

THE STRENGTH OF THE INTERFACIAL BOND IN THE CERAMIC MATRIX COMPOSITES Al_2O_3 -Ni

SUMMARY

Using the results of High Resolution Transmission Electron Microscopy studies of epitaxial layers fcc metal/corundum we have proposed atomistic model of the interfacial structure of the Al_2O_3 -Ni composite. Then, we have carried out the verification of the CTIP+EAM model in the application to the description of interatomic interactions in the region of the interface. The assumed model of interactions has allowed us to identify the structure in the neighborhood of the interface. The obtained structure is consistent with experimental data.

Keywords: ceramic matrix composites, Al_2O_3 -Ni interface

WYTRZYMAŁOŚĆ WIĄZANIA WARSTWY PRZEJŚCIOWEJ W KOMPOZYTACH O OSNOWIE CERAMICZNEJ Al_2O_3 -Ni

Wykorzystując wyniki mikroskopowych badań warstw epitaksjalnych fcc metal/ korund zaproponowano atomowy model struktury warstwy przejściowej w kompozytach Al_2O_3 -Ni. Następnie przeprowadzono weryfikację modelu CTIP+EAM w zastosowaniu do opisu oddziaływań międzyatomowych występujących w warstwie przejściowej. Założony model pozwolił zidentyfikować strukturę obszaru znajdującego się w sąsiedztwie warstwy przejściowej. Otrzymana struktura ta jest zgodna z danymi doświadczalnymi.

Słowa kluczowe: kompozyty o osnowie ceramicznej, warstwa przejściowa Al_2O_3 -Ni

1. INTRODUCTION

At present composites formed by metallic particles dispersed within ceramic matrix, the so called cermets (CMC), find a wide range of technological applications. Due to high toughness, wear resistance and low specific gravity the composites are used in aircraft and automobile industry as structural components, for example: brake disks, couplings. On the other hand, optical, electrical and magnetic properties make the CMC multifunctional materials.

Behaviour of a composite subjected to load depends on the way of load transfer between the ceramic matrix and the metallic inclusions. Therefore, the bond of the ceramic/metal interface determines the mechanical properties of the CMCs. Improvement of fracture toughness with respect to brittle ceramic is mainly obtained by the crack bridging mechanism. The mechanism works only if the interfacial bond is sufficiently strong. Otherwise a crack propagates along the ceramic/ metal interface and final toughness of the composite can be even worse than the ceramic matrix alone. The Al_2O_3 -Ni and ZrO_2 -Ni are examples of composites of different fracture toughness K_{Ic} . In the first case, due to strong ionic – covalent bonds formed across the interface (Shi *et al.* 2007b), K_{Ic} increases (Moya *et al.* 2007). In the second case, bonds arise mainly by the weak Ni-Zr hybridization interactions (Moya *et al.* 2007). Therefore K_{Ic} of the ZrO_2 -Ni composite is close to K_{Ic} of the ceramic matrix (Moya *et al.* 2007). In a similar way strength of the interfacial bond influences the wear resistance of composites. In the case of a strong bond, the load applied to a composite induces plastic deformation metallic particles and arising

microcracks are forced to pass through the ductile inclusions. While, in the case of a weak bond microcracks propagate along the ceramic/metal interfaces; thus, the metallic inclusions are easily drug out increasing the wear rate (Moya *et al.* 2007).

Effective assessment of the interfacial bond strength is possible by two methods: *ab initio* and Molecular Dynamic (MD). Both methods require to assume a model of the considered interface in the form of an atomistic structure. In *ab initio* calculations interactions between atoms are determined by Density Functional Theory (DFT) from the so called *first principles* (Payne *et al.* 1992; Nalepka 2005). Thanks to the solution of the Kohn-Sham equation, one obtains the electron density distributions $\rho(\mathbf{r})$ expressed in the following way:

$$\rho(\mathbf{r}) = 2 \sum_i |\psi_i(\mathbf{r})|^2 \quad (1)$$

where the wave functions $\psi_i(\mathbf{r})$ describe quantum mechanical states of the electrons.

