

# INTERATOMIC POTENTIALS FOR DESCRIBING IMPURITY ATOMS OF LIGHT ELEMENTS IN FCC METALS

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**Abstract.** Parameters of Morse potentials for describing the interactions of atoms of light elements C, N, O with atoms of fcc metals Al, Ag, Ni are found. This set of three metals is unique in that two of them have almost the same radii of atoms, while the other two have almost identical electronegativities. The search for potential parameters was carried out according to the empirical relationships observed for a large number of metals having C, N or O impurities. For this purpose, the most studied characteristics were chosen: the melting or decomposition temperature of the corresponding chemical compound of the metal with the light element and the activation energy of diffusion of the impurity atom in the crystal lattice of the metal. In the paper, in addition, we have corrected the potentials found earlier to describe interatomic interactions in Pd-H and Ni-H systems.

**Keywords:** interatomic potential, molecular dynamics, impurity, interstitial, fcc metal, carbon, nitrogen, oxygen

## 1. Introduction

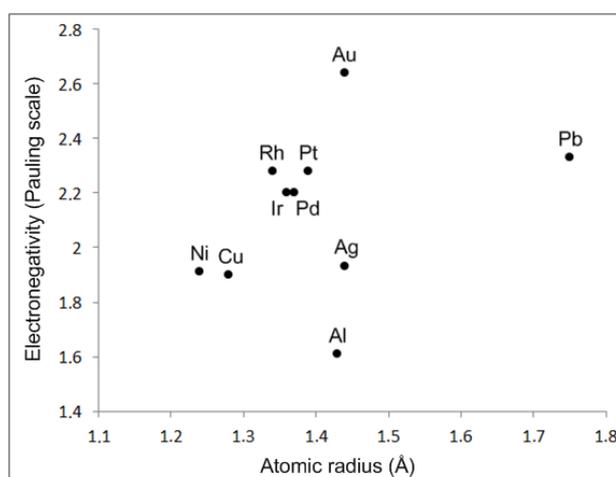
Interaction of impurity atoms with metals is a significant scientific and technological interest, which has a wide range of applications in materials science. Atoms of light elements (primarily the most common ones: hydrogen, oxygen, nitrogen, carbon), forming interstitial defects and phases in metals, have high chemical activity and already at low concentrations strongly influence on the properties of metals. Being effective stoppers of vacancies, dislocations and grain boundaries, the impurities of light elements significantly increase the strength, hardness, frictional properties simultaneously, as a rule, with brittleness [1-3]. A high melting temperature and chemical resistance are typical for many interstitial alloys. Despite the importance of understanding the mechanisms and processes underlying the effect of doping light elements on the properties of metals, now there are many questions regarding the behavior of impurities at the atomic level in the metallic matrix. In particular, the questions of interaction at the atomic level of various interstitial impurities with defects in the crystal lattice, especially dislocations and grain boundaries, remain insufficiently studied. In this case, computer simulation is an effective research tool. However, not so many interatomic potentials are known in the literature describing interactions of impurity atoms with metal atoms, which are necessary for modeling. Moreover, there are no potentials for a number of metals and various impurities found within the framework of one approach, which would allow to judge in the course of studies about any regularities associated with certain characteristics of impurities or metals.

The present paper is devoted to the search for the potentials of the interaction of C, N, O impurity atoms with fcc metals Al, Ag, Ni. The choice of these fcc metals will be explained below. As for the type of crystal lattice, the interstitial alloys, which are usually formed on the basis of metals with hcp and bcc lattices, are more widely known and studied. At the same time, in molecular dynamics models at high temperatures, as a rule, fcc and hcp metals are modeled. Various processes, for example, diffusion and deformation, migration of defects and others, from the position of molecular dynamics, have been studied much better for the fcc lattice, which creates a good foundation for future studies of the influence of impurities on these processes in fcc metals. In the paper, in addition, we have corrected the potentials found earlier [4] to describe interatomic interactions in Pd-H and Ni-H systems.

