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Sol-gel protective coatings for black chrome solar selective films

R. B. Pettit
Thermophysical Properties Division 5824, Sandia National Laboratories
Albuquerque, New Mexico 87185
C. J. Brinker
Ceramics Development Division 5845, Sandia National Laboratories
Albuquerque, New Mexico 87185

Abstract

Electrodeposited black chrome solar selective films degrade rapidly when heated to temperatures above 300°C in air. The application of sol-gel protective coatings to the black chrome films has been investigated as a possible means to improve the oxidation resistance of black chrome at high temperatures. The sol-gel coating process consists of applying an alcoholic solution containing polymeric glass precursors. After the coating is fired for about one-half hour at a moderate temperature (~450°C), a glass layer is obtained. Because of the wide range of sol-gel processing parameters, initial studies have concentrated on determining the effect of the following variables on the thermal stability of sol-gel coated black chrome: (1) sol-gel composition; (2) firing temperature; (3) firing atmosphere; (4) sol-gel coating thickness; (5) pre-aging of the black chrome films. Of the compositions studied, only SiO_2/B_2O_3 and $SiO_2/B_2O_3/Al_2O_3/Na_2O/BaO$ resulted in improved thermal stability. Of the other processing parameters, the firing temperature had the most significant effect on the resulting black chrome thermal stability, with 500°C firing being optimum. For the best combination of process variables studied to date, the solar absorptance of a sol-gel coated sample decreased from 0.97 to 0.95 after 100 hrs at 400°C, while, for an uncoated control sample, the solar absorptance decreased to 0.89. For most of the sol-gel coated films, continued aging at 400°C resulted in continued protection of the black chrome film.*

Introduction

Electrodeposited black chrome solar selective films are currently the primary candidate for use in parabolic trough solar concentrators[1] that operate near 300°C. Recent studies[2] have shown that the thermal stability of the black chrome films that are electroplated from Harshaw Chemical Co. Chromonyx bath [3] is a strong function of both the bath chemistry and contaminants in the bath. Degradation of films deposited onto nickel substrates results in a rapid decrease in the solar absorptance by ~10%. Investigation of changes in the film microstructure and composition with thermal aging have shown that metallic chromium (Cr) within the film oxidizes to form Cr_2O_3.[4] Therefore if the rate of oxidation of the metallic chromium could be reduced through the use of a protective coating, the useful lifetime of the black chrome film may be extended or the maximum permissible operating temperature might be increased.

Suitable protective coatings would include inorganic oxides that are stable at high temperature, such as SiO_2, TiO_2, MgO, Al_2O_3, etc. There are two areas of concern in using such a protective coating. First, the coating itself may adversely affect the optical properties of the black chrome film and thereby reduce the collector operating efficiency. This can occur either because of a reduction in the solar absorptance (probably caused by increasing the reflectance at the coating/black chrome interface) or because of an increase in the emittance (probably caused by increased infrared absorption in the coating). Thus the thickness of the protective coating may have to be carefully controlled. The second area of concern involves the cost and ease of application of the coating to the solar collector receiver surface. In the case of Sandia's parabolic collector, the receiver is a ~3.6 m long tube, approximately 33 mm in diameter.

A coating technique that allows various inorganic oxides to be deposited on large surfaces at relatively low cost is the sol-gel process. In this process, glasslike macromolecules are formed in solution at room temperature by chemical polymerization.[5] Before the solution transforms to a stiff, amorphous gel, it can be diluted and applied to a surface by dipping, spraying or other thin film coating techniques. After drying, the porous gel coating is heated to a moderate temperature (less than the softening point) where it converts to a dense, transparent glass layer.

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In this study, various sol-gel protective coatings were applied to black chrome films and the resulting optical properties and thermal aging behavior were studied. The coatings were applied using a straight forward dipping and firing process and involved low cost materials such as SiO_2, B_2O_3, TiO_2, etc.