The calculated $\rho(\mathbf{r})$ allows to determine the total energy E_{tot} of the considered atomic system according to the formula:

$$\begin{aligned} E_{tot}(\{\psi_i\}) = & 2 \sum_i \int \psi_i \left(\frac{-\hbar^2}{2m} \right) \nabla^2 \psi_i d^3 \mathbf{r} + \\ & + \int v_{ion}(\mathbf{r}) \rho(\mathbf{r}) d^3 \mathbf{r} + \frac{e^2}{2} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r} d^3 \mathbf{r}' + \\ & + E_{xc}[\rho(\mathbf{r})] + E_{ion}[\{\mathbf{R}_I\}] \end{aligned} \quad (2)$$

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E_{tot} is the sum of the following contributions: the kinetic energy of the non-interacting electrons, the energy of electron – ion interactions, the energy of electron – electron interactions, the exchange-correlation energy and the energy of ion – ion interactions. The exchange-correlation functional E_{xc} introduces the correction of the first summand. In the MD method, the electron density distribution, as well as the total energy, are approximated by assumed functions, whose forms result from the analysis of physical properties of the considered system. The formulated E_{tot} is a function of atomic positions. Using the well known relation (Phillips 2001):

$$f(\mathbf{r}) = -\nabla E_{tot}(\mathbf{r}) \quad (3)$$

one can determine force field acting on atoms system. Thanks to this, according to Newton's Second Law, one can observe how atomic positions are changing in time under the influence of the temperature or the applied load. Thus, it is possible to reconstruct the system of dislocations in the interface and to trace the propagation of a crack.

In order to characterize the bonding formed in the interfacial zone, two kinds of tensile tests are carried out (Yang *et al.* 2005). In the first one, the so called *relaxed tensile test*, the sample cut out from the surroundings of the interface is being stretched in the direction normal to the interface. The test is conducted very slowly so in each of its stages the atoms can relax to the ground state. In the second test, the so called *rigid tensile test*, only the selected interface or interlayer distance is increased, without relaxation. The stress arising during each of the tests can be evaluated as follows (Phillips 2001):

$$\sigma(\epsilon) = \frac{dE(\epsilon)}{d\epsilon} \quad (4)$$

where $E(\epsilon)$ is the total energy per the considered sample referred to the volume of the sample in the equilibrium state.

The maximum value of the stress obtained in the relaxed tensile test is the strength of the interface bond, while σ_{max} from the rigid test describes the strength of the local bonding formed across the interface or the selected interlayer.

The *ab initio* method allows determination of the accurate electron density distribution and hence the kinds of bonds formed across the interface. However, *ab initio* calculations are computationally expensive and thus limited to relatively small systems (about 200 atoms). One analyzes accordingly coherent interfaces (without defects), in the temperature 0 K. The MD method uses an approximate form of E_{tot} . Therefore, the method enables studies of the interfaces containing misfit dislocations and other structural defects in the temperature different from 0 K. Additionally, the MD method gives possibility to introduce a crack and trace its propagation (Zhou *et al.* 2009). Thanks to this, fracture toughness K_{Ic} of CMC composites can be deter-

mined. *Ab initio* results are used to verify the model of interatomic interactions assumed in the MD method but also they give the premises for the production conditions of the composites in which strong enough bonds of interfaces arise.

2. ATOMISTIC MODEL OF THE STRUCTURE OF THE Ni-Al₂O₃ INTERFACE

The structure of the Ni-Al₂O₃ interface is represented by an assumed computational cell, which is repeated parallel to the interface. The computational cell contains a metallic and a ceramic elementary cell. One assumes that their mutual orientation is such as in the epitaxial layers fcc metal/Al₂O₃. Thus, according to High Resolution Transmission Electron Microscopy (HRTEM) studies (Medlin *et al.* 1997), the closed packed planes of Ni crystal and Al₂O₃ crystals are parallel to each other: (111) || (0001). Fulfilling the above assumptions, in the case of the Ni crystal, one forms a hexagonal elementary cell instead of the conventional cubic one. In the computational cell, the Ni cell is supported by the standard, hexagonal cell of corundum crystal. Using the symmetry elements characterizing each of the crystals (Nalepka and Pecherski 2009) as well as the experimental values of the lattice constants and the internal parameters z_{Al} , x_O (Villars 1991) the atoms positions have been generated. The Al₂O₃ and Ni elementary cells are depicted in Figures 1, 2 and the characteristics of the geometries of the cells are contained in Table 1.

