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Influence of Temperature and Orientation on Elastic, Mechanical, Thermophysical and Ultrasonic Properties of Platinum Group Metal Carbides

Ultrasonic properties of PGM carbides

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Abstract

The elastic, mechanical, thermophysical and ultrasonic properties of platinum group metal (PGM) carbides XC (X: Rh, Pd, Ir) have been investigated at room temperature. The Coulomb and Born-Mayer potential model has been used to compute second and third order elastic constants (SOECs and TOECs) at 0K and 300K. The obtained values of SOECs are used to evaluate the mechanical properties such as Young's modulus, bulk modulus, shear modulus, Pugh's indicator, Zener anisotropic constant and Poisson's ratio at room temperature. The materials show the brittle nature as the value of Pugh's indicator for PGM carbides has been achieved less than or nearly equal to 1.75. Again the values of SOECs are used to compute the ultrasonic velocities along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions for the longitudinal and shear modes of wave propagation. Further the values of Debye temperature, thermal conductivity, specific heat per unit volume, energy density, average value of ultrasonic Grüneisen parameter, thermal relaxation time, non-linear parameter have been calculated with the help of SOECs, TOECs, ultrasonic velocities, density and molecular weight. Finally, the ultrasonic attenuation

due to phonon-phonon interaction and due to thermoelastic relaxation mechanisms have been calculated with the use of all associated parameters. The calculated values of elastic, mechanical, thermophysical and ultrasonic properties are compared with available literature and discussed.

1. Introduction

During the last few years much attention has been given to the study of different properties of platinum group metals and their alloys especially the carbides due to their peculiar applications in science and engineering (1-5). The platinum group metal carbides have excellent mechanical and thermophysical properties such as a great hardness, large strength, wear resistance and high melting point. Many theoretical and experimental studies have been done about the structural, mechanical, dynamical, electronic and optical properties of the platinum metal carbides by the investigators (6-14). Li et al. (1) synthesized the platinum carbide (PtC) under extreme conditions and considered as a potential candidate for superhard materials. Ono et al. (2) reported the synthesis of platinum carbide by the synchrotron X-ray diffraction method at pressure greater than 75 GPa at high temperature. Jyoti et al. (3) presented a comprehensive study of elastic, mechanical, thermophysical and ultrasonic properties of novel platinum carbide in rock-salt and wurtzite structural phases at room temperature. Iridium carbide with various stoichiometry were investigated by Li et al. (4) using the first principle method. Rabah et al. (5) carried out the stabilities and mechanical properties of ideal stoichiometric palladium mono carbide in five different phases. A study of the cohesive energies of 4d- transition metal carbides has been performed by Guillermet et al. (6). Bugaev et al. (7) focussed on the formation of carbide phase in the bulk region and on the surface of supported palladium nano particles. They also investigated X-ray absorption spectroscopy study of carbide formation. The structural, electronic, vibrational and thermodynamical

properties of transition metal carbides RuC, RhC, PdC, and AgC have been investigated by Soni et al. (8) using the plane wave pseudopotentials method with the generalised gradient approximation (GGA) in the frame of density functional theory. Ateser et al. (9) studied structural, mechanical and dynamical properties of PdC to predict most stable structure using GGA approximation based on Perdew-Burke-Ernharf (PBE) function synthesis, properties and simulation of platinum group metal carbides have been done by Ivanovski (10). First principle computation method has been performed to understand the peculiarities of mechanical stability, elastic, electronic properties and chemical bonding for platinum group metal carbides RhC, PdC and IrC by Bannikov et al. (11). Li (12) investigated the structural and electronic properties of PdC using local density approximation and GGA. Tan et al. (13) studied potential energy curves and spectroscopic constants of 23 states of rhodium carbide (RhC) using complete active space multi configuration self-consistent field (CASMCSCF) followed by first order configuration interaction (FOCI) calculation. A new synthesis method to make rhodium carbide has been investigated by Wakisaka et al. (14). Ksouri et al. (15) has been investigated structural, elastic and thermodynamical properties of metal carbides MC (M=Ir, Rh, Ru). Spectroscopic characterization of chain to ring structural evolution in platinum carbide clusters has been studied by Zhang et al. (16).

In view of these circumstances and taking into account that there are no precise and complete analysis available from elastic properties to ultrasonic properties of PGM carbides, the authors have investigated temperature dependent elastic, mechanical, thermodynamical and ultrasonic properties of platinum group metal (PGM) carbides XC (X: Rh, Pd, Ir) along $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ crystallographic directions.

The layout of this paper is given as follows: the theoretical background in Section 2, the results and discussions are presented and discussed in section 3. Section 4 includes the concluding remarks of the investigation.

