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Calculation of mechanical properties of hypothetic eutectic nanocomposites LaB_6–MeB_2

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Abstract

This effort is to investigate the possibility of developing new eutectic composite materials based on quasi-binary systems LaB_6–MeB_2 (Me stands for Ti, Zr, Hf, etc.), where reinforcing fibers of MeB_2 are nano-size in cross-section while having a comparatively long generatrix. The composites were assumed to be produced by the method of directed solidification of eutectic melts. A model of morphology showed very close agreement to the technological sample that was obtained by directional solidification. Algorithm of calculation of mechanical properties was based on an asymptotic method of averaging by Bakhvalov–Sanches Palencia [Sanches-Palencia, E., *Non-Homogeneous Media and Vibration Theory*. Springer-Verglag, New York, 1980; Bakhvalov, N. S. and Panasenko, G. P., *Averaging of processes in periodic media*. Nauka, Moscow, 1984, [in Russian]]. Geometry of a material (a representative cell) are accepted the same as for eutectic alloys, but a ratio of nano-whisker radius and cell size varies in some limits. The numerical experiment shows considerable increase of values of elastic constants for nanocomposites. Fields of thermo-deformations were calculated both for real eutectic systems LaB_6–MeB_2 and for hypothetical nanocomposites of these systems with different volume fraction of reinforcing whiskers. The macrocomposite results are in good agreement with its experimental observations, and for nanocomposites, the predicted characteristics are very attractive, which offers a solution for modification of technology of directed solidification of eutectic systems for the case of nano-size whisker reinforcements.
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Keywords: Directed solidification; Nano-wisker; Eutectic material; Hypothetic nanocomposites; Quasi-binary system

1. Introduction

While polycrystal materials obtained by sintering of powders lose some strength due to a presence of interphase boundaries which concentrate impurities and defects, eutectic materials have the advantage due to a formation of “pure” semi-coherent interphase boundaries with neither impurities nor large defects which suppress macroscopic strength of the material.

Presented here is an effort to investigate a possibility of development of new eutectic composite materials based on quasi-binary systems LaB_6–MeB_2 (Me = Ti, Zr, Hf), where reinforcing fibers of MeB_2 are nano-size in cross-section while having a comparatively long generatrix (Fig. 1). Let us assume that the composites are produced by the method of directed solidification of eutectic melts. In this processing approach, the labor-intensive operations of producing rather perfect fibers and introducing those to matrix are excluded; a technological process represents a single operation which, at optimal parameters, provides the uniform distribution of fibers within a matrix, well bounded to the matrix. Besides that, thanks to almost thermodynamically stable condition of the whole composite system at temperature of crystallization, eutectic composites possess rather high temperature stability.

Previous work[1] confirms that for in situ eutectic composites with high modulus whiskers of strengthening phase, fibers optimal sizes should be in section 0.5–1.0 μm for their length of 50–100 μm. However this work had been carried out before the concerted effort nano-structured material research began. A rapid development of research on materials nanostructural condition highlighted uniquely high mechanical properties of nanofibers as well as a wide spectrum of chemical compositions where they are realized. Thus, of importance is computer design of nanocomposites, especially in systems which involve only non-metallic substances as only they keep a high level of strength properties while employed at high temperature.

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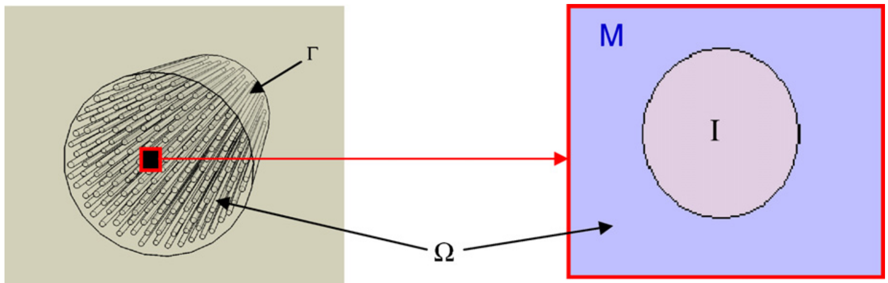

Fig. 1. Geometrical model of the material. I – MeB_2 inclusion (fiber), M – LaB_6 matrix, surface Γ – boundary of the sample, Ω – 3D area representing the sample.