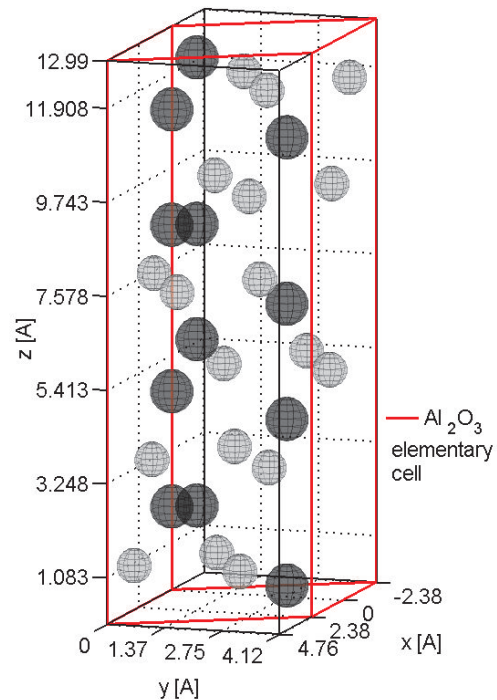
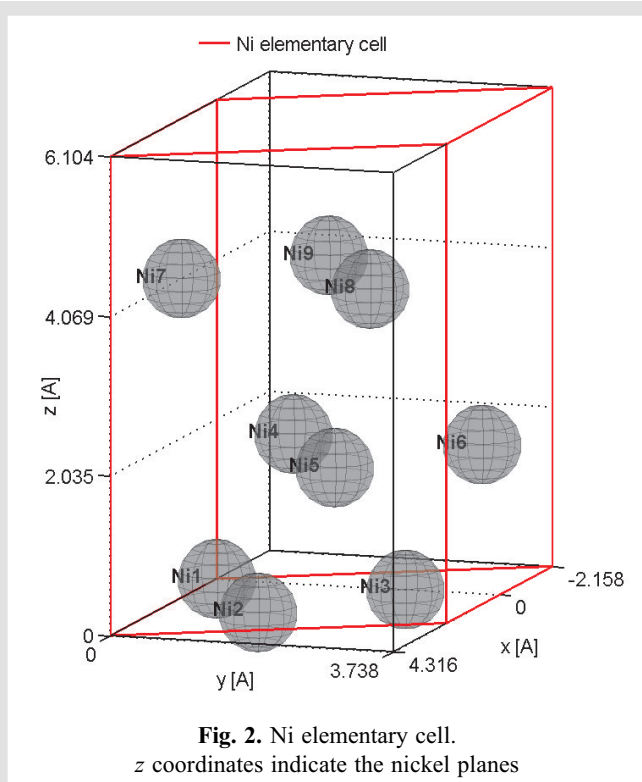


Fig. 1. Al₂O₃ elementary cell. Oxygen atoms (white spheres) are located in the six planes determined by z coordinates.

Aluminum atoms (black spheres) are arranged in three verticals determined by x and y coordinates



The study of the microstructure of the fcc metal/corundum epitaxial layers showed that, depending on the production conditions, the corundum crystal can be terminated by the Al layer (the stoichiometric interface) or by the O layer (the O rich interface) (Scheu *et al.* 2006). The presented model approximates the first type of the interface. In the second case the model is similar, but in the corundum crystal, the last Al layer is removed (Zhang *et al.* 2006).