2. Theoretical Background

The Coulomb and Born-Mayer potential has been applied to compute the second and third order elastic constants (SOECs and TOECs) at temperature 0K and 300K for the PGM carbides. The theoretical calculation of elastic constants is based upon stress strain method expressed by Hooke's law (17).

Hooke's law for an anisotropic medium can be given as

$$\sigma_{ij} = C_{ijkl}\eta_{kl} \quad (i)$$

here $i, j, k, l = 1, 2, 3$ and C_{ijkl} is a fourth rank tensor called elastic stiffness constant. σ_{ij} is second rank stress tensor for the anisotropic material and η_{kl} is the Lagrangian strain tensor.

$$\partial\eta_{kl} = \frac{1}{2} \left[\left(\frac{\partial x_k}{\partial a_1} \right) \left(\frac{\partial x_l}{\partial a_K} \right) - \delta_{ij} \right] \quad (ii)$$

where a and x are initial and final position of a material point and δ_{ij} is the Kronecker's delta.

To deform any solid elastically work is stored in form of potential energy. The elastic energy density is defined as the energy per unit volume of a cubical structure. The elastic energy density for a deformed solid can be expanded as a power series of strains. The coefficients of terms higher than quadratic in strains are defined as higher order elastic constants. The elastic constant of n^{th} order defined by (17) is

$$C_{ijklmn} = \left(\frac{\partial^n F}{\partial \eta_{ij} \partial \eta_{ij} \partial \eta_{ij} \dots} \right)_{\eta=0} \quad (iii)$$

The tensor notation can be written as

$$C_{IJK \dots} = C_{ijklmn \dots} = \left(\frac{\partial^n F}{\partial \eta_{ij} \partial \eta_{ij} \partial \eta_{ij} \dots} \right)_{\eta=0} \quad (iv)$$

the indices are contracted as $ij=I, jk=J, 11 \rightarrow 1, 22 \rightarrow 2, 33 \rightarrow 3, 23 \rightarrow 4, 31 \rightarrow 5, 12 \rightarrow 6$. Here F is the free energy density of the undeformed material.

The free energy density of the material at temperature T is given as

$$F^{Total} = U + F^{Vib} \quad (v)$$

Where U stands for internal energy per unit volume of the crystal when all ions are at rest on their lattice point, which is given by

$$U = \frac{1}{2V_C} \sum \phi_{\mu\nu}(r) \quad (vi)$$

Where r is the distance between the μ^{th} and ν^{th} ions, $\phi_{\mu\nu}(r)$ is the interaction potential between μ^{th} and ν^{th} ions. It is the sum of long-range Coulomb potential $\phi_{\mu\nu}(C)$ and the short range Born Mayer repulsive potential $\phi_{\mu\nu}(B)$. V_C is the volume of elementary cell. The interaction potential $\phi_{\mu\nu}(r)$ can be expressed as

$$\phi_{\mu\nu}(r) = \phi_{\mu\nu}(C) + \phi_{\mu\nu}(B) \quad (vii)$$

$\phi(C)$ and $\phi(B)$ may be expressed as

$$\phi_{\mu\nu}(C) = \pm \left(\frac{e^2}{r_0} \right) \text{ and } \phi_{\mu\nu}(B) = A \exp\left(-\frac{r_0}{b}\right) \quad (viii)$$

\pm sign is used for like and unlike ions. Here e is the electronic charge, r_0 is the nearest neighbour distance, A is strength parameter and b is hardness parameter respectively.

Strength parameter A is defined as

$$A = -3b \left(\frac{e^2}{r_0^2} \right) \left[6 \exp\left(\frac{-r_0}{b}\right) + 12\sqrt{2} \exp\left(\frac{-\sqrt{2}r_0}{b}\right) \right]^{-1} \quad (ix)$$

Vibrational free energy F^{Vib} is given by

$$F^{Vib} = \frac{k_B T}{NV_C} \sum_{i=0}^{3sN} \ln 2 \sinh(h\omega_i / 2k_B T) \quad (x)$$

Where N is the number of the cells in the crystal, and s is the number of ions per unit cell, ω_i is vibrational frequency corresponding to i^{th} mode of atomic vibration and k_B is the Boltzmann constant.

Elastic constants of second and third order at temperature T from Eqn (iv), (v) and (vi) are written as

$$C_{IJ} = C_{IJ}^0 + C_{IJ}^{Vib} \quad \text{and} \quad C_{IJK} = C_{IJK}^0 + C_{IJK}^{Vib} \quad (\text{xii})$$

The SOECs and TOECs are obtained as the sum of static elastic constants at absolute zero temperature and vibrational energy contribution at particular temperature. Where the superscript 0 indicates the static constant at 0K and superscript 'vib' indicates the vibrational portion of elastic constant at a certain temperature. The expression to compute SOECs and TOECs are given in literature (18).

