THE EFFECTS OF ALUMINUM OR SCANDIUM ON THE TOUGHNESS, DENSITY AND PHASE STABILITY OF IRIDIUM, PLATINUM, RHODIUM AND PALLADIUM

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ABSTRACT

The effects of the substitution of aluminum or scandium on the density, toughness as well as the stability of the phases formed by such an addition on platinum, iridium, rhodium and palladium metals were evaluated with the density functional quantum mechanical calculation methods. All the metals had four atoms per formula unit. When one atom (25%) of the metals was substituted with aluminum or scandium, the densities reduced by about 42% (platinum with aluminum); about 32% (palladium with aluminum) and about 36% (rhodium with aluminum). The density drop was about 41% (platinum with scandium); about 33% (rhodium with scandium) and about 29% (palladium with scandium). Both aluminum and scandium led to a debilitating reduction in the toughness of platinum and rhodium, while the toughness of iridium and palladium were systematically improved. The substitution of some atoms of platinum with scandium was predicted with highest prospects on the account of improved density, toughness and structure stability.

Keywords: Density, Toughness, Platinum, Palladium, Rhodium, Iridium

INTRODUCTION

Commercially, pure metals are rarely used. They are used in the form of an intermetallic (alloy) according to their required physical properties. Intermetallics are particularly attractive, because they can be achieved with good oxidation and corrosion resistances, low density, high strength and stiffness at room temperature. Iridium (Ir), platinum (Pt), rhodium (Rh) and palladium (Pd) are promising candidates for developing new generation superalloys (Yamabe-Mitarai *et al.*, 1996; Wolf and Hill, 2000; Cornish et al., 2003). These metals have the face centered cubic structure (fcc) and high melting points. The major concerns in using these metals are their densities and strength at room temperature (Yamabe-Mitarai *et al.*, 1996). When a solid solution is formed between two or more metals, several things, including formation of new phases, improvement or otherwise in ductility and strength are possible. The effects of the addition of aluminum or scandium on the density and toughness of platinum, iridium, palladium and rhodium as well as the stability of the phases formed by the addition are evaluated. Scandium and aluminum were chosen as the alloying elements because they have comparable and low ($\approx 3\ g.cm^{-}3$) densities. The crystal structure for iridium, platinum, rhodium and palladium is fcc (Fig. 1) with the space group Fm-3m. This structure has four atoms per formula unit, with atoms at positions: (0, 0, 0), (0, ½, ½), (½, 0, ½), (½, ½, 0). Each atom in an fcc lattice has 12 nearest-neighbours, giving the structure a closed pack arrangement of atoms.

In evaluating the effects of scandium or aluminum on the density and toughness of platinum, iridium, rhodium and palladium, one atom of these metals (at position 0, 0, 0) was substituted with scandium or aluminum. The new structure arrangement is shown in Figure 1. This structure type is designated as $L1_2$ (Pearson, 1967) in the Strukturbericht notation or as *cP*4 in the Pearson's symbol (space group Pm-3m). All the evaluations done in this paper are theoretical, and the intention is to provide a guide on the effects of scandium or aluminum at improving or otherwise the toughness, density and to see if the phases formed with these metals are stable at ground state.