3. THE MODEL OF THE INTERATOMIC INTERACTIONS ACROSS THE Ni- Al_2O_3 INTERFACE

Identification of an appropriate formula of E_{tot} is difficult because of the complex interactions which arise across the ceramic/metal interface (Nalepka and Pecherski 2009). The only of the existing models, which describes both ionic-covalent bonds and metallic ones is the CTIP+EAM (Charge Transfer Ionic Potential + Embedded Atom Method). We have chosen its corrected version proposed by (Zhou *et al.* 2004, 2005). The total energy of the system E_{tot} consists of two contributions:

$$E_{tot} = E_q + E_n \quad (5)$$

The first of them E_q (CTIP) originates from ionic interactions occurring in the ceramic layer. The value of the energy depends on magnitudes of local atomic charges. The second contribution E_n (EAM) describes the covalent and metallic interactions occurring in the ceramic layer and metal layer correspondingly:

$$E_n = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_i \sum_{\substack{j \\ i \neq j}} \phi_{ij}(r_{ij}) \quad (6)$$

The function F_i is the energy of embedding of the i -th atom in the electron density ρ_i and ϕ_{ij} is the energy of the interaction of a pair of atoms.

The presented model of interatomic interactions had not been applied to the Ni- Al_2O_3 interface before. Therefore, its verification has been performed with use of the experimen-

Table 1

	Symmetry group	Lattice constants/internal parameters	Atom positions relative to the elementary cell	Primitive vectors of the assumed elementary cell
Al_2O_3	$R\bar{3}c$	$a_s = 4.758 \text{ \AA}$ $c_s = 12.99 \text{ \AA}$ $x_O = 0.03064 \text{ \AA}$ $z_{Al} = 0.35228 \text{ \AA}$	basis positions: $O(x_O, 0, \frac{1}{4})$ $Al(0, 0, z_{Al})$	$a = [1, 0, 0]a_2$ $b = [\sqrt{3}/2, -1/2, 0]a_s$ $c = [0, 0, 1]c_s$
Ni	$Fm\bar{3}m$	$a_{fcc} = 3.5236 \text{ \AA}$	Ni1(0, 0, 0), Ni2($\frac{1}{2}, \frac{\sqrt{3}}{6}, 0$) Ni3($0, \frac{1}{\sqrt{3}}, 0$), Ni4($\frac{1}{6}, \frac{\sqrt{3}}{6}, \frac{1}{3}$) Ni5($\frac{2}{3}, \frac{\sqrt{3}}{3}, \frac{1}{3}$), Ni6($\frac{1}{6}, \frac{\sqrt{3}}{2}, \frac{1}{3}$) Ni7($\frac{1}{3}, 0, \frac{2}{3}$), Ni8($\frac{1}{3}, \frac{1}{\sqrt{3}}, \frac{2}{3}$) Ni9($-\frac{1}{6}, \frac{\sqrt{3}}{6}, \frac{2}{3}$)	$a = [1, 0, 0]\sqrt{3/2}a_{fcc}$ $b = [\sqrt{3}/2, -1/2, 0]\sqrt{3/2}a_{fcc}$ $c = [0, 0, 1]\sqrt{3}a_{fcc}$

tal and *ab initio* data (Villars 1991; Shi *et al.* 2007b). For the purpose we have used the program for MD calculations: LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) (Plimpton 1995). The input data were: the identified geometry of the Ni, Al₂O₃ elementary cells (Tab. 1) and the numerical implementations of the CTIP+EAM formulas for the atoms system: Ni, Al, O. The second set of data was obtained by MATLAB package and introduced into LAMMPS in the DYNAMO 86 format (LAMMPS 2003). The diagrams of the CTIP+EAM functions are presented in Figures 3–6.