The SOECs are applied to compute the mechanical properties of PGM carbides such as bulk modulus (B), shear modulus (G), Young modulus (Y), Poisson ratio (σ), Zener anisotropy (A_n) and Pugh's ratio (B/G) at room temperature (17,18). The expression for B , Y , G , σ and A_n are given below:

$$B = \frac{(C_{11} + C_{12})}{2} \quad (\text{xiii})$$

$$G = \frac{(C_{11} - C_{12} + 3C_{44})}{10} + \frac{2.5(C_{11} - C_{12})C_{44}}{(4C_{44} + 3(C_{11} - C_{12}))} \quad (\text{xiv})$$

$$Y = \frac{9GB}{(G + 3B)} \quad (\text{xv})$$

$$\sigma = \frac{(3B - 2G)}{(6B + 2G)} \quad (\text{xvi})$$

$$A_n = \frac{2C_{44}}{(C_{11} - C_{12})} \quad (\text{xvii})$$

Further SOECs of PGM carbides have been used to compute the ultrasonic velocities along different directions. When acoustical wave propagates through PGM carbides, it gets diffuse into one longitudinal and two shear acoustic waves. There are three modes of acoustical

velocity i.e. V_L , V_{S1} and V_{S2} along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ crystallographic directions. The acoustical velocity depends on SOECs and mass density by the following ways.

Along $\langle 100 \rangle$ direction

$$V_L = \sqrt{(C_{11}/\rho)}; \quad V_{S1} = V_{S2} = \sqrt{(C_{44}/\rho)}; \quad (xvii)$$

Along $\langle 111 \rangle$ direction

$$V_L = \sqrt{(C_{11} + 2C_{12} + 4C_{44})/3\rho}; \quad V_{S1} = V_{S2} = \sqrt{(C_{11} - C_{12} + C_{44})/3\rho}; \quad (xviii)$$

Along $\langle 110 \rangle$ direction

$$V_L = \sqrt{(C_{11} + C_{12} + 2C_{44})/2\rho}; \quad V_{S1} = \sqrt{C_{44}/\rho}; \quad V_{S2} = \sqrt{(C_{11} - C_{12})/\rho}; \quad (xix)$$

From ultrasonic velocities the Debye average velocity (V_D) can be calculated in the following way.

Along $\langle 100 \rangle$ and $\langle 111 \rangle$ direction

$$V_D = \left[\frac{1}{3} \left\{ \frac{1}{V_L^3} + \frac{2}{V_{S1}^3} \right\} \right]^{-1/3} \quad (xx)$$

Along $\langle 110 \rangle$ direction

$$V_D = \left[\frac{1}{3} \left\{ \frac{1}{V_L^3} + \frac{1}{V_{S1}^3} + \frac{1}{V_{S2}^3} \right\} \right]^{-1/3} \quad (xxi)$$

The Debye average velocity is used to calculate the Debye temperature (θ_D) (17) as follows-

$$\theta_D = \frac{h}{k_B} \left(\frac{3nN\rho}{4\pi M} \right)^{1/3} V_D \quad (xxii)$$

where k_B is Boltzmann constant, N is Avogadro's number, h is the Planck's constant, M is the molecular weight, ρ is the density and n is number of atoms per unit cell. The Debye temperature is used to compute the thermal conductivity. The expression for κ is given below.

$$\kappa = \frac{A \bar{M}_a \delta \theta_D^3 n^{1/3}}{\gamma^2 T} \quad (xxiii)$$

Where δ (in Å) is the cube root of volume per atom, $A=3.04 \times 10^{-8}$, \bar{M}_a is defined as average atomic mass in amu. γ is defined as Grüneisen parameter. Grüneisen parameter along different directions has been computed by using the (θ_D/T) Tables in literature (19). κ is defined as thermal conductivity which has been calculated by Morelli and Slack's approach (20). When ultrasonic waves pass through PGM carbides, the energy is dissipated. The loss in the material occur due to different reasons for example electron-phonon interaction, phonon-phonon interaction, thermoelastic relaxation, grain boundaries and magnon-phonon interaction etc. At high temperature ($\geq 100\text{K}$) the most conspicuous causes of ultrasonic losses in the PGM carbides are Akhieser loss (phonon-phonon interaction) and loss due to thermal relaxation mechanisms. The computation of ultrasonic attenuation in the chosen PGM carbides has been done by Mason's approach (21). The ultrasonic attenuation due to Akhieser loss is given by

$$\left(\frac{\alpha}{v^2}\right)_L = \frac{4\pi^2 \tau_L E_0 D_L}{6\rho V_L^3} \quad (\text{xxiv})$$

$$\left(\frac{\alpha}{v^2}\right)_{S1} = \frac{4\pi^2 \tau_{S1} E_0 D_{S1}}{6\rho V_{S1}^3} \quad (\text{xxv})$$

$$\left(\frac{\alpha}{v^2}\right)_{S2} = \frac{4\pi^2 \tau_{S2} E_0 D_{S2}}{6\rho V_{S2}^3} \quad (\text{xxvi})$$

