fjrs.futa.edu.ng

FUTA Journal of Research in Sciences

ISSN: 2315-8239

FUTA Journal of Research in Sciences, 2014 (1): 72-76

SUTTON-CHEN TYPE FORCE FIELDS FOR OSMIUM AND RUTHENIUM

A.I. Popoola* and I.A. Fuwape
Department of Physics, Federal University of Technology, Akure, Nigeria.
*Email: ispopoola71@gmail.com.

ABSTRACT
The Sutton-Chen type of force fields was derived for osmium and ruthenium using the Finnis-Sinclair form of embedded atom model. The newly derived force fields were used to calculate the compressibility (or bulk modulus) and melting points of Osmium and Ruthenium. The theoretical bulk modulus calculated for osmium was 428 GPa and this falls within the experimental data range (395 GPa – 462 GPa) that have been reported for osmium. The experimental bulk modulus for ruthenium is 321 GPa, while the theoretical bulk modulus obtained with the derived force fields was 322 GPa – giving a difference of only 0.3%. The trends in the results of the newly derived force fields and those in existence for other platinum group metals was similar, indicating that the derived force fields would be suitable and reliable for modeling the mechanical properties of osmium, ruthenium and their related phases.
Key words: Osmium, Ruthenium, Force Fields, Molecular Dynamics

INTRODUCTION

Experimental material design, synthesis and optimization are plagued with many difficulties, including lack of requisite data needed on the physical, thermodynamic and mechanical properties. There are also difficulties with the processing of refractory alloys, due to the high temperature requirements. With the availability of fast computers and efficient algorithms, it is now a routine to compliment experimental alloy developments with theoretical modeling. This does not only help in understanding new material properties, it prevents the expensive and time consuming "trial and error" approach that goes with experimental investigations. Within the Materials Physics community, both the *ab initio* Density Functional Theory (DFT) (Kohn and Sham, 1965; Perdew and Zunger, 1981) and semi-empirical molecular dynamics (MD) (Alder and Wainwright, 1959; Daw and Baskes, 1984) have provided the important theoretical foundations for modern quantum calculation of materials properties. The *ab initio* method is capable of providing direct information regarding a system, but limited in the number of atoms it can handle due to computer time and resources. The semi-empirical molecular dynamics is more appropriate for systems with large numbers of atoms. It is an established tool to evaluate material properties, even at the atomic level (Cagin *et al*., 1999; Papanicolaou *et al*., 2003). Popular models for describing many-body problems such as metallic systems include Embedded Atom Model (EAM) (Daw and Baskes, 1984). The EAM was developed and have been used to study elemental metals and their alloys (Adams *et al*, 1989; Johnson, 1990). The advantage of EAM is its easy empirical descriptions of interatomic forces and all pairwise interactions. Other variants of EAM includes the Glue Model (Ercolessi *et al*., 1988), the Finis-Sinclair for the body centered cubic (bcc) elemental metals (Finnis and Sinclair, 1984) and the noble metals (Ackland and Vitek, 1990), the Sutton-Chen potentials for ten specified fcc elemental metals (Sutton and Chen, 1990) and the Rafii-Tabar and Sutton potentials for the fcc random binary alloys (Rafii-Tabar, 2000).

The platinum group metals (PGMs), have been indicated to play a major role in the design of new class of superalloys (Yamabe-Mitarai *et al*., 1996; Wolf and Hill, 2000; Cornish *et al.*, 2003). The platinum group metals are: platinum, iridium, rhodium, ruthenium, palladium and osmium. Apart from the high melting point of these metals, they mostly have the face centered cubic (fcc) structure and good oxidation and corrosion resistance. The Sutton-Chen (SC) type force fields have been reported for platinum, rhodium, iridium and palladium while those for osmium and ruthenium are yet to be published. The melting point of osmium is the fourth highest of all elements and its compressibility is comparable to that of diamond. Ruthenium is a hard metal, which does not tarnish at normal temperatures. Ruthenium is resistant to acids (Chemicool, 2012; Heraeus-Catalysts, 2012) and its addition to other metals can increase the hardness and corrosion resistance of the alloy (periodic.lanl.gov, 2010). In view of the enormous potentials possessed by these elements, it is important to develop force fields for them so that they can be adequately studied. Given the success of SC potentials at describing pure metals and their related phases, the purpose of the present work is to develop, within the framework of the SC-EAM, force fields for osmium and ruthenium.