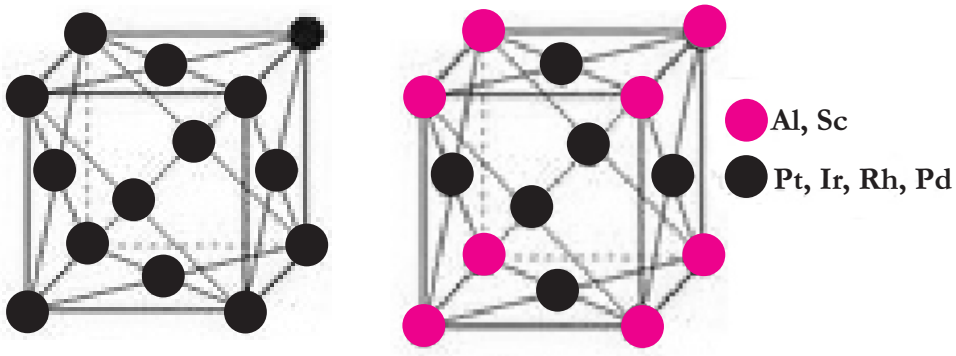


Figure 1: Crystal Structure for Pure Iridium, Platinum, Rhodium and Palladium (left). Crystal Structure in which one Atom of Iridium, Platinum, Rhodium and Palladium have been replaced with either Aluminum or Scandium (right). This latter structure type is designated as $L1_2$ in the Strukturbericht notation or as *cP*4 in the Pearson's symbol (space group Pm-3m).

CALCULATION METHODS

All the three elastic constants (c_{11}, c_{12}, c_{44}) needed to describe a cubic structure was evaluated using the VASP computer code (Kresse and Furthmüller, 1996). VASP is a package for performing quantum mechanical calculations on molecules and solids. It uses the variation method (Hafner, 2008) to solve the Kohn-Sham equation for each unit cell. All approximations to the Kohn-Sham equation, was obtained, using the generalized gradient approximation (GGA) (Perdew *et al.*,1996). Integration over the Brillouin zone was performed on an 8×8×8 grid according to the Monkhorst-Pack (Monkhorst and Pack, 1976) scheme. Forces on the atoms were allowed to relax to less than 0.001eV/Å during geometrical optimizations. From the elastic constants, the bulk modulus (B) and the shear modulus (G) were evaluated. The relationship between the bulk modulus, shear modulus and the elastic constants are defined in Equations 1 – 6.

$$B_V = \frac{c_{11} + 2c_{12}}{3} \quad (1)$$

$$G_V = \frac{c_{11} - c_{12} - 3c_{44}}{5} \quad (2)$$

$$B_R = \frac{c_{11} + 2c_{12}}{3} \quad (3)$$

$$G_R = \frac{5(c_{11} - c_{12})c_{44}}{[4c_{44} + 3(c_{11} - c_{12})]} \quad (4)$$

where B_V and G_V are the bulk and shear moduli as defined according to the Voigt approximations (Voigt, 1928) and B_R and G_R are the bulk and shear moduli according to the Reuss approximations (Reuss, 1929). The results were obtained according to Equations 5 and 6, because these averages have been found to give a better estimation of elastic properties (Hill, 1952):

$$B = \frac{1}{2}(B_V + B_R) \quad (5)$$

$$G = \frac{1}{2}(G_V + G_R) \quad (6)$$

The density (ρ^{cal}, in g.cm^{-3}) was calculated using Equation 7.

$$\rho^{cal} = \frac{M_W \times Z}{Cell\ Vol. \times 0.60225} \quad (7)$$

where Z = number of atoms per formula unit, M_W = molecular weight of the elements, $Cell\ Vol$ = cell volume in Å^3.

The microscopic electronic structure is used to evaluate many physical properties of an intermetallic compound. When an alloy is formed, electron redistribution does take place, and this leads to many different structures and phases. The density of states (DoS) plots is a valuable tool for evaluating the phase stability of a structure. The DoS describes the number of states per interval of energy available to be occupied by electrons. For a free electron gas, the DoS can be defined as:

$$N(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} \quad (8)$$

Where m is the atomic mass, $\hbar$ is the Planck's constant and E is the energy of the system.

RESULTS AND DISCUSSION

Density

The calculated results alongside experimental values are given in Table 1. For platinum, iridium, rhodium and palladium, the proximity between the calculated results and experimental data showed that the calculated results are reliable enough to make predictions. When one atom (25%) of platinum, iridium, rhodium and palladium was substituted with aluminum or scandium, the calculated density results (ρ^{cal}) showed a decrease in the density by about 43% (iridium with aluminum); about 42% (platinum with aluminum); about 32% (palladium with aluminum); about 36% (rhodium with aluminum). The density of iridium dropped from 22 $g.cm^{-3}$ to 12.79 $g.cm^{-3}$ (about 42% drop in density) when one atom of iridium was substituted with scandium. The density drop was about 41% (platinum with scandium); about 33% (rhodium with scandium) and about 29% (palladium with scandium).