Where α is the ultrasonic attenuation constant, v is the frequency of ultrasonic wave, V_L is the ultrasonic velocity for longitudinal wave, E_0 energy density which is defined by (θ_D/T) Table of AIP handbook (19). The required time in which thermal phonons regain its original shape distorted by ultrasonic waves for exchange of acoustic and thermal energy is known as thermal relaxation time (τ_{th}) and is given as

$$\tau_{th} = \tau_s = \frac{\tau_L}{2} = \frac{3\kappa}{C_V V_D^2} \quad (\text{xxvii})$$

Where C_V is specific heat capacity at constant volume and it has been computed using data from the AIP handbook (21). D is non-linearity parameter (acoustic coupling constant) which is given by

$$D = 9 \langle (\gamma_i^j)^2 \rangle - \frac{3 \langle \gamma_i^j \rangle^2 C_V T}{E_0} \quad (\text{xxviii})$$

The thermoelastic attenuation caused by thermoelastic relaxation is given by (21)

$$\left(\frac{\alpha}{v^2} \right)_{th} = \frac{4\pi^2 \langle \gamma_i^j \rangle^2 \kappa T}{2\rho V_L^5} \quad (\text{xxix})$$

3. Results and Discussion

The computed values of SOECs and TOECs for the chosen PGM carbides are obtained using Coulomb and Born-Mayer potential model. The two parameters i.e., nearest neighbour distance and hardness parameter play important role to evaluate SOECs and TOECs for the PGM carbides. The nearest neighbour distance (r_0) for RhC, PdC and IrC are 2.172 Å, 2.215 Å and 2.20 Å respectively (11) which is assumed to be constant at temperature 0K and 300K and hardness parameter b is selected 0.303 Å (22) for all materials.

Table I SOECs and TOECs (10^{11}Nm^{-2}) of PGM carbides at 0K and 300K

Material	Temp(K)	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}
RhC	0	7.39	4.67	4.67	-106.67	-19.04	7.03	7.03	-19.04	7.03
	300	8.39	4.58	4.73	-114.46	-19.76	5.60	7.09	-19.34	7.03
		2.927 ^a	1.819 ^a	0.454 ^a						
		4.25 ^b	2.51 ^b	0.43 ^b						
PdC	0	4.39 ^c	2.56 ^c							
		7.27	4.29	4.29	-105.85	-17.50	6.50	6.50	-17.50	6.50
	300	8.24	4.19	4.34	-113.64	-18.20	5.06	6.56	-17.79	6.50
		3.76 ^b	1.73 ^b	0.56 ^b	-114.67 ^f	-12.59 ^f	4.09 ^f	4.75 ^f	-13.12 ^f	4.67 ^f
Pd	300	2.76 ^c	1.81 ^c	0.49 ^f						
		3.72 ^f	3.07 ^f							
		3.21 ^h	2.44 ^h	1.11 ^h						
IrC	0	1.94 ⁱ	1.50 ⁱ	0.72 ⁱ						
		7.31	4.41	4.42	-106.16	-18.02	6.68	6.68	-18.02	6.68
		8.29	4.32	4.47	-113.90	-18.72	5.24	6.74	-18.31	6.68
IrC	300	4.39 ^c	2.57 ^c							

Ir	300	5.80 ^g	2.42 ^g	2.56 ^g
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^a See Ref. (9); ^b See Ref. (11); ^c See Ref. (23); ^f See Ref. (3); ^g See Ref. (32); ^h See Ref. (33); ⁱ See Ref. (34)

The computed values of SOECs and TOECs using Equations (i)-(xi) for the PGM carbides have been presented in **Table I** at 0K and 300K with existing comparable SOECs (9,11,23,3,32,33,34). There are some variations in the obtained results and existing results as we have neglected the polarizability of the ions, van der Waal's forces and many body forces. It is obvious from **Table I** that values of elastic constants have been found highest for RhC and lowest for PdC, which shows that RhC has better intrinsic properties among the chosen PGM carbides. **Table I** depicts that the values of C_{11} and C_{44} increase while C_{12} decreases with increase in temperature for the chosen materials. The TOECs C_{111} , C_{112} , C_{116} have been found negative and decreases with increase in temperature, C_{123} decreases with temperature while C_{144} increases with temperature and the value of C_{456} remains constant due to absence of vibrational part of energy. C_{11} , C_{12} , C_{44} , C_{123} , C_{144} have positive temperature coefficients and C_{111} , C_{112} , C_{166} have negative temperature coefficients while C_{456} remains constant irrespective of temperature change. Because of no contribution of vibrational part of energy, Cauchy's relations defined by Cousin (24) at 0K are satisfied $C_{12}^0 = C_{44}^0$; $C_{112}^0 = C_{166}^0$; $C_{123}^0 = C_{456}^0 = C_{144}^0$ in our case. Cauchy's relation holds good at 0K but does not hold good on higher temperature because on increasing temperature the nature of interacting forces becomes more ionic. The orders of the elastic constants of the investigated materials are comparable with PtC (3). The SOECs obeyed the Born stability criterion ($C_{11}+2C_{12}>0$, $C_{44}>0$, $C_{11}-C_{12}>0$) (25) which prove that chosen materials are elastically stable at room temperature in B1 Phase. The TOECs are greater for RhC and lesser for PdC. TOECs values are not available for direct comparison for PGM carbides, so the results of TOECs for the chosen PGM carbides have been compared with our recent publication on PtC (3), the order of the TOECs have the same quantum. SOECs of PGM carbides have been compared with existing values of PGMs and we have found that