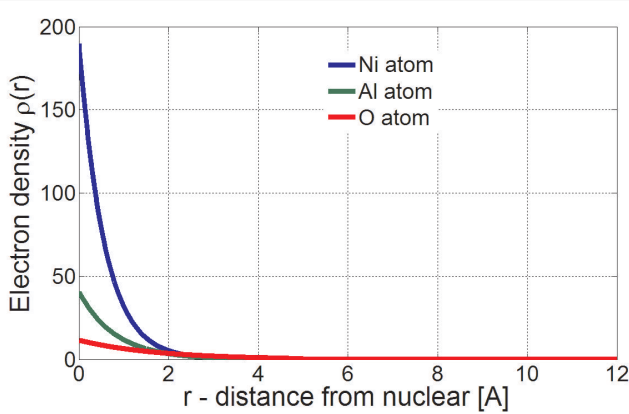


Fig. 3. Distribution of electron density for the Ni, Al, O atoms

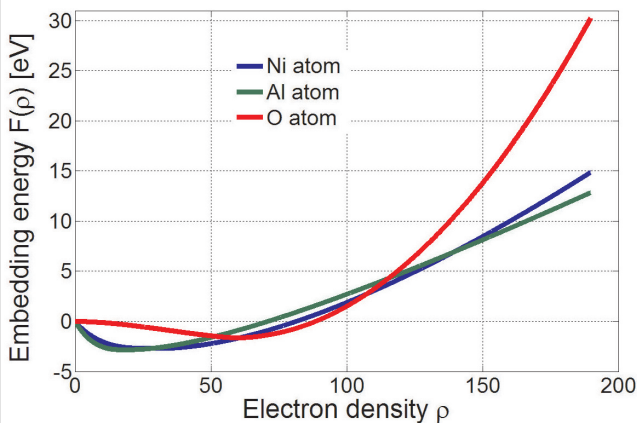


Fig. 4. Embedding energies for atoms: Ni, Al, O as functions of electron density

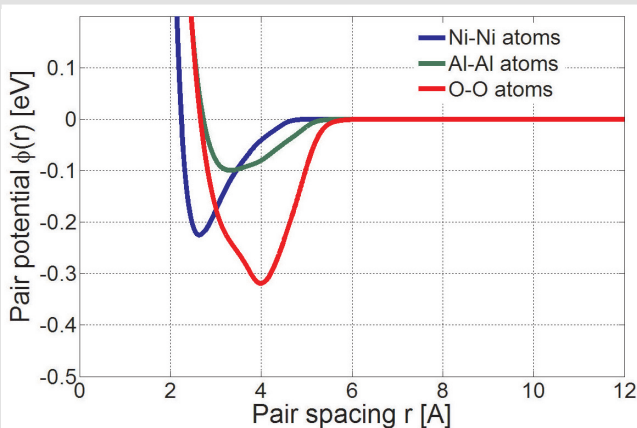


Fig. 5. Energies of pair interactions: Ni-Ni, Al-Al, O-O as functions of the interatomic distance

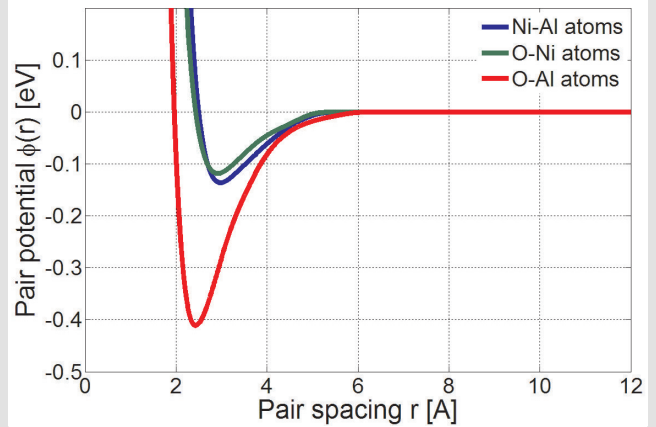


Fig. 6. Energies of pair interactions: Ni-Al, O-Ni, O-Al as functions of the interatomic distance

According to the HRTEM studies of interfaces of the Al₂O₃-Ni composite, the structures of the regions in the distance of $\sim 5\text{Å}$ from the interface remain undisturbed (Sekino *et al.* 1997). Thus, the geometries of the elementary cells of these regions should be the same as in the case of the bulk crystals. The corundum elementary cell has been assumed in the standard form. According to this, the verification of its geometry was performed by X.W. Zhou and H.N.G Wadley (Zhou *et al.* 2005). The obtained lattice constants are consistent with the experimental data. The originally assumed hexagonal elementary cell of the Ni crystal demands an individual verification. For this purpose, the Ni crystal has been subjected to two independent deformation processes. In the first of them there occurs the uniform stretching/compression of the planes parallel to the base of the Ni cell and the lattice constant $a = 4.30 + 0.001 \cdot i$, $i = 1, \dots, 50$. In the second deformation process crystal is uniformly stretched/ compressed in the direction perpendicular to the base and the lattice constants $c = 6.05 + 0.001 \cdot i$, $i = 1, \dots, 50$. In each step of the strain processes there has been performed the minimization of the energy E_{tot} with respect to the position of atoms inside the elementary cell. In the ground state the lattice constants of face centered crystal should satisfy the relation (Kraft and Marcus 1993):

