Anomalous concentration dependence of the thermal conductivity of refractory sintered binary nano-composites TiN-ALN and ZrC-ZrB₂

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Abstract. An abnormal concentration dependence of the thermal conductivity of nano-composites Titanium Nitride-Aluminum Nitride and zirconium carbide-zirconium diboride has been experimentally established from the volume fraction of components. An explanation of the nature of the anomalous dependence and a technique for an approximate estimation of the dependence of the thermal conductivity of a nanocomposite on the volume fraction of components are proposed. Oxygen-free refractory compounds - covalent and metal-like active investigated in the development of new ceramic materials used for achieving higher physical and mechanical characteristics as well as for use in extreme conditions in mechanical engineering, nuclear engineering, aviation, special equipment. The development of technology is constantly stimulates the creation of new materials, which must manifest a complex of properties rarely show by one substance, such decisions cannot find the formation of composite (hetero) materials. In the case of eutectic systems with diffusive non-interacting refractory components, used for the synthesis of composite ceramic materials in a highly thermodynamic state, the possibility of co-building a new group of ceramics with interphase boundary (of eutectics "coarse conglomerate") with anomalous concentration dependences of the physical and mechanical characteristics of composite materials (flexural strength and modulus of elasticity, super plasticity – elongation more than 500%, tensile, strength and fracture toughness) and thermal properties (thermal conductivity and thermal diffusivity) [1-3].

1. Introduction

In the literature over the past decades, was information about the patterns of interaction between the actions of refractory compounds belonging to different classes, in other words you, about the structure of polythermal sections Me₄X 'Me₅X "in the ternary systems Me₄X 'X "(for example, the phase diagram of type-Me₄C- Me₅B₂, Me₄N-Me₅B₂, Me₄C-SiC, etc.) [1-3].

It is important to note that most of these systems are described by the description diagrams of the eutectic type. Since the system Me₄C(N)-Me₅C [2], Me₅B₂- Me₄C [3], Me₄B₂ [4], Me₄N-Me₄B₂ [5], LnB₆-Me₄B₂, B₄C-Me₄B₂, SiC-Me₄B₂, SiC-Me₄C [6] - are eutectic.

The authors of these publications established regularities of the eutectic composition and temperature according to the most important parameters of the electronic structure of components. These systems formed the basis for a large variety of composition ceramics and directionally crystallized materials, so-called "ceramic eutectics".
2. Technology of synthesis of binary composites from ultradispersed powders

When the eutectic crystallization process interphase particle boundaries must be characterized by the lowest energy, which is determined by their specific structure. In particular, for systems MeC (MeN) - MeB2 presented by cubic and hexagonal crystals can form a nearly ideal (coherent) interphase boundary in the conjugation of planes \{111\} MeC and \{001\} MeB2, the planes with a maximum surface energy $\sigma_{hkl}$.

The existing method of plasma-chemical synthesis (PHS), refractory compounds can produce powders with dispersion, sufficient to create a eutectic structure of "coarse conglomerate"

It should highlight the system TiN - AlN, in which both individual components and mixtures can be obtained by means of plasma chemical synthesis. This system is of interest to a large group of ceramics for various purposes - structural, wear-resistant (including rolling elements for bearings) and resistive (as represented by highly conductive TiN and AlN insulator AlN to the different components of the conductivity at 19 orders of magnitude).

Despite a significant difference in the nature of chemical bonding and the probable structure of the phase diagram of a system of no interacting components (non-eutectic), and sintering the mixture of powders with $d < 0.1$ mm is also possible to the formation of special boundaries in the resulting pair of planes \{111\} TiN and \{0001\}-typical type of dependence of conductivity on concentration of components AlN, in which the interatomic distances Ti-Ti (0.303 nm) and Al - Al (0.309 nm), respectively, differ only slightly.

The simplest and most common method of making composites of refractory components is the method of powder technology - ceramic. To date, created a variety of options for this technology, allowing to receive advanced ceramic products from micro- and nano-powders of different substances in a wide range of particle sizes from 10 nm to $10^8$ nm [1,2].