Table 1: The Calculated Elastic Constants (c_{11}, c_{12}, c_{44}), Bulk Modulus (B), Shear Modulus (G), B/G Ratio, Poisson's Ratio (v) and Density (ρ^{cal}) for Platinum, Iridium, Rhodium and Palladium as well as their alloy with Aluminum and Scandium. Experimental data are in square brackets and are from **(**Simmons and Wang, 1971; Eric *et al.*, 1992).

Mater.	c_{11} (GPa)	c_{12} (GPa)	c_{44} (GPa)	B (GPa)	G (GPa)	B/G	v	ρ^{cal} ($g.cm^{-3}$)
Pt	306 [347]	231 [251]	76 [76]	256 [278]	65 [61]	3.95	0.38 [0.38]	21 [21]
Ir	570 [590]	251 [249]	237 [262]	357 [355]	226 [210]	1.58	0.24 [0.26]	22 [22]
Pd	202 [227]	159 [176]	73 [72]	174 [180]	52 [44]	3.35	0.37 [0.39]	11 [12]
Rh	408 [413]	192 [194]	174 [184]	264 [270]	161 [150]	1.63	0.25 [0.26]	12 [12]
Ir_3Al	389	239	164	289	136	2.34	0.30	12.63
Pt_3Al	327	179	115	228	108	2.12	0.30	12.24
Pd_3Al	171	125	87	140	60	2.33	0.31	7.43
Rh_3Al	271	196	128	220	91	2.42	0.32	7.64
Ir_3Sc	358	198	164	358	198	1.81	0.27	12.79
Pt_3Sc	292	162	115	292	162	1.99	0.29	12.36
Pd_3Sc	201	124	89	201	124	2.19	0.30	7.78
Rh_3Sc	258	159	119	258	159	2.01	0.29	8.06

Toughness

The toughness (ductility) of a material correlates with the Poisson's ratio. The higher the Poisson's ratio of crystalline or amorphous metals at low temperatures, the better the ductility (Pugh, 1954; Lewandowski *et al.,* 2005). Brittle materials would have Poisson's ratio that is less than 1/3, while ductile materials would have higher values (Frantsevich *et al.*, 1982). Another empirical relation linking materials ductility with its elastic moduli showed that a high bulk (*B*) to shear (*G*) modulus (*B*/*G*) ratio would signify ductility while a low value would signify brittle nature (Pugh, 1954). The value separating ductile and brittle materials is around 1.75. If B/G > 1.75, the material would behave in a ductile manner, otherwise the material would behave in a brittle manner (Pugh, 1954). The trends given by both the Poisson's and B/G ratios are similar and are shown in Figure 2. Out of the pure metals, platinum is predicted with the highest toughness, followed by palladium, rhodium and with iridium having the least toughness. The toughness of platinum and palladium are predicted to reduce with addition of aluminum and scandium, while the toughness of iridium and rhodium are predicted to be systematically improved with addition of aluminum and scandium.

