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Elastic, Electronic and Vibrational Properties of Ir-based Refractory Superalloys

Selgin Al*[1] and Nihat Arıkan[2]

ABSTRACT

The mechanical, electronic and vibrational properties of Ir-based refractory superalloys (Ir_3Hf and Ir_3Nb) in the $L1_2$ structure were studied in the framework of *ab initio* calculations. The obtained equilibrium lattice constants and bulk modulus were reported and compared with the existing data. The elastic constants of alloys were determined using energy strain method. The results were utilised to evaluate mechanical stability of alloys in the crystal structure of $L1_2$. Both alloys were found to be mechanically stable based on the Pugh's criteria. Subsequently, electronic band structures and partial and total densities of states have been obtained for Ir_3Hf and Ir_3Nb. The band structures of alloys demonstrated metallic behaviour whilst the conductivity was mostly governed by Ir 5d states for both alloys. Moreover, phonon distribution curves of both alloys were obtained by employing the linear response technique within the density functional theory. Both alloys are found to be dynamically stable based on phonon modes evaluation.

Keywords: DFT, band structure, phonon modes, stability, superalloys.

1. INTRODUCTION

The iridium based refractory superalloys especially hafnium or nickel containing alloys are promising materials owing to their exceptional ultra-high temperature features such as high melting temperature (2443°C) and high density (22.65 kg/m^3), high corrosion resistance and thermal stability [1-4]. Yamabe *et al.* [5-7] suggested superalloys build on iridium (Ir) and rhodium (Rh) alloys which can endure high temperatures. Single Ir crystals exhibit brittle manner whereas its alloys show enhanced high temperature strengths [8, 9] which made them attractive as a protective coating materials in extreme environments. The common applications of Ir alloys include rocket combustion chambers, gas turbines, nuclear power fuel containers, sources of radiation for medical treatments, coatings, and engine ignition tools [7, 10-12]. Improvement of ductility of Ir has taken great interest by the researchers. In this sense, several Ir-based alloys have been considered as high temperature materials. Several experimental and theoretical studies were conducted to reveal physical features of these alloys. Sundareswari *et al.* [13] studied electronic structures several Ir-based alloys using TB-MMTO (Self-Consistent Tight Binding Linear Muffin Tin Orbital) method under pressures. Elastic features were evaluated by Chen *et al.* [14]. Kontsevoi *et al.* [2] explored dislocation properties and mechanical behavior of

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Ir_3X by means of first principle calculation and PN (Peierls-Nabarro) model. Yamabe [7] studied high temperature strength of Ir-Nb superalloys. Moreover, thermodynamic features and lattice misfits were discussed by Liang *et al.* [15] in the framework of first principle calculations. However, only a few full electronic and elastic properties are found in the literature. Our study is dedicated to investigate elastic, mechanical strength, electronic and vibrational features of Ir-based refractory superalloys; Ir_3Hf and Ir_3Nb in the framework of greatly accurate ab initio calculations. To the best of authors' knowledge, phonon modes of these alloys have not presented all together from first principle calculation perspective.

2. METHOD

The computations were conducted by employing ab initio density functional theory (DFT) [16, 17] within the Quantum-Espresso software package [18]. Perdew-Burke-Ernzerhof, generalized gradient approximation (PBE-GGA) was utilized for the exchange correlation potential [19]. The electronic wave functions were enlarged in plane-wave basis to initiate a kinetic energy cut off to 60 Ry, while the cut off energy for the electronic charge density was taken as 600 Ry. A 8x8x8 k-points mash was utilized to represent the Brillouin zone. A Methfessel-Paxton [20] smearing parameter with a width of $\sigma = 0.05$ Ry was applied for the integration up to the Fermi surface so as to achieve a smooth density of states. The lattice dynamic computations were done within the framework of the DFPT [21, 22]. The phonon frequencies were collected on a 4x4x4 q-point mesh to obtain ten dynamic matrices. Fourier deconvolution was adopted to this mesh to evaluate these dynamical matrices at arbitrary wave vectors.