## 2. Choosing of fcc metals

Impurities of light elements in metals are in the atomar state. Because of their relatively small size, the C, N and O atoms usually occupy octahedral sites (i.e. voids with the largest free volume) in the fcc, hcp and bcc crystal lattices of metals [1,5]. With an ordered arrangement of light atoms in the interstitial sites of the metals, interstitial phases are formed. The first criterion for the possibility of formation of interstitial phases in the metal under consideration is usually indicated the ratio of the radii of the interstitial atom and metal atom. The radii of C, N and O atoms differ slightly in the literature and depend on the chemical bond involved. This is usually 0.77 Å for C, 0.71 Å for N and 0.65 Å for O [1,2]. According to Hagg's rule, with the ratio of the radii of less than 0.59, the metal tends to form interstitial phases with the formation of simple structures [1,3]. All fcc metals, except Ni and Cu, have the ratio of the radii of less than 0.59, but only aluminum forms the stable carbides and nitrides, which indicates the influence of one more factor.

The second important criterion is the strength of the chemical bond, which, according to, for example, [2], indirectly depends on the difference in the electronegativities of the interacting elements. As a rule, the lower the electronegativity of a metal, the higher the tendency to interact with light elements and to the formation of strong bonds with them with the transition from a metallic type to a covalent one. The light elements C, N, O themselves have one of the highest values of electronegativity, i.e. the ability to attract electrons at the formation of a chemical bond: C – 2.55, N – 3.04, O – 3.44 [2,6].



**Fig. 1.** Distribution of fcc metals by electronegativity and atomic radius

Figure 1 shows the distribution of fcc metals by the radius of atoms and electronegativity. The values are taken from [1,6]. Platinum group metals, gold and plumbum practically do not form carbides and nitrides (they are usually unstable and require special

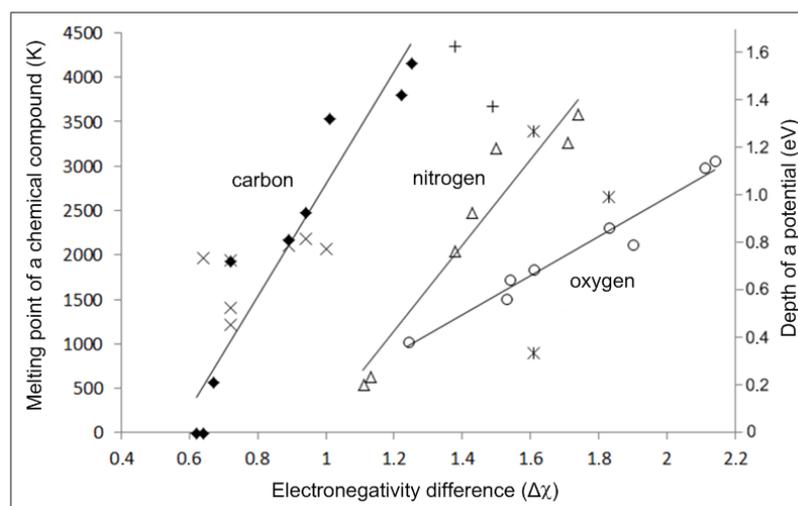
conditions for their formation). Aluminum forms very strong carbides, nitrides and oxides with high values of hardness and melting point. Ni, Cu, Ag are between these metals by electronegativity and, indeed, can form low-stable or unstable carbides and nitrides.

For further study and search of the potentials, fcc metals Ni, Ag, Al were chosen. This set of three metals is unique in that two of them have almost the same radii of atoms, while the other two have almost identical electronegativities. Radii of atoms: Al – 1.43 Å, Ag – 1.44 Å, Ni – 1.24 Å [1]. Electronegativities (Pauling scale): Al – 1.61, Ag – 1.93, Ni – 1.91 [6]. Thus, when obtaining different dependencies for these three metals, the relationship either with the size of atoms or with electronegativity will be seen.

### 3. Empirical relationships for the calculation of the potentials

The search for potential parameters was carried out according to the empirical relationships observed for a large number of metals having C, N or O impurities. For this purpose, the most studied characteristics were chosen: the melting or decomposition temperature of the corresponding chemical compound of the metal with the light element and the activation energy of diffusion of the impurity atom in the crystal lattice of the metal.

