

# Effects of some rare earth oxides and/or SiO<sub>2</sub> additions to a commercial ZrO<sub>2</sub> paint for coating SiGe thermoelectric materials

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The effects of some rare earth oxides (Y<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Sm<sub>2</sub>O<sub>3</sub> or Er<sub>2</sub>O<sub>3</sub>) and/or SiO<sub>2</sub> additions to a commercial oxide paint (mainly ZrO<sub>2</sub>) were studied as coatings for SiGe thermoelectric materials. No spalling occurred in the samples prepared from coatings containing small amounts of Er<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> or both CeO<sub>2</sub> and SiO<sub>2</sub> while heating for 1322 h at 1080° C in vacuum, and the sublimation of silicon and/or germanium was reduced significantly. The improvements imparted by these oxide additions to the commercial oxide paint is thought to be due to decreased internal stress of the surface oxides. The addition of Y<sub>2</sub>O<sub>3</sub> and Sm<sub>2</sub>O<sub>3</sub> had a detrimental effect.

## 1. Introduction

Si-Ge alloys which are being used as thermoelectric materials for radioisotopic thermoelectric generators are exposed to high temperatures to maximise their efficiency. Because silicon, germanium and the dopants are slowly lost due to sublimation at high temperatures [1-5], coatings of Si<sub>3</sub>N<sub>4</sub> or SiO<sub>2</sub> are used to suppress sublimation of the alloy elements [6, 7]. We have found that the application of a commercial oxide paint (mainly ZrO<sub>2</sub>) [8] as coatings for SiGe thermoelectric materials showed good adherence to the surface oxides and significantly reduced the sublimation of the alloy [9], also see preceding paper [10].

In the present study, the effect of rare earth oxides and/or SiO<sub>2</sub> additions to a ZrO<sub>2</sub> commercial oxide paint on the vapour-suppression properties of SiGe alloys was examined. In addition to establishing the conditions for applying coatings of these materials to SiGe, their effectiveness at 1080° C in vacuum was

studied. Metallographic, X-ray diffraction and electron probe microanalyser (EPMA) studies were used to obtain a better understanding of the oxide adherence at the oxide/alloy interface.

## 2. Experimental details

The experimental details are presented in the preceding paper [10]. The oxide paints used in this aspect of our study were made by mixing small amounts of rare earth oxides (Y<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Sm<sub>2</sub>O<sub>3</sub>, or Er<sub>2</sub>O<sub>3</sub>) and/or SiO<sub>2</sub> to the commercial oxide paint "Z-prime" [8]. These oxide paints were applied to the sample surface by using a spray gun. The coated samples were then heated in air at 1100° C for 200 h before the weight loss measurements were begun.

## 3. Results and discussion

Fig. 1 shows the loss rate by sublimation of the coated n-type SiGe (GaP) samples. Low loss rates were