Experimental details

Black chrome film preparation

All black chrome films were prepared from carefully prepared baths using Harshaw's Chromonyx black chrome solution.[3] The substrate was high purity (99.5%) nickel foil that was carefully cleaned and activated prior to electrodeposition.[2] The plating current density was typically 188 mA/cm^2 (175 A/ft^2) with the sample size being 7.6 cm x 10 cm. Because measurable changes in the optical properties with thermal aging are required in order to assess the protective nature of any applied coatings, black chrome films of only "moderate" thermal stability were plated. Thus, uncoated films, when heated for ≈100 hrs at 400°C in air, exhibited a decrease in solar absorptance of ~6-7%. As a point of comparison, our most stable coatings require over 1500 hrs at 400°C to show a decrease in solar absorptance of 6-7%.[2] It is presumed, but has not yet been shown, that any beneficial effect exhibited for these films at this aging temperature will also apply for more thermally stable black chrome films operated at lower temperatures.

Sol-gel coatings

The sol-gel coating process consists of applying an alcoholic solution containing polymeric glass precursors to a substrate at room temperature and then firing at a moderate temperature to obtain a glass layer. Sol-gel compositions of SiO_2/ZrO_2, SiO_2/TiO_2, SiO_2/B_2O_3 and $SiO_2/B_2O_3/Al_2O_3/Na_2O/BaO$ were fabricated using procedures reported in detail elsewhere.[5,6] The important sol-gel processing parameters include the coating thickness, firing temperature, firing time and firing atmosphere. These variables can affect the density, surface area, refractive index and pore structure of the sol-gel coating.[7]

Optical property measurements

The solar absorptance, α_s, was determined by appropriately averaging hemispherical reflectance data obtained using either a Beckman Model DK-2 or Model 5270 Spectroreflectometer over the wavelength range 350-2500 nm. The reference material used for these measurements was packed Halon powder. The 100°C emittance values [$\varepsilon(100°C)$] were measured using a Gier Dunkle Infrared Reflectometer, Model DB-100, as described in Ref. 8. Changes in α_s of more than ±0.01 absorptance units and in $\varepsilon(100°C)$ of more than ±0.02 emittance units should be considered significant.

Experimental results and discussion

As stated in the previous section, there are a large number of sol-gel processing parameters that may affect the protective nature of the sol-gel coatings when applied to black chrome films. In order to access the importance of these variables, a systematic experimental approach was utilized. In the first series of experiments (phase I), different sol-gel compositions were tested, while the processing parameters were held constant. In phase II experiments, the "best" composition from phase I was selected while several process parameters were varied. Finally in phase III experiments, selected process parameters were varied in order to "optimize" the results. The results of each experimental phase are detailed below.

Phase I experiments: Initial screening experiments investigated the protective nature of several different sol-gel compositions. The sol-gel coatings tested included (wt %) 63% SiO_2/37% TiO_2; 65% SiO_2/35% ZrO_2; 66% SiO_2/34% B_2O_3; and 66% SiO_2/18% B_2O_3/7% Al_2O_3/6% NaO/3% BaO (5-component glass). Prior to application, the gel solutions were diluted with solvent (ethanol) to optimize the coating quality and uniformity. The equivalent weight % oxides of the diluted solutions are listed in Table I for each composition studied. The black chrome films were dipped, dried and then fired at 450°C for 30 minutes in a N_2/5% H_2 atmosphere. The thickness of a single coating applied to a glass slide was ~150-200 nm before firing. The change in α_s for an uncoated sample after heating to 450°C for 30 minutes is less than 0.02 absorptance units.

The solar absorptance and 100°C emittance values are listed in Table I for coated and uncoated control samples both before and after they were aged at 400°C in air for 96 hrs. The solar absorptance values for both the SiO_2/TiO_2 and SiO_2/ZrO_2 coated samples after the thermal aging are lower than the uncoated samples, indicating no beneficial effect. In addition the $\varepsilon(100°C)$ values for these coated samples were 0.04-0.08 emittance units higher than the uncoated samples.