One of the universal criteria by which it is possible to evaluate the strength of interatomic interactions and, correspondingly, the depth of the energy well of the interatomic potential, is the melting or decomposition temperature of the substance. Figure 2 shows the dependences of melting or decomposition temperatures of a chemical compound of a metal with carbon, nitrogen or oxygen on the difference in the electronegativities  $\Delta\chi$  of the metal and the impurity. The temperature values are taken from [1, 7, 8]. As an argument, the melting point of the metal  $T_m$  and the product of these values  $T_m \cdot \Delta\chi$  were also considered. The highest correlation was observed in the first case. As can be seen in Fig. 2, within the framework of one type of chemical compound (carbides, nitrides or oxides), the dependence on the difference of electronegativities has a clearly noticeable linear character. It can be concluded that the potential well is indeed proportional to  $\Delta\chi$ , but within the same type of compound.



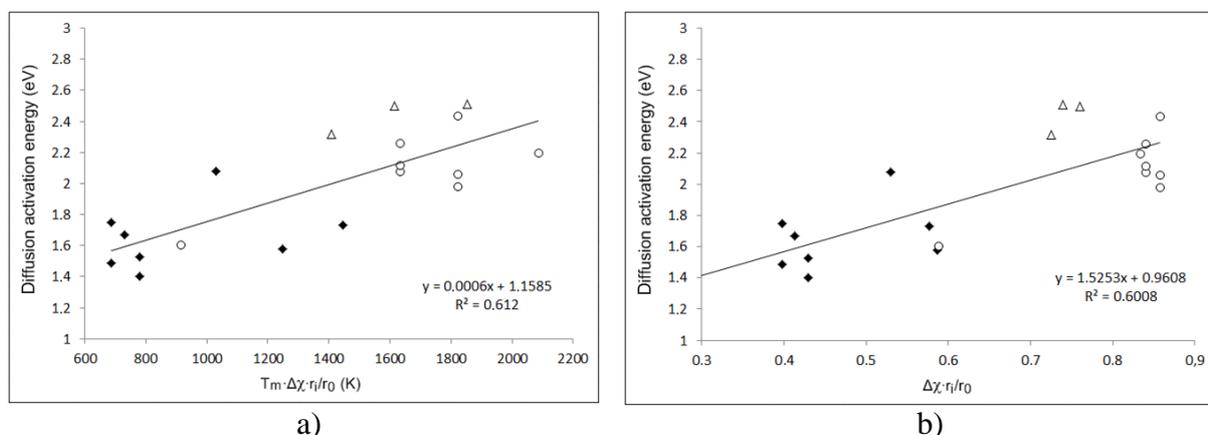
**Fig. 2.** Dependences of the melting or decomposition temperature of a chemical compound (carbide, nitride or oxide) and the depth of potentials from different works of the interaction of the metal and impurity atoms on the difference of electronegativities of the metal and impurity ( $\times$  – metal-carbon potentials,  $+$  – metal-nitrogen potentials,  $*$  – metal-oxygen potentials)

On the right vertical scale in Fig. 2, it is shown the corresponding values of the potential depths, which we found in the literature for the bonds of various metals with atoms of light

elements. When calibrating the right scale, we guided by the most studied and most frequently encountered potentials for such bonds as Fe-C, Al-O, Al-C. The values of the potential depths in the figure for metal-carbon systems are taken from [5, 9-12], for metal-nitrogen systems – from [12], for metal-oxygen systems – from [13-15]. It is seen that in the case of the interaction of metals with carbon (the crosses in the figure), the coincidence, with the exception of a pair of points, is quite good. For the impurities of nitrogen and oxygen, there is very little information in the literature, large depths of the potentials in Fig. 2 for them are explained, as a rule, in that they were not found for solid solutions, but for nitrides and oxides, which as is known are more stronger compounds.

Using the above-mentioned dependencies, empirical values of potential depths for bonds of Al, Ag, Ni with C, N, O have been found, which will be given below in the general table.

