# Gehlenite as a potential material for thermal barrier coatings

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### Abstract

Here we explore available natural gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>) as a possible material for thermal barrier coatings (TBCs), which protect metal parts of gas turbine blades from high temperatures. Our theoretical calculations show a rather low thermal conductivity and sufficiently high thermal expansion of gehlenite. We also measured the heat capacity and thermal conductivity of natural samples of gehlenite, and performed tests of stability of its TBC to thermal cycling. We found that gehlenite can indeed improve TBCs, reducing both thermal conductivity and CMAS corrosion and could be used in double ceramic TBCs as a protective top coat on a YSZ layer.

Keywords: Ceramics; gehlenite, heat capacity; thermal expansion; machine learning

interatomic potentials; molecular dynamics simulations.

## **1** Introduction

Thermal barrier coatings are widely used to protect metallic components of aircraft engines and gas turbines, in order to support their work at high operating temperatures and engine powers. A typical TBC is a system composed of the oxidation resistant alloy MCrAlYX (M = Ni/Co, X = Hf, Ta, Re, Si) as a bond coat on superalloy substrates and a refractory oxide ceramic material as a corrosion-resistant heat insulating top coat. Ceramic top coatings are usually deposited by such methods as atmospheric plasma spraying (APS) or electron-beam physical vapor deposition (EB-PVD) [1,2]. The currently used top coat material is partially (6-8 wt%) yttria-stabilized zirconia (YSZ), which provides the best hightemperature performance, has low thermal conductivity (~2 W/mK at 1273 K), and a relatively high linear coefficient of thermal expansion (CTE) (11×10<sup>-6</sup> K<sup>-1</sup> at 293-1273 K) [3] close to that of the superalloy (16×10<sup>-6</sup> K<sup>-1</sup> [2]). The major disadvantages of YSZ are sintering, metastability, and high oxygen diffusion which limit the operating temperatures (< 1473 K) and the number of thermal cycles [3,4]. Therefore, there is a need to search for new TBC materials having a high melting point, high phase stability, low thermal conductivity, a relatively high coefficient of thermal expansion, no oxygen diffusion, and good chemical and mechanical stability at the operating temperatures [1,3-5]. Many refractory oxides based on alumina, titania, zirconia, hafnia, rare earths (e.g. fluorites (Ce, RE)O<sub>2-x</sub>, pyrochlores A23+B24+O7, garnets Y3Al5O12, Y3AlxFe5-xO12, Dy3Al5O12, monazite-type LaPO4, perovskites  $A^{2+}B^{4+}O_3$ , hexaaluminates CaAl<sub>12</sub>O<sub>19</sub>, LaMgAl<sub>11</sub>O<sub>19</sub>, etc.) are considered to be potential TBC materials [1,2,4,5]. Most of these compounds have framework structures, but some of them exhibit layered (BaLa<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>,  $RE_2$ SrAl<sub>2</sub>O<sub>7</sub>) or chain (Y<sub>4</sub>Al<sub>2</sub>O<sub>9</sub>) structures [1,5].

Most of the mentioned promising TBC materials have natural minerals as prototypes. One of the roles of the TBC is to protect alloys to resist oxidation by the high temperature/pressure in the combustion environment [6]. Therefore, successful TBC should be dense and thermally stable, highly impervious to oxygen transport, phase-stable over the temperature range of interest, tolerant to thermal strains arising from the cyclic nature of the operation, and resistant to the influence of external objects.

Our idea is to search for possible TBC candidates among readily available hightemperature oxide minerals. Gehlenite  $Ca_2Al_2SiO_7$  (2CaO·Al\_2O\_3·SiO\_2, C2AS) is an interesting candidate for TBC for the following reasons:

- It is an abundant mineral, exhibiting high-temperature stability in nature and is also one of the main stable products of TBC degradation in aero engines because of the interaction at ~1473 K with molten Ca–Mg–Al–silicates (CMAS) [7-9], which are typical for desert sands or volcanic ashes.
- Its layered and relatively complex crystal structure suggests lower thermal conductivity: heat is most efficiently transferred by acoustic phonons, which constitute only a small fraction of all phonons in complex structures.
- Relatively weak Ca—O bonds imply good thermal expansion and strong anharmonicity, which lowers thermal conductivity.