values of SOECs for PGMs carbides are higher than PGM pure metals. These elastic constants are further applied to compute various mechanical constants like Young's modulus (Y), bulk modulus (B) and shear modulus (G), Pugh's ratio (B/G), Poisson's ratio (σ) and Zener anisotropic ratio (A_n) using Equations (xii)-(xvi) and are presented in **Table II**.

Table II Mechanical properties of PGM carbides at room temperature

Material	$Y(10^{11} \text{Nm}^{-2})$	$B(10^{11} \text{Nm}^{-2})$	$G(10^{11} \text{Nm}^{-2})$	B/G	σ	A_n
RhC	8.31 1.23 ^b	5.85 2.844 ^a 3.09 ^b 2.82 ^e	3.29	1.78	0.26 0.43 ^b	2.48
Rh	3.86 ^j	2.80 ^j	1.53 ^j	1.83 ^j	0.26 ^j	
PdC	8.05 1.56 ^d 1.17 ^e	5.54 2.68 ^a 2.188 ^b 2.78 ^c 2.41 ^d 2.13 ^e 2.70 ^h	3.20 0.49 ^b 0.42 ^e	1.73 4.456 ^b	0.26 0.396 ^b 0.39 ^d	2.14 3.2 ^e
Pd	1.28 ^j	1.90 ^j	0.46 ^j	4.13 ^j	0.39 ^j	
IrC	8.14	5.64 3.18 ^e	3.23	1.75	0.26	2.25
Ir	5.38 ^j	3.78 ^j	2.14 ^j	1.78 ^j	0.26 ^j	

^a See Ref. (26); ^b See Ref. (9); ^c See Ref. (12); ^d See Ref. (11); ^e See Ref. (23); ^h See Ref. (33) ^jSee Ref. (35)

From **Table II** it is clear that bulk modulus and Young's modulus for RhC is highest and for PdC is lowest which predicts that RhC is stiffer and less compressible than any other PGM carbides. The higher value of shear modulus for RhC shows that it is much harder than PdC and IrC. The Pugh's ratio (B/G) (27) fracture-toughness ratio is calculated and we find that the B/G ratios for chosen materials are less or nearly equal to 1.75 which shows that the chosen PGM carbides are brittle in nature (28). The Poisson's ratio limit for non-central nature of inter atomic forces is given by $0.2 < \sigma < 0.5$. In present case calculated values of Poisson ratio

is 0.26 which shows that applied forces are non-central in PGM carbide materials (29). For covalent materials the Poisson ratio is almost 0.1 while 0.25 for ionic bond. The calculated Poisson's ratio is greater than 0.25 which shows that ionic contributions in inter atomic bonding are dominant for chosen materials. With the help of Poisson's ratio (σ) and Cauchy pressure ($C_{12} - C_{44}$) the intrinsic ductility and brittleness can be predicted in case of PGM carbides. For ductile materials Poisson's ratio $\sigma > 0.3$ and Cauchy pressure ($C_{12} - C_{44}$) > 0 while for brittle materials Poisson's ratio $\sigma < 0.3$ and Cauchy pressure ($C_{12} - C_{44}$) < 0 . From Table II values of Poisson's ratio for PGM carbides are less than 0.3 ($\sigma < 0.3$) and Cauchy's pressure is less than zero ($C_{12} - C_{44} < 0$) for all chosen PGM carbides. This confirms chosen PGM carbides are brittle in nature. For isotropic materials A_n should be equal to 1 but in our case A_n is greater than 1 which indicates the chosen materials are anisotropic in nature. The obtained values are compared with existing values in available literatures (9,11,12,23,26,35). The variations in the results are due to different computational methods. Our calculations are based on computer programming MATLAB and manually which gives precise results.