The second experimentally determined value, which was used to search for the potentials, was the activation energy of the diffusion of light atoms in a metal. In [16], for example, it is said that this quantity depends linearly on the melting point of the metal. We have analyzed the dependences of the diffusion activation energy found in the literature on various combinations of three parameters: the melting point of the metal  $T_m$ , the difference in the electronegativities  $\Delta\chi$  and the ratio of the radii of the interstitial and the metal atoms  $r_i/r_0$ . The values of the diffusion activation energy for different systems were taken from [16-24]. The values of the activation energy even for the same system can differ significantly in different works. Nevertheless, some general regularities have been found. The activation energy better correlates with the products  $T_m \cdot \Delta\chi \cdot r_i/r_0$  (Fig. 3a) and  $\Delta\chi \cdot r_i/r_0$  (Fig. 3b). As it turned out, the main argument in this case again is the difference of the electronegativities  $\Delta\chi$ . The relative size of the atoms and the melting point of the metal to a lesser extent affect the activation energy of diffusion of the interstitials in metals.



**Fig. 3.** Dependences of the activation energy of the diffusion of impurity atoms in the crystal lattice of a metal from: a)  $T_m \cdot \Delta\chi \cdot r_i/r_0$ ; b)  $\Delta\chi \cdot r_i/r_0$

With the help of the found approximations, the empirical activation energies of the diffusion of C, N and O atoms in Al, Ag and Ni were calculated, which were used in the search for the potential parameters (they will be given in the table below).

#### 4. Potential parameters

The search for the potential parameters for the systems under consideration was carried out using the molecular dynamics method. Interactions of metal atoms with each other were described by the multi-particle EAM Cleri-Rosato potentials [25], built within the tight-binding model. In this case, the energy of the  $i$ -th atom is found using expression

$$U_i = \sum_j A \exp\left(-p\left(\frac{r_{ij}}{r_0} - 1\right)\right) - \sqrt{\sum_j \xi^2 \exp\left(-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right)} \quad (1)$$

Here  $A$ ,  $p$ ,  $q$ ,  $\xi$ ,  $r_0$  are the potential parameters;  $r_{ij}$  is the distance between the  $i$ -th and  $j$ -th atoms. The parameters of the Cleri-Rosato potentials were taken from [25].

To describe the interactions of impurity atoms of light elements with metal atoms and impurity atoms with each other the Morse potential was chosen:

$$\varphi(r_{ij}) = D\beta e^{-\alpha r_{ij}} \left(\beta e^{-\alpha r_{ij}} - 2\right), \quad (2)$$

where  $\alpha$ ,  $\beta$ ,  $D$  are the parameters of the potential. Cleri-Rosato and Morse potentials have proved themselves in numerous calculations performed by the molecular dynamics method [26-30]. Pair potentials are relatively often used by various researchers to describe interatomic interactions in metal-impurity systems. Multi-particle potentials are physically more reasonable, but taking into account the high error of the experimental data on which the potential parameters are selected, as well as the error of the search methods of the parameters themselves, the choice of pair potentials is justified.

Table 1 shows the empirical values of the potential depths  $h$  and the values of the activation energy of impurity diffusion in the metal ( $Q_1$  and  $Q_2$  – for the dependences in Figures 3a and 3b respectively). The right-hand side of the table lists the parameters of the Morse potentials found in the work for the considered bonds, as well as the values of the activation energy of impurity diffusion calculated in the molecular dynamic model.

The activation energy of the diffusion of the atom of a light element in the crystal lattice of a metal was calculated by the technique described by us in [26], which consists in finding the difference in the energy of the calculation block containing the interstitial at the position of the saddle point (between three atoms in the (111) plane) upon passage from the octahedral site to the tetrahedral one and the energy of the calculation block containing the interstitial in the octahedral site. In each case, a thorough dynamic relaxation of the structure was carried out.