Gehlenite Ca<sub>2</sub>Al[AlSiO<sub>7</sub>] is an Al-rich member of the melilite group of minerals, which forms solid solutions with åkermanite Ca<sub>2</sub>Mg[Si<sub>2</sub>O<sub>7</sub>], alumoåkermanite NaCaAl[Si<sub>2</sub>O<sub>7</sub>], Fegehlenite (Ca<sub>2</sub>Fe<sup>3+</sup>AlSiO<sub>7</sub>) and Fe-åkermanite (Ca<sub>2</sub>Fe<sup>2+</sup>Si<sub>2</sub>O<sub>7</sub>) [10]. The crystal structure of gehlenite is tetragonal (a = 7.684, c = 5.065 Å,  $P \ \overline{4}2_1m$ , Z = 4) [11,12] and contains layers parallel to plane (001), which consist of corner-sharing AlO<sub>4</sub> and (Al<sub>0.5</sub>Si<sub>0.5</sub>)O<sub>4</sub> tetrahedra forming five-membered rings. The Ca<sup>2+</sup> cations are in the eightfold coordination (Thomson cubes) between the tetrahedral layers (Fig. 1). Pure and doped gehlenite crystals and ceramics were considered as laser hosts, high-temperature piezoelectric sensors, pigments, dielectric materials, bone regeneration scaffolds [12-16]. The available data are scarce, but do indicate high promise of gehlenite for TBC applications: it undergoes no solid-solid phase transitions under ambient pressure, has relatively high congruent melting point (1863 K) [8,17] and volumetric thermal expansion coefficient ( $28.3 \cdot 10^{-6}$  K<sup>-1</sup>) values [10], low thermal conductivity (1.5-2.9 W m<sup>-1</sup> K<sup>-1</sup> at room temperature) [18,19], good mechanical, and anti-hydration properties [20,21]. Interestingly, mesoporous C2AS ceramic sintered at 1173–1723 K has a very low thermal conductivity value of 0.30–0.42 W m<sup>-1</sup> K<sup>-1</sup> at 1273 K [21].

The purpose of the present work is to find out whether natural gehlenite ceramics can be used as a TBC material. To understand better the properties of gehlenite, we computed its thermal conductivity and thermal expansion as a function of temperature. Then we selected natural gehlenite crystals, checked their properties, prepared ceramic samples and performed tests of gehlenite-based TBCs.

Fig. 1. Structure of gehlenite Ca<sub>2</sub>Al[AlSiO<sub>7</sub>] projected onto (001).

### 2 Materials and methods

#### 2.1 Computational methodology.

We have computed the thermal conductivity of gehlenite by using two different computational methods. First solving the phonon Boltzmann transport equation (BTE) with an iterative self-consistent algorithm [22,23], using the ShengBTE package [24] and second using molecular dynamics (MD) simulation by homogeneous nonequilibrium molecular dynamics (HNEMD) approach [25,26] as implemented in the GPUMD package [27].

To obtain the initial training set, we used the *ab initio* molecular dynamics (AIMD) approach as implemented in the VASP code [28] with projector-augmented-wave (PAW) [29] pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) functional [30] for the exchange-correlation energy. The AIMD calculations were performed using a supercell of 192 atoms and  $\Gamma$ -point for sampling the Brillouin zone [31]. Plane waves with kinetic energies below the 600 eV cutoff were used as the basis set to represent the Kohn-Sham wave functions. AIMD

simulations were used for producing data to train a machine learning interatomic potential (MLIP). First, the *NPT* thermostat was used to obtain the initial training set to obtain a preliminary MLIP. Then the active learning method [32,33] was utilized to increase the reliability of the potentials. The time step was 2 fs, and the total simulation time was 6 ps. We used two different MLIPs – both based on the same training data sets, and validated on 100 randomly selected configurations (not included in the training set).