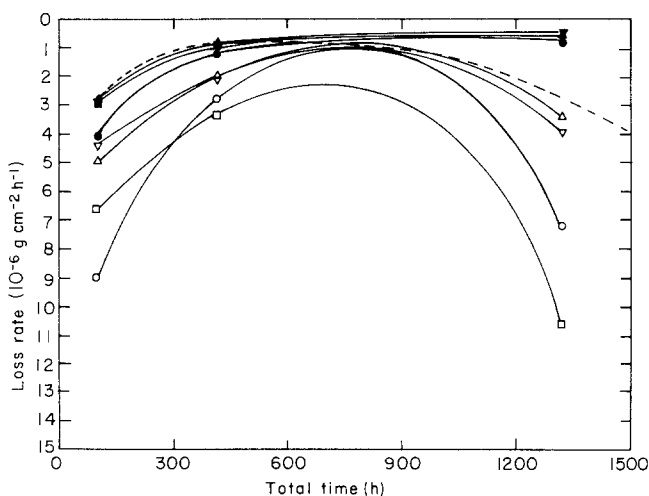


Figure 1 Sublimation of n-type SiGe (GaP) alloys coated with "Z"-prime containing some rare earth oxides and/or SiO<sub>2</sub> in vacuum at 1080° C. (●) S-29 (1.0% Er<sub>2</sub>O<sub>3</sub>), (○) S-33 (0.2% Y<sub>2</sub>O<sub>3</sub>), (△) S-34 (0.2% Sm<sub>2</sub>O<sub>3</sub>), (▽) S-43 (1.0% Sm<sub>2</sub>O<sub>3</sub>), (□) S-44 (5.0% Sm<sub>2</sub>O<sub>3</sub>), (▲) S-58 (0.2% SiO<sub>2</sub>), (▼) S-59 (1.0% SiO<sub>2</sub>), (■) S-60 (0.2% SiO<sub>2</sub> + 0.5% CeO<sub>2</sub>), (---) S-41 (Z-prime). The number in parenthesis after sample number shows weight per cent of the oxide added to "Z-prime".

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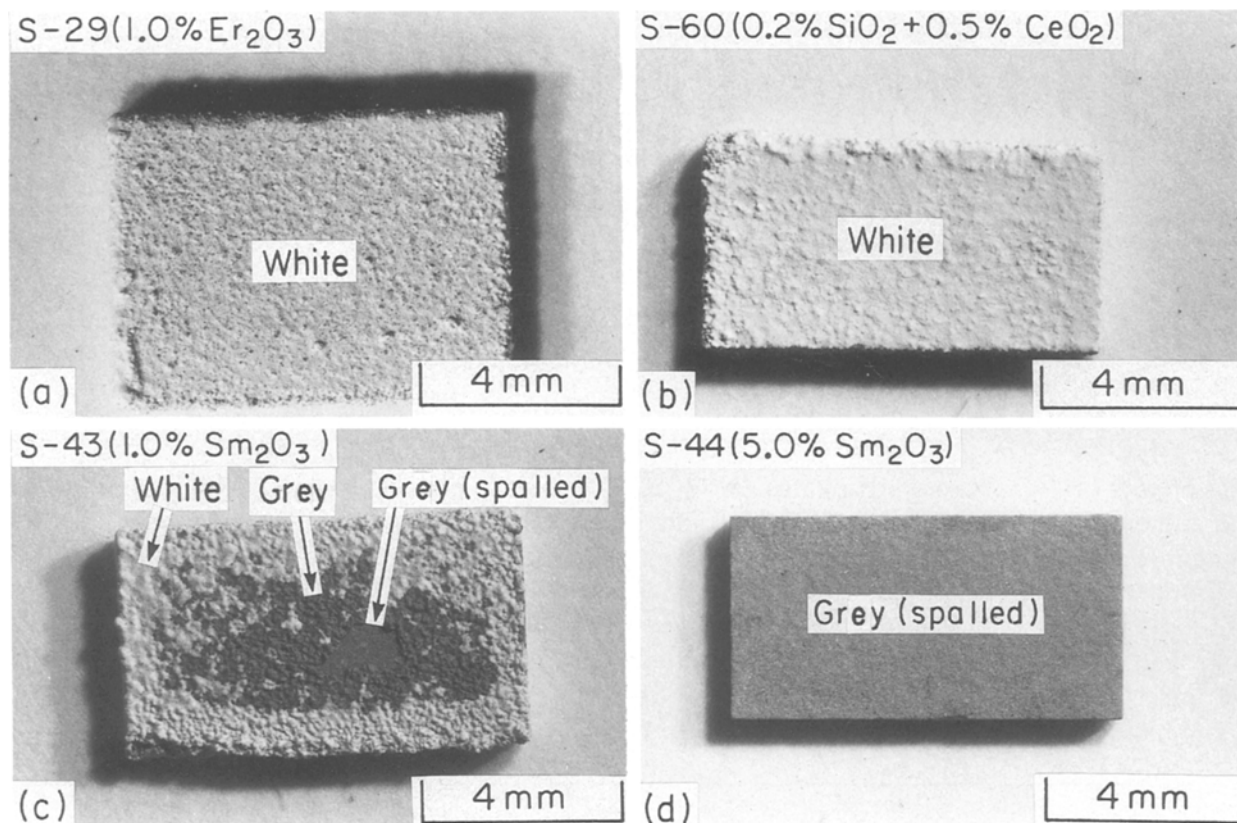