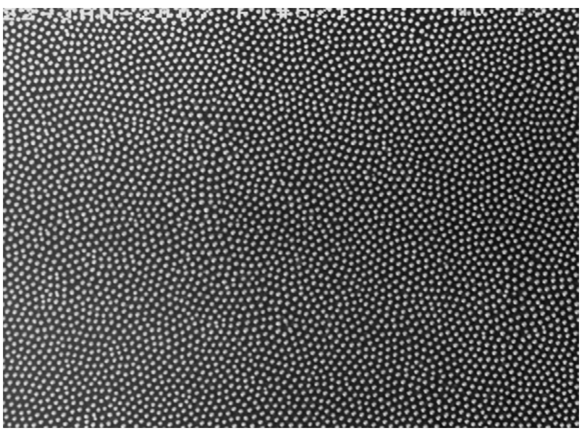

Fig. 2. Photo of microstructure of LaB_6–ZB_2 sample (provided by Dr. V. Filippov, IPMS).

2. Theoretical approach and results

A model object is very close to technological sample obtained by the method of directed solidification. A cylinder with typical sizes of L, S and appropriate mechanical characteristics of matrix and inclusions (E – Young modulus, ν – Poisson's ratio), which suffers given external deformation and also can work in cooling mode (temperature difference) undergoing thermo-deformations, is considered.

Algorithm of calculation of mechanical properties is based on asymptotic method of averaging by Bakhvalov–Sanches Palencia,[2,3] i.e. in some area Ω correspondent to a sample of the investigated material a boundary problem is considered as

$$\sum_{j=1}^{3}\frac{\partial\sigma_{ij}(\vec{x})}{\partial x_j}=0, \qquad i=1,2,3 \tag{1}$$

$$\sigma_{ij}(\vec{x})=\sum_{kl=1}^{3}C_{ij}^{kl}(\vec{x})\varepsilon_{kl}(\vec{x}), \qquad i,j=1,2,3 \tag{2}$$

where $\sigma_{ij}(\vec{x})$ – local stresses, $C_{ij}^{kl}(\vec{x})$ – local modules of elasticity and local deformations $\varepsilon_{ij}(\vec{x})$ are defined through displacements $\vec{u}(\vec{x})$:

$$\varepsilon_{ij}(\vec{x})=\frac{1}{2}\left(\frac{\partial u_i(\vec{x})}{\partial x_j}+\frac{\partial u_j(\vec{x})}{\partial x_i}\right) \tag{3}$$

Boundary conditions of the problem (1)–(3) are given as

$$\vec{u}(\vec{x})=0, \quad x\in\Gamma_1 \tag{4}$$

$$\sum_{j=1}^{3}\sigma_{ij}(\vec{x})n_j=F_i(\vec{x}), \quad x\in\Gamma_2, \quad i,j=1,2,3 \tag{5}$$

where Γ_1 and Γ_2 – parts of boundary Γ of area Ω, and $\vec{F}(\vec{x})$ – given force field, applied to area surface, $\Gamma=\Gamma_1\cup\Gamma_2$, $\Gamma_1\cap\Gamma_2=\emptyset$.