Moment tensor potentials (MTPs) [34] were used as an accurate and computationally efficient model of MLIPs [33,35]. The MTP parameters were obtained by solving the following minimization problem (fitting, training):

$$\sum_{k=1}^{K} \left[ w_{e} \left( E_{k}^{AIMD} - E_{k}^{MTP} \right)^{2} + w_{f} \sum_{i}^{N} \left| f_{k,i}^{AIMD} - f_{k,i}^{MTP} \right|^{2} + w_{s} \sum_{i,j=1}^{3} \left| \sigma_{k,ij}^{AIMD} - \sigma_{k,ij}^{MTP} \right|^{2} \right] \rightarrow \min \left[ \frac{1}{2} \left( \frac{1}{2} \left( \frac{1}{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \right)^{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \left( \frac{1}{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \right)^{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \left( \frac{1}{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \right)^{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \left( \frac{1}{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \right)^{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \left( \frac{1}{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \right)^{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \left( \frac{1}{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \right)^{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \left( \frac{1}{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \right)^{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \left( \frac{1}{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \right)^{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \left( \frac{1}{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \right)^{2} \right)^{2} + \frac{1}{2} \left( \frac{1}{2} \right)^{2} + \frac{1}{2} \left($$

where  $E_k^{\text{AIMD}}$ ,  $f_{k,l}^{\text{AIMD}}$  and  $\sigma_{k,lj}^{\text{AIMD}}$  are the system's total energy, atomic forces, and stresses in the training set, respectively; *K* is the total number of configurations;  $E_k^{\text{MTP}}$ ,  $f_{k,l}^{\text{MTP}}$ , and  $\sigma_{k,lj}^{\text{MTP}}$ are the corresponding values predicted by MTP;  $w_f$ ,  $w_f$ , and  $w_s$  are the non-negative weights equal to 1.0, 0.1, and 0.1 and expressing the importance of energies, forces, and stresses. The cut-off radius of the potential was 6.0 Å. Using MTP potentials, we extracted second- and third-order interatomic force constants for solving the Boltzmann transport equation (BTE) [22-24] in the lattice dynamics (LD) and effective harmonic method (EHM) [36,37] as implemented in the Hiphive package [38]. The PHONOPY package [39] interfaced with the MLIP code was used to compute interatomic force constants (IFCs). After testing the convergence of phonon frequencies as a function of supercell size, the dynamical matrix was constructed using the finite-displacement method; the matrix was then symmetrized and the translational invariance was ensured by imposing the acoustic sum rule. The vibrational frequencies were obtained as a result of diagonalization.

The second type of MLIP used here is the neuroevolution potential (NEP) [40], implemented in GPUMD package [27]. Thermal conductivities were calculated with NEP

using molecular dynamics simulations. The GPU-based implementation of the NEP potential gives extreme efficiency and enables calculations of thermal conductivities of large simulation cells over longer time periods.

#### 2.2 Sample preparation and characterization

Natural light-grey gehlenite (ref. FMM\_1\_41299) composed of crystals with maximum size 3-5 mm from the Fersman Mineralogical Museum collection (Moscow, Russia) was chosen for the experimental study. This sample was found in 1930s in the skarns of Vesuvianite hills near the Kedabek mine (Azerbaijan). Electron microprobe analysis gave composition Ca<sub>2.0</sub>(Mg<sub>0.4</sub>Al<sub>0.6</sub>)[Si<sub>1.4</sub>Al<sub>0.6</sub>O<sub>7</sub>], which corresponds to the solid solution of gehlenite and åkermanite (60 : 40). Likewise, indexing of the XRD pattern gives unit cell parameters (space group  $P\overline{4}2_1m$ ) a = 7.7330(4) Å, c=5.0400(5) Å, V = 301.39(6) Å<sup>3</sup>, intermediate between the corresponding gehlenite and åkermanite values [10].

The crystal, grinded and post-annealed powder samples were characterized by PXRD, thermal analysis and other methods (see some details in Supplementary Materials).