The solar absorptance values for both the SiO_2/B_2O_3 and the 5-component glass were higher than the uncoated samples after thermal aging, with the largest difference being 0.06 absorptance units. In addition, the ε(100°C) values for these coated samples were within 0.01 emittance units of the uncoated samples. It is interesting to note that although all these sol-gel coatings are predominately SiO_2 (63-66 wt %), the two best coatings both consist primarily of SiO_2/B_2O_3.

The solar absorptance values listed in column 3 of Table I represent the decrease that occurred after both the thermal aging test and the sol-gel firing process. For the SiO_2/ZrO_2 and SiO_2/TiO_2 protected films, about 1/2 of this decrease in solar absorptance occurred after the sol-gel firing process. For the two more stable sol-gel coatings, the solar absorptance decreased only 0.01-0.02 absorptance units after the sol-gel firing process.

Table I. Solar absorptance and emittance values of sol-gel coated and uncoated black chrome samples from phase I experiments. The α_s values listed in column 1 were obtained as-plated, in column 2 after the sol-gel coating process and in column 3 after thermal aging at 400°C in air for 96 hrs. The emittance values are shown only after the thermal aging test. All compositions are in wt %.

		α_s			
Sol-Gel Coating	# Coats	1	2	3	ε(100°C)
63% SiO_2/37% TiO_2 (Diluted to 7.6 wt % oxides)	1 coat	0.97	0.94	0.91	0.12
	uncoated	0.97	----	0.92	0.08
	2 coats	0.97	0.94	0.91	0.13
	uncoated	0.97	----	0.93	0.08
65% SiO_2/35% ZrO_2 (Diluted to 3.8 wt % oxides)	1 coat	0.97	0.94	0.91	0.12
	uncoated	0.97	----	0.92	0.08
	2 coats	0.97	0.93	0.88	0.16
	uncoated	0.97	----	0.91	0.08
66% SiO_2/34% B_2O_3 (Diluted to 4.5 wt % oxides)	1 coat	0.97	0.96	0.93	0.09
	uncoated	0.97	----	0.90	0.08
	2 coats	0.96	0.96	0.92	0.09
	uncoated	0.97	----	0.89	0.08
66% SiO_2/18% B_2O_3/ 7% Al_2O_3/6% NaO/3% BaO (Diluted to 2.8 wt % oxides)	1 coat	0.96	0.96	0.93	0.07
	uncoated	0.97	----	0.87	0.08
	2 coats	0.97	0.95	0.91	0.08
	uncoated	0.97	----	0.89	0.08

Phase II experiments: Because of the success of the 5-component glass sol-gel system, a series of experiments were set up that utilized this sol-gel coating in order to illuminate the importance of several processing parameters. The processing parameters studied included (1) the firing temperature, (2) the firing atmosphere, (3) the sol-gel coating thickness and (4) the effect of pre-aging the black chrome film. The latter treatment involved heating the black chrome film to 350°C for 96 hrs prior to the application of the sol-gel coating. It was felt that the sol-gel coating might adhere better to the resulting layer of Cr_2O_3 that forms on the black chrome film and thereby offer better protection.

In order to extract the maximum amount of information from these experiments, a 2^4 factorial experimental design was constructed for the four process variables.[8] The values for each variable were set as follows: firing temperature (500°C; 600°C); firing atmosphere (N_2; dry H_2); coating thickness (dilution to 2.8 and 1.4 wt % oxide); pre-aging of the black chrome film (yes;no). The firing time was held constant at 20 min. The full 16 combinations of these variables are listed in Table II. Black chrome films used for these experiments were prepared from identical bath solutions, so that all sol-gel coated samples had initial α_s values of 0.96 or greater and α_s values after thermal aging can be directly compared (i.e., each corresponding uncoated sample would have the same aging characteristics).

