

Thermal expansion behavior of a model ceramic–metal composite

C.L. Hsieh, W.H. Tuan*

Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan

Received 5 February 2006; received in revised form 17 January 2007; accepted 19 January 2007

Abstract

In the present study, dense Al_2O_3 –NiAl composites containing 0–100 vol.% Al_2O_3 are prepared, and their linear coefficient of thermal expansion (CTE) determined. Comparison is made between the experimental data and several model predictions. Among the model predictions, the Kerner and Turner models not only offer respectively the highest and lowest values but also cover most the experimental data. As the CTEs of the two phases are close to each other, the two model predictions can serve as the upper and lower bounds for the CTE of two-phase materials up to 400 °C. © 2007 Elsevier B.V. All rights reserved.

Keywords: Composites; Thermal expansion

1. Introduction

The thermal expansion behaviour of composite is important when it is used in conjunction with other material. Different from monolithic materials, it is possible to tailor the coefficient of thermal expansion (CTE) of composite by varying its phase ratio. Therefore, it is important to establish the relationships between CTE and phase ratio of the composite.

A dilation strain is generated as a body is subjected to a temperature change. The expansion strain of one phase in a two-phase material is constrained by the rigidity of another one, and its magnitude of such strain depends on the shear transfer at the interface. Therefore, the strain induces by thermal stress shows strong dependence on elastic constants [1–5]. Many theoretical models are available to predict the elastic constants of two-phase composites [1,6]. Some models provide specific value for composite; some offer a pair of upper and lower bounds instead.

There are not so many models available for the thermal expansion coefficient of composites. The reported experimental data on the CTE of two-phase materials are also sparse [7,8]. The experimental data which covers the entire composition range is even less. Therefore, an experimental study that provides the CTE data over the entire composition range is still in need.

The CTEs of two-phase materials depend strongly on their microstructural characteristics. In order to cover the scatter of the experimental data, several theoretical models provide the upper and lower bounds for the CTEs [4,5]. However, none of a pair of bounds is satisfactory to cover the experimental data [9]. Ashby thus used the upper bound of Schapery bounds and lower bound of Levin–H–S bounds to compare their experimental data.

The present study aims to explore the following issues:

1. To provide a set of experimental data that cover the entire composition range of a two-phase material.
2. To suggest a suitable pair of upper and lower bounds for the thermal expansion coefficients of ceramic–metal composites from the available theoretical models. The pair of the bounds should cover not only our experimental data and but also cover most data of other composites.

In the present study, two phases, Al_2O_3 and NiAl, are chosen to prepare the ceramic–metal composites. The melting points of these two materials are close to each other. Therefore, it is possible to prepare the Al_2O_3 –NiAl composites with various compositions at the same processing temperature. The chemical interactions between the two materials are limited during processing in a reducing atmosphere [10]. The chemical issue between the two materials can thus be ignored. The elastic constants of the composites have been measured and compared with the theoretical models for the elastic constants. The elastic constants of the Al_2O_3 –NiAl composites fall within the Hasin and Shtrikman (H–S) bounds [6]. Therefore, the Al_2O_3 –NiAl sys-

* Corresponding author. Tel.: +886 2 23659800; fax: +886 2 23634562.
E-mail address: tuan@ccms.ntu.edu.tw (W.H. Tuan).

tem is also used as the model system in the present study to investigate the CTE of two-phase materials.

2. Theoretical models

The equations used in the present study to describe the CTEs of composites are shown in Table 1. Since the Al_2O_3 –NiAl composite prepared in the present study is an isotropic one, only the equations for isotropic two-phase materials are collected. The review and the derivation of the available models are out of the scope of the present study. A brief summary for the background of the equations is given below.

The simplest equation to estimate the thermal expansion of two-phase materials is the rule of mixtures (ROM), Eq. (1). The equation has been applied to the ZrO_2 –Ni system that the elastic constants of the two phases are the similar [7]. The rule of mixtures was also used to predict the CTE of Ni– Al_2O_3 composites [8], though the elastic modulus of Al_2O_3 is twice that of Ni. Turner is the first scientist who took the elastic constant into account in his CTE equation, Eq. (2). The shape of the second phase is then considered by Kerner, Eq. (3), and Schapery, Eq. (4); though a simple shape, spherical, is considered.

