Metal matrix composites based on valence-unstable systems

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Abstract. The work is focused on the thermal expansion of composites based on valence-unstable systems. The main motivation was to create invar-like materials of a new type and to develop approaches to the quantitative description of coefficients of thermal expansion (CTE) of both the composite itself and its key component - a material with a negative contribution to thermal expansion due to valence fluctuations. The experimental data on the linear CTE of Al/SmB6 composite was performed by capacitive dilatometry in the temperature range 5-220K. It turned out that this composite shows invar properties up to 60K. Several models were used to describe thermal expansion in Al/SmB6. A quantitative approach is proposed for describing the negative magnetic contribution and the lattice contribution to the CTE of systems based on intermediate-valence samarium hexaboride.

1. Introduction

The terminology accepted in solid state physics reserves the names “invar” and “invar alloys” for transition metal compounds, usually based on iron and nickel [1-3]. These compounds exhibit close to zero CTE values over a wide temperature range due to the competition of the magnetic and lattice contributions to thermal expansion [4]. Invars have found many application niches, but there are still many open questions in the physics of this class of materials. Compounds that do not contain magnetic constituents based on d-elements, but at the same time demonstrate CTE values less than |2|x10⁻⁶ K⁻¹ in a given temperature range are called invar-like, and the related physical mechanisms may be different in origin. One of the ways to obtain an invar-like material is to synthesize a composite of two components with negative and positive contributions to the CTE and their compensation in a fairly wide temperature range. Reviews with a detailed description of such composites, which are characterized by invar-like properties in terms of their thermal expansion are given in [5]. The choice of material with a positive CTE is quite wide, while there are very few materials with a negative CTE. Most of invar-like composites described in the literature are based on the use of complex oxides such as: ZrW₂O₈, Sc₂W₃O₁₁₂, Y₃W₆O₁₁₂ and others [6-8]. In these systems the negative thermal expansion is driven by transversal thermal motion of oxygen atoms leading to apparent decrease in cation-anion distances [9]. Meanwhile, systems with a pure electronic mechanism of negative thermal expansion are known. The electronic degrees of freedom associated with this anomalous contribution to thermal expansion rely on phenomena such as strong electronic correlations and valence instabilities. These phenomena are observed in some compounds of f-elements like samarium, ytterbium, and europium. Such compounds are classified in condensed matter physics as systems with strongly correlated electrons (SCES). Systems with intermediate valence (IV) represent a special class of SCES. Valence instability in IV systems leads to strong fluctuations between two valence configurations. In the case of samarium ions, fluctuations occur between electron configurations with Sm²⁺ and Sm³⁺ ions, which have very different radii. A strong dependence of the samarium valence on temperature, coupled with a strong difference in the size of the configurations, leads to a negative contribution to the CTE, since a smaller configuration (namely, Sm³⁺) is populated as the temperature increases.
Table 1. Negative thermal expansion values of selected IV systems

| Materials          | NTE temperature range, K | Minimum CTE value, x10^-6 K^-1 | Reference |
|--------------------|--------------------------|---------------------------------|-----------|
| Sm0.8B6            | 5-90                     | -4                              | 10        |
| SmB6               | 10-130                   | -4.2                            | 10        |
| Sm0.8La0.1B6       | 55-156                   | -3.1                            | 10        |
| Sm0.7La0.22B6      | 20-200                   | -3.1                            | 11        |
| Sm0.5La0.5B6       | 10-160                   | -1.3                            | 11        |

SmB6 is one of the most interesting objects in the SCES domain. Samarium hexaboride, which belongs to the class of IV systems, shows numerous anomalies of physical properties and continues to attract the attention of both theorists and experimenters. SmB6 and systems based on it show a significant negative contribution to CTE. Table 1 shows the quantitative parameters of several SmB6-based systems, as well as the temperature range of negative CTE values and the amplitude of this anomalous contribution.

