

CHEMICALLY VAPOR-DEPOSITED ZrB_2 AS A SELECTIVE SOLAR ABSORBER*

E. RANDICH

• *Sandia National Laboratories, Albuquerque, NM 87185 (U.S.A.)*

D. D. ALLRED

• *Energy Conversion Devices, Troy, MI 48084 (U.S.A.)*

• (Received March 27, 1981; accepted April 7, 1981)

Coatings of ZrB_2 and TiB_2 for photothermal solar absorber applications were prepared using chemical vapor deposition (CVD) techniques. Oxidation tests suggest a maximum temperature limit for air exposure of 600 K for TiB_2 and 800 K for ZrB_2 . Both materials exhibit innate spectral selectivity with an emittance at 375 K ranging from 0.06 to 0.09, a solar absorptance for ZrB_2 ranging from 0.67 to 0.77 and a solar absorptance for TiB_2 ranging from 0.46 to 0.59. ZrB_2 has better solar selectivity and more desirable oxidation behavior than TiB_2 . A 0.071 μm antireflection coating of Si_3N_4 deposited onto the ZrB_2 coating leads to an increase in absorptance from 0.77 to 0.93, while the emittance remains unchanged.

1. INTRODUCTION

Efficient solar photothermal conversion at high temperatures benefits from spectrally selective absorber surfaces. The optical properties of these surfaces are such that they possess both a high solar absorptance α_s , to maximize the fraction of the solar insolation transformed to heat, and a low thermal emittance ϵ , to suppress IR reradiation losses. These favorable optical properties must be maintained during long-term operation at elevated temperatures and in many cases exposure to the atmosphere. Economic considerations favor simplicity of design and the use of coatings rather than bulk materials^{1,2}. One of the chief materials problems in the use of coatings is the preparation of high temperature surfaces of IR reflector materials which are stable at elevated temperatures in air. Except for platinum, which is expensive, no elemental coatings appear to be suitable for use in air at elevated temperatures². Some transition metal compounds (particularly some of the borides, nitrides, carbides and silicides) appear to have desirable high temperature oxidation properties³. Although the emittances for most of these compounds are not known, the low d.c. resistivities of the group IV metal diborides relative to the parent metals suggests that they will be low⁴. Another advantageous property of the transition metal borides is their high hardness. TiB_2 and ZrB_2 have reported hardnesses of

* Paper presented at the International Conference on Metallurgical Coatings, San Francisco, CA, U.S.A., April 6–10, 1981.

3300 HV 25 and 2300 HV 25 respectively (both harder than WC)⁵ which means that they will be extremely resistant to scratching and erosion damage. This and the fact that these borides can easily be deposited by chemical vapor deposition (CVD) recommends their use for solar selective surfaces.

We prepared coatings of TiB₂ and ZrB₂ using CVD techniques and determined α_s and $\epsilon(375\text{ K})$ for the as-deposited materials. These properties were measured for ZrB₂ after extended aging in air at 675 K. High temperature oxidation properties were also measured using ramp-type oxidation tests. The possibility of enhancing the solar absorptance of ZrB₂ using antireflection coatings of Si₃N₄ was also explored.

2. PROCEDURE

The coatings were deposited onto Poco AXF-5Q graphite by H₂ reduction of BCl₃ and either TiCl₄ or ZrCl₄. The CVD apparatus and procedures have been described in detail elsewhere⁵. The deposition temperature for TiB₂ and ZrB₂ were 1200 K and 1225 K respectively. All coatings were deposited at our laboratory atmospheric pressure of 635 Torr. Reactant gas flows were adjusted so that, for TiB₂, B/Ti = 1.0 and H/Cl = 10.0 and, for ZrB₂, B/Zr = 1.0 and H/Cl = 20.0 (atomic ratios). The thicknesses of the coatings ranged from 15 to 30 μm as determined by weight gain.

The ramp-type oxidation tests were performed in O₂ at 100 Torr using a heating rate of 4 K min⁻¹. A Cahn RH electrobalance was used to monitor weight change. Environmental aging tests of the ZrB₂ were carried out in air at 675 \pm 5 K.

Antireflecting Si₃N₄ coatings were deposited by plasma-enhanced CVD at 575 K using SiH₄ and NH₃ in an N₂ carrier gas. The Si₃N₄ thicknesses were determined by ellipsometry on silicon wafers which were coated with Si₃N₄ together with the ZrB₂ samples.