To study changes in elastic, mechanical, thermophysical and ultrasonic properties exhibited by platinum group metal carbides we have compared the properties of PGMs carbides with the existing properties of platinum group metals. If we compare mechanical properties of platinum group metal carbides (RhC, PdC and IrC) to existing values of pure platinum group metals (Rh, Pd and Ir) we find that values of Young modulus, bulk modulus and shear modulus of PGMs are less than PGMs carbides. The Pugh's ratio for PGMs is greater than 1.75 which shows ductile nature of PGMs. Thus platinum group metals are softer and ductile while platinum group metal carbides are harder and brittle in nature.

The values of ultrasonic velocity for any material depends on SOECs and density along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions for longitudinal and shear modes of wave propagation. The ultrasonic velocities (V_L and V_S) have been computed using Equations (xvii)-

(xix). Further the Debye average velocity V_D has been computed using Equations (xx)-(xxi) along different directions. The computed values of V_L , V_S and V_D are presented in **Table III**.

Table III Orientation dependent ultrasonic velocities (in 10^3ms^{-1}) of PGM carbides at room temperature

Material	Direction	V_L	V_{S1}	V_{S2}	V_D
RhC	<100>	3.00	2.25	2.25	2.42
	<110>	3.47	2.25	1.43	1.88
	<111>	3.61	1.75	1.75	1.97
PdC	<100>	3.02	2.19	2.19	2.37
		5.85 ^f	1.98 ^f	1.98 ^f	2.25 ^f
	<110>	3.42	2.19	1.50	1.93
		5.60 ^f	1.98 ^f	2.88 ^f	2.34 ^f
	<111>	3.54	1.76	1.76	1.98
		5.593 ^a	2.324 ^a	1.75 ^f	2.63 ^a
Pd	<100>	5.65 ^f	1.75 ^f		1.99 ^f
		4.743 ^k			
	<110>	2.436 ^k			
IrC	<111>	1.456 ^k			
	<110>	2.28	1.68	1.68	1.81
	<111>	2.60	1.68	1.12	1.45
	<111>	2.70	1.33	1.33	1.49

^a See Ref. (9); ^f See Ref. (3); ^k See Ref. (36)

The Debye average velocity for RhC is highest along <100> direction and lowest for IrC along <110> direction. The calculated values are compared with the values obtained by Ateser et al. (9) which is in approximately agreement with the values of PdC along <100>. The decreasing value of ultrasonic velocity from RhC to IrC is due to increase in density. The Debye temperature (θ_D) is the temperature of a crystal's highest normal mode of vibration and it correlates the elastic properties with the thermodynamic properties such as phonons, thermal expansion, thermal conductivity, specific heat and lattice enthalpy (26,30). θ_D has been computed using the Equation (xxii). The computed values of θ_D along different directions are presented in **Figure 1**.

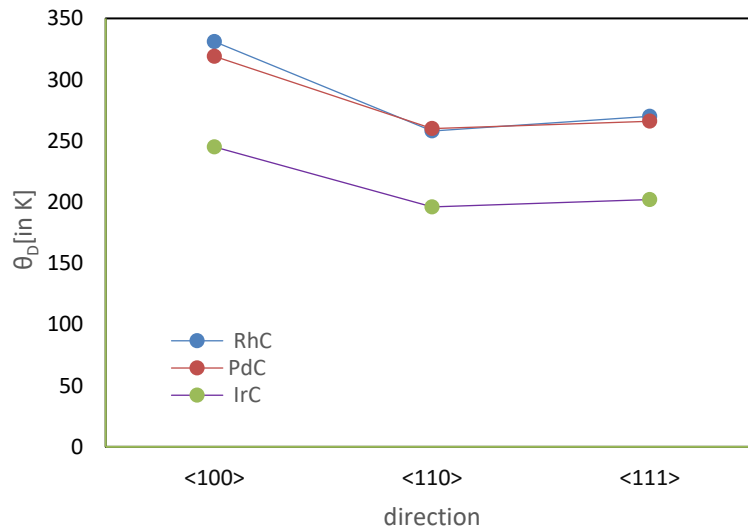


Fig. 1 Direction dependent Debye temperature of PGM carbides

It is depicted from **Figure 1** that the value of θ_D has been found lowest along $\langle 110 \rangle$ direction for all the materials. It has been also mentionable here that the value of θ_D is smallest for IrC, because θ_D is proportional to the cube root of the molecular weight. The value of θ_D along $\langle 100 \rangle$ for PdC is found 319K in our case while Ateser et. al (9) presented θ_D 353K. A standard value of Debye temperature of Rh, Pd and Ir are 275K, 150K and 228K respectively (31). Average Grüneisen parameter $\langle \gamma_i^j \rangle$ has been evaluated with the help of SOECs and TOECs. Further θ_D and $\langle \gamma_i^j \rangle$ are applied to compute thermal conductivity (κ) using the Equation (xxiii). The specific heat per unit volume (C_V) and energy density (E_0) have been found out with θ_D/T Tables of AIP Hand book (19). The computed values of $\langle \gamma_i^j \rangle$, κ , C_V and E_0 are presented in **Table IV**.