![Figure 1](image)

Figure 1. Concentration dependences of thermal conductivity $\lambda(V_B)$ and electric conductivity $\sigma(V_B)$ of binary heterogeneous systems of different nature, the nature of the structure and interaction of components: 1 - mechanical mixtures of macro- and micro-level, 2 - continuous solid solutions - components are mixed in the sub-nano level ($< 1$ nm), 3 - eutectics of "coarse conglomerate" with an anomalous concentration dependence.
Figure 1 shows the typical type of dependence of conductivity on concentration of components of macro- (d > 1 mm) and micro- (1 < d < 100 microns) heterogeneous systems (mechanical mixes) - line 1, sub-nanodispersed system (d < 1 nm) solid solution allows - line 2, and an unexpected (anomalous) type of concentration dependence for some ultradisperse (mesoscopic level) composite materials system (10 < d < 300 nm) - line 3, [7-14].

In the works [1-4,6] shows that the type of concentration dependence of aggregate size is determinate by physic-chemical factors and the technology of synthesis of composite material or alloy (static or dynamic compaction of powder components, sintering in the solid phase or with the participation of the molten phase, the melting)

Heterogeneous systems with refractory non-interacting components of the diffusion in the solid state and eutectic alloys are a group of "mechanical mixtures" with the dimensions of the inhomogeneities in the macro- (d > 1 mm) and micro- (10 < d < 500 microns) range. The dependence of thermal conductivity and electrical conductivity of such "mechanical mixtures" is monotonic concave to the axis of the volume concentration of the components $V_b$ (curve 1 in figure 1).

The components of heterogeneous systems belonging to the group of continuous or limited (in the region of solubility) solid solutions are mixed at the level of atoms and chemical compounds (sub-nanometer range d <10 nm). The dependence of thermal conductivity and electrical conductivity of such solid solutions has extreme character with a pronounced minimum near equiatomic or equimolar concentrations of the components $X_i$ (curve 2 in figure 1).

One would expect that the concentration dependence of thermal conductivity of heterogeneous structures whose components are mixed at the intermediate level will be located between the extreme cases discussed above, i.e., between curves 1 and 2 in figure 1.

However, contrary to expectations, in the papers [2,6] concentration dependence of thermal conductivity of the investigated ceramics with developed interphase boundary (eutectic “coarse conglomerate ”) differed from the discussed above (line 3 in figure 1) with a local or a general excess of the maximum effective thermal conductivity with respect to composites of a group of mechanical mixtures.

A qualitative explanation of the physical nature of the anomalous type of con-traditional relationships proposed in the papers [1,2].

Features compression heterophase systems - the composite ceramics in eutectic systems with the initial particle size of 0.1 - 0.3 micron at $T > 0.6 T_{\text{eutectic}}$ manifested in the fact that close to the eutectic becoming demonstrate significantly greater rate of compaction.

Such particles obtained by vibrogrinding are characterized not only high level of specific surface area, but also by the presence of a significant number of dislocations, depending on the nature of the compounds, i.e., increased surface "activity" [2]. This is explained by the fact that different contact name, small particles are developing a much more powerful diffusive flows - providing sliding particles (seal) and accommodation (adjustment) of contacting lattices of two different particle components.

Given the difference in interatomic distances of Me-Me in these compounds can be expected, that interphase boundaries will characterized by the presence of so-called misfit dislocations. At such small sizes of grains in the composite (<1 micron) internal volumes of these compounds with predominant share of the covalent bond should be characterized by a low dislocation density (or their absence) and high hardness.

It should be noted that the eutectic metallic systems at low temperatures show a higher hardness in comparison with pure metals, which is associated with the manifestation in metals primarily intragranular dislocation slip and braking at the last of the grain boundaries [6].