Cylindrical samples with sizes 7.0×1.9 mm and 6.0×1.8 mm were prepared from the chosen gehlenite crystals for thermal diffusivity and heat capacity measurements, respectively. The crystal end faces were polished, the parallelism of the upper and lower parts of the samples was less than 0.1 arcmin. Since gehlenite is semi-transparent in the IR region, its end faces were coated with chromium, while all other sides were uniformly coated with a thin layer of graphite (using the GRAPHIT 33 graphite spray) to enhance the absorption of the surfaces.

Thermal diffusivity was measured on a NETZSCH LFA-427 apparatus by the laser flash method in high-purity static argon (99.998 wt.%) at temperatures 293-973...1073 K. The thermal diffusivity value was determined from the heating curve of the surface opposite to the irradiated one. The radiation heat losses were accounted for within the Cape and

Lehman model [44]. Corrections for the length of the laser pulse and its real shape were considered [45]. Depending on the temperature, the error of thermal diffusivity measurements varied from 2 to 5%.

The specific heat capacity ( $c_p$ ) of a 87.83 mg gehlenite sample was measured by differential scanning calorimetry. The experiment was carried out on a NETZSCH DSC 404 F1 calorimeter using platinum crucibles with corundum inserts and platinum lids at 300-1270 K with a heating rate of 10 K/min in a 20 mL/min argon flow. A 63.44 mg sapphire sample was used as the calibration reference. The estimated measurement error of this setup was 2–4%, which was confirmed by the experiments with high-purity platinum and sapphire samples.

From powders of gehlenite, the coatings were deposited on two types of substrates using detonation spraying from a gehlenite powder. First, 40-60  $\mu$ m gehlenite powder was deposited on a 70×50×2 mm steel plate subjected to sandblasting. The steel plate played here the role of model metal bond coat of TBCs. The spraying was performed with a CCDS2000 detonation gun developed in the Lavrentyev Institute of Hydrodynamics SB RAS [41] using a 1000 × 20 mm barrel. An acetylene-oxygen mixture C<sub>2</sub>H<sub>2</sub> + 2.5O<sub>2</sub> with mainly oxidative detonation products (O, O<sub>2</sub>, OH, CO) was used to prevent the mineral from reduction during the spraying process. The spraying mode was established based on previous experiments on obtaining oxide coatings [42,43]. The powder was injected into the barrel at a distance of 400 mm from the barrel exit. The samples were placed at 100 mm from the barrel end, and the coating was sprayed in a series of shots to form a ~ 5  $\mu$ m thick layer in one shot. The coating thickness varied from 20 to 500  $\mu$ m.

Then the data obtained for the model coating samples were used to choose the optimal conditions for the preparation of TBCs based on gehlenite deposited on heat-resistant alloys of the Inconel<sup>TM</sup> family that are used as the substrates. To counteract the difference between thermal expansion coefficients of gehlenite and Inconel<sup>TM</sup>, the alloy surface was coated with a

NiAl layer and a YSZ-Nd (or  $ZrO_2$ -Nd) layer with a thickness of 40-60  $\mu$ m and 20-25  $\mu$ m, respectively. The thickness of the gehlenite layer was 40-50  $\mu$ m in all cases.

The thermal cycling tests were conducted on an apparatus that can periodically change the thermal load of the test sample at a specified rate (see Supplementary Materials, Fig. SM5). The position of the studied object was controlled with a PLLM-11-500 linear module equipped with a PL57H76-D8 bipolar stepper motor. The positioning system was controlled by a SMSD-4.2 programmable stepper motor controller. The temperature at control points was recorded using chromel-alumel thermocouples and an OPTRIS CT pyrometer.

## **3 Results and Discussion**

### 3.1 Calculations of thermal expansion and thermal conductivity

We used two different methods to calculate thermal expansion coefficient (TEC): quasiharmonic approximation [40,46,47] (QHA) and molecular dynamics (MD) simulation. The PHONOPY and LAMMPS packages were used to calculate the TEC within QHA and MD simulations, respectively [48,49]. Fig. 2 shows the volumetric TEC of gehlenite calculated as a function of temperature and its comparison with experimental data. Accurate calculations of TEC must take into account quantum statistics of phonons (important below Debye temperature and done in the QHA, but not in MD) and all anharmonic effects (QHA includes them approximately, but ignores so-called intrinsic anharmonicity, which becomes important at high temperatures – whereas MD takes full account of anharmonicity. Below Debye temperature the QHA is more accurate, whereas at higher temperatures MD is to be preferred.