Mechanical stability of materials can be evaluated using elastic constants. Elastic constants of materials demonstrate stiffness against externally applied strain. In addition, it allows to estimate other features such as strength and melting temperature [23]. It is also possible to obtain elastic constants from the slopes of the acoustic modes in the full phonon spectra [24, 25]. Small waves in the acoustic phonons correspond to sound velocities which are correlated to C_{11}, C_{12} and C_{44} as described in references [26, 27]. Subsequently, using the elastic constants the relevant polycrystalline features such as Bulk modulus (B), Shear modulus (G), Young's modulus (E), anisotropy factor (A) and Poisson's ratio (σ) can be collected using the following standard relationships:

$$B = \frac{C_{11}+2C_{12}}{3} \quad (1)$$

$$G = \frac{G_v+G_R}{2}, G_v = \frac{C_{11}-C_{12}+3C_{44}}{5}, G_R = \frac{5\,(C_{11}-C_{12})C_{44}}{3(C_{11}-C_{12})+4C_{44}} \quad (2)$$

$$E = \frac{9BG}{3B+G} \quad (3)$$

$$A = \frac{2C_{44}}{(C_{11}-C_{12})} \quad (4)$$

$$\sigma = \frac{1}{2}\left(1-\frac{E}{3B}\right) \quad (5)$$

3. RESULTS AND DISCUSSION

3.1. Structural and Elastic Properties

The Ir-based superalloys crystallise in Cu_3Au type structure with the space group $Pm\bar{3}m$ (221) where Hf orNb atoms sit at (0,0,0) positions whilst Ir atoms sit (0,1/2,1/2) positions. The total energy is computed based on the unit cell. The obtained total energy is then matched to Murnaghan's equation of state [28] to collect lattice constants (a) in the equilibrium phase and bulk modulus (B). The obtained lattice constants, bulk modulus and elastic constants of alloys are presented in Table 1. As it is easily notable from Table 1 that the obtained lattice constants and bulk modulus for the alloys are greatly in line with both existing theoretical and experimental data. Bulk modulus of a solid is an indication of the average bond strength within the solid since it is correlated to atoms' the binding energy. Based on this, the bond strength of alloys are expressed as $Ir_3Nb > Ir_3Hf$.

Elastic constants of a solid are knows as the quantitative numbers that can provide valuable data on mechanical and dynamical behaviour of a solid [29]. The elastic constants in this study are computed using strain-stress method at the optimised lattice. A cubic structure has three elastic constants which are defined as follows; C_{11},

C_{12} and C_{44}. The general Born criteria [30] for mechanical stability of a cubic structure is given as;

$$(C_{11}+2C_{12})>0,\ C_{44}>0,\ C_{11}>0 \text{ and } C_{11}-C_{12}>0 \quad (6)$$

As Table 1 demonstrates that both alloys fulfil the mechanical stability condition, indicating that the studied superalloys are mechanically stable.

The Born stability criteria also brings a restriction for the bulk modulus of alloys. The bulk modulus of a cubic structure should take a value between C_{11} and C_{12} as follows;

$$C_{11} > B > C_{12} \quad (7)$$

As can be seen from Table 1 that both conditions given in equations 6 and 7 are fulfilled for both superalloys.

Table 1: The obtained equilibrium lattice constants *a(Å),* bulk modulus *B* (GPa) and elastic constants of Ir_3Hf and Ir_3Nb in the $L1_2$ structure.

Alloys	***Ref.***	***a(Å)***	***B***	***C_{11}***	***C_{12}***	***C_{44}***
Ir_3Hf	This work	3.935	315.117	471.890	236.730	235.760
	VASP-GGA [3]	3.970	270	403	203	205
	Exp. [1]	3.933				
	FLPAW [2]		271			
	Exp. and LAPW [31]	3.931	297			
	VASP [14]	3.972	285.310	442.880	206.530	221.720
Ir_3Nb	This work	3.934	317.218	520.859	215.397	246.981
	VASP-GGA [3]	3.930	307	510	206	240
	Exp. [1]	3.892				
	FLPAW [2]		315			
	VASP [14]	3.970	379.270	631.94	252.94	303.39

Table 2: The computed bulk modulus *B* (GPa), shear modulus G (GPa), B/G ratio, Young's modulus E (GPa), Anisotropy factor A (GPa), Poisson's ratio (σ) and Cauchy Pressures ($C_{12} - C_{44}$) of alloys.