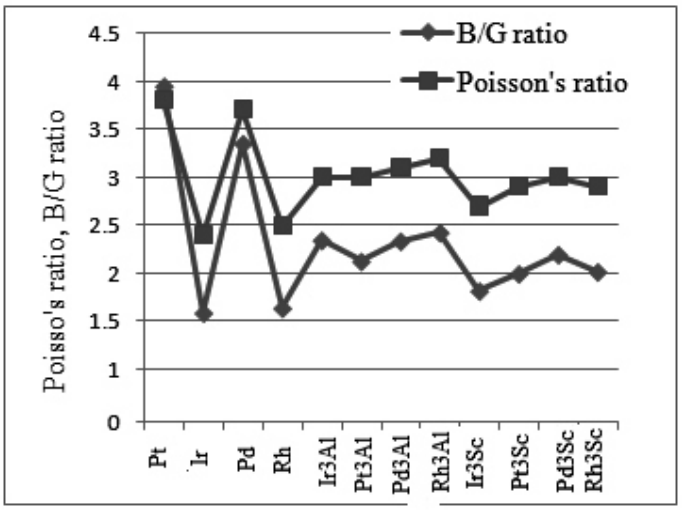


Figure 2: Comparison of B/G and the Poisson's Ratios between Platinum, Iridium, Rhodium and Palladium as well as their alloy with Aluminum or Scandium in the $L1_2$ Structure. The Poisson's Ratio are Magnified by a Factor of 10

Phase Stability