RESULTS

For structural materials, mechanical properties are the main concern. The elastic properties (i.e bulk modulus, shear modulus etc) have been used with success to identify many superalloys. The newly derived SC type potential was used to calculate the bulk modulus and melting points of osmium and ruthenium. To ascertain the correctness of the newly derived potentials, results obtained were compared with those of existing SC potentials. All structure relaxation and bulk modulus calculation was done on a super-cell consisting of 6912 atoms.

CALCULATION METHODS

The total potential energy in the Sutton-Chen form of EAM (Sutton and Chen, 1990) is given as:

$$\Phi_i^{SC} = \varepsilon\left[\frac{1}{2}\sum_i\sum_{j\neq i}\phi_{rep}(r_{ij}) - c\sum_i(\rho_i)\right]^{\frac{1}{2}} \quad (1)$$

Where $\phi_{rep}(r_{ij})$ is a pair potential accounting for repulsion between *i* and *j* atomic cores and ρ_i is a local density accounting for the cohesion associated with *i*.

$\phi_{rep}(r_{ij})$ is given by:

$$\phi_{rep}(r_{ij}) = \left(\frac{a}{r_{ij}}\right)^n \quad (2)$$

and

$$\rho_i = \sum_{j\neq i}\left(\frac{a}{r_{ij}}\right)^m \quad (3)$$

In (1), c is a dimensionless quantity, r_{ij} is the spacing between atoms i and j, ε is a quantity with the unit of energy, a, is the lattice parameter and m and n are positive integers with $n > m$. The potential for Os and Ru was deduced from the density functional calculations wherein m and n completely defines (1). The value of c was fixed by the equilibrium condition for each crystal structure (Sutton and Chen, 1990). Table 1, contains the parameters ε, c, m and n fitted for osmium and ruthenium. Other potential parameters for platinum, rhodium, iridium and palladium in Table 1 are from (Cagin *et al.*, 1999).

Each cell was simulated first with the constant temperature-pressure Berendsen ensemble (Berendsen, 1984), to obtain the equilibrium volume, after which it was switched to the constant temperature-volume ensemble (Hoover, 1985) to distort the cell and obtain change in energy. A least-square fit of the energy-volume data was done using the Birch-Murnaghan equation of state (Birch, 1978) to obtain the bulk moduli. The melting points were obtained from the phase transition phenomena. The phase transition from the solid state into the liquid was determined by evaluating the temperature at which a jump in the total energy occurred. All calculations were done with the DL-POLY computer code (Turodov *et al*., 2006). DL-POLY is a molecular dynamics (MD) simulation package that is capable of simulating ten-of-thousands of atoms, in most popular ensembles and boundary conditions. The relaxation time was fixed at 0.1ps. For interacting atoms, cubic periodic boundary condition was applied during the solution of the equations of motion. The Velocity Verlet (VV) algorithm was used to solve all equations at a time-step of 10^{-15}s. All calculations were carried out for 100000-steps of equilibration, with a

production time of 1ps. The derived trends in the MD results are shown in Table 2. For osmium, the theoretical bulk modulus was 428 GPa and this falls within the experimental data range (395 GPa – 462 GPa) that have been reported for osmium. The experimental bulk modulus for ruthenium is 321 GPa, while the theoretical bulk modulus obtained with the derived force fields was 322 GPa - an observed difference of about 0.3%. These results suggest that the force fields are valid and suitable for modeling. However, the melting points of osmium and ruthenium were overpredicted by the derived force fields. The melting point of osmium was overpredicted by about 12% and ruthenium by about 22%. It should be noted also that previously published force fields overpredicted the melting points. For example, the melting point of platinum was overpredicted by about 13%, palladium by about 7%, iridium by about 31% and the melting point of rhodium was overpredicted by about 27%.