Alloys	***Ref.***	***B***	***G***	***B/G***	***E***	***A***	***σ***	***$C_{12} - C_{44}$***
Ir_3Hf	This work	315.117	178.321	1.767	420.067	2.005	0.261	0.97
	LAPW [31]	297	163	1.822	413	-	0.269	
	VASP [14]	285.310	180.3	1.582	446.8	-	0.239	-15.2
Ir_3Nb	This work	317.218	203.683	1.557	503.320	1.617	0.235	-31.584
	VASP [14]	379.270	257.8	1.471	630.6	-	0.223	-50.45

The bulk and shear modulus of alloys in Table 2 can be used to estimate resistance to volume change under pressure. It can be said that both alloys can show a resistance towards a volume

change under pressure since the value of bulk modulus (B) is higher than the value of shear modulus (G) for both alloys. Moreover, B/G ratio is computed in order to evaluate brittleness and ductility of alloys. These features are extremely important for high temperature strength. Based on the Pugh criteria [32], if this ratio is higher than 1.75, the solid is ductile if not it is brittle. According to the ratios given in Table 2, Ir_3Hf is ductile whereas Ir_3Nb is brittle. These results are in well accordance with Chen *et al.* [14]. In addition, the bonding characteristics of alloys are examined via Poisson's ratio and Cauchy pressure. It is accepted that if the Poisson's ratio is around 0.1, the solid shows covalent bonding characteristics, if it is around 0.25, it demonstrates ionic bonding characteristics [32, 33]. For the values between 0.25 and 0.5, the central forces dominate [34]. As shown in Table 2 that the inter atomic forces of Ir_3Hf seem to be central forces whereas Ir_3Nb seems to have ionic bonding characteristics. Cauchy pressure ($C_P=C_{12}-C_{44}$) can be used to predict angular atomic bonding characteristics of metals and compounds. On the assumption that Cauchy pressure is more positive, the solid exhibits more metallic characteristics, otherwise the solid shows angular character in the bonding [32, 35, 36].Thus, it can be said that Ir_3Nb is brittle with angular bonding at zero pressure whereas Ir_3Hf is ductile and more metallic.

The Young modulus and elastic anisotropy are also important physical parameters. As Young modulus of a solid increases it gets much stiffer [37]. Therefore, Ir_3Nb is much stiffer than that of Ir_3Hf. If A=1, the solid is isotropic. The value of higher or lower than unity indicates anisotropy. Table 2 displays that both alloys are anisotropic owing to A>1.

3.2. Electronic and Phonon Properties

Electronic band structure and density of states were calculated along high symmetry directions in the Brillouin zone in order to evaluate the electronic properties of the alloys. Figure 1 and 2 exhibits the electronic band structures of Ir_3Hf and Ir_3Nb, respectively. The total and partial density of states of alloys are depicted in Figure 3 and 4. The electronic structure of alloys shows metallic character due to the fact that the conduction and valence band cut Fermi energy level and also no gap is seen at the Fermi energy level in Figure 3 and 4. Both alloys have similar trend in the electronic structure. For Ir_3Hf, hybridizations of Ir-5d and Hf-5d bands are observed at a peak of around 3 eV. The biggest contribution to the Fermi energy level and thus conductivity is due to Ir-5d bands. Below the Fermi energy level, Ir-5d bands have the biggest contribution whilst other bands have relatively small effect. In the case of Ir_3Nb, there is also a hybridization around 3 eV due to Ir-5d and Nb-4d bands. The contribution to the band above the Fermi energy level is due to Ir-5d bands.

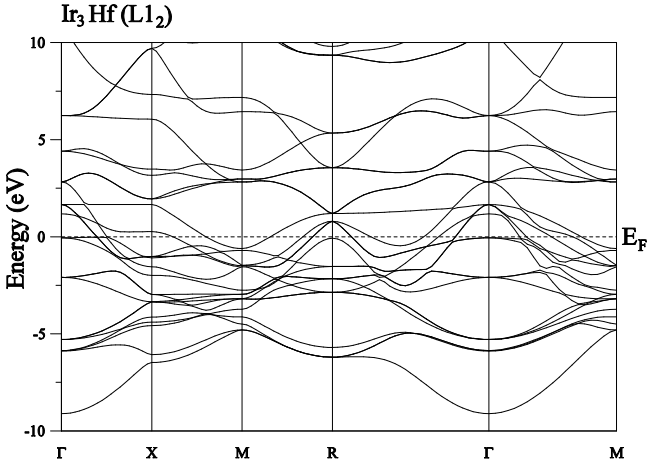

Figure 1. The calculated electronic structure of Ir_3Hf in the $L1_2$ structure.