Let us find a solution of the above said problem as

$$u_i(\vec{x})=\sum_{j=1}^{3}e_{ij}x_j+w_i(\vec{x},\hat{e}), \qquad i=1,2,3 \tag{6}$$

where e_{ij} – components of tensor of external (macroscopic) deformations $\hat{e}$, and functions $w_i(\vec{x},\hat{e})$ are periodic with a period equal to the representative cell of material. In linear approximation we obtain:

$$w_i(\vec{x},\hat{e})=\sum_{p,q=1}^{3}e_{pq}w_i^{pq}(\vec{x}), \tag{7}$$

where $w_i^{pq}(\vec{x})$, symmetrical on p, q and are solutions of six systems of equations:

$$\sum_{i,k,l=1}^{3}\frac{\partial}{\partial x_i}\left(C_{ij}^{kl}\left(e_{kl}^{pq}+\frac{1}{2}\left(\frac{\partial w_k^{pq}}{\partial x_l}+\frac{\partial w_l^{pq}}{\partial x_k}\right)\right)\right)=0 \tag{8}$$

for six linearly independent single external deformations e_{ij}^{pq} (three one-axis compressions and three displacements). Thus the effective modules of elasticity $\tilde{C}_{ij}^{kl}$ are defined by integrals:

$$\tilde{C}_{ij}^{pq}=\int_V\sum_{k,l=1}^{3}C_{ij}^{kl}\left(e_{kl}^{pq}+\frac{1}{2}\left(\frac{\partial w_w^{pq}}{\partial x_l}+\frac{\partial w_l^{pq}}{\partial x_k}\right)\right)\mathrm{d}V \tag{9}$$

on volume of a representative cell.

Thus, for given distribution of elasticity modules by the volume of representative cell the system of Eq. (8) was numerically solved on 3-d grid to compute $w_i^{pq}(x)$ in each node of the cell. Then integral (9) over the cell was used to compute effective elasticity modules, and for given "macroscopic" deformation e_{ij} Eqs. (4) and (5) were used to compute local details of deformations. Then simple counting (due to discrete form of the problem after applying the grid) allowed compute distribution of deformations in a cell per volume unit independently for matrix and inclusion.

A number of materials based on LaB_6 matrix were simulated as infinite space filled by parallel round cylinders with axes passing through nodes of a 2-d periodic grid. This geometry reasonably corresponds to the structure of materials in scope, which is represented by a photo in Fig. 2, the fibers have approximately the same diameter and are placed uniformly, with no significant local concentrations.

The requirement to initial melt to be eutectic specifies components concentrations in the material. Observation (uniform distribution of sizes and density of the fibers) allows to choose representative cell with single cylindrical inclusion of length which significantly exceeds its diameter. Specific concentration, relative position and shape of fibers define uniquely possible ratios of linear sizes in the representative cell. Thus, ratio of typical distance between centers of the fibers (in the model—linear size of representing cell) to their diameters is defined by solidification conditions, meaning they correspond to volume concentration of the fibers material in eutectic.

Initial data used to compute effective modules of a number of materials LaB_6–MeB_2 are presented in Table 1. As a result of computing experiment to define mechanical characteristics of eutectic composites the following effective modules of elasticity are obtained and calculated by the above described technique (see Table 2). The well-known ideas of reinforcing materials by nanotubular structures with the aim of introducing their unique mechanical properties in operational characteristics of composites touched eutectics as well. In [4] it is shown that even eutectic temperature for pseudo-binary eutectic systems TiN–AlN, TiC–TiB_2, TiN–NB_2 at reduction of characteristic

Table 1
Initial data: E – Young's modules, x_{mass} – mass share, MeB_2 ρ_g/ρ_m – ratio of inclusions density to matrix one, c_{vol} – volume share, calculated by formula $c_{vol} = x_{max}\rho_m/\rho_g$; α_g/α_m – ratio of coefficients of volume expansion of inclusion and matrix

	HfB_2	NbB_2	TaB_2	TiB_2	ZrB_2
$E \times 10^{-11}$ Pa	4.7971	6.736	6.867	5.4053	4.958