This effect allows you to specifically use it when developing materials for use in conditions of rapid temperature change (especially regulated heating rate), suggesting that the processes of microplastic deformation of the boundary will contribute to the relaxation of thermal stresses occur.

Consequently, the structure of the planned heterophase sintered ceramic material must be close to that of the eutectic, which is difficult to implement. However, comparable in sophistication interfaces sin-
tered composition (heterophase ceramics) can be created, focusing on the use of ultrafine (nano-) powders with the size of particles \( d = 20 \div 60 \) nm

Naturally, the simulation of eutectic structures following a convention to consider \( \tau \) blows, but the approach to the "course eutectic conglomerate" is possible.

For example, earlier in \([1-4,6]\), using submicron powders of carbides and borides \( \text{MeC}-(\text{MeB}_2\text{LaB}_6) \) received sintered at \( T=2000^\circ \text{C} \) composites in the system \( \text{TiC-TiB}_2 \) \( (T_{\text{eutectic}}=2650^\circ \text{C}) \), \( \text{ZrC-ZrB}_2 \) \( (T_{\text{eutectic}}=2850^\circ \text{C}) \), \( \text{ZrB}_2\text{LaB}_6 \) \( (T_{\text{eutectic}}=2470^\circ \text{C}) \) and in other systems throughout the concentration range studied, and their most important structure-sensitive physical and mechanical characteristics.

A characteristic feature of the structure to equal the porosity of the sintered heterophase composites (porosity \( \sim 2-3\% \)) is an approximate equality of the components of particle sizes in the range of 25-75\% (2-4 microns).

During sintering mono-powders each source component the particle size of both phases during sintering increases markedly - to 12-16 microns. Mutual "obstacle screening" of the phases plays the role of preventing the growth of grains of each of them is obvious. Sintering heterophase (two-component) mixtures in this concentration range (when the initial particle size of the phase components) against a background of advanced network interfaces, which are vacancy sinks.

In the end, with the free sintering of the structure is formed summarizes the properties of two closely "matched" frames, this stage and perhaps formation of a special "special" (coherent or semi-coherent) boundaries.

An important role in their formation processes are the relative rotation of the particles upon application of external forces, it is difficult implemented with increasing particle size \( (d_{\text{initial}} \gg 1 \) microns)

The growth of the size of the contacting particles requires a substantial increase in the time required for diffusive mass transport in the contact zone and the reversal of the particles. External forces prevent such a turn, providing the appearance of large-conventional boundaries \([4]\).

Consequently, the "force" (pulse, dynamic), compaction (without the necessary adjustment of the diffusion boundary) and "free" sintering, there may be different in structure, almost "perfect contact at the interface ("interpenetrating", "mutually penetrating") lattices of the two dissimilar components of the structure and properties of each sub lattice is close to the structure and properties of monocrystalline components.

3. The model of the composite structure and the method of calculating the effective thermal conductivity of binary composites

To develop a model of the structure and the approximate method of calculating/predicting the thermal conductivity we use the experiences and recommendations of operations \([11-14]\) and represent the considered binary heterogeneous system \( \text{A-B} \) in figure 1 as a quasi-ternary composition with a variable components \( \text{A, B} \) and \( \text{AB} \) component of the corresponding structure of two interpenetrating sublattices with coherent boundaries and coherent or semi-coherent phase microstructure which is close to single crystal of each of the initial components at \( V_A=V_B=0.5 \).

The third "quasi-component" in the studied systems is the frame structure is formed in an equal volume concentrations of components \( V_A=V_B=0.5 \) as a result of diffusion of the active manifestation of the interaction at the interfaces of contacting nanoparticles crossing the starting components in a particular state - with a coherent, or semi-coherent phases border, microstructure which is close to monocrystalline of each of the initial components.

Approximation to the single crystal of each of the components reduces the scattering of phonons in the bulk of the particles, and the boundaries of different components and leads to an increase in thermal conductivity of each of the contacting the components and, consequently, a local excess of the thermal conductivity of ordinary mechanical mixture or a general maximum effective thermal conductivity of the composite material.