Table IV Direction dependent ($\langle \gamma_i^j \rangle$), κ (in $\text{Wm}^{-1}\text{K}^{-1}$), C_V ($\text{J mole}^{-1}\text{K}^{-1}$), E_0 (J mole^{-1}) for PGM carbides at 300°K

Material	Direction	$\langle \gamma_i^j \rangle$	κ	C_V	E_0
	$\langle 100 \rangle$	1.38	15.29	2.356	4.856

RhC	<110>	1.47	6.31	2.402	5.361
	<111>	1.60	6.09	2.402	5.274
	<100>	1.35	14.80	2.356	4.936
PdC			9.08 ^f		
	<110>	1.43	7.10	2.402	5.339
	<111>	1.56	6.41	2.402	5.295
IrC	<100>	1.36	11.34	2.432	5.448
	<110>	1.45	5.17	2.440	5.831
	<111>	1.58	4.77	2.440	5.785

^f See Ref. (3)

It is obvious from **Table IV** that the ultrasonic Grüneisen parameters are calculated using Mason's approach and found highest along <111> direction. The thermal conductivity directly depends on atomic weight and Debye temperature. It can be seen in **Table IV** that the thermal conductivity increases with increasing atomic weight and Debye temperature. The value of the thermal conductivity for PGM carbides are highest along <100> direction. The largest value of thermal conductivity is for RhC and lowest for IrC because the thermal conductivity is directly proportional to the Debye temperature. The existing values of κ of Rh, Pd and Ir are $150 \text{ Wm}^{-1}\text{K}^{-1}$, $72 \text{ Wm}^{-1}\text{K}^{-1}$, $150 \text{ Wm}^{-1}\text{K}^{-1}$ respectively which indicates pure PGMs are more thermally strong than PGMs carbides (37). The values of specific heat capacity (C_v) and energy density (E_0) have been found out highest for IrC along <110> and lowest for RhC along <100> direction. The values of C_v for RhC and PdC materials are approximately equal.

The thermal relaxation time (τ_{th}) have been calculated using Equation (xxvii) The value of acoustic coupling constants (D_L and D_S) for longitudinal and shear waves has been computed with average Grüneisen parameter $\langle \gamma_i^j \rangle$ and average of the square of the Grüneisen parameter, specific heat per unit volume and energy density from Equation (xxviii)-(xxix).

All obtained thermal parameters are applied to compute the ultrasonic attenuation due to thermoelastic mechanism $(\alpha/v^2)_{th}$ and due to phonon-phonon interaction mechanism for

longitudinal and shear wave $[(\alpha/v^2)_L$ and $(\alpha/v^2)_S]$ using Equations (xxiv)-(xxvi). The computed values of τ_{th} , D_L , D_S , $(\alpha/v^2)_{th}$, $(\alpha/v^2)_L$ and $(\alpha/v^2)_S$ have been presented in **Table V**.

Table V Direction dependent τ_{th} [in ps], D_L , D_{S1} , D_{S2} , $(\alpha/v^2)_{th}$, $(\alpha/v^2)_L$, $(\alpha/v^2)_{S1}$ and $(\alpha/v^2)_{S2}$ (all (α/v^2) in 10^{-16} Nps²m⁻¹)

Material	Direction	τ_{th}	D_L	D_{S1}	D_{S2}	$(\alpha/v^2)_{th}$	$(\alpha/v^2)_L$	$(\alpha/v^2)_{S1}$	$(\alpha/v^2)_{S2}$
RhC	<100>	33.25	26.51	32.97	32.97	0.760	22.37	32.86	32.86
	<110>	22.34	26.74	44.56	324.82	0.172	10.83	32.93	937.93
	<111>	19.68	33.55	196.13	196.13	0.161	10.44	268.90	268.90
PdC	<100>	33.58	25.67	29.50	29.50	0.702	22.48	33.79	33.79
			105.5 ^f	43.8 ^f		0.58 ^f	7.93 ^f	34.78 ^f	34.78 ^f
	<110>	23.79	25.00	39.91	338.03	0.205	11.57	35.02	93.02
IrC	<100>	43.00	26.51	30.60	30.60	1.260	43.19	62.90	62.90
	<110>	30.30	26.13	41.34	333.63	0.337	21.66	64.09	1748.40
	<111>	26.31	32.811	201.45	201.45	0.307	20.96	538.76	538.76

^f See Ref. (3)

It is depicted in **Table V** that the value of the thermal relaxation time (τ_{th}) is of the order of 10^{-11} s order which confirms the metallic character of PGM carbides. The value of (τ_{th}) is highest along <100> direction and lowest along <111> direction for RhC, PdC and IrC and it plays a crucial role for the computation of ultrasonic attenuation.