$$c_0 = \sqrt{2}a_0 \quad (7)$$

In order to check if in the case of the assumed model CTIP+EAM the above relationship is preserved, the precision of calculations have been increased. Finally, the following quantities characterizing the equilibrium state have been obtained: $a_0 = 4.31065 \text{ Å}$, $c_0 = 6.09618 \text{ Å}$, $E_0 = 40.049722 \text{ Å}$. The evaluated lattice constants fulfilled the relation (7) and $a_{fcc} = a_0\sqrt{2/3} = 3.51963 \text{ Å}$ is consistent with the experimental value up to the second place (Tab. 1). The described above complex process of deformation is presented in Figure 7.

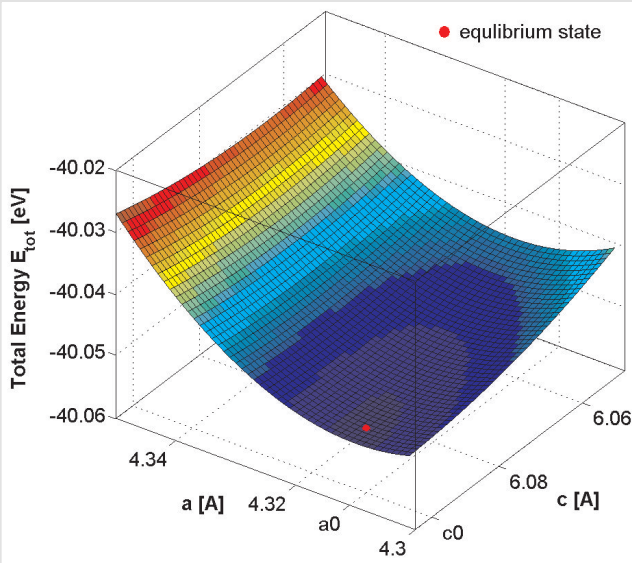


Fig. 7. Total energy of the Ni crystal per the elementary cell as a function of the lattice constants

With regard to complexity of calculations, the *ab initio* method considers ideal systems. Therefore, in the case of metal/ ceramic interface the Ni elementary cell (Fig. 2) is being uniformly stretched in order to the lattice constant a attains the value identical as in the case of corundum (Fig. 1, Tab. 1). For the purpose of obtaining of the equilibrium system, in which the Ni cell is spanned by Al₂O₃ cell, the change of c dimension has been also performed. The presented deformation processes are defined by the following tensor:

$$\varepsilon = \begin{pmatrix} \varepsilon_p & 0 & 0 \\ 0 & \varepsilon_p & 0 \\ 0 & 0 & \varepsilon_z \end{pmatrix} \quad (8)$$

where: $\varepsilon_p = \frac{1}{2} \left[\left(\frac{a}{a_0} \right)^2 - 1 \right]$, $\varepsilon_z = \frac{1}{2} \left[\left(\frac{c}{c_0} \right)^2 - 1 \right]$.

The process of strain determined by Eq. (8) has been applied to the Ni crystal in which the interatomic interactions have been described by means of the CTIP+EAM model. The dependence of the density of the elastic strain energy Φ on the parameters ε_p and ε_z describes the course of above deformation process. The density $\Phi(\varepsilon)$ has been evaluated from the expression (Nalepka 2005):

$$\Phi(\varepsilon) = \frac{E_{tot}(\varepsilon) - E_0}{V_0} \quad (9)$$

where V_0 is the volume of the elementary Ni cell in the equilibrium state. The results are presented in Figure 8.