Then, in the range of volumetric concentrations of \( I \) \((0 < V_B <0.5)\) heterogeneous system will be considered as a binary mechanical mixture with a thermal conductivity \( \lambda_A \) of component \( A \) and quasi compo-
tern AB with a thermal conductivity $\lambda_{AB}$ corresponding thermal conductivity of the system with $V_A=V_B=0.5$.

In the range II ($0.5 < V_B < 1$) heterogeneous system will be considered as a binary mechanical mixture of component AB with $\lambda_{AB}$ with a thermal conductivity and thermal conductivity $\lambda_B$ of component B.

Thermal conductivity of components A and B are taken from the reference data. Thermal conductivity of the component AB is taken from either from experiment (a more reliable value) [2], or calculated in the presence of background data, the thermal conductivity of $\lambda_{AB}$ max max (maximum maximorum) as the mechanical mixture of two monocristalline components A and B with an equivolume concentration.

We now consider the method of calculation in the range of I-1 ($0 < V_B < (0.075 - 0.1)$). In the process of sintering of components A and B at the interface between them is formed of a coherent (semi coherent) boundaries are at a low volume concentration distribution in the matrix component A in the form of droplets non contacting quasicomponent AB. Volume fraction of inclusions quasicomponent AB (reduced volume concentration of $V_{AB\ rel}$) is determinate by ratio.

$$V_{AB\ rel}=2V_B$$

(1)

Effective thermal conductivity $\lambda_{eff}$ structures interspersed with concentrations in the range above $0 < V_{AB\ rel} < (0.15-0.2)$ is calculated according to any one set of relations for a given structure, for example, the formula proposed by V. Odelevsky [9].

$$\lambda_{eff} = \lambda_{mat}(1 - V_{AB\ rel})/((1 - \lambda_{rel}) - (1 - V_{AB\ rel}))/3)$$

(2)

where: $\lambda_{mat}=\lambda_A$, $\lambda_{incl}=\lambda_{AB}$, $\lambda_{rel}=\lambda_{incl}/\lambda_{mat}$

The matrix component is structurally dominant (in effect on the effective thermal/electric conductivity) with respect to the inclusions.

In the range I-3 ($0.8-0.85 < V_{AB\ rel} < 1$ and $0.4 < V_B < 0.425$ in figure 1 composite material has heterogeneous structure of the matrix quasicomponent AB with droplets non contacting original component A.

Effective thermal conductivity of the structure $\lambda_{eff}$ with a splash of A is also calculated by the formula (2) with an appropriate substitute index components - the dominant component of the matrix and inclusions, namely,

$$\lambda_{mat}\lambda_{AB}, \lambda_{incl}=\lambda_A, \lambda_{rel}=\lambda_{incl}/\lambda_{mat}$$

In the range of I-2 ($0.15-0.2 < V_{AB\ rel} < (0.8-0.85)$ in Fig. 1 heterogeneous structure is a chaotic binary mixture of geometrically equal components A and AB which is the effective thermal conductivity can be calculated by the relation [14].

$$\lambda_{eff}=\lambda_A (1 - V_{AB\ rel})^2 + \lambda_{AB} (V_{AB\ rel})^2 + 4V_{AB\ rel} (1 - V_{AB\ rel}) \lambda_A \lambda_{AB} / (\lambda_A + \lambda_{AB})$$

(3)

In the range of II-1 in figure 1 ($0.5 < V_B < 1$) the heterogeneous system is considered as a binary mechanical mixture of component AB with a thermal conductivity $\lambda_{AB}$ and component B with thermal conductivity $\lambda_B$.

In the range of I-4 $0.5 < V_B < (0.575 - 0.6)$ in figure 1 heterogeneous structure is a quasicomponent AB matrix with droplets non contacting original component B.