Figure 2 The coated surfaces of the samples (a) S-29, (b) S-60, (c) S-43 and (d) S-44 after 1322 h in vacuum at 1080°C.

observed for samples S-59, S-58, S-29 and S-60. High loss rates are observed for samples S-44, S-33, S-43 and S-34. A dotted line in Fig. 1 shows the loss rate of a pure “Z-prime”-coated n-type SiGe (GaP) alloy taken from Fig. 1 of the preceding paper [10]. The loss rate of the “Z-prime”-coated alloy was found to lie between the low loss rate and the high loss rate groups.

The oxide additions from the low loss rate group ( $\text{Er}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{CeO}_2 + \text{SiO}_2$ ) to “Z-prime” were thought to be effective because they decreased the internal stress of the surface oxide coatings on the SiGe alloys. Fig. 2 shows the coated surfaces of the samples S-29, S-60, S-43, and S-44 (parts a to d, respectively) after 1322 h in vacuum at 1080°C. Grey-coloured oxides for S-43 sample were observed in the central area of the specimen. Some spalled areas were observed in the grey-coloured oxides. The grey-coloured oxides might be formed by sublimation of n-type SiGe (GaP) alloys, and might lead to spallation

TABLE 1 Summary of X-ray diffraction analysis of oxides on n-type SiGe (GaP) alloys heat-treated for 1322 h in vacuum at 1080°C

Sample No.	Oxides
S-29 (1.0% $\text{Er}_2\text{O}_3$ )	$\text{ZrO}_2$ (s) $\text{ZrSiO}_4$ (s)
S-33 (0.2% $\text{Y}_2\text{O}_3$ )	$\text{ZrO}_2$ (s)
S-34 (0.2% $\text{Sm}_2\text{O}_3$ )	$\text{ZrO}_2$ (s) $\text{ZrSiO}_4$ (w)
S-43 (1.0% $\text{Sm}_2\text{O}_3$ )	$\text{ZrO}_2$ (s) $\text{ZrSiO}_4$ (w)
S-44 (5.0% $\text{Sm}_2\text{O}_3$ )	$\text{ZrO}_2$ (s)
S-58 (0.2% $\text{SiO}_2$ )	$\text{ZrO}_2$ (s) $\text{ZrSiO}_4$ (m)
S-59 (1.0% $\text{SiO}_2$ )	$\text{ZrO}_2$ (s) $\text{ZrSiO}_4$ (s)
S-60 (0.2% $\text{SiO}_2 + 0.5\% \text{CeO}_2$ )	$\text{ZrO}_2$ (s) $\text{ZrSiO}_4$ (m)

s, strong; m, medium; w, weak.