**Fig. 2.** Volumetric thermal expansion of gehlenite as a function of temperature. Experimental data: a [10] and b [50]. Note that linear TEC (equal to 1/3 of the volumetric TEC) of gehlenite is very close to that of YSZ.

In our calculations we have considered third-order interatomic force constants up to the

fourth nearest neighboring shell in a  $3 \times 3 \times 3$  supercell [51]. When solving the BTE, the Brillouin zone was sampled using a  $10 \times 10 \times 10$  q-point mesh. Anisotropic structure of gehlenite implies anisotropic thermal conductivity, see Fig. 3.

**Fig. 3.** Thermal conductivity of gehlenite as a function of temperature calculated by three different methods. The most reliable results are from HNEMD.

To use the EHM, first we perform MD simulations with MTP potentials in the *NVT* ensemble in a  $3 \times 3 \times 4$  supercell constructed using an equilibrium lattice constant at each temperature for 100 ps. To construct the force constant model, we used 300 randomly selected snapshots from the MD trajectories. The cutoff for second- and third-order interactions up to 8.0 Å and 5.0 Å, respectively were chosen. Thus, renormalized second- and third-order IFCs were calculated. The temperature-dependent interatomic force constants (TDIFCs) obtained by the EHM are valid only at temperatures close to the temperature of the MD simulation. Therefore, we performed several MD simulations at different temperatures. Fig. 4 (a) shows the phonon dispersion curves and (b) density of states (pDOS) calculated at different temperatures using the EHM model. As can be clearly seen in Fig. 4 (b), the contribution of acoustic phonons in pDOS shifts to higher frequencies with temperature. As a result of this strong renormalization of phonons at high temperatures, the thermal conductivity values calculated with TDIFCs differ significantly from those calculated with IFCs using the harmonic lattice dynamics (zero temperature) method (Fig. 3). The temperature dependence of thermal conductivity in the EHM model changes from  $\kappa \propto T^{-1}$  to  $\kappa \propto T^{-0.5}$ .

Fig. 4. Phonon density of states of gehlenite at different temperatures calculated with the EHM.

The EHM results were verified by homogeneous nonequilibrium molecular dynamics HNEMD simulations [25,26] with the NEP potential as implemented in the GPUMD package using a large (9 × 9 × 12) supercell containing 23328 atoms that was large enough to reduce size effect in thermal conductivity calculations nearly to zero. The total time of each simulation was 2 ns, and the magnitude of the external driving force was  $5 \times 10^{-5} \text{ Å}^{-1}$ . Several individual simulations were performed for each temperature, and thermal conductivity was obtained by averaging their results. These results agree with thermal conductivities from EHM calculations. Our calculations show that gehlenite has sufficiently low thermal conductivity (as well as sufficiently high TEC and chemical inertness) for TBC applications. Our experimental values of thermal conductivity (~1-3 W/m·K at temperatures 300-1000 K, see Supplementary Materials) are already very low, but include the contribution from radiative heat transport – removing which one will obtain even lower values. In practical applications, radiative heat transfer is usually not important and can be suppressed by doping.

#### 3.2 Thermal cycling tests of deposited gehlenite samples

The XRD pattern of the gehlenite coating deposited on a steel substrate (Fig. 5) shows that the sample contains a small admixture of grossular  $Ca_3Al_2Si_3O_{12}$  (PDF 01-073-2372) in addition to the main phase. This phase could be formed during spraying due to the interaction with  $Al_2O_3$  micropowder (the surface of the sample was treated with  $Al_2O_3$  micropowder before spraying to increase the surface roughness).

Fig. 5. XRD pattern of a gehlenite coating (120  $\mu$ m) produced by detonation spraying on a steel plate.

