristo P, Mantyli T, Kettunen P and Lappalainen R 1991 Stoichiometry and impurities in sputtered alumina films on copper Thin Solid Films 204 297–311

Segal B G, Jacquet J M and Besse J 2001 Elaboration, characterization and dielectric properties study of amorphous alumina thin films deposited by r.f. magnetron sputtering Vacuum 62 27–38

Voigt M and Sokolowski M 2004 Electrical properties of thin rf sputtered aluminum oxide films Mat. Sci. Eng. B 109 99–103

Bhatia CS, Guthmiller G and Spool AM 1989 Alumina films by sputter deposition with Ar/O2: preparation and characterization J. Vac. Sci. Technol. A 7 1298–302

Radnick J, Mohr C and Claus P 2003 On the origin of binding energy shifts of core levels of supported gold nanoparticles and dependence of pretreatment and material synthesis Phys. Chem. Chem. Phys. 5 172–7

Choi J G and Thomson L T 1996 XPS study of as-prepared and reduced molybdenum oxides Appl. Surf. Sci. 93 143–9

Scanlon D O, Watson G W, Payne D J, Atkinson G R, Egdell R G and Law D S L 2010 Theoretical and experimental study of the electronic structures of MoO3 and MoO2 J. Phys. Chem. C 114 4636–45

Dias D, Rebouta L, Costa P, Al-Rjoub A, Benelmeki M, Tavares C J, Barradas N P, Alves E, Santilli P and Pischow K 2017 Optical and electronic structures of MoO3 and MoO2 Thin Solid Films 663 35–43

Mikheev A Y, Kharlamov V A, Kruchek S D, Cherniati A A and Khomenko II 2015 Analyzing the contents of residual and plasma-supporting gases inside a vacuum deposition unit chamber IOP Conf. Ser.: Mater. Sci. Eng. 70 012001

Usman M, Arshad M, Suwanam S S and Hall A 2018 Influence of annealing environment on the ALD–Al2O3/4H-SiC interface studied through XPS J. Phys. D: Appl. Phys. 51 105111

Ning Y et al 2016 Effects of substrates, film thickness and temperature on thermal emittance of Mo/substrate deposited by magnetron sputtering Vacuum 128 73–9

Bardin T, Pronkoz J G, Budhani R, Lim J S and Bunshah R 1988 The effects of oxygen concentration in sputter-deposited molybdenum thin films Thin Solid Films 156 243–9

Dai X, Zhou A, Feng L, Wang Y, Xu J and Li J 2014 Molybdenum thin films with low resistivity and superior adhesion deposited by radio-frequency magnetron sputtering at elevated temperature Thin Solid Films 567 64–71

Carver G E 1980 Optical properties of molybdenum thin films The University of Arizona Doctoral dissertation http://hdl.handle.net/10150/565472

Kending L P, Rek Z U, Yalisove S M and Bilello J C 2000 The role of impurities and microstructure on residual stress in nanoscale Mo films Surf. Coat. Technol. 132 124–9

Pachlhofer J M, Jachs C, Franz R, Franzke E, Köstenbauer H, Winkler J and Mitterer C 2016 Structure evolution in reactively sputtered molybdenum oxide thin films Vacuum 131 246–51

El-Hady K A, Soliman H, Abou G H, Poussy A I and Fathy M 2011 Preparation and characterization of DC sputtered molybdenum thin films Alex. Eng. J. 50 57–63

Lahiri S, Angello J and Natan M J 1982 Precise lattice parameter determination of PtHg4 Thin Solid Films 15 100–1

Akter N, Becerril-Gonzalez JJ, Karabiyik M, Alam F, Pala N, Oskam G and Ares-Muzio O 2021 FDTD modeling of sputtered Mo–Al2O3 nanocomposites Sol. Energy. Mat. Sol. C 225 111027

Radnick J, Mohr C and Claus P 2003 On the origin of binding energy shifts of core levels of supported gold nanoparticles and dependence of pretreatment and material synthesis Phys. Chem. Chem. Phys. 5 172–7

Choi J G and Thomson L T 1996 XPS study of as-prepared and reduced molybdenum oxides Appl. Surf. Sci. 93 143–9

Scanlon D O, Watson G W, Payne D J, Atkinson G R, Egdell R G and Law D S L 2010 Theoretical and experimental study of the electronic structures of MoO3 and MoO2 J. Phys. Chem. C 114 4636–45

Dias D, Rebouta L, Costa P, Al-Rjoub A, Benelmeki M, Tavares C J, Barradas N P, Alves E, Santilli P and Pischow K 2017 Optical and structural analysis of solar selective absorbing coatings based on AlSiOxW cerments Sol. Energy 150 335–44

Mostako A T T and Khare A 2012 Molybdenum thin films via pulsed laser deposition technique for first mirror application Laser Part. Beams 30 559–67

Al-Kuhaili M F, Durrani S M A and Bakhtiari L A 2010 Pulsed laser deposition of molybdenum oxide thin films Appl. Phys. A 98 609

Lakshmi-Narayana A, Hussain O M, Ramana CV, Camacho-Lopez M, Abdel-Ghany A, Hashem A, Mauger A and Julián C M 2020 Molybdenum-suboxide thin films as anode layers in planar lithium microbatteries Electrochem. 1 1160

Mateen F, Li Y, Saeed M A, Sun Y, Zhang Y, Lee S Y and Hong S K 2021 Large-area luminescent solar concentrator utilizing donor-acceptor luminesphore with nearly zero reabsorption: indoor/outdoor performance evaluation J. Lumin. 231 117837

Kim S H, Saeed M A, Lee S Y and Shim J W 2021 Investigating the indoor performance of planar heterojunction based organic photovoltaics IEEE J. Photovolt. 11 997–1003

Saeed M A, Kim SH, Baek K, Hyun J K, Lee S Y and Shim J W 2021 PEDOT:PSS: CuNW-based transparent composite electrodes for high-performance and flexible organic photovoltaics under indoor lighting Appl. Surf. Sci. 567 150852