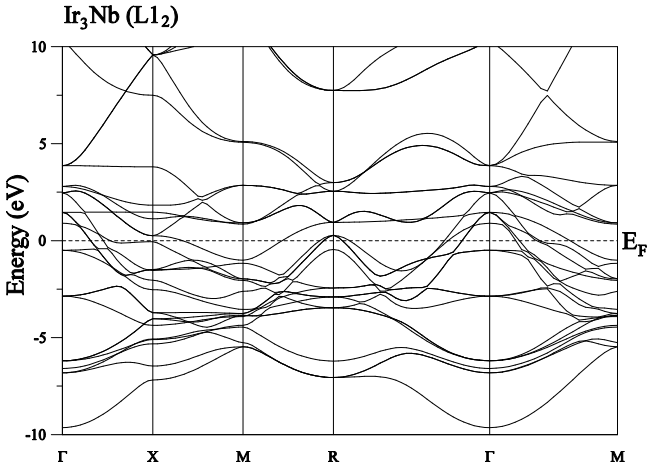

Figure 2. The calculated electronic structure of Ir_3Nb in the $L1_2$ structure.

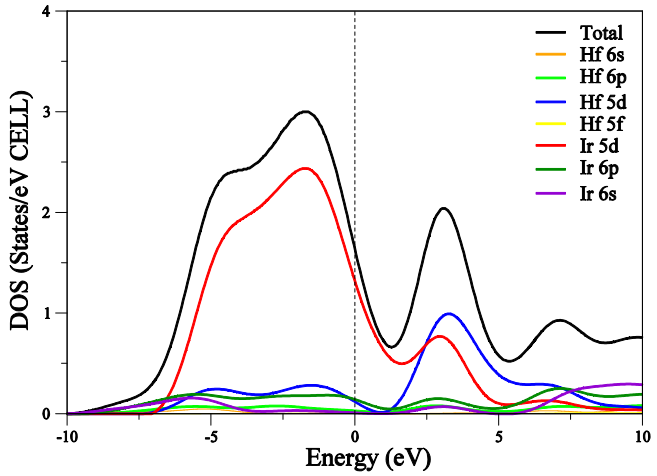

Figure 3. The calculated total and partial density of states of Ir_3Hf in the $L1_2$ structure.

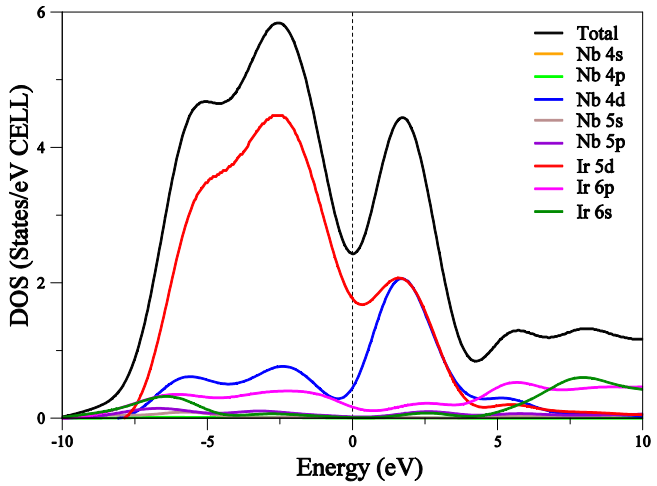

Figure 4. The calculated total and partial density of states of Ir_3Nb in the $L1_2$ structure.