Table 1: Sutton-Chen potential parameters for PGMs. Parameters for osmium and ruthenium are new, while those for platinum, rhodium, iridium and palladium are from (Cagin *et al*., 1999)

Metal	n	m	ε (eV)	c	a(Å)
Pt	11	7	9.7894E-3	71.336	3.9163
Rh	13	5	2.4612E-3	305.499	3.7984
Pd	12	6	3.2864E-3	148.205	3.8813
Ir	13	6	3.7674E-3	224.815	3.8344
Os	13	6	3.8665E-3	230.728	3.8640
Ru	14	5	2.6060E-3	323.468	3.8330

Table 2: Calculated bulk modulus and melting temperature for osmium, ruthenium and other platinum group metals using the potentials listed in Table 1. Experimental data are in curly brackets and are from the cited references.

Metal	B (GPa)	MP (K)	Refs.
Pd	195, {180}	1950, {1828}	(James and Lord, 1992)
Pt	387, {278}	2300, {2041}	(Kaye and Laby, 1995)
Ir	422, {306 - 355}	3600, {2739}	(Yngve and Leonid, 2000; Kittel, 2004)
Rh	398, {380}	2850, {2237}	(Kaye and Laby, 1995)
Ru	322, {321}	3200, {2607}	(Eric and Brook, 1992)
Os	428, {395 - 462}	3700, {3306}	(Hyunchae *et al*., 2002; Takemura, 2004; Florent *et al.*, 2004)

CONCLUSIONS

The results obtained from the newly derived SC type force fields for osmium and ruthenium showed similar trends to the results obtained with existing force fields for other platinum group metals. The proximity between the bulk modulus results and existing experimental data showed that the force fields are reliable and suitable for modeling the mechanical properties of these metals and are therefore predicted to work well for their related phases. Melting points was over-predicted both by existing and the newly derived force fields. Defects in crystals are one of the factors known to promote melting and as different defect types were not considered in obtaining the theoretical melting points, it is suggested that the melting point results are suitable only for guiding experiments.

We profoundly thank Prof. J.E. Lowther and Prof. L.A. Cornish for useful discussions. One of us (AIP) acknowledges research support from the

African Materials Science and Engineering Network (AMSEN- an ias-carnegie foundation).

REFERENCES

Ackland, G.J. and Vitek, **V** (1990). Many-body potentials and atomic scale relaxations in noble metal alloys. Physical Review B 41: 3 - 7.

Adams, J.B., Foiles, S.M. and Wolfer, **W.G (**1989). Self-diffusion and impurity diffusion of FCC metals using the 5-frequency model and the Embedded Atom Method. Journal of Materials Research 4: 102 – 112.

Alder, B.J. and Wainwright, T.E (1959). Studies in Molecular Dynamics - General Method. Journal of Chemistry and Physics 31: 459 – 466.

Berendsen, H.J.C., Postma, J.P.M., van Gunsteren, W.F., DiNola, A. and Haak, J.R (1984). Molecular dynamics with coupling to an external bath. Journal of Chemistry and Physics 81: 3684 – 3690.

Birch, F.J (1978). Finite strain isotherm and velocities for single-crystal and polycrystalline NaCl at high pressures and 300 K. Journal of Geophysical Research 83: 1257 – 1268.

Cagin, T., Dereli, G., Uludogan, M. and Tomak, M (1999). Thermal and Mechanical Properties of some FCC Transition Metals. Physical Review B 59: 3468 – 3473.

Cagin, T., Qi, Y., Li, H., Kimura, Y., Ikeda, H., Johnson, W.L. and Goddard III, **W.A (**1999). Calculation of thermal, mechanical and transport properties of model glass formers. In Inoue, A., Johnson, W. L. and Liu, C.T., (Eds.). Bulk Metallic Glasses. Materials Research Society Symposium Series 554: 43-48.