As we can see, these systems based on valence-unstable samarium look promising for creating a composite with invar-like properties in the temperature range below 100 K. The main goal of the present work was to create and investigate invar-like material of a new type – a composite based on a metal and an IV system. Additional important goals were to develop model approaches to the description of the CTE of the composite itself, as well as the electronic and lattice contributions to the CTE for a key component – a system with negative thermal expansion.

2. Experimental results

A sample with a component ratio of 25% SmB6 and 75% Al was prepared by hot pressing. All details concerning the initial components, the synthesis process, diagnostics, and primary characterization of the sample (optical and electron microscopy, x-ray microtomography, and elemental composition analysis) will be described in a separate publication. In this paper in the chapter related to sample characterization we show the results of a study of the composite by x-ray diffraction (XRD) technique.

The composites were characterized by XRD using synchrotron-generated X-Ray beam with E = 15.2 keV (\( \lambda = 0.826 \) Å) at the STM beamline of Kurchatov synchrotron radiation source KSRS (Figure 1). XRD pattern is fully defined by peaks attributed to Al and SmB6 thereby indicating that no chemical reactions occurred to form novel phases.

![XRD pattern of Al/SmB6 composite at room temperature. Symbols correspond to the experimental data. Line is a result of Rietveld refinement using the FullProf software package.](image1)

The key experiment of this work and the feasibility study of creating composite invar-like materials based on samarium hexaboride was the measurement of relative elongation on a dilatometer. The dilatometric method allows calculating the value of such a thermodynamic parameter as CTE. The measurements of Al/SmB6 composite were carried out by capacitive dilatometry using a measuring cell/option installed in the PPMS (Quantum Design) system (for more details see [12]) in the temperature range 5-210 K.
Figure 2. Relative thermal expansion of Al/SmB$_6$ composite.

Figure 2. shows relative expansion (elongation) (dL/L) as a function of temperature for the composite sample under study. The contribution of the cell material to the relative elongation was estimated by separate measurements and was extracted from the data. CTE of Al/SmB$_6$ was calculated based on the measurements of relative elongation. The temperature dependence of CTE is depicted in Figure 3. It should be noted that to prevent oscillations of the CTE, the temperature dependence of relative elongation was preliminarily smoothed using the spline function.

Figure 3. Linear coefficient of thermal expansion of Al/SmB$_6$ composite.

3. Discussion
The results of fitting of the X-ray diffraction pattern showed the compliance of the sample with the claimed composition and proved the absence of parasitic phases in the accuracy of X-ray phase analysis. Measurements of the thermal expansion of the sample under study allow us to conclude that as a result of compensation of the positive contribution of aluminum by the negative contribution to the CTE from the intermediate-closed component of the composite, the sample is indeed an invar-like material up to a temperature of 60 K.

Several models have been developed aiming to quantitatively describe the thermal expansion of composites. Many of them are listed in [13]. The simplest approach is the rule of mixtures (ROM) (1):

$$\alpha_c = \alpha_f v_f + \alpha_m v_m$$  

where the subscripts c, f and m denote the composite, filler and matrix respectively; $\alpha$ – CTE; $v$ – volume fraction. More sophisticated treatments are based on widely used Turner (2) and Kerner (3) models:
\[ \alpha_c = \frac{(\alpha_f \nu_f K_f + \alpha_m \nu_m K_m) / (\nu_f K_f + \nu_m K_m)}{K_f - K_m} \tag{2} \]

\[ \alpha_c = \alpha_m \nu_m + \alpha_f \nu_f + \nu_m \nu_f (\alpha_f - \alpha_m) \frac{K_f - K_m}{\nu_m K_m + \nu_f K_f + 3K_m K_f / 4 G_m} \tag{3} \]

where \( K \) – bulk modulus; \( G \) – shear modulus.

In the following part we analyze the dilatometric experimental data based on the thermo-elastic models given by Eqs. (1-3). In our calculations we used literature values for thermal expansion and elastic properties of Al and SmB\(_6\) [10,14]. A comparison of experimental and computed data is depicted in Figure 4.