The phonon modes distributions and phonon density of states of Ir_3Hf and Ir_3Nb are given in Figure 5. As can be seen from the Figure, there is no soft mode in computed phonon dispersion curves, indicating that both alloys are dynamically stable. Ir_3Hf and Ir_3Nb alloys have a total of 12 phonon modes due to the fact that they contain 4 atoms in the unit cell. The mass divergence of anions and cations affect the shape of phonon modes distribution. As the mass difference gets larger, the divergence of acoustic and optical phonon modes become clearer. In this study, Ir_3Nb alloy dominates the high-frequency range above 4.8 THz due to the lighter Nb atoms whilst Ir_3Hf vibrates in the frequency region below this frequency owing to heavier Ir atoms. On the other hand, the vibration frequency of Ir and Hf atoms are very close to each other, probably very little mass difference between atoms.

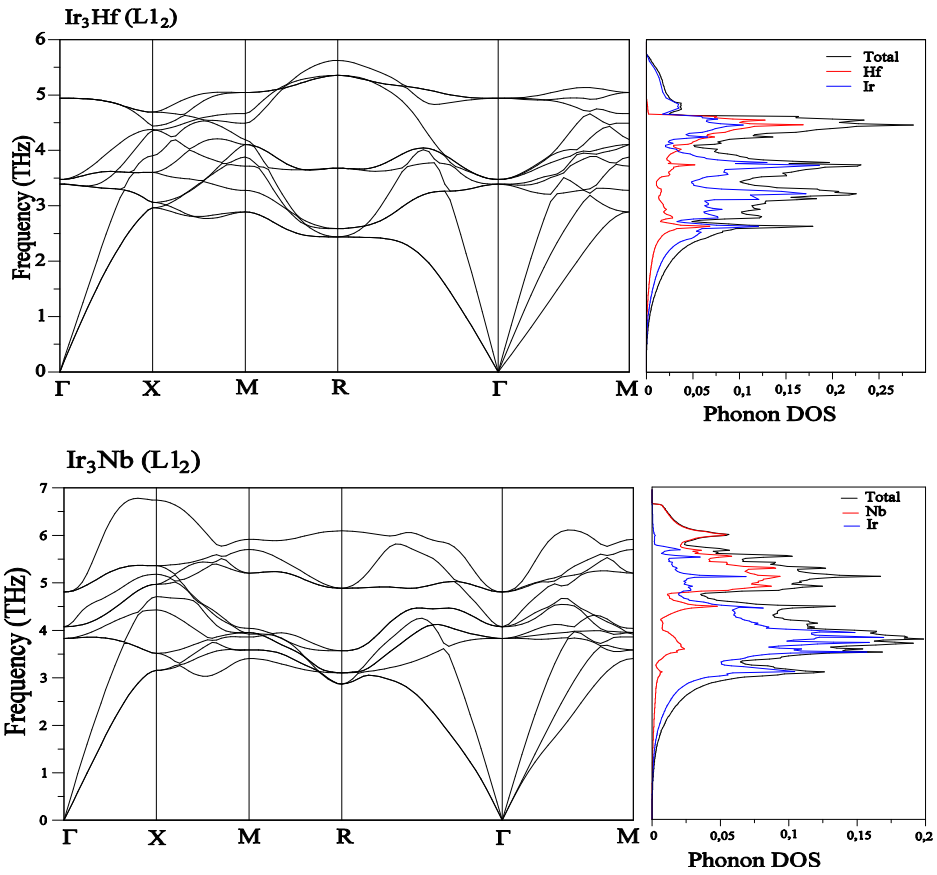

Figure 5. The phonon dispersion curves and phonon density of states of Ir_3Hf and Ir_3Nb in the $L1_2$ structure.

4. CONCLUSIONS

In this paper, elastic, electronic and vibrational features of Ir-based superalloys have been examined in the density functional theory framework. The obtained lattice parameters and elastic constants are in line with the existing experimental and theoretical results in literature. The Young modulus, anisotropy factor, Poisson's ratio and Cauchy pressures of alloys have also been evaluated. It is found that Ir_3Nb is brittle at zero pressure. The electronic band structures of alloys indicated metallic character for both alloys. The original object of this paper is to reveal elastic, mechanical and phonon characteristics of these alloys all together. The phonon modes distribution and phonon density of states of alloys showed that these superalloys are dynamically stable in nature.

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