It is obvious from **Table V** that the value of acoustic coupling constant for shear wave is highest along <110> direction and polarization along $\langle 1\bar{1}0 \rangle$ direction of the chosen B1 structured RhC, PdC and IrC single crystals, which indicates that maximum conversion of ultrasonic energy into thermal energy or vice-versa. The values of acoustic coupling constants are not available for direct comparison so we compare the results of D_L and D_S with PtC (3) which shows similar trend.

The ultrasonic attenuation for the chosen materials PGM carbides i.e. $(\alpha/v^2)_{total} = (\alpha/v^2)_{th} + (\alpha/v^2)_L + (\alpha/v^2)_{S1} + (\alpha/v^2)_{S2}$ is shown in **Figure 2**.

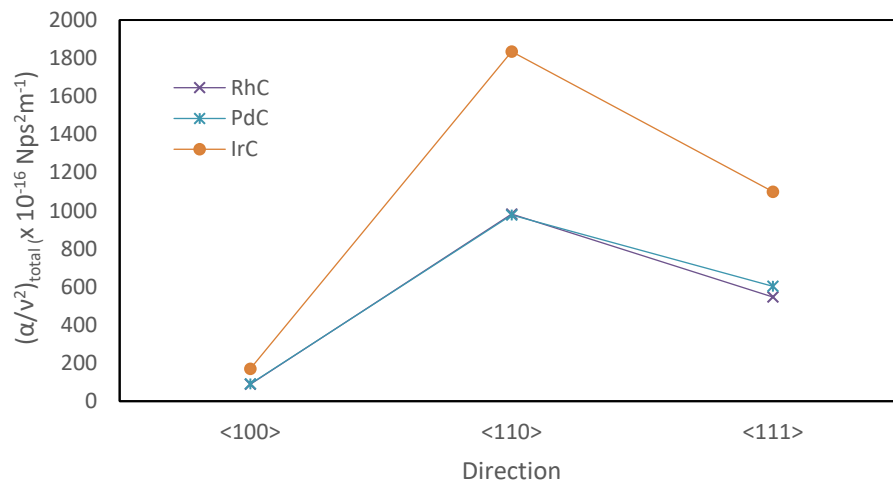


Fig. 2 Direction dependent total ultrasonic attenuation of PGM carbides

From **Table V** it is clear that values of thermal attenuation loss $(\alpha/v^2)_{th}$ for XC (X: Rh, Pd, Ir) is highest along <100> and lowest along <111> direction. The thermal attenuation is highest for IrC which indicates that time for conversion of acoustic to thermal energy is longest for IrC. From **Table V** it is also clear that thermal attenuation loss is very less in comparison to loss due to phonon-phonon interaction. Computed values of Akhieser damping for chosen materials are highest along <110> directions and lowest along <100> direction. It is also shown in **Figure 2** that total ultrasonic attenuation is highest <110> direction at room temperature. Uncertainty in ultrasonic attenuation depends on several parameters like SOECs, TOECs, material density, heat capacity, thermal energy density, thermal relaxation time, frequency and acoustic coupling constants. The results on ultrasonic attenuation for RhC, PdC and IrC are not available for comparing directly. So the comparison has been done with PtC (3) and found good agreement with that.

4. Concluding Remarks

On the basis of obtained results and their analysis, we conclude following points:

- The temperature and orientation dependent elastic, mechanical, thermal and ultrasonic properties of rock salt structured PGM carbides have been analysed.
- Behaviour of SOECs and TOECs are like other rock salt structured materials of B1 type.
- Cauchy's relation has been satisfied at 0K and they deviate at higher temperature for the chosen PGM carbides.
- Born stability criterion for mechanical stability has been satisfied by RhC, PdC and IrC.
- Pugh's ratio and Cauchy's pressure confirms the brittle nature of the investigated materials.
- The ultrasonic velocities are dependent on direction rather than temperature and the most suitable direction of ultrasonic wave propagation is $\langle 100 \rangle$ for all PGM carbides.
- Direction dependent Debye temperature at which all the vibrational modes are excited, is highest along $\langle 100 \rangle$ direction for all materials.
- The highest value of thermal conductivity is for RhC and lowest for IrC because the thermal conductivity is directly proportional to the Debye temperature.
- Order of thermal relaxation time confirms the semi metallic nature of PGM carbides.
- The value of ultrasonic attenuation is lowest along $\langle 100 \rangle$ direction for all chosen materials, which indicates that $\langle 100 \rangle$ direction is most suitable for wave propagation for PGM carbides.

The achieved results explore the base for further studies of these materials as well as for their engineering application in industries.

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