The upper and lower bounds for elastic modulus have been well established [6]. Among these bounds for elastic constants, the H–S bounds can cover most experimental data on elastic modulus [5,6]. The H–S bounds have thus become very popular. The H–S bounds for elastic constants were used in the equations for thermal expansions coefficient, the bounds for CTE are then established (see Eqs. (5)–(10)).

3. Experimental

3.1. Preparation of Al_2O_3 –NiAl composites

Detailed procedures for the preparation of the Al_2O_3 –NiAl composites can be found elsewhere [10]. A brief description is given here. An alumina powder (TM-DAR, mean particle size = 0.2 μm , Taimei Chem. Co. Ltd., Tokyo, Japan) and various amounts of nickel aluminide powder (NiAl, mean particle size = 5.9 μm , Xform Inc., New York, USA) were milled together in ethyl alcohol with an attritor (Model 01-HD, Union Process Inc., USA) for 12 h. The milling media was ZrO_2 balls. Sintering was performed by hot pressing at 1450 °C in a graphite die for 1 h under an applied pressure of 24.5 MPa. The resulting NiAl content varied from 0 to 100% with increments of 10 vol.%. The final density of the composites was larger than 98%. The basic properties of each phase in the Al_2O_3 –NiAl composites are shown in Table 2. The microstructure was observed with scanning electron microscopy (SEM).

3.2. Measurement of CTE

The CTE measurements were performed from 25 to 1200 °C with a thermal mechanical analyzer (TMA, SETSYS 1600, SETARAM, France). The heating rate was 5 °C/min. The measurement was conducted in air. The dimensions of the CTE specimens were 3 mm × 3 mm × 12 mm. Correction was made by measuring the linear expansion of the equipment without specimen. Comparison has also been made between the CTE of pure Al_2O_3 specimen and the reported data from National

Table 1
Model predictions for the CTE of two-phase materials

| Model | Predictions | References |
|---------------------|--|------------|
| ROM | $\alpha_c = \alpha_p V_p + \alpha_m V_m$ (1) | |
| Turner | $\alpha_c = \frac{\alpha_m K_m V_m + \alpha_p K_p V_p}{K_m V_m + K_p V_p}$ (2) | [2] |
| Kerner | $\alpha_c = \alpha_m V_m + \alpha_p V_p + V_m V_p (\alpha_p - \alpha_m) \frac{K_p - K_m}{V_m K_m + V_p K_p + 3K_m K_p / 4G_m}$ (3) | [1,3] |
| Schapery | $\alpha_c = \alpha_p + (\alpha_m - \alpha_p) \frac{(1/K_c) - (1/K_p)}{(1/K_m) - (1/K_p)}$ (4) | [4] |
| Schapery bounds | $\alpha_c^u = \alpha_m V_m + \alpha_p V_p + \frac{4G_m (K_c - K_p)(\alpha_m - \alpha_p)V_p}{K_c (4G_m + 3K_p)}$ (5) | [4] |
| | $\alpha_c^l = \alpha_m V_m + \alpha_p V_p + \frac{4G_p (K_c - K_m)(\alpha_p - \alpha_m)V_m}{K_c (4G_p + 3K_m)}$ (6) | |
| Rosen–Hashin bounds | $\alpha_c^u = \frac{4V_m V_p G_p (K_m - K_p)(\alpha_m - \alpha_p)}{3K_m K_p + 4G_p \bar{K}} + (\alpha_m V_m + \alpha_p V_p)$ (7) | [5] |
| | $\alpha_c^l = \frac{4V_m V_p G_m (K_m - K_p)(\alpha_m - \alpha_p)}{3K_m K_p + 4G_m \bar{K}} + (\alpha_m V_m + \alpha_p V_p)$ (8) | |
| Levin–H–S bounds | $\alpha_c^u = \alpha_m - \frac{(\alpha_m - \alpha_p)K_p(3K_m + 4G_m)V_p}{K_m(3K_p + 4G_m) + 4(K_p - K_m)G_m V_p}$ (9) | [4] |
| | $\alpha_c^l = \alpha_p - \frac{(\alpha_p - \alpha_m)K_m(3K_p + 4G_p)V_m}{K_p(3K_m + 4G_p) + 4(K_m - K_p)G_p V_m}$ (10) | |

E: elastic (Young's) modulus; G: shear modulus; K: bulk modulus; V: volume fraction; subscript c: composite; subscript m: matrix phase; subscript p: second phase; superscript u: upper bound; superscript l: lower bound.