The DoS plot for all the $L1_2$ structures formed between platinum, iridium, palladium, rhodium with aluminum are shown in Figure 3 while those with scandium are shown in Figure 4. At zero temperature, the $L1_2$ phase is not feasible in Pt_3Al, Ir_3Al, Pd_3Al and Rh_3Al.

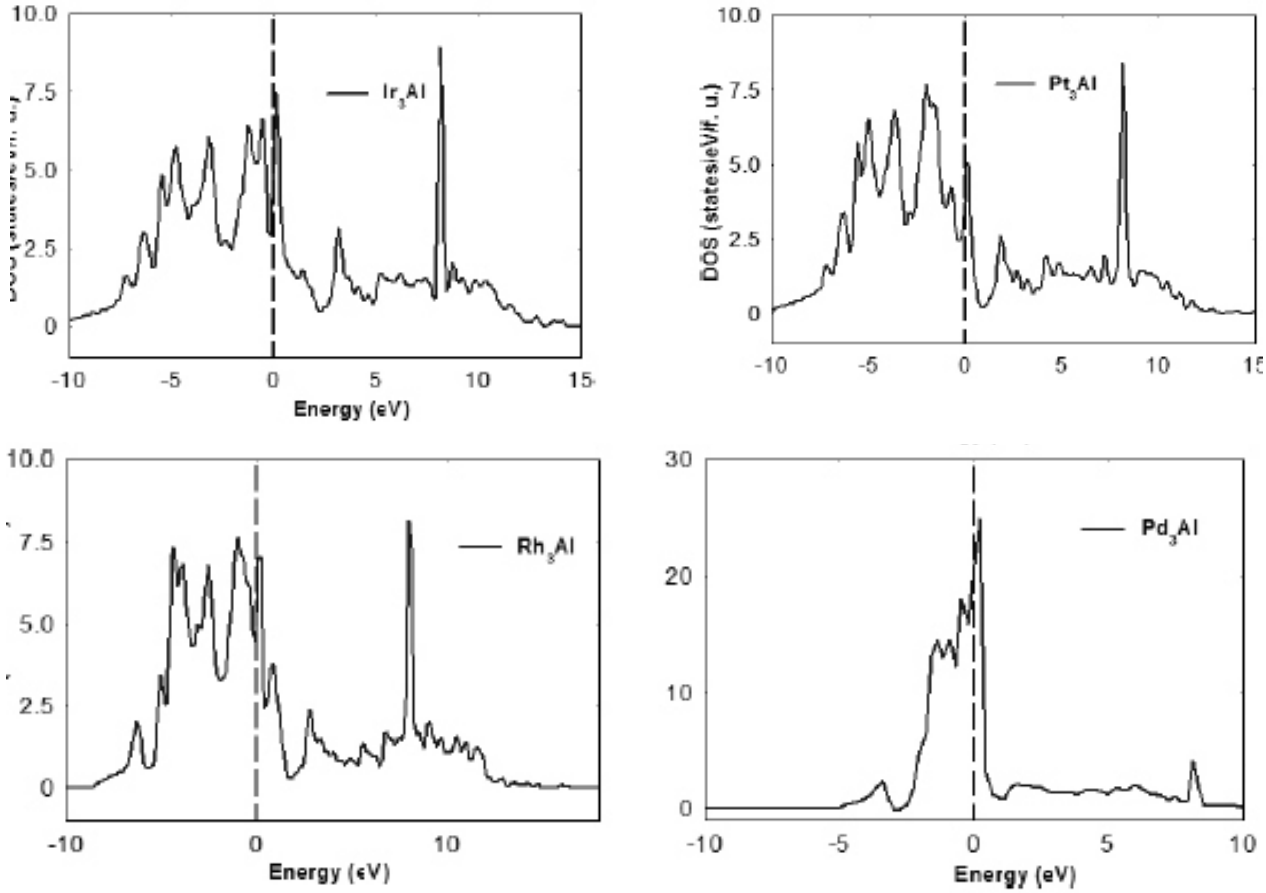
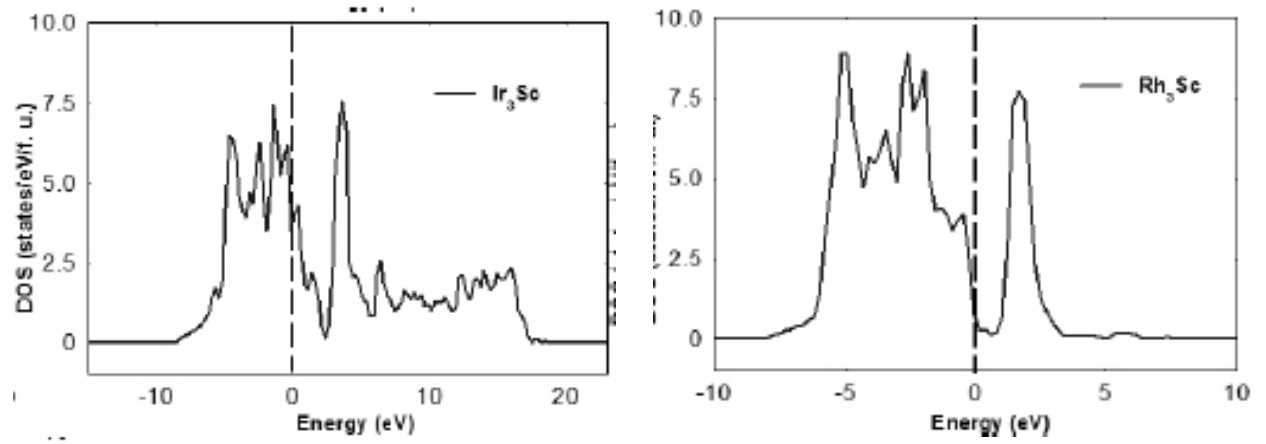