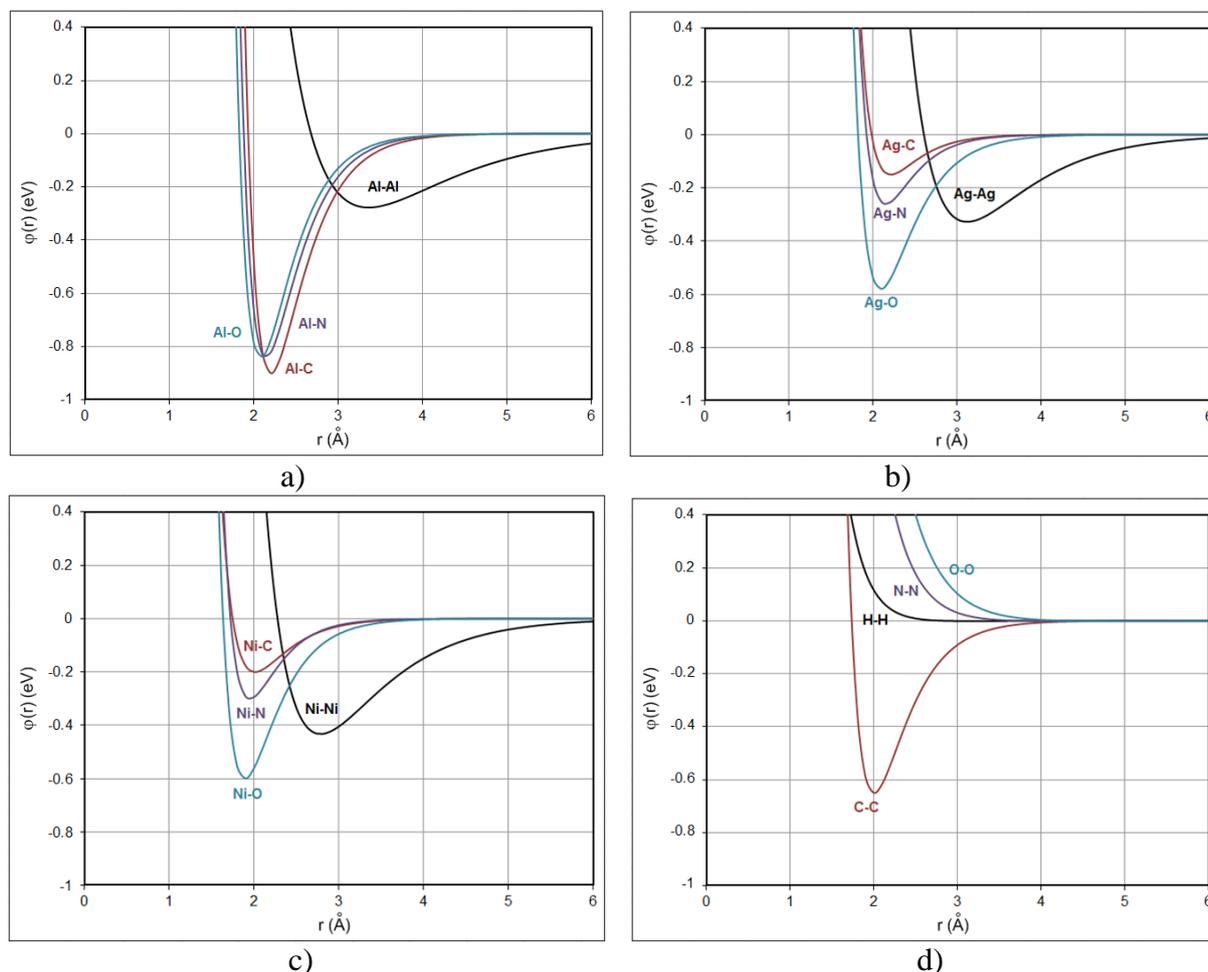
Table 1. Empirical quantities for the search for the potentials and found with their help the parameters of the Morse potentials of the interaction of metal and impurity atoms

Bond	$r_1+r_0, \text{\AA}$	$h, \text{eV}$	$Q_1, \text{eV}$	$Q_2, \text{eV}$	$\alpha, \text{\AA}^{-1}$	$\beta$	$D, \text{eV}$	$Q, \text{eV}$
Al-C	2.20	0.90	1.44	1.73	2.59263	300	0.90	1.34
Ag-C	2.21	0.15	1.40	1.47	2.96429	700	0.15	1.43
Ni-C	2.01	0.20	1.57	1.57	2.63598	200	0.20	1.57
Al-N	2.14	0.84	1.56	2.04	2.66532	300	0.84	1.51
Ag-N	2.15	0.26	1.56	1.80	3.01255	650	0.26	1.64
Ni-N	1.95	0.30	1.83	1.95	3.03257	370	0.30	1.86
Al-O	2.08	0.84	1.62	2.23	2.74220	300	0.84	1.76
Ag-O	2.09	0.58	1.66	2.00	2.58068	220	0.58	1.87
Ni-O	1.89	0.60	1.99	2.18	2.71735	170	0.60	2.04

To describe the interactions of impurity atoms with each other in metals, the potentials proposed by other authors have been taken as a basis. For the C-C bond, the pair potentials from [10,11] were transformed into Morse potentials. For N-N and O-O bonds, potentials were taken from [31,32]. The potential parameters are given in Table 2. Figure 4 shows all the potentials found in this paper.