The solar absorptance and 100°C emittance values after aging at 400°C in air for 96 hrs are listed in Table II. The optical properties of two uncoated samples aged in the same way were $\alpha_s = 0.89-0.90$ and $\varepsilon(100°C) = 0.08$ (see Table II). Clearly the sol-gel coating had no measureable affect on the emittance values; however the processing variables did affect the solar absorptance values.

Table II. Solar absorptance and emittance properties of sol-gel coated black chrome samples from phase II experiments after thermal aging at 400°C in air for 96 hrs. Samples #17, 18 are uncoated control black chrome samples. The pre-heating conditions are discussed in the text.

Sample	Temp.	Atm.	Dilution (wt % oxides)	Preheating	α_s	$\varepsilon(100°C)$
1	600°C	Dry H_2	2.8	No	0.86	0.08
2	"	"	2.8	Yes	0.87	0.08
3	"	"	1.4	No	0.86	0.08
4	"	"	1.4	Yes	0.89	0.08
5	"	N_2	2.8	No	0.94	0.08
6	"	"	2.8	Yes	0.90	0.08
7	"	"	1.4	No	0.93	0.08
8	"	"	1.4	Yes	0.90	0.08
9	500°C	Dry H_2	2.8	No	0.93	0.08
10	"	"	2.8	Yes	0.94	0.08
11	"	"	1.4	No	0.93	0.08
12	"	"	1.4	Yes	0.93	0.08
13	"	N_2	2.8	No	0.95	0.08
14	"	"	2.8	Yes	0.93	0.08
15	"	"	1.4	No	0.95	0.08
16	"	"	1.4	Yes	0.92	0.08
17	Uncoated	---	----	---	0.90	0.08
18	Uncoated	---	----	---	0.89	0.08

Using standard factoral analysis procedures,[8] the most significant change in α_s resulted from the temperature variations, with 500°C being considerably better than 600°C. The next most significant process variable was the firing atmosphere, where N_2 was better than dry H_2. The pre-aging procedure had only a small effect on the α_s values (no aging better than aging) while the coating thickness (dilution) had no measurable effect on the α_s values. Because the sol-gel coating dilution had no significant effect on the resulting optical properties, we may consider samples that differ only in the coating dilution as identical. A graphic visualization of the effect of the other process variables can be obtained by averaging the two α_s values for the samples that differ only in the dilution (i.e., averaging the results for samples 1 and 3, 2 and 4, 5 and 7, etc.) and plotting the remaining eight experimental points as shown in Fig. 1. It can be easily seen that the best coatings were obtained in the lower left corner (500°C; N_2; no pre-aging). For these conditions, α_s maintained a value of 0.95 compared to the values 0.89 and 0.90 for the uncoated samples.

As previously mentioned, the α_s values listed in Table II result after both the thermal aging test and the sol-gel firing process. It is interesting to note that the decrease in α_s caused by the aging at 400°C for 96 hrs was very nearly the same for all of the experimental conditions investigated (the decrease was ~0.02 absorptance units). Therefore the major differences in the final α_s values were due to the sol-gel firing process itself and not the thermal aging test.

Phase III experiments: Several additional experiments were performed in order to determine the effect of certain selected variables. For these experiments, one process parameter was varied while all other processing parameters were fixed at the values which produced the best coatings in the phase II experiments (i.e., dilution to 2.8 wt % oxides; temperature 500°C; firing time 20 min; atmosphere N_2; no pre-aging). The experimental conditions and the resulting optical properties are listed in Table III.