Table 2
Elastic constants and CTE of Al₂O₃ and NiAl

| | Young's modulus ^a (GPa) | Poisson's ratio ^a | Shear modulus ^a (GPa) | Bulk modulus ^a (GPa) | CTE ^b (ppm °C ⁻¹) |
|--------------------------------|------------------------------------|------------------------------|----------------------------------|---------------------------------|--|
| Al ₂ O ₃ | 401 | 0.24 | 162.3 | 253.5 | 7.3 |
| NiAl | 186 | 0.31 | 71.2 | 161.9 | 14 |

^a Note: Determined by an ultrasonic technique [6].

^b Note: Present study, from room temperature to 500 °C.

Physical Laboratory [11]. The CTE measurement was parallel to the hot-pressing direction.

4. Results and discussion

Fig. 1 shows one typical micrograph of the Al₂O₃–NiAl composites. The NiAl particles are slightly elongated in a direction perpendicular to the hot-pressing direction. However, the aspect ratio of the NiAl particles is smaller than 3 [10], the Al₂O₃–NiAl composites can thus be treated as isotropic two-phase materials.

4.1. The calibration of the CTE measurements

Fig. 2 shows the percentage of linear change of a 50% Al₂O₃–50% NiAl composite up to 800 °C as a function of temperature. The length changes with the temperature increase and temperature decrease are recorded. The expansion curve matches closely with the shrinkage curve. It implies that there is no damage within the specimens, which may affect the values of CTE significantly [8]. It may also imply that the oxidation, if any, of the Al₂O₃–NiAl composites during CTE measurement is negligible as the temperature is below 800 °C.

Fig. 3 shows the CTE and percentage of linear change of pure Al₂O₃ specimen as a function of temperature. The CTE is calculated from the linear expansion, $\Delta L/L_0$, as a function of temperature change, ΔT , as

$$\bar{\alpha}_T = \frac{\Delta L}{L_0} \frac{1}{\Delta T}. \quad (11)$$

The reported data [11] for the CTE of pure Al₂O₃ are also shown in the figure. The CTE values obtained in the present

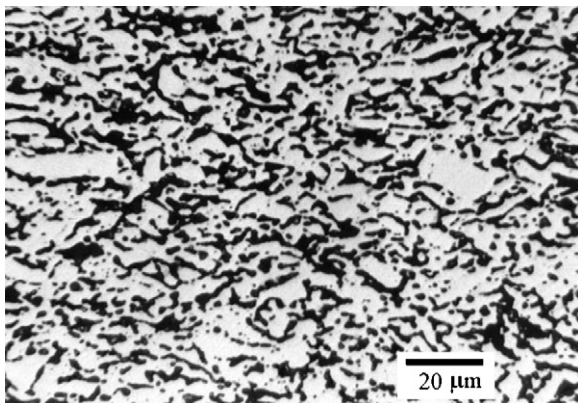


Fig. 1. Typical micrograph of 30 vol.% Al₂O₃–70 vol.% NiAl composite (black phase is Al₂O₃, white phase NiAl).

study match well with the reported value. The above procedures confirms the accuracy of the CTE values obtained in the present study.

4.2. The CTE of Al₂O₃–NiAl composites

Fig. 4 shows the percentage of linear change of the Al₂O₃–NiAl composites as a function of temperature. The $\Delta L/L_0$ of the composites decreases with the increase of Al₂O₃ content at a fixed temperature. It demonstrates that the expansion

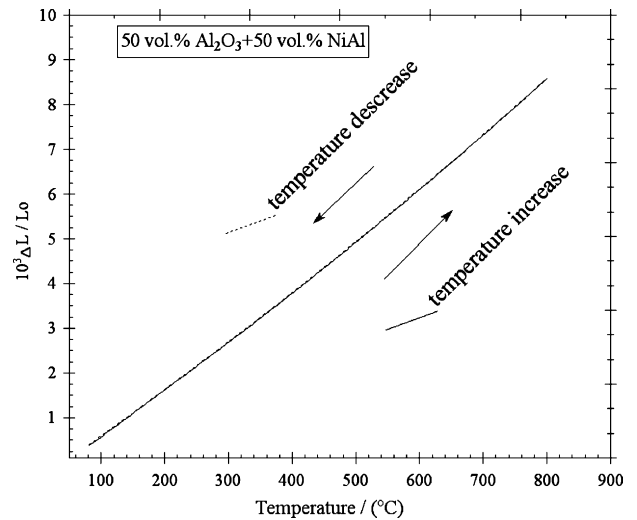


Fig. 2. Length change vs. temperature for 50 vol.% Al₂O₃–50 vol.% NiAl composite. The temperature increases from 80 to 800 °C then decreases to 80 °C at 5 °C/min.