The hemispherical reflectance properties of samples were measured from a wavelength of 0.35–2.5 μm using a Beckman DK2 spectroreflectometer and Halon reflectance standards. The solar absorptance values of the samples were determined from hemispherical reflectance curves using a 20-point solar absorptance technique and are accurate to ± 0.01 absorptance units⁶. The emittances (375 K) of the samples were determined using a model DB-100 Gier Dunkle reflectometer and are accurate to ± 0.02 emittance units.

3. RESULTS AND DISCUSSION

The oxidation behavior of both ZrB₂ and TiB₂ has two distinct temperature domains (Fig. 1). Below a critical temperature of 600 K for TiB₂ and 800 K for ZrB₂ the measured weight gain due to oxidation is quite slow. Above 725 K for TiB₂ and 925 K for ZrB₂ the weight gain is quite rapid. Between these two domains is a transition region of approximately 125 K. These results are in excellent agreement with reported results for powder samples^{7,8} which showed that in the low temperature domain an amorphous protective oxide is formed while in the high temperature domain a crystalline non-protective oxide is formed. In the transition range between these domains an amorphous oxide film stabilized by boron oxide is

formed⁸. In the low temperature domain the growth rate of the amorphous oxide is reported to be parabolic while in the high temperature domain the oxidation rate obeys a linear growth relationship. These results suggest an absolute maximum temperature limit for air exposure applications of 700 K for TiB_2 and 900 K for ZrB_2 in order to maintain long-term optical stability. More conservative temperature limits of 600 K and 800 K respectively might prevent a potentially rapid degradation of the absorber to provide a safety margin in case of a brief accidental high temperature excursion. In consideration of these temperature limits, ZrB_2 coatings alone were selected for high temperature aging tests in air.

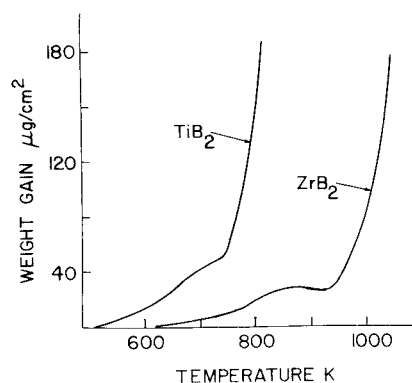


Fig. 1. The oxidation behavior of CVD TiB_2 and ZrB_2 coatings heated at 4 K min^{-1} in O_2 at 100 Torr.

The emittances at 375 K of the ZrB_2 and TiB_2 coatings were essentially equal, ranging from 0.06 to 0.09. The solar absorptance of the TiB_2 coatings ranged from 0.46 to 0.59 and the solar absorptance of the ZrB_2 coatings ranged from 0.67 to 0.77. These values seem to correlate with the surface morphology of the sample. In Fig. 2 we show scanning electron microscope photographs of two ZrB_2 samples whose as-deposited α_s values were 0.69 (Fig. 2(a)) and 0.76 (Fig. 2(b)). The surface microroughness of the sample shown in Fig. 2(a) is greater (an estimated feature size of about 2–3 μm) than that of the sample shown in Fig. 2(b) (an estimated feature size of about 0.5–2.0 μm). It appears that the finer roughness is effective in increasing the solar absorptance of ZrB_2 . This corresponds to observations for many different kinds of selective surface systems^{1,2}. Since both ZrB_2 samples show substantial microscopic roughness they can be expected to have increased values for α_s above that which would be measured for a smooth sample.

The zirconium boron oxide which is formed on the ZrB_2 coating on exposure to air at 675 K apparently acts as an antireflection coating. The observed changes in the hemispherical reflectance are shown in Fig. 3. After 668 h, α_s increases from 0.67 to 0.73 while ϵ remains unchanged at about 0.06. The rate of change in α_s decreases with exposure time which is consistent with a parabolic growth rate for the oxide. Long-term exposure of unprotected ZrB_2 in air at 675 K would be expected to result in a peaking and eventual decrease in α_s with an eventual increase in ϵ . We cannot estimate the time when this will occur, however, from the data at hand.