Table 2. Parameters of Morse potentials for interactions of impurity atoms with each other in a metal

Bond	$\alpha, \text{\AA}^{-1}$	$\beta$	$D, \text{eV}$
C-C	2.62351	190	0.65
N-N	1.55580	700	0.001
O-O	1.26829	500	0.001



**Fig. 4.** Pair potentials of interactions of impurity atoms of light elements with: a) Al; b) Ag; c) Ni. Figure (d) shows the potentials of interaction of impurity atoms with each other in a metal

Unfortunately, in the literature there is very little information on the binding energy of light-element atoms with defects of the crystal lattice of metals. This value would be useful for additional approbation of potentials. For fcc metals, we found only the binding energy of a carbon atom with a vacancy in  $\gamma$ -Fe: 0.37–0.41 eV [33]. These values in the mentioned work were found experimentally and with the help of first-principles calculations. Of the metals under consideration, the characteristics of  $\gamma$ -Fe are closest to Ni (atomic radii: 1.29  $\text{\AA}$  ( $\gamma$ -Fe) and 1.24  $\text{\AA}$  (Ni); differences of electronegativities with carbon: 0.72 (Fe) and 0.64 (Ni)). The binding energy of a carbon atom with a vacancy in nickel, found using the potentials obtained in this paper, turned out to be 0.35 eV, which is close to the values in [33].

In this paper, we also present the potentials found earlier for describing the Pd-H and Ni-H interactions and the corrected potentials for the H-H bond (Table 3). The potential parameters for the Pd-H and Ni-H bonds were calculated by us in [4] using experimental data

on the absorption energy, the activation energy of the above-barrier diffusion of hydrogen in a metal (at normal and high temperatures), the binding energy with a vacancy and dilatation. When searching for potentials for H-H bond, in [4] we relied on the potentials known in the literature. However, it was found that even in the presence of a relatively small well at the H-H potential, in the case of molecular dynamic modeling of a high concentration of hydrogen in metal, hydrogen atoms attract each other and form aggregates consisting of several dozen atoms. There is no mention of the formation of aggregates of impurity hydrogen atoms in real metals in the literature. Therefore, it was decided to use the potential proposed in [34], according to which the hydrogen atoms in a metal matrix repel each other. This potential was transformed into a Morse potential (Fig. 4d), the parameters of which are shown in Table 3.

Table 3. Parameters of Morse potentials for interactions in Pd-H and Ni-H systems

Bond	$\alpha, \text{\AA}^{-1}$	$\beta$	$D, \text{eV}$
Pd-H	0.9	9.76	0.10737
Ni-H	1.2	14	0.1331
H-H	2.11	800	0.001

## 5. Conclusion

In the work, we have found parameters of Morse potentials for describing the interactions of atoms of light elements C, N, O with atoms of fcc metals Al, Ag, Ni. The parameters of the potentials were calculated taking into account empirical dependencies and known characteristics, such as the melting or decomposition temperature of the corresponding chemical compound of a metal with a light element, activation energy of the diffusion of an impurity atom in the crystal lattice of the metal. It was found that the dependences of the melting or decomposition temperature of a chemical compound of a metal with one or another impurity (carbides, nitrides, oxides) on the difference between the electronegativities of the metal and the impurity are clearly linear. When considering the influence of various factors on the activation energy of diffusion of an impurity atom in a metal lattice, it was found that the activation energy is more dependent on the difference between the electronegativities of the metal and the impurity, and on the ratio of the radii of their atoms.

In addition, we have corrected the potentials found earlier to describe interatomic interactions in Pd-H and Ni-H systems. The potentials proposed in this work are intended for computer simulation, in particular by the molecular dynamics method, of impurity atoms of light elements in metals containing various structural defects.

**Acknowledgements.** No external funding was received for this study.

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