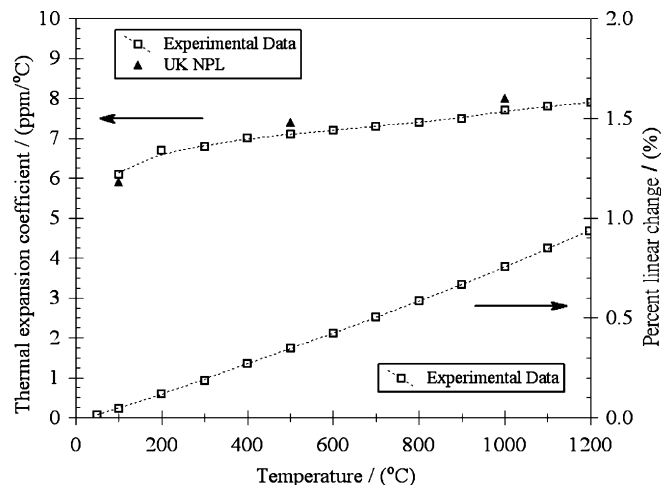


Fig. 3. Comparison between the thermal expansion coefficient of pure Al₂O₃ specimen and the reported data [11].

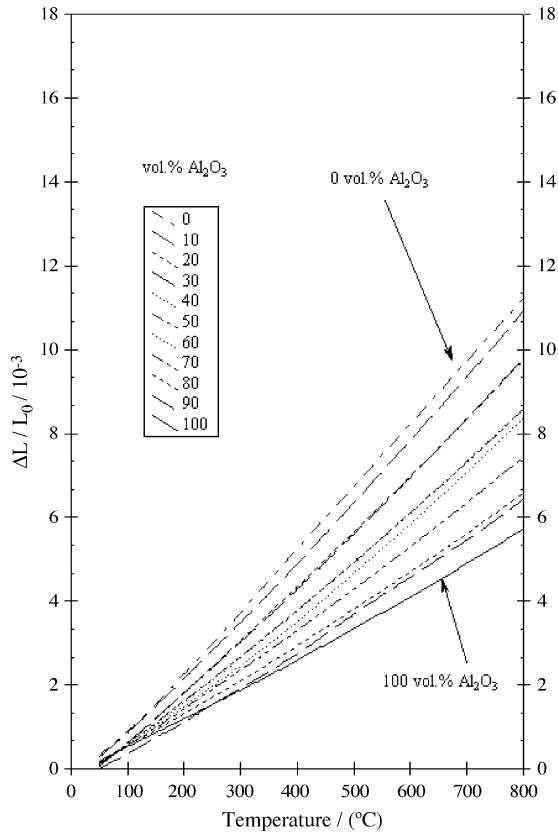


Fig. 4. Length change vs. temperature for the Al_2O_3 -NiAl composites.

sion of NiAl grains in the composite is constrained by the nearby Al_2O_3 grains.

Fig. 5 shows the CTE of the Al_2O_3 -NiAl composites as a function of temperature. The CTE values of the pure Al_2O_3 , pure NiAl and Al_2O_3 -NiAl composites all increase with the increase of temperature. For pure NiAl, the CTE increases significantly below 400°C . Nevertheless, the CTE increase of pure Al_2O_3 below 400°C is relatively minor. With the increase of Al_2O_3 content, the Al_2O_3 -NiAl composites show less sensitivity to temperature change below 400°C . The CTE of NiAl is nearly a constant above 600°C . It further confirms the need to compare the experimental data and theoretical models over entire composition range.