The foregoing results show that ZrB_2 is sufficiently resistant to oxidation at

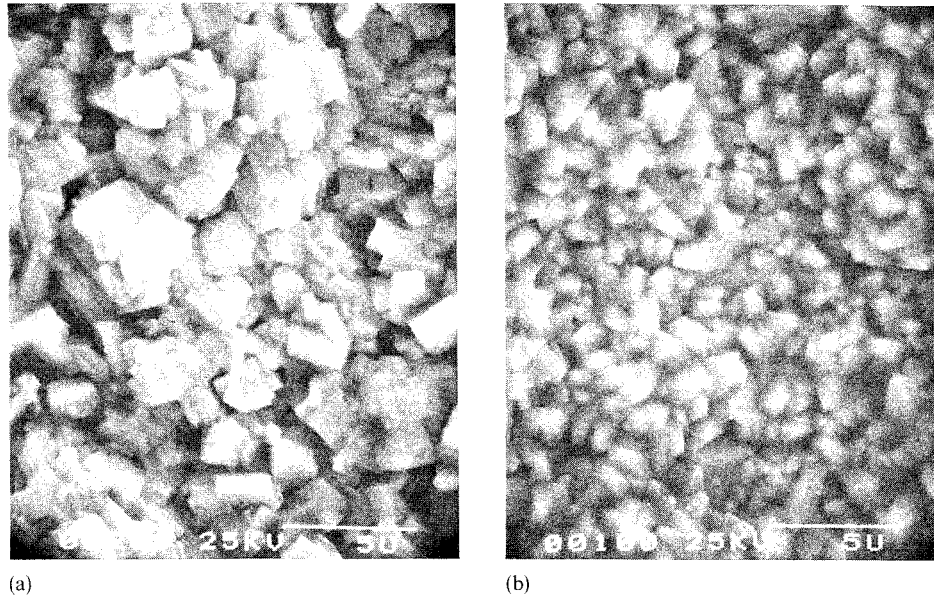


Fig. 2. Scanning electron microscope photographs of CVD ZrB_2 showing the surface morphologies for coatings with (a) $\alpha_s = 0.69$ and $\epsilon = 0.08$ and (b) $\alpha_s = 0.76$ and $\epsilon = 0.07$.

675 K and possesses a sufficiently low ϵ to recommend its use as a solar absorber material with a variety of absorber stack configurations. We, therefore, prepared two-layer selective coatings consisting of CVD ZrB_2 which was overcoated with $0.071 \mu\text{m}$ of Si_3N_4 . The function of the Si_3N_4 film is only to act as an antireflection layer for the underlying ZrB_2 to enhance its solar absorptance. We also expect the Si_3N_4 to enhance the oxidation stability of ZrB_2 further. These two-layer coatings have α_s values ranging from 0.89 to 0.93 depending on the initial absorptance (morphology) of the CVD ZrB_2 coating. A thickness of $0.071 \mu\text{m}$ for the Si_3N_4 was determined as the optimum thickness for a high α_s as this places the reflectance minimum near a wavelength of $0.55 \mu\text{m}$, the peak of the solar spectral distribution. In Fig. 4 the hemispherical reflectance is shown as a function of wavelength for the two ZrB_2 samples whose surface morphologies are shown in Fig. 2. In Fig. 4 the upper curve for each case is for the as-deposited film and the lower curve is after the antireflection coating of Si_3N_4 has been deposited onto the ZrB_2 . For the coating shown in Fig. 2(a), α_s increases from 0.69 to 0.89 while ϵ increases from 0.08 to 0.10. For the coating shown in Fig. 2(b), α_s increases from 0.76 to 0.93 while ϵ increases from 0.07 to 0.09. The refractive index of Si_3N_4 appears to be reasonably close to the optimum required for an antireflection coating for ZrB_2 since it reduces the reflectance to only 0.02 at the minimum point. The reflectance at the minimum point is relatively constant regardless of the initial reflectance of the ZrB_2 coating.