Figure 3: The Total Electronic Density of States for Phases of Iridium with Aluminum (Ir_3Al), Platinum with Aluminum (Pt_3Al), Rhodium with Aluminum (Rh_3Al) and Palladium with Aluminum (Pd_3Al). Energies Relative to Fermi Level are Indicated by the Dotted Vertical Lines.

The Fermi level, E_F, on the DoS plot for these compounds were on the anti-bonding (high energy) side (Fig. 3). Therefore, replacing one atom (25%) out of the four atoms per formula unit of platinum, iridium, rhodium or palladium with aluminum is predicted to result into the formation of not a $L1_2$ but a metastable structure. According to the DOS plots (see Fig. 4), the addition of scandium into platinum in the stoichiometry Pt_3Sc is predicted to give a stable $L1_2$ phase at zero temperature. The Fermi level for this compound was exactly at the pseudogap. The E_F was on the non-bonding (low energy) part of the DoS spectrum for Ir_3Sc, Pd_3Sc and Rh_3Sc.



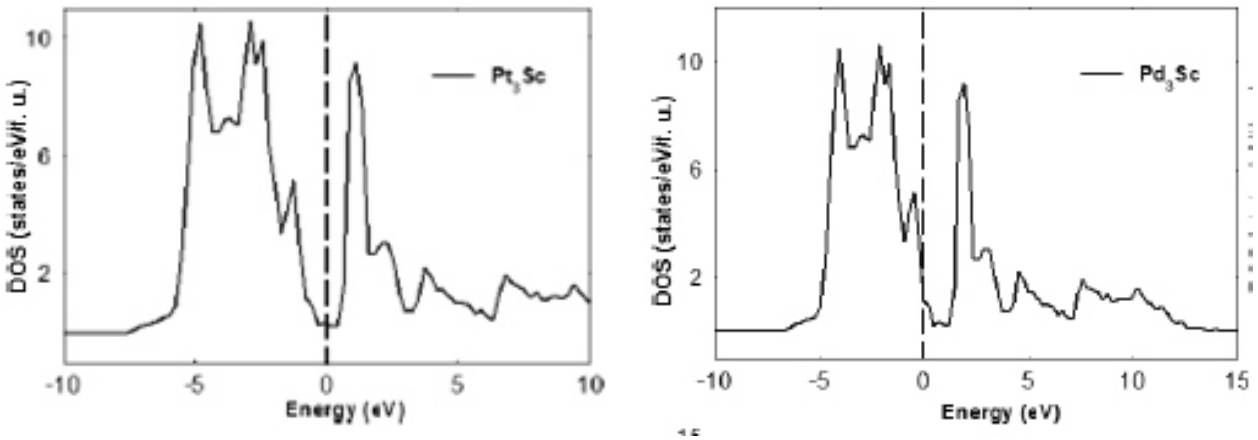


Figure 4: The Total Electronic Density of States for Phases of Iridium with Scandium (Ir_3Sc), Rhodium with Scandium (Rh_3Sc), Platinum with Scandium (Pt_3Sc) and Palladium with Scandium (Pd_3Sc). Energies Relative to Fermi Level are Indicated by the Dotted Vertical Lines.

The tendency for the formation of the $L1_2$ phase is highly predicted only with additional elements. To attain a more stable structure, the E_F needs to move further into the pseudogap. Elements such as cobalt and chromium that have high electrons could play a crucial role in this regard.

CONCLUSIONS

The toughness, density as well as the stability of the structure formed when about 25% of platinum, iridium, rhodium and palladium are substituted with aluminum or scandium was evaluated. The reduction in the density when one atom of platinum or iridium was substituted with one atom of aluminum was comparable with the density obtained when one atom of iridium or platinum was replaced with scandium. Density differential of about 3% was however observed when one atom of rhodium or palladium was substituted with scandium as against rhodium/palladium with aluminum. Despite lower density in favor of the intermetallics when compared with the pure metals, toughness are predicted to be badly affected in platinum plus aluminum, platinum plus scandium, palladium plus aluminum and palladium plus scandium. Toughness is predicted to improve in iridium when alloyed with aluminum/scandium and in rhodium plus aluminum or scandium.

The phase stability studies showed that replacing 25% of platinum, rhodium, palladium and iridium with aluminum would not produce the $L1_2$ structure. Rather, the structures are predicted to be metastable at the ground state. Without any additional element, replacing 25% of platinum with scandium is predicted to produce the $L1_2$ structure at ground state. Additionally, $L1_2$-Ir_3Sc, $L1_2$-Pd_3Sc and $L1_2$-Rh_3Sc can be achieved but with some additional elements. The $L1_2$ structure has closed packed planes and many directions for slip. For cold temperature workability, any material with the $L1_2$ structure is expected to show good properties, including strength. From the foregoing, the prospect of the addition of aluminum or scandium to platinum, iridium, rhodium and palladium in terms of reduction in density, toughness improvements and phase stability without any additional elements is predicted highest between platinum with scandium, followed by palladium with scandium, rhodium with scandium and finally iridium with scandium.

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REFERENCES

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

Eric A. Brandes, and Brook, G.B. (Editors). 1992. *Smithells Metals Reference Book*. Butterworth-Heinemann Ltd., UK.

Frantsevich, I.N. Voronov, F.F. & Bokuta, S.A. 1982. *Handbook of Elastic Constants and*

Moduli of Metals and Insulators. Kievl, Naukova Dumka.