4.3. Comparison

Fig. 6 shows the CTE of the composites at 400 , 600 and 800°C as a function of Al_2O_3 content. The model predictions are also shown in the figures. The experimental data do not follow the rule of mixtures (the straight line between the values of Al_2O_3 and NiAl, not shown in the figure). Though the upper and lower bounds of the Shapery, Rosen-Hasin, Levin-H-S bounds are relatively close to each other, they fail to cover the experimental data above 600°C . The largest and smallest values are provided by the Kerner and Turner models, respectively. The Kerner and Turner models can cover all the CTE data as the temperature is lower than 400°C . A few experimental data are out of the Kerner and Turner bounds as the temperature

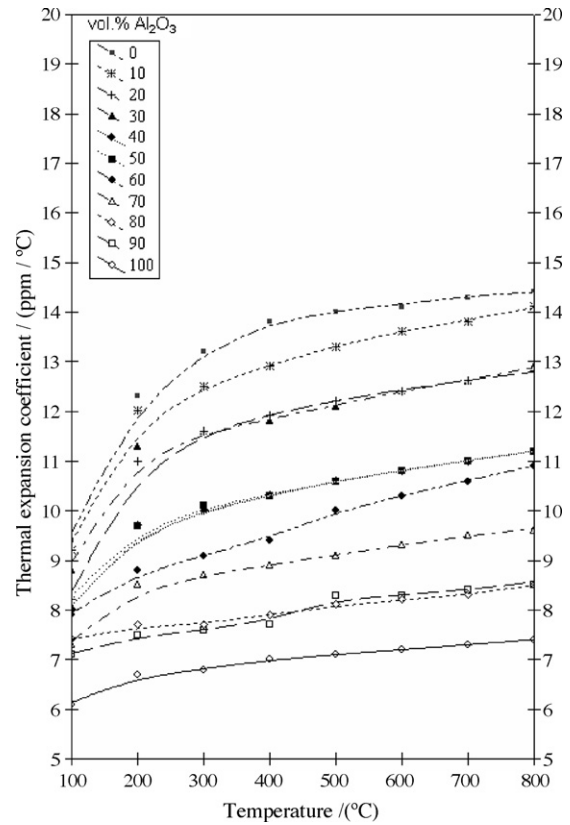


Fig. 5. Thermal expansion coefficient versus temperature for the Al_2O_3 -NiAl composites.

is higher than 600°C . Metallic NiAl exhibits good oxidation resistance [12], and our preliminary study indicated that there is no detectable oxidation during the thermal expansion measurement (see Fig. 2). The CTE of NiAl shows different temperature dependence at low and high temperature (see Fig. 5); the match between the experimental data and models can only be found at a temperature below 400°C .

4.4. The bounds for CTE

The above comparison suggests that the Kerner and Turner models provide the highest and lowest values for the experimental data at 400°C , respectively. They may serve as the upper and lower bounds for the CTE of two-phase composites. The elastic modulus ratio (E_p/E_m) of Al_2O_3 over NiAl is 2.2 and CTE ratio (α_p/α_m) 0.52, the difference of the elastic constants and CTEs between Al_2O_3 and NiAl is relatively small (see Table 2). Therefore, it is necessary to carry out the same comparison for the systems with larger difference in basic properties. Since the elastic modulus reflects the bonding strength of materials [1], the CTE value depends on the dilation strain induced by temperature change. Therefore, there is a strong correlation between the values of elastic modulus and CTE. Assuming that the elastic modulus ratio (E_p/E_m) of two-phase material is inversely proportional to the CTE ratio (α_p/α_m), the effect of CTE ratio on the model predictions can be estimated.

By assuming that $E_p/E_m = \alpha_m/\alpha_p$ is 2, 5 and 10, the models predictions are shown in Fig. 7. As the system with similar elas-