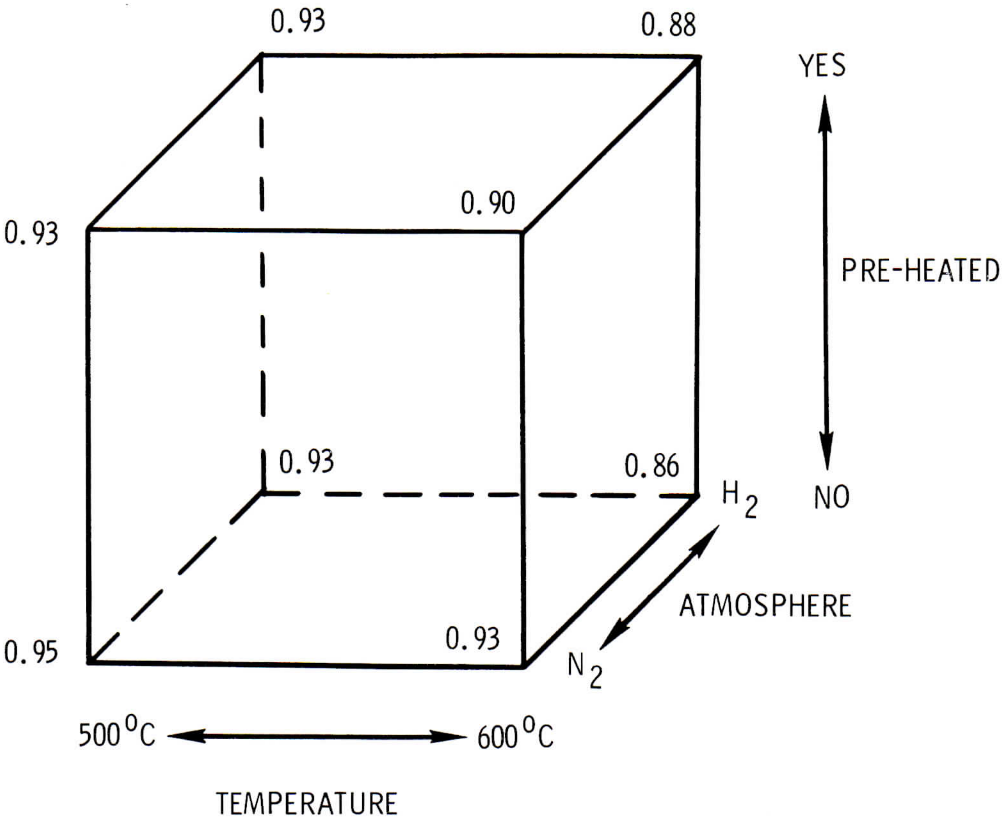

Figure 1. Schematic representation of the average solar absorptance values obtained from the phase II experiments. The experimental variables included the sol-gel firing temperature, firing atmosphere and pre-heating of the black chrome film as discussed in the text.

Table III. Solar absorptance and emittance properties of sol-gel coated samples from phase III experiments after thermal aging at 400°C in air for 96 hrs. The 5-component glass consists of 66% SiO_2/18% B_2O_3/7% Al_2O_3/6% NaO/3% BaO. All compositions are in wt %. The vacuum corresponded to 1.33×10^{-4} Pa.

Sample	Sol-Gel Coating	Temp.	Atm.	Time	Dilution (wt % oxides)	α_s	ε(100°C)
1	5-component glass	500°C	N_2	20 min.	6.6	0.89	0.17
2		500°C	N_2	20 min.	0.7	0.93	0.08
3	5-component glass	450°C	N_2	20 min.	2.8	0.91	0.07
4		425°C	N_2	20 min.	2.8	0.88	0.09
5	5-component glass	500°C	VAC.	20 min.	2.8	0.86	0.09
6	5-component glass	500°C	AIR	20 min.	2.8	0.86	0.09
7		450°C	AIR	20 min.	2.8	0.89	0.09
8	70% SiO_2/30% B_2O_3	500°C	N_2	20 min.	4.5	0.93	0.09
9	92% TiO_2/8% SiO_2	500°C	N_2	20 min.	4.4	0.84	0.09

It was very surprising that the sol-gel thickness did not affect the protective nature of the sol-gel coating. One might have expected thicker coatings to provide more oxidation resistance, but possibly result in higher emittance values; thinner coatings would have the reverse effect. Therefore the effect of the sol-gel coating thickness was investigated further by diluting the coating solution to 6.6 and 0.7 wt % oxides. As shown for samples #1 and #2 in Table III, the 0.7 wt % dilution produced similar optical properties compared to the 2.8 and 1.4 wt % dilution of phase II (see samples #13 and #15 of Table II) while the 6.6 wt % dilution resulted in a lower α_s value and a higher $\varepsilon(100°C)$ value. Thus dilution in the range 2.8 to 0.7 wt % oxides provide acceptable protective coatings for the 5-component sol-gel.