	LaB_6–HfB_2	LaB_6–NbB_2	LaB_6–TaB_2	LaB_6–TiB_2	LaB_6–ZrB_2
x_{mass}	0.220	0.202	0.324	0.103	0.210
ρ_g/ρ_m	4.25	2.61	4.27	1.72	2.08
c_{vol}	0.062	0.087	0.101	0.062	0.114
α_g/α_m	0.719	0.922	0.984	1.250	1.281

Young's modules for LaB_6 is accepted as $E = 4.88 \times 10^{11}$ Pa

Table 2
Effective modules of elasticity of composites C_{ij} obtained at calculations, and Poisson coefficient $\nu = C_{12}/(C_{12} + C_{11})$, Young's modulus $E = (C_{11} + 2C_{12})(C_{11} - C_{12})/(C_{11} + C_{12})$ and shear modulus in the plane (x, y) $\mu = C_{44}$

	LaB_6–HfB_2	LaB_6–NbB_2	LaB_6–TaB_2	LaB_6–TiB_2	LaB_6–ZrB_2
$C_{11} \times 10^{-11}$ Pa	5.105	5.235	5.312	5.144	5.118
$C_{12} \times 10^{-11}$ Pa	0.827	0.845	0.856	0.833	0.825
$C_{44} \times 10^{-11}$ Pa	2.139	2.193	2.224	2.156	2.146
$E \times 10^{-11}$ Pa	4.874	5.000	5.074	4.912	4.889
ν	0.139	0.139	0.139	0.139	0.139
$\mu \times 10^{-11}$ Pa	2.139	2.193	2.224	2.156	2.146

Table 3
Effective and average on volume characteristics for LaB_6, reinforced by nano-whiskers, depending on bulk concentration of nano-whiskers

c_{vol}		0.041	0.077	0.112	0.197
effective on Bakhvalov - Sanchez- Palencia					
C_{11}, C_{22}	10^{-11}	6.552	7.805	9.066	12.082
C_{33}	10^{-11}	6.955	8.548	10.140	13.923
C_{12}	10^{-11}	1.040	1.219	1.399	1.827
C_{23}, C_{31}	10^{-11}	0.996	1.139	1.284	1.634
C_{44}, C_{55}	10^{-11}	2.609	3.018	3.434	4.435
C_{66}	10^{-11}	2.605	2.999	3.394	4.342
average on volume					
C_{11}		6.955	8.548	10.140	13.923
C_{12}		1.105	1.340	1.576	2.135
C_{66}		2.925	3.604	4.282	5.894

linear size of inclusion up to 10–20 nm falls by 600–900 °C and in previous work[5] it is shown that Vickers's hardness for the system $TiN–Si_3N_4–TiSi_2$ at characteristic linear size of 3 nm reaches 100 GPa. It gives a hope, that in case of realization of the technology of directed solidification an opportunity of achievement of nanosizes for diameters of fibers of inclusion of reinforced phase the obtained nanocomposites will possess very attractive mechanical properties (see Table 2).

At calculations for model LaB_6, reinforced by nano-whiskers, Young's modulus of nano-whisker is accepted as 47.971×10^{10} Pa. Geometry of a material (and, thus a representative cell) are accepted the same as for eutectic alloys, but a ratio of nano-whiskers radius and cell size varies in some limits, as requirements to observance of concentration equal to eutectic are absent. Table 3 includes the effective characteristics obtained as a result of calculations depending on bulk concentration of nano-whiskers using the proposed algorithm and for comparison—values, average on composite volume.

Table 3 shows a substantial growth of elastic constants, and control calculations of common average on volume values show a rather close results that means a qualifying character of Bakhvalov–Sanchez–Palencia asymptotic technique.

To obtain the distribution of thermo-deformations we accepted the following assumptions:

1. Stresses in composite at temperature of crystallization are equal to zero.
2. Coefficients of linear expansion of composite components are isotropic.