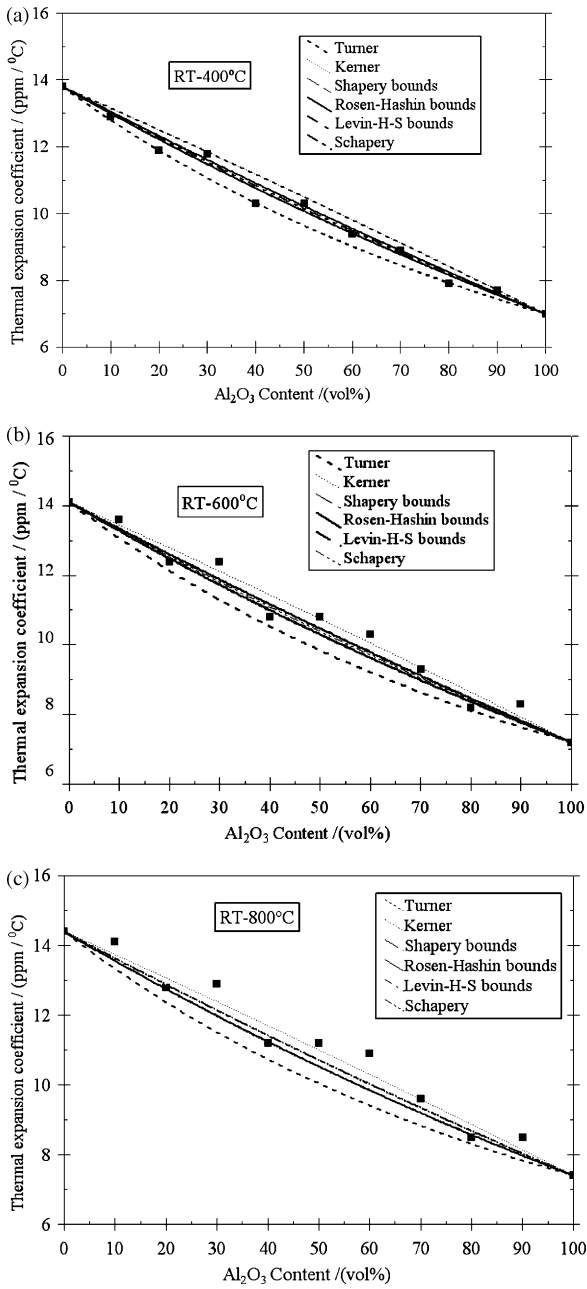


Fig. 6. Comparison between experimental data at (a) 400 °C, (b) 600 °C and (c) 800 °C and model predictions.

tic constants and CTE values ($E_p/E_m = \alpha_p/\alpha_m = 2$, the case of Al₂O₃–NiAl system), the CTE of the composites varies within a narrow region. For such case, all model predictions are close to the values predicted by the rule of mixtures. Previous studies on ZrO₂–Ni ($E_p/E_m = 1$) and Al₂O₃–Ni ($E_p/E_m = 1.9$) composites suggested that the CTEs of their composites are close to the values of the rule of mixtures [7,8]. In fact, the CTEs of these composites can be predicted by most theoretical models simply because the two phases within their composites are similar in elastic properties.

As the ratios of elastic modulus and CTE increase, the bounds for the CTE values are wider. However, the Kerner predictions are always the highest. Furthermore, the Kerner predictions are