Fig. 6 shows a SEM image of the surface of a gehlenite layer deposited on the steel substrate and an optical image of its transverse cross-section. As can be seen, the coating is melted through and has low porosity. No long cracks and defects were found. The SEM image (Fig. 6a) of the transverse cross-section of the gehlenite coating shows a distinct interface layer, the elemental composition of which differs significantly from that of the coating. The main elements in the interface composition are aluminum and iron. The interface layer was formed during detonation sputtering when the local temperature on the substrate surface rises up to 2500 K.

Fig. 6. Surface of the 350  $\mu$ m thick gehlenite layer: (a) SEM image of the surface, (b) optical image of a transverse cross-section. Grey and white layers indicate the gehlenite coatings and steel substrate, respectively.

The thermal cycling tests were conducted at 1123-1323 K for two samples of coatings on a steel substrate to determine their thermal stability. The thickness of the gehlenite coating was 150-250  $\mu$ m. As can be seen (see Supplementary Materials Fig. SM6), the samples at t<sub>max</sub>=1123 K on the hot surface and at t<sub>min</sub>=1033 K on the cold surface have no visible cracks or fractures after 50 cycles.

At higher temperatures up to  $t_{max} = 1323$  K on the hot surface and up to  $t_{min} = 1213$  K on the cold surface, the gehlenite coatings degrade already after 5 cycles even if we nearly double the thickness of the layer (300-460 µm). Rapid degradation of the gehlenite layer at 1323 K is mainly due to the interaction of the coating with iron from the steel substrate.

For a more detailed study of the interaction of gehlenite with the substrate, mixtures of gehlenite and steel powders and gehlenite and zirconium oxide powders were prepared. Based on the DTA and XRD, it was found that (1) gehlenite begins to react with the steel at oxidizing conditions below 1000 K; (2) gehlenite does not interact with YSZ in an oxidizing atmosphere up to 1250 K (and above, See Supplementary Materials for TG/DTA curves (Fig. SM7) and XRD (Figs. SM 8 and 9).

Fig. 7 shows SEM images of transverse cross-sections of a sample with a gehlenite coating on a steel substrate. A 330  $\mu$ m thick continuous coating (Fig. 7a) is formed after the deposition of gehlenite on the surface of the steel substrate. No large macropores appear, but small cracks with a length of 20-40  $\mu$ m are observed. According to our elemental analysis

(see Supplementary Materials section (Table SM1)), the sample contains phases corresponding to gehlenite and to the steel substrate. At the same time, the heat-treated sample contains a 3-5  $\mu$ m thick intermediate (interface) layer at the substrate-coating boundary. This interface layer is most probably formed due to the chemical interaction of gehlenite with the metal substrate in an oxidizing atmosphere during testing (elemental analysis of this intermediate layer is shown in Supplementary Materials Table SM1).

Note that the thickness of the gehlenite coating after the heat treatment decreased by 41.8% down to 192  $\mu$ m. The SEM images indicate that the number and the total length of small (shorter than 20  $\mu$ m) cracks decreased by 12%, while the total length of cracks larger than 20  $\mu$ m increased significantly.

**Fig. 7.** SEM images of transverse cross-sections of coating samples on a steel substrate (a) before and (b) after the heat treatment. Panel (b) also shows the gehlenite coatings (1); TGO coatings (2) and steel substrate (3).

The thermal cycling data obtained for the samples of model coatings were used to choose optimal conditions for the preparation of fractured porous media using gehlenite coatings deposited on standard samples of a heat-resistant alloy of the Inconel<sup>TM</sup>(IN792-5A) family that is employed in the fabrication of turbine blades. The heat-resistant binder was a 40–60  $\mu$ m thick NiCrAlY layer. It should be noted that at high temperature, the MCrAlY binder coating is oxidized to form a thermally grown oxide layer (TGO). This layer can slow down further oxidation of the bond coat by acting as a diffusion barrier. YSZ layers with a thickness of 5-10  $\mu$ m were additionally deposited on the samples. This layer was applied to compensate for the TEC. In all cases, the thickness of the gehlenite layer was 20-25  $\mu$ m. The structure and composition of the coatings were studied by SEM and EDX (see Supplementary Materials Table SM2) on transverse cross-sections of the samples. Fig. 8 shows the SEM images of transverse cross-section of the obtained sample.