4. CONCLUSIONS

Both CVD TiB_2 and ZrB_2 are refractory hard coatings which have low thermal emittances and innate solar spectral selectivities. However, ZrB_2 has substantially

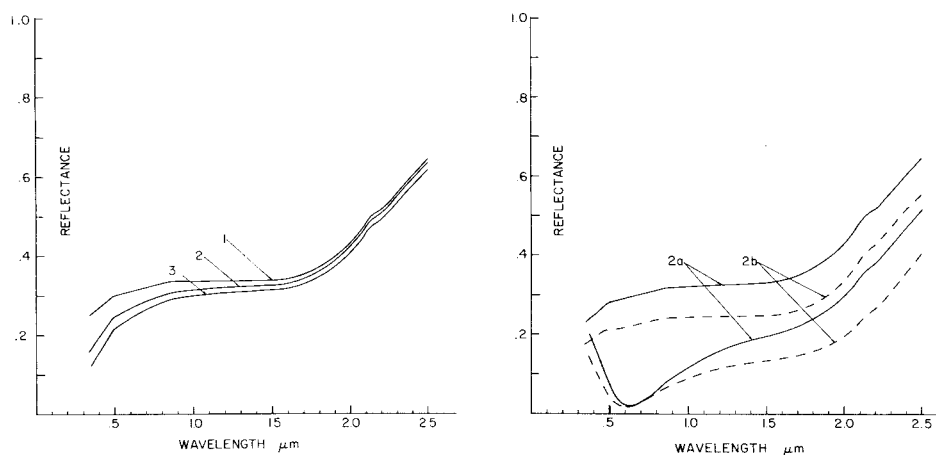


Fig. 3. Aging of ZrB_2 in air at 675 K: curve 1, as deposited, $\alpha_s = 0.67$, $\varepsilon = 0.06$; curve 2, aged for 245 h, $\alpha_s = 0.70$, $\varepsilon = 0.07$; curve 3, aged for 668 h, $\alpha_s = 0.73$, $\varepsilon = 0.06$.

Fig. 4. Changes in the hemispherical reflectance as a function of wavelength by applying a $0.071 \mu\text{m}$ coating of Si_3N_4 on the ZrB_2 coatings shown in Figs. 2(a) (—) and 2(b) (---).

superior high temperature oxidation properties and a better solar selectivity which make it a better choice for use as a spectrally selective surface at elevated temperatures. The formation of a reasonably protective amorphous oxide film at 675 K changes α_s and ε only slowly. At temperatures below 800 K this oxide remains amorphous and appears to grow at a parabolic rate, suggesting that ZrB_2 could be used at temperatures up to 800 K without undergoing rapid or catastrophic changes in α_s and ε . Initial results using an antireflection (and oxidation protection) coating of Si_3N_4 show gains in α_s to 0.93 from 0.77 while maintaining ε at 0.09. In light of its superior oxidation behavior this places antireflected ZrB_2 among the best high temperature selective solar absorbers. Higher absorptances might be obtained if other antireflection coatings were used instead of or in addition to Si_3N_4 . Optimization of the surface morphology of the CVD ZrB_2 may also further increase α_s . Future work will focus on the determination of the stability of Si_3N_4 -antireflected ZrB_2 coatings which have been deposited onto metallic substrates such as Kovar during aging in air at 675 K and 775 K.

ACKNOWLEDGMENTS

The authors wish to express their thanks to R. B. Pettit and J. J. Clement, Sandia National Laboratories, for their help in the sample preparation and the measurement of optical properties.

Sandia National Laboratories is a U.S. Department of Energy facility. This work was supported by the U.S. Department of Energy under Contract DE-AC04-76-DP00789.

REFERENCES

- 1 R. E. Hahn and B. O. Seraphin, *Phys. Thin Films*, 10 (1978) 1.

- 2 D. M. Mattox, *Opt. News*, (Summer 1976).
- 3 J. C. Haygarth, *Thin Solid Films*, 72 (1980) 51.
- 4 C. F. Powell, I. E. Campbell and B. W. Gonser, *Vapor Plating*, Wiley, New York, 1955, p. 117.
- 5 E. Randich, *Thin Solid Films*, 63 (1979) 309.
- 6 M. A. Lind, R. B. Pettit and K. D. Masterson, *J. Sol. Energy Eng.*, 102 (1980) 34.
- 7 A. Lebugle and G. Montel, *C.R. Acad. Sci., Sér. C*, 273 (1971) 546.
- 8 A. Lebugle and G. Montel, *C.R. Acad. Sci., Sér. C*, 274 (1972) 1512.