Because lowering the firing temperature improved the optical properties of the sol-gel coated samples in phase II experiments, the effect of an additional reduction in the firing temperature was investigated. As shown for samples #3 and #4 in Table III, temperatures of 450°C and 425°C do not produce coatings which protect as well as coatings fired at 500°C. This probably results from a lack of coating densification at the lower firing temperatures, as previously shown.[7]

For sample #5 in Table III, the firing atmosphere was changed to a vacuum (pressure of 1.33×10^{-4} Pa) but the resulting α_s value was 0.07 absorptance units lower than the value obtained for the N_2 atmosphere (compare sample #5 to sample #2 in Table III). This indicates a significant oxidation of the black chrome film had occurred at the pressure utilized. Therefore a moderate vacuum is not sufficient to protect the black chrome film during the firing process. Similar results were obtained for an air atmosphere, with a 450°C firing temperature slightly better than the 500°C firing temperature.

Finally, the sol-gel composition was changed to 70% SiO_2/30% B_2O_3 and 92% TiO_2/8% SiO_2 (all percentages in wt %). As in the phase I experiments, the SiO_2/B_2O_3 coating produced similar results to the 5-component glass coating. The high TiO_2 content coating did not protect the black chrome film as the α_s value was 0.07 absorptance units below the value for the uncoated film.

Longer term aging experiments: In order to confirm that the protective nature of the sol-gel coatings would persist for longer times, the "best" coatings from each experimental phase were selected for additional aging at 400°C together with the corresponding uncoated control samples. From the phase III experiments, the 5-component glass coating at 0.7 wt % dilution and the SiO_2/B_2O_3 coated sample were selected. Solar absorptance values as a function of aging time are shown in Figure 2 and are listed in Table IV for times up to 400 hrs. Although α_s continues to decrease with time for both the coated and uncoated samples, the α_s values for the sol-gel coated samples remain higher than the α_s values for the uncoated samples. The aging behavior of the coated and uncoated samples can be made to overlap if the heat treatment times for the coated samples are multiplied by 0.37 (= 1/2.7) as shown in Fig. 2. Similar results were obtained for phase I samples. Thus it is necessary to age the coated sample 2.7 times longer than the uncoated sample in order to obtain the same α_s value. If this relationship holds for other aging temperatures and longer times, then the sol-gel coated black chrome samples would improve the operating lifetime of the black chrome film by at least a factor of 2.

Different aging behavior was obtained for samples #13 and #15 (see Table II) from the phase II experiments. For these samples, additional heating at 400°C resulted in a rapid drop in α_s between 200 and 400 hrs of aging. Thus, after 430 hrs, the α_s values of the sol-gel coated and uncoated samples were equal, within experimental error. At the present time, this unusual aging behavior is not understood. Experiments are in progress to determine the nature of the degradation for these films.

Table IV. Solar absorptance values as a function of heat treatment time at 400°C in air for samples #1 and #5 from Table III. Also included is an uncoated sample from the same black chrome film.