**Fig. 8.** Samples of the coated alloy before thermal cycling. (a) Optical images of the substrate after the deposition of the gehlenite coating; (b) SEM images of the transverse cross-section of a sample coated with gehlenite (the regions of interest (ROI) (b) are shown in the Supplementary Materials Section (Table SM2).

The SEM images (Figs. 8 and 9) show that the gehlenite coated sample made of a heatresistant alloy of the Inconel<sup>™</sup> family contains four distinct regions corresponding to four different layers, as is evidenced by the EDX data (See also Supplementary Materials for EDX (Table SM2). As can be seen, dense low-porous continuous coatings were formed after the deposition. No exfoliations or laminations, neither in the volume of a single layer nor between the layers, were observed.

**Fig. 9.** SEM image of a transverse cross-section of a multilayer coating on an Inconel substrate (Numbers 1-4 indicate intermediate layers: 1 - Gehlenite; 2 – Intermetallide; 3 – TGO layer; 4 - Inconel<sup>TM</sup>).

**Fig. 10.** Samples of the coated alloy after thermal cycling. (a) Optical images of the substrate after thermal cycling (number of cycles: 30;  $\tau_{heat}$ : 140 s,  $\tau_{cool}$ : 45 s;  $T_{hot}$ : 1423 K,  $T_{cold} < 1263$  K); (b) SEM images of a transverse cross-section of a gehlenite coated sample after thermal cycling (the regions of EDX analysis 1-4 are shown in the Supplementary Materials Section (Table SM3)).

Fig. 10 shows that certain extreme conditions of thermal cycling lead to the destruction of the protective layer of the gehlenite-coated sample (Fig. SM6b). SEM images of transverse cross-sections of the sample confirm the degradation of the gehlenite protective coating: it becomes looser, contains large macropores, and thins down to complete vanishing. As can be seen, the NiAl sublayer is also destroyed, and local sites of delamination from the substrate are observed. The EDX data on the composition of deposited layers indicate no distinct boundaries between the layers after thermal cycling (Table SM3).

# 4 Concluding remarks

Thermal conductivity and thermal expansion of gehlenite are very attractive for applications in thermal barrier coatings, being better than or equal to those of yttriumstabilized zirconia. Using machine learning interatomic potentials and fully anharmonic nonequilibrium molecular dynamics, we made the first and very reliable calculations of thermal conductivity of gehlenite in the relevant temperature range: it is found to decrease from 3.5 W m<sup>-1</sup> K<sup>-1</sup> at 300 K to 1.5 W m<sup>-1</sup> K<sup>-1</sup> at 1500 K. We found that anharmonic renormalization of phonon frequencies has great effect on thermal conductivity at high temperatures and changes its temperature dependence from T<sup>-1</sup> to T<sup>-0.5</sup>. Our experimental data confirm very low thermal conductivity, even though they cannot be compared directly as they contain a radiative heat transfer contribution.

The experimental data on thermal cycling of gehlenite coatings based on the natural mineral are encouraging. The temperature of layer destruction (1600 K) is high enough. Other parameters of gehlenite, such as its high melting point (1863 K), absence of phase transitions at least up to 1273 K, together with the already mentioned low thermal conductivity and high thermal expansion coefficient make this material very promising for thermal barrier coatings.

One of major advantages is that gehlenite contains Ca, Mg, Al, Si, O, i.e. the same elements that cause calcium-magnesium-aluminosilicate (CMAS) corrosion, a critical factor provoking the destruction of thermal barrier coatings, and should not be susceptible to the CMAS corrosion. Gehlenite does not suffer from CMAS corrosion. The destruction of thermal barrier coatings in jet engines due to CMAS corrosion has been a significant problem in recent years. For example, the standard 7YSZ coating dissolves quite easily in the CMAS melt [56,57]. Various aspects of this problem and its possible solutions are widely discussed

[58-61].