Cornish, L.A., Fischer, B. and Völkl, **R** (2003). Development of Platinum-Group-Metal Based Superalloys for High-Temperature Use. Materials Research Society Bulletin 28: 632 – 638.

Daw, M.S. and Baskes, M.I. (1984). Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals. Physical Reviews B 29: 6443 – 6453.

Ercolessi, F., Parrinello, M. and Tosatti, E. (1988). Simulation of gold in the glue model. Philosophical Magazine A 58: 213 – 226.

Eric, A.B. and Brook, G.B. (1992). Smithells Metals Reference Book. Butterworth-Heinemann. United Kingdom.

Finnis, M.W. and Sinclair, J.E. (1984). A simple empirical N-body potential for transition metals, Philosophical Magazine A 50: 45 – 55.

Florent, O., Daniel, L.F., James, B., Chantel, M.A., David, M.T., Michael, H., Bernard, C. and Bernard, C (2004). Experimental Evidence for a High-Pressure Isostructural Phase Transition in Osmium. Physical Review Letters 93: 095502 (1 – 4).

Hoover, W.G (1985). Canonical dynamics: Equilibrium phase-space distributions. Physical Review A. 31: 1695 – 1697.

Hyunchae, C., Klepeis, J.E., Yeo, C.S. and Young, D.A (2002). Osmium has the lowest experimentally determined compressibility. Physical Review Letters 88: 135701–135704.

James, A.M. and Lord, M.P (1992). Macmillan's Chemical and Physical Data. Macmillan, London.

Johnson, R.A (1990). Phase stability of fcc alloys with the embedded-atom method. Physical Review B 41: 9717 – 9720.

Kaye, G.W.C. and Laby, T.H (1993). Tables of physical and chemical constants. Longman Press. London.

Kittel, C (2004). Introduction to Solid State Physics. Wiley and Sons, India.

Kohn, W. and Sham, L.J (1965). Self-Consistent Equations Including Exchange and Correlation Effects. Physical Review A 140: 1133 – 1138.

Papanicolaou, N.I., Chamati, H., Evangelakis, G.A. and Papaconstantopoulos, **D.A (**2003). Second- moment interatomic potential for Al, Ni and Ni-Al alloys, and molecular dynamics application. Computational Materials Science 27: 191 – 198.

Perdew, J.P. and Zunger, A (1981). Self-interaction correction to density-functional approximations for many-electron systems. Physical Review B 23: 5048 – 5079.

Rafii-Tabar, H (2000). Modelling the nano-scale phenomena in condensed matter physics via computer-based numerical simulations. Physics Reports 325: 239 – 310.

Sutton, A.P. and Chen, J (1990). Long-range Finnis–Sinclair potentials, Philosophical Magazine Letters 61: 139 – 146.

Takemura, K (2004). Bulk modulus of osmium: High-pressure powder x-ray diffraction experiments under quasihydrostatic conditions. Physical Review B 70: 012101 (1 – 4).

Turodov, I.T., Smith, W., Trachenko, **K. and** D**ove**, **M.T (**2006). New dimensions in molecular

dynamics simulations via massive parallelism. Journal of Materials Chemistry 16: 1911 – 1918.

Wolf, I.M. and Hill, P.J (2000). Platinum Metals-Based Intermetallics for High-Temperature Service. Platinum Metals Review 44: 158 – 165.

www.chemicool.com/elements/ruthenium. Accessed May 18, 2012.

www.heraeus-catalysts.com. Accessed April 12, 2012.

www.periodic.lanl.gov/rhodium. Accessed December, 2010.

Yamabe-Mitarai, Y., Ro, Y., Maruko, T. and Harada, **H (**1996). Ir-Base Refractory Superalloys for Ultra- High Temperatures. Scripta Materiala 35: 211 – 215.

Yngve, C. and Leonid, D. (2000). Compressibility measurements on iridium. Journal of Alloys and Compounds 306: 26 – 29.