Sample	0	24 hrs	96 hrs	193 hrs	303 hrs	402 hrs
#1 (5-component glass)	0.97	--	0.93	0.92	0.89	0.89
#5 (70% SiO_2/30% B_2O_3)	0.96	--	0.93	0.91	0.89	0.89
Uncoated	0.97	0.93	0.91	0.88	--	0.85

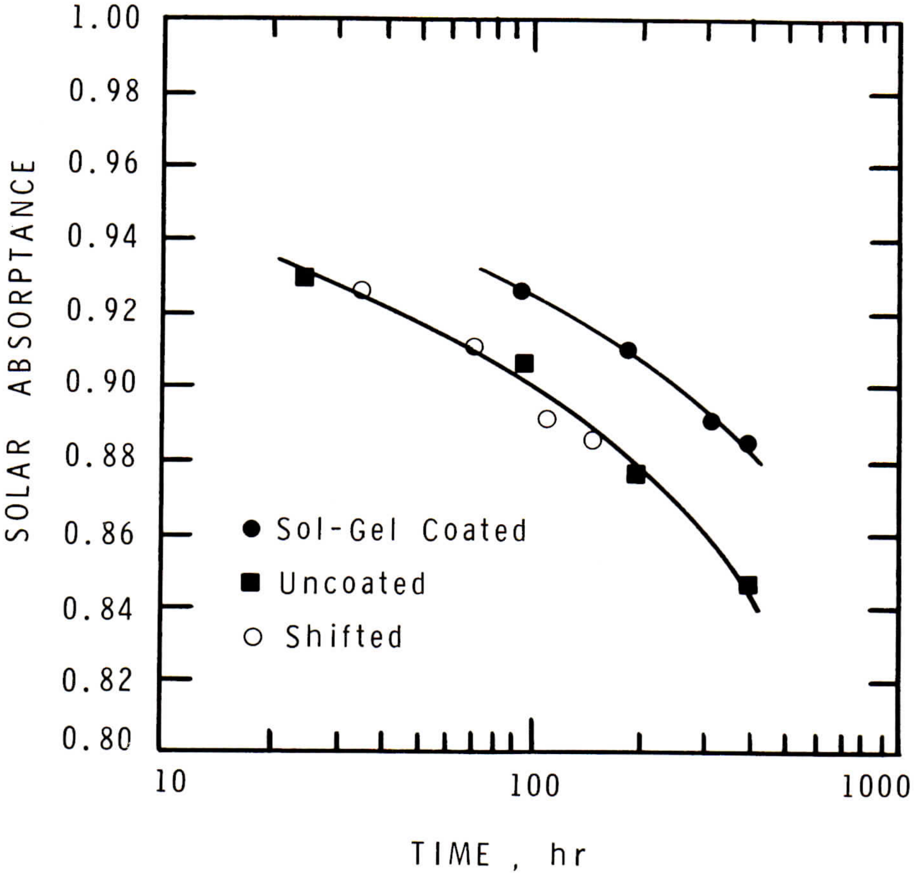

Figure 2. Plot of the solar absorptance as a function of time of aging at 400°C in air for sol-gel coated and uncoated black chrome films. The coated samples include sol-gel coatings of SiO_2/B_2O_3 and a 5-component glass (samples #1 and #5 from Table III). Also shown is the effect of shifting the time axis by a factor of 0.37 for the sol-gel coated samples.

Conclusions

The improvement in the thermal stability of sol-gel coated black chrome solar selective films was studied for a variety of sol-gel compositions and processing parameters. When properly applied, the sol-gel coating could improve the lifetime of some black chrome films when aged at 400°C in air by at least a factor of 2. Sol-gel coatings made of primarily SiO_2/B_2O_3 performed significantly better than coatings composed of SiO_2/TiO_2 and SiO_2/ZrO_2. Of the processing variables investigated in the phase II and III experiments, the firing temperature had the largest effect on the resulting solar absorptance values, with ~500°C being optimum. In addition the firing atmosphere was important, with a N_2 atmosphere better than dry H_2, air or vacuum. For the best coatings, the increase in the 100°C emittance values was less than 0.01-0.02 emittance units.

When several sol-gel coated black chrome films were aged for longer times at 400°C in air, the solar absorptance values remained higher than the uncoated control samples, as expected. However, for a few coated films, the solar absorptance decreased significantly after 430 hrs at 400°C. Experiments are in progress to determine the nature of this unusual degradation.

Acknowledgements

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