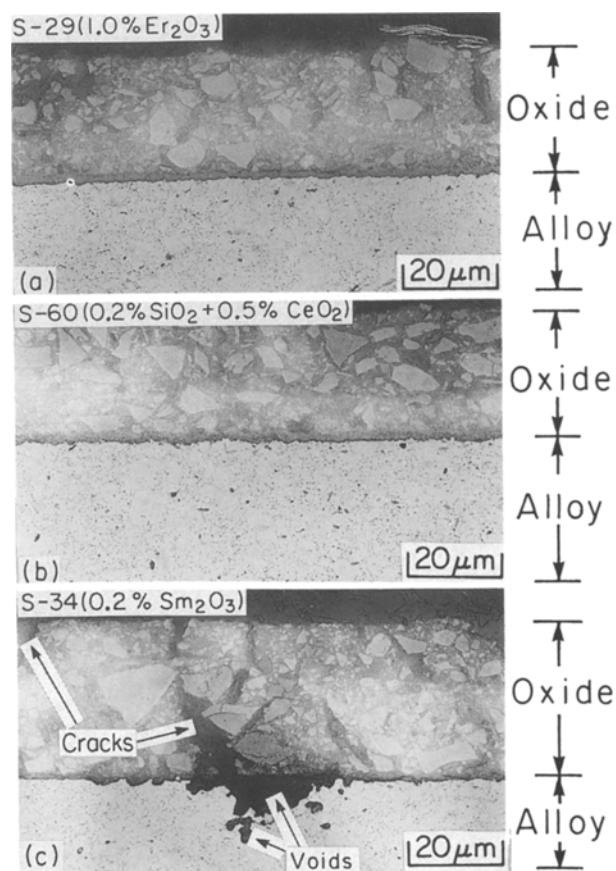


Figure 3 Microstructures of the cross-section of the n-type SiGe (GaP) alloys coated with “Z-prime” containing rare earth oxides and/or  $\text{SiO}_2$  after annealing 1322 h in vacuum at 1080°C.

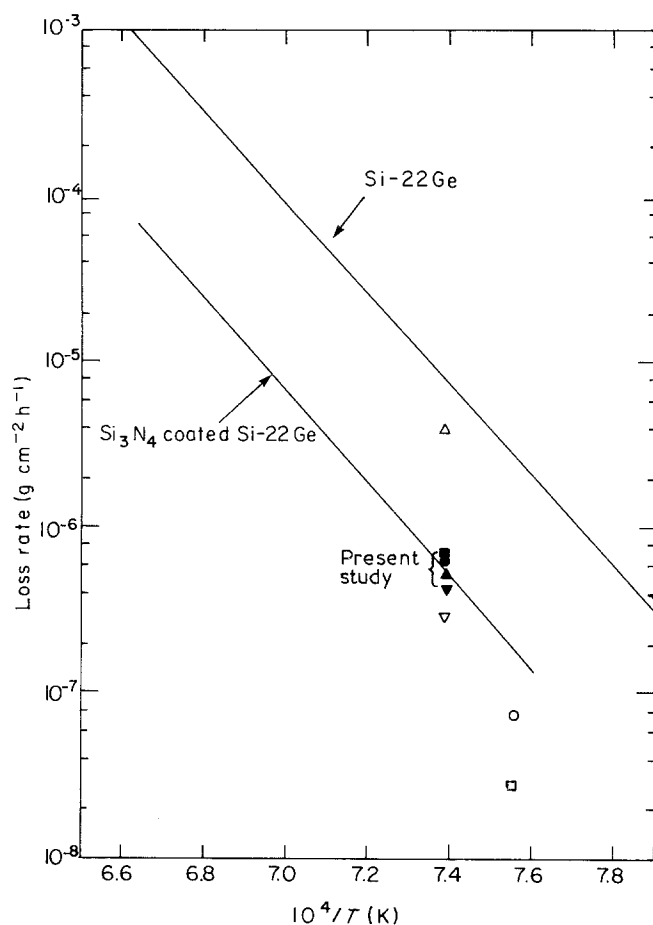


Figure 4 Loss rate for various ceramic-coated SiGe alloys. The results of the uncoated and Si<sub>3</sub>N<sub>4</sub>-coated and Si<sub>78</sub>Ge<sub>22</sub> were taken from Shields and Noon [7]. Present study: (●) S-29 (1.0% Er<sub>2</sub>O<sub>3</sub>), (▲) S-58 (0.2% SiO<sub>2</sub>), (▼) S-59 (1.0% SiO<sub>2</sub>), (■) S-60 (0.2% SiO<sub>2</sub> + 0.5% CeO<sub>2</sub>). (Δ) Z-prime, one coat; (▽) Z-prime, two coats; (○) SiO<sub>2</sub>-coated p-type SiGe (GaP); (□) SiO<sub>2</sub>-coated n-type SiGe (GaP).

of the surface oxides. The smooth grey-coloured surface of S-44 sample occurred by spallation of the surface oxides. On the other hand, white-coloured oxides were observed over the entire surface for samples S-29 and S-60, and no evidence was found for spallation on the surfaces of these samples.