The effective thermal conductivity of the $\lambda_{eff}$ structures interspersed with B is also calculated by the formula (2) with an appropriate substitute index components - the pre-dominating component of the matrix and inclusions, namely,

$$\lambda_{mat}=\lambda_{AB}, \lambda_{incl}=\lambda_B, \lambda_{rel}=\lambda_{incl}/\lambda_{mat} V_{B\ rel}=2(V_B-0.5)$$

$$\lambda_{eff} = \lambda_{mat}(1 - V_{B\ rel})/((1 - \lambda_{rel}) - (1 - V_{B\ rel}))/3$$

(4)

In the range of II-3 in figure 1 ($0.9 - 0.925) < V_B < 1$ a heterogeneous system is a matrix of component B with a thermal conductivity $\lambda_B$ with non-contacting droplets of quasicomponent AB with a thermal conductivity $\lambda_{AB}$. Effective thermal conductivity structures interspersed with AB as calculated by the formula (2), with an appropriate substitute index components - the dominant component of the matrix and inclusions, namely.
\[ \lambda_{\text{matr}} = \lambda_B, \lambda_{\text{incl}} = \lambda_{AB}, \lambda_{\text{rel}} = \lambda_{\text{incl}} / \lambda_{\text{matr}}, V_{AB_{\text{rel}}} = 2(1 - V_B) \]

Finally, in the range of II-2 (0.575 - 0.6 < V_B < 0.8 - 0.85) in figure 1 hetero-structure is a binary mixture of chaotic geometrically equal components AB and B, effective thermal conductivity which can be calculated by the relations [14].

\[ V_{B_{\text{rel}}} = 2(V_B - 0.5) \]

\[ \lambda_{\text{eff}} = \lambda_{AB}(1 - V_{B_{\text{rel}}})^2 + \lambda_B(V_{B_{\text{rel}}})^2 + 4V_{B_{\text{rel}}}(1 - V_{B_{\text{rel}}})\lambda_{AB}/(\lambda_{AB} + \lambda_B) \]

In accordance with the principles of the theory of generalized conductivity checked the relations obtained in the limit transitions.

If V_B = 0, then for the range of I-1 by the formula (3) the apparent \( \lambda_{\text{eff}} = \lambda_A \); when V_B = 0.5 for the range I-3 and I-4, we \( \lambda_{\text{eff}} = \lambda_{AB} \), when V_B = 1.0 for range II-6, \( \lambda_{\text{eff}} = \lambda_B \).

Below in figure 2 shows a comparison of calculation results with experimental data obtained in the papers [1, 2].

![Figure 2](image-url)

**Figure 2.** Abnormal concentration dependences of the thermal conductivity of eutectic structures of the "coarse conglomerate"-sintered nanocomposites: ○ TiN – AlN - experimental data, 1 - calculation; △ ZrC-ZrB2 - experimental data, 2 - calculation.

4. Conclusion
The explanation for the experimental established type of abnormal concentration dependence of thermal conductivity of the binary composites sintered from ultra-dispersed (mesoscopic level 10 < d < 300 nm) powders and method of the calculation/forecasting of the thermal conductivity of such composites are offered.

The method allows to predict thermal conductivity of such composites with the minimum volume of basic data at a development stage of composite material with the required thermal conductivity that reduces expenses of time and funds for synthesis of samples and carrying out measurements.

5. Symbols
$V_A, V_B, V_{AB}$ - the volume fractions of components A and B and the quasi-component AB; $V_{AB\,\text{rel}}$ - reduced volume concentration of the quasi-component of the AB in the range I in figure 2 ($0 < V_B < 0.5$).

$\lambda_A, \lambda_B, \lambda_{AB}$ - thermal conductivity of the initial components A and B and the quasi-component AB; $\lambda_{\text{eff}}$ - the effective thermal conductivity of binary nanocomposite; $\lambda_{\text{matr}}, \lambda_{\text{incl}}$ - thermal conductivity of the matrix component and inclusions; $\lambda_{\text{rel}} = (\lambda_{\text{incl}} / \lambda_{\text{matr}})$ - the relative thermal conductivity of the inclusions.

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