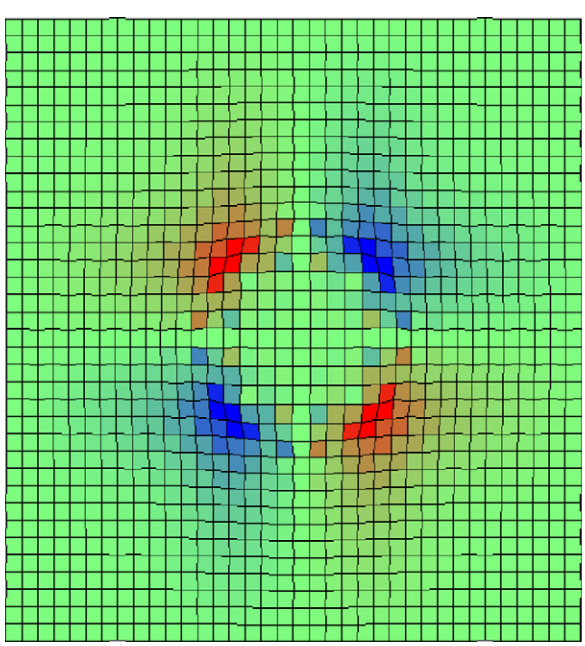

Fig. 3. Distribution of shear component of thermo-deformations in representative cell of composite $LaB_6–HfB_2$. Green color corresponds to not deformed material. Intensity of red and blue colors corresponds to an intensity of shear in a plane, perpendicular to fiber axis, a color is defined by a sign of shear deformation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

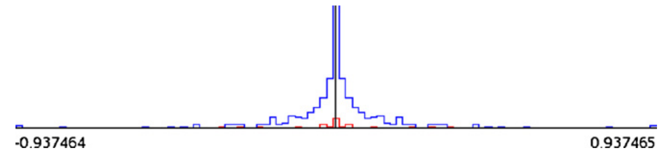

Fig. 4. Distribution of a degree of shear component of deformation in volume. Blue curve – matrix LaB_6, red – fiber HfB_2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3. Coefficients of linear expansion and modules of elasticity of components are constant and suffer a jump on interface inclusion—matrix.

Then Eq. (6) can be re-written as

$$\varepsilon_{ij}(\vec{x}) = e_{ij} + \frac{1}{2}\sum_{p,q=1}^{3}\left(\frac{\partial w_i^{pq}}{\partial x_j} + \frac{\partial w_j^{pq}}{\partial x_i}\right)e_{pq} + \delta_{ij}\theta(\vec{x}, T), \quad (10)$$

where $\theta(\vec{x}, T)$, piecewise-constant function of coordinates equal to zero when $T = T_m$: $\theta(\vec{x}, T_m) = 0$. In linear approximation with respect to T: $\theta(\vec{x}, T) = \alpha(\vec{x})(T - T_m)$, where α—coefficient of linear expansion.

After substitution of Eq. (10) in Eqs. (1) and (2) and their numerical solution with respect to $\vec{w}^{pq}(\vec{x})$, under the condition of binding (the functions $u_i(\vec{x}) = \sum_{j=1}^{3}\varepsilon_{ij}(\vec{x})x_j$ should be continuous) micro-distributions of thermo-deformations illustrated in Figs. 3 and 4 are calculated.

3. Conclusions

From the results of calculations it is concluded that the most part of materials of matrix and inclusion suffers only weak internal deformations associated with composite matrix structure and only the area of matrix around fiber is strongly deformed. Asymptotic method of Bakhvalov–Sanchez–Palencia allowed to calculate the elastic constants and fields of thermo-deformations both for real eutectic systems $LaB_6–MeB_2$ and for hypothetical nanocomposites of these systems with different volume fraction of nanotubular strengthening whiskers. For macrocomposites we obtained the results which are in a good agreement with experimental ones and for nanocomposites the predicted characteristics are very attractive that makes the problem of modification of technology of directed solidification of eutectic systems for the case of nanotubular whiskers actual.

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