Fig. 3 shows microstructures of the cross-section of the coated n-type SiGe (GaP) alloys (S-29, S-60 and S-34, parts a, b and c, respectively) which had been heat-treated at 1080°C in vacuum for 1322 h. The oxide adherence of the samples (S-29, S-60) which showed low loss rate was good. On the other hand, for the high loss rate sample (S-34) voids were observed at the oxide/alloy interface and cracks were detected in the surface oxides. This is consistent with results noted above concerning the spalling of surface oxides.

Table I shows the phases identified by X-ray diffraction of oxide coatings on the samples. ZrO<sub>2</sub> was detected in all the samples after heat treatment in vacuum. ZrSiO<sub>4</sub> was also detected except in samples S-33 and S-44. The intensities of the Bragg peaks of

ZrSiO<sub>4</sub> were greater for low loss rate samples (S-29, S-58, S-59, S-60) than for the high loss rate samples (S-34, S-43). Because linear expansion coefficients of the n-type SiGe (GaP) alloy and ZrSiO<sub>4</sub> are similar, it is suggested that the oxide adherence is improved by the formation of ZrSiO<sub>4</sub> [9, 10].

Fig. 4 shows the loss rates for various ceramic-coated SiGe alloys, including data which were obtained after annealing 1322 h in vacuum at 1080°C. The loss rates for the samples S-29, S-58, S-59 and S-60 were found to lie on the line for the Si<sub>3</sub>N<sub>4</sub>-coated alloys, and to lie between the once-“Z-prime”-coated and twice-coated “Z-prime” n-type SiGe alloys (see our previous paper [10]).

Studies on the compositional distribution of cross-sections of the alloys after heat treatment in vacuum were carried out using a Cambridge Stereoscan 200 with Tracor X-ray spectrometer. A gallium-enriched area, similar to that schematically shown in Fig. 10 of the preceding paper [10], was observed at the coated oxide/alloy interface (see Table II). The gallium contents of the boundary in samples S-29, S-43, S-59 and S-60 were found to vary from 89 to 93 at %, which is similar to the values found for “Z-prime”-coated n-type SiGe (GaP) alloys and the explanation for this gallium enrichment is probably the same as discussed in our previous paper [10].

TABLE II Electron probe microanalysis of gallium-enriched area of n-type SiGe (GaP) alloys coated with “Z-prime” with some rare earth oxides and/or silicon oxide after 1322 h in vacuum at 1080°C

Sample No.	Analysed composition (at %)
S-29 (1.0% Er <sub>2</sub> O <sub>3</sub> )	92 Ga, 5 Si, 3 Ge
S-43 (1.0% Sm <sub>2</sub> O <sub>3</sub> )	89 Ga, 5 Si, 2 Ge, 2 Al, 1 Zr, 1 Ca
S-59 (1.0% SiO <sub>2</sub> )	93 Ga, 3 Si, 2 Ge, 1 Al, 1 Zr
S-60 (0.2% SiO <sub>2</sub> + 0.5% CeO <sub>2</sub> )	91 Ga, 3 Si, 2 Ge, 2 Al, 2 Zr

## Acknowledgements

The authors thank R. F. Hartman of General Electric Company (Philadelphia, Pennsylvania) for supplying n-type SiGe (GaP), and Dr J. F. Nakahara of Ames Laboratory (Ames, Iowa) for making the X-ray

diffraction measurements. Ames Laboratory is supported by the US Department of Energy, Office of Defense Energy Projects and Special Applications, Office of Nuclear Energy, under contract no. W-7405-ENG-82.

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*Received 1 September 1988  
and accepted 12 January 1989*