The red curve is the set of the strain states, subjected to which Ni elementary cell takes new, non-equilibrium forms spanned by the Al₂O₃ cell. According to the assumption of *ab initio* calculations (Shi *et al.* 2007a, b) one of the Ni

cells together with the undeformed corundum cell create the system in the equilibrium state. In the studied strain range, the density of the energy $\Phi(\varepsilon)$ has only one minimum corresponding the identified equilibrium configuration of the Ni cell. This indicates the lack of the metastable states, in which $\Phi(\varepsilon)$ should attain local minima. The result is consistent with the existing *ab initio* calculations (Kraft and Marcus 1993), what confirms correctness of the assumed model of interatomic interactions. Additionally, the conducted calculations reveal, that when the Ni cell takes non-equilibrium forms, spanned by the undeformed corundum cell, the Ni atoms remain in the unchanged positions in reference to the actual edges of the elementary cell. Accordingly, the disturbance of the ordered system of atoms (Fig. 2) pointed out in the *ab initio* calculation (Shi *et al.* 2007a) is invoked only by the bonds arising between atoms of: Ni and O or Al. The configuration of Ni atoms after the formation of the interfacial bond and its strength will be the subject of the further studies.

4. CONCLUSIONS

The application of the CTIP+EAM model to describe interatomic interactions across the interface of the Al₂O₃-Ni composite has been verified. The above model has been specified for the system of atoms: Ni, O, Al. Using the obtained formula for the total energy we have determined the equilibrium configuration of the unconventional, hexagonal elementary cell representing the Ni crystal in the interfacial zone. The evaluated lattice constants are consistent with the

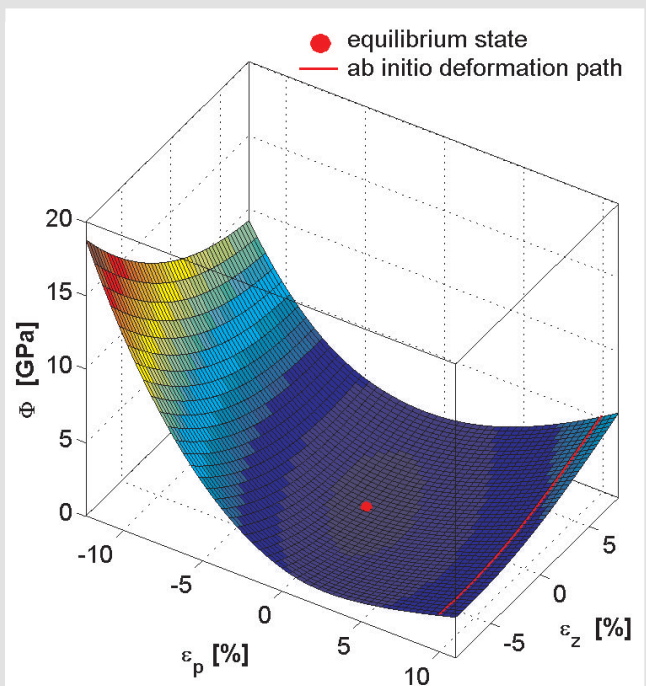


Fig. 8. The density of elastic strain energy Φ stored in the complex process of deformation (8) applied to the Ni crystal. The deformation path employed in the *ab initio* calculation is marked with the red curve

experimental data and preserve the relation specific for the fcc crystal. The last feature is confirmed by the HRTEM studies of the epitaxial layers fcc metal/corundum. The identified elementary cell has been subjected to the complex process of deformation, which enables obtaining of the model used in *ab initio* calculations. In the studied range of strains, the metastable states do not appear, what is consistent with *ab initio* results.

The presented model of interatomic interactions allows determination the strength of the bond formed across the interface free from defects or the interface containing misfit dislocations. In the first case the value should be consistent with the existing *ab initio* calculations. Evaluation of the second quality demands determination of the system of misfit dislocations and thus creation of a model of the interface close to reality. Such a structure can be obtained by identification of the equilibrium configuration of a large computational cell. In the case of Al_2O_3 -Ni interface, the cell consist of $10 \times 10 \times 2$ Al_2O_3 elementary cells and $11 \times 11 \times 4$ Ni elementary cells. Application of the specified model of interatomic interactions to the evaluation of the strength of the bond in the case of the ideal interface and the interface close reality will be the subject of further studies.

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