Hafner, *J. 2008*. *Ab-initio* simulations of materials using VASP: Density-functional theory and beyond. *J. of Comput. Chem.* 29, 2044–2078 .

Hill, R. 1952. The Elastic Behaviour of a Crystalline Aggregate. *Proc. Phys. Soc.* 65, 349 -354.

Kresse, G. and Furthmüller J. 1996. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **6,** 15-50.

Lewandowski, J.J. Wang, W.H. and Greer, A.L. 2005. Intrinsic plasticity or brittleness of metallic glasses. *Phil. Mag. Lett.* 85, 77 - 87.

Monkhorst, H.J. and Pack, J.D. 1976. Special points for Brillouin-zone integrations. *Physical Review B. 1***3,** 5188 – 5192.

Pearson, W.B. 1967. *A Handbook of Lattice Spacings and Structures of Metals and Alloys*. Pergamon, Oxford.

Perdew, J.P. Burke, K. and Ernzerhof, M. 1996. Generalized gradient approximation made simple. *Physical Review Letters* 77, 3865 – 3868.

Pugh, S.F. 1954. Relations between elastic moduli and plastic properties of polycrystalline pure metals. *Philosophical Magazine* 45, 823 – 843 .

Reuss, A. 1929. Berechnung der Fliessgrenze von Mischkristallen auf Grund der Plastizitätsbedingung für Einkristalle. *Z. Angew. Math. Mech.* 9, 49 - 58.

Simmons, G.and Wang, H. 1971. *A Handbook of Single Crystal Elastic Constants and Calculated Aggregate Properties*. MIT Press, Cambridge.

Voigt, W. 1928. *Lehrbuch der Kristallphysik. Teuibner, Leipzig*. 830 - 831.

Wolf, I.M. and Hill, P.J. 2000. Platinum Metals-Based Intermetallics for High-Temperature Service. *Plat. Met. Rev.* 44, 158 – 165.

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

Moduli of Metals and Insulators. Kievl, Naukova Dumka.

Hafner, *J. 2008. Ab-initio* simulations of materials using VASP: Density-functional theory and beyond. *J. of Comput. Chem.* 29, 2044–2078.

Hill, R. 1952. The Elastic Behaviour of a Crystalline Aggregate. *Proc. Phys. Soc.* 65, 349 -354.

Kresse, G. and Furthmüller J. 1996. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **6,** 15-50.

Lewandowski, J.J. Wang, W.H. and Greer, A.L. 2005. Intrinsic plasticity or brittleness of metallic glasses. *Phil. Mag. Lett.* 85, 77 - 87.

Monkhorst, H.J. and Pack, J.D. 1976. Special points for Brillouin-zone integrations. *Physical Review B. 1***3,** 5188 – 5192.

Pearson, W.B. 1967. *A Handbook of Lattice Spacings and Structures of Metals and Alloys.* Pergamon, Oxford.

Perdew, J.P. Burke, K. and Ernzerhof, M. 1996. Generalized gradient approximation made simple. *Physical Review Letters* 77, 3865 – 3868.

Pugh, S.F. 1954. Relations between elastic moduli and plastic properties of polycrystalline pure metals. *Philosophical Magazine* 45, 823 – 843.

Reuss, A. 1929. Berechnung der Fliessgrenze von Mischkristallen auf Grund der Plastizitätsbedingung für Einkristalle. *Z. Angew. Math. Mech.* 9, 49 - 58**.**

Simmons, G.and Wang, H. 1971. *A Handbook of Single Crystal Elastic Constants and Calculated Aggregate Properties.* MIT Press, Cambridge.

Voigt, W. 1928. *Lehrbuch der Kristallphysik. Teuibner, Leipzig.* 830 - 831.

Wolf, I.M. and Hill, P.J. 2000. Platinum Metals-Based Intermetallics for High-Temperature Service. *Plat. Met. Rev.* 44, 158 – 165.

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