**Figure 4.** Plot of experimental CTE values (orange solid line) along with curves representing CTE values calculated using thermo-elastic models for the Al/SmB\(_6\). Black filled circles – CTE of Al; red open circles – CTE of SmB\(_6\); dashed line – results of the ROM model assuming SmB\(_6\)-25 vol.%; blue open squares – results of the ROM, Terner and Kerner models assuming various SmB\(_6\) volume fraction (30%, 25% and 29%, respectively). The shaded area corresponds to the linear CTE values typical for invar alloys.

Our calculations have shown that in the case of SmB\(_6\), two model approaches can be applied to simplify the problem. These approaches rely on phenomenological models with a relatively small number of parameters. To calculate the lattice contribution to CTE, we can use the superatom model, which was previously successfully used to describe the dispersion of phonons, the density of phonon states, and the specific heat of higher borides, including hexaborides [15]. At the same time negative electronic contribution to CTE caused by intermediate valence of samarium ions can be described using the Weiss phenomenological model (the invar model) [16], which was previously successfully used to describe CTE in classical invar alloys, as well as in intermediate-valence systems based on plutonium [17]. In the domain of SCES, plutonium is considered as a 5f electron homologue of the 4f element samarium due to a similar structure of the partially filled electron shells and related anomalous properties.

Figure 5 shows the Weiss model fit of the electronic contribution to the CTE of samarium hexaboride. The anomalous electronic part of CTE was estimated by subtracting the lattice contribution calculated within the superatom model from the experimental data obtained by XRD.
4. Conclusion

The synthesis of a new type of composite and its study by several experimental techniques methods demonstrate that intermediate-valence systems can be successfully used to create invar-like materials. In particular, the negative anomalous electronic contribution to CTE caused by valence-unstable samarium ions allowed to fully compensate for the positive lattice contribution to CTE in the composite Al/SmB6-25% at temperatures up to 60K. The Turner model was proved to perform very well to reproduce the thermal expansion in Al/SmB6. So this model is probably well-suited for the new type of metal matrix composites based on intermediate-valence systems. Two model approaches have been successfully applied to describe both the electronic contribution (phenomenological invar Weiss model) and the lattice contribution (phenomenological superatom model) to the CTE in SmB6.

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References

[1] Wasserman E F, Acet M in Magnetism and Structure in Functional Materials (eds Planes A, Manosa L, Saxena A) Springer, 2005, 177-196
[2] Shiga M 1996 Current Opinion in Solid State and Materials Science 1 340-348
[3] Wasserman E F in Ferromagnetic Materials Vol. 5 (eds Buschow K H J & Wohlfarth E), North-Holland, Amsterdam, 1990, 237-322
[4] van Schilfgaarde M, Abrikosov I A, Johansson B 1999 Letters to Nature 400 46-49
[5] Sidhu S S, Kumar S, Batish A 2016 Critical Reviews in Solid State and Materials Sciences 41 132-157
[6] Holzer H, Dunand D C 1999 J. of Materials Research 14 780-789
[7] Gao S, Zhao N, Liu Q. et al. 2019 J. of Alloys and Compounds 779 108-114
[8] Das Sa, Das Si, Das K 2014 Ceramics International 40 6465-6472
[9] Sleight A W 1998 Annu. Rev. Mater. Sci. 28 29-43
[10] Nefedova E V , Alekseev P A, Klement’ev E Sm et al. 1999 JETP 88 565-573
[11] Nefedova E V , Alekseev P A, Lazukov V N, Sadikov I P 2003 JETP 96 1113-1121
[12] Freidman A L , Popkov S I, Semenov S V, Turchin P P 2018 Technical Physical Letters 44 123-125
[13] Hsien C L, Tuan W H 2007 Materials Science and Engineering A 460-461 453-458
[14] Nakamura S, Goto T, Kunii S, et al 1994 J. Phys. Soc. Jpn. 63 623-636
[15] Serebrennikov D A, Clementyev E S, Alekseev P A 2016 JETP 3 452-460
[16] Weiss R J 1963 Proc. Phys. Soc. 82, 281
[17] Lawson A C, Roberts J A, Martinez B, et al. 2006 Phil. Mag. 86 2713;