The only drawback is that gehlenite coating reacts with a metal (steel) substrate at relatively low temperatures, which suggests the need for a protective intermediate barrier layer. In our experiments, a 5–10  $\mu$ m thick protective YSZ layer allowed us to significantly increase the temperature of coating degradation. No interaction of gehlenite with YSZ was observed. Gehlenite is an extremely effective barrier preventing the penetration of molten CMAS components to the base thermal barrier coating.

From our results it is clear that gehlenite could be a potential component for improved thermal barrier coatings. There are several possible avenues. First, it can be used as the second (top) layer in the preparation of CMAS-resistant thermal barrier coatings. Second, it can be used as a component of promising TBC composite systems providing high porosity of the ceramics [20,21] and, therefore, low thermal conductivity. For example, CaAl<sub>12</sub>O<sub>19</sub>/Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> samples [20] demonstrated high sintering temperatures (> 1300°C), high porosity (46–64%) and flexural strength values of the composite that can be possibly be used as a thermal barrier material. Third, properties can be tuned by solid solutions or by exploring structural analogs. For example, within the gehlenite-åkermanite series of melilite solid solutions, gehlenite is more promising due to its higher melting point. On the other hand, among the numerous structural analogues of gehlenite [62,63], aluminates CaLnAl<sub>3</sub>O<sub>7</sub> [63] promise to have even higher thermal stability than gehlenite, e.g., CaYAl<sub>3</sub>O<sub>7</sub> [64].

#### Acknowledgments

Calculations of thermal expansion and thermal conductivity of gehlenite were supported by the Russian Science Foundation, grant No. 23-13-00117 (https://rscf.ru/project/23-13-00117/).

#### Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study. All data will be made available upon request.

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This preprint research paper has not been peer reviewed. Electronic copy available at: https://ssrn.com/abstract=4837899

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#### Figures

Fig. 1. Structure of gehlenite Ca<sub>2</sub>Al[AlSiO<sub>7</sub>] projected onto (001).

**Fig. 2.** Volumetric thermal expansion of gehlenite as a function of temperature. Experimental data: a [10] and b [50]. Note that linear TEC (equal to 1/3 of the volumetric TEC) of gehlenite is very close to that of YSZ.

**Fig. 3.** Thermal conductivity of gehlenite as a function of temperature calculated by three different methods. The most reliable results are from HNEMD.

**Fig. 4.** Phonon density of states of gehlenite at different temperatures calculated with the EHM.

Fig. 5. XRD pattern of a gehlenite coating (120  $\mu$ m) produced by detonation spraying on a steel plate.

Fig. 6. Surface of the 350  $\mu$ m thick gehlenite layer: (a) SEM image of the surface, (b) optical image of a transverse cross-section. Grey and white layers indicate the gehlenite coatings and steel substrate, respectively.

**Fig. 7.** SEM images of transverse cross-sections of coating samples on a steel substrate (a) before and (b) after the heat treatment. Panel (b) also shows the gehlenite coatings (1); TGO coatings (2) and steel substrate (3).

**Fig. 8.** Samples of the coated alloy before thermal cycling. (a) Optical images of the substrate after the deposition of the gehlenite coating; (b) SEM images of the transverse cross-section of a sample coated with gehlenite (the regions of interest (ROI) (b) are shown in the Supplementary Materials Section (Table SM2).

**Fig. 9.** SEM image of a transverse cross-section of a multilayer coating on an Inconel substrate (Numbers 1-4 indicate intermediate layers: 1 - Gehlenite; 2 – Intermetallide; 3 – TGO layer; 4 - Inconel<sup>TM</sup>).

Fig. 10. Samples of the coated alloy after thermal cycling. (a) Optical images of the substrate after thermal cycling (number of cycles: 30;  $\tau_{heat}$ : 140 s,  $\tau_{cool}$ : 45 s;  $T_{hot}$ : 1423 K,  $T_{cold} < 1263$ 

K); (b) SEM images of a transverse cross-section of a gehlenite coated sample after thermal cycling (the regions of EDX analysis 1-4 are shown in the Supplementary Materials Section (Table SM3)).















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Fig. 7



Fig. 8

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Fig. 9





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