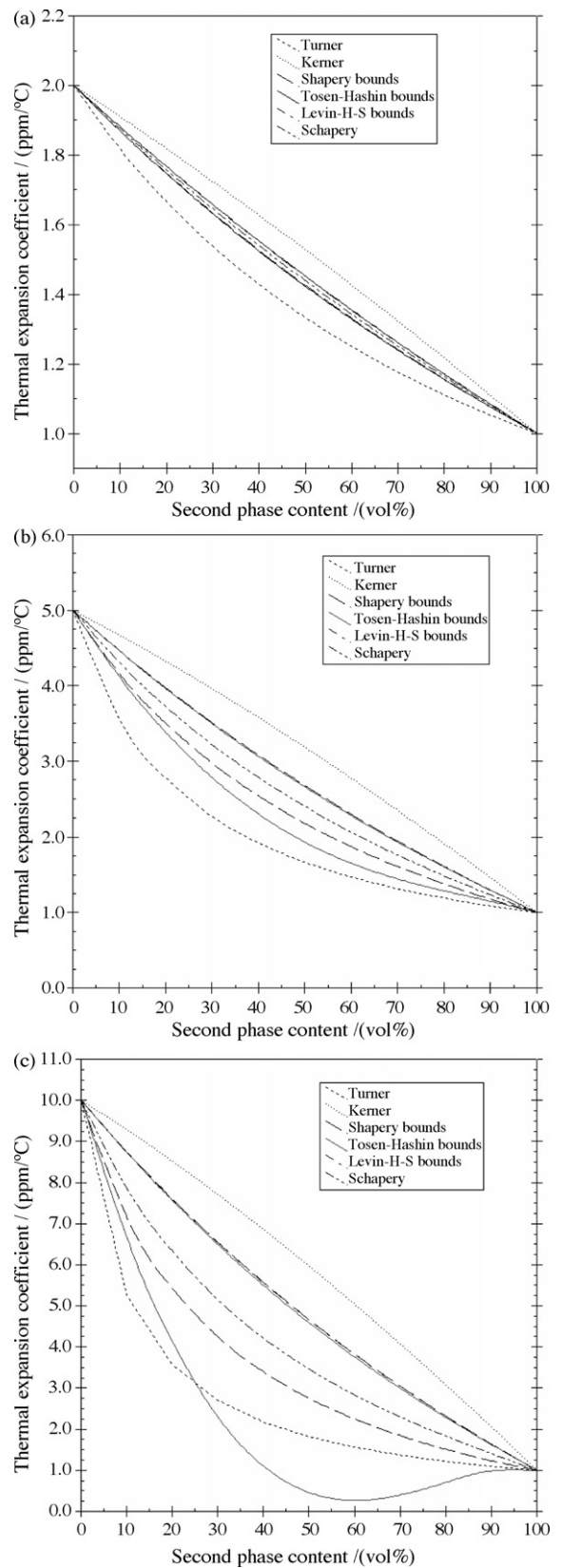


Fig. 7. Model predictions for the cases that (a) $E_p/E_m = \alpha_m/\alpha_p = 2$, (b) $E_p/E_m = \alpha_m/\alpha_p = 5$, and (c) $E_p/E_m = \alpha_m/\alpha_p = 10$.

close to the rule of mixtures. It suggests that either Kerner model or rule of mixtures can be used to estimate the highest possible value for the CTE of composites. The predictions offer by the other models are all lower than the values predicted by the rule of mixtures.

The Turner model offer the lowest predictions as the α_m/α_p is lower than 10. As the α_m/α_p is high, say 10, the Turner model can no longer provide the lowest prediction for the composites with high second phase content. The Turner model prediction can only serve as the lowest bound for two-phase material as the elastic modulus ratio (or CTE ratio) is relatively small.

A pair of bounds, Kerner and Turner model predictions, can be used to cover the experimental data over the entire composition range. However, some experimental data at $>600^\circ\text{C}$ are outside the bounds (see Fig. 6b and c). Most theoretical models neglect the interactions (or coupling) between 2 phases in the composites [13]. As indicates in Fig. 5, such interactions are temperature-dependent. More works are thus needed to solve the problems involving such interactions.

5. Conclusions

In the present study, the coefficient of thermal expansion of $\text{Al}_2\text{O}_3\text{-NiAl}$ is measured and compared with several theoretical models. The CTE of the composites shows strong dependence not only on the amount of each phase but also on the temperature. After comparing the models predictions with the experimental

data, only the Kerner and Turner model predictions are wide enough to cover most the experimental data up to 400°C . Various possible values for the CTE of the two phases in the composite are assumed, confirming that the Kerner and Turner models can be used as the upper and lower bounds for the CTE of two-phase materials, respectively.

Acknowledgments

The present work was supported by the National Science Council, Taiwan ROC, through contract nos. NSC87-2216-E002-032 and NSC92-2216-E002-029.

References

- [1] D.K. Hale, *J. Mater. Sci.* 11 (1976) 2105.
- [2] P.S. Turner, *J. Res. Natl. Bureau Stand.* 37 (1946) 239.
- [3] E.H. Kerner, *Proc. Phys. Soc.* 69 (1956) 808.
- [4] R.A. Schapery, *J. Comp. Mater.* 2 (1968) 380.
- [5] B.W. Rosen, Z. Hashin, *Int. J. Eng. Sci.* 8 (1970) 157.
- [6] C.L. Hsieh, W.H. Tuan, T.T. Wu, *J. Eur. Ceram. Soc.* 23 (2004) 2789.
- [7] W. Hu, H. Guan, X. Sun, S. Li, *Mater. Lett.* 32 (1997) 59.
- [8] H.A. Bruck, B.H. Rabin, *J. Am. Ceram. Soc.* 82 (1999) 2927.
- [9] M.F. Ashby, *Acta Metall. Mater.* 51 (1993) 1313.
- [10] W.H. Tuan, Y.P. Pai, *J. Am. Ceram. Soc.* 82 (1999) 1624.
- [11] R. Morrell, *Handbook of Properties of Technical & Engineering Ceramics, Part I*, National Physical Laboratory, London, 1987, p. 82.
- [12] R.D. Noebe, R.R. Bowman, M.V. Nathal, *Int. Mater. Rev.* 38 (1993) 193.
- [13] C.L. Hsieh, W.H. Tuan, *Mater. Sci. Eng. A* 425 (2006) 349.