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Theoretical Approach on Characterizing Structural and Mechanical Properties of Industrial Alloys

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Abstract

With the goal of entering Indonesia's golden dream 2045 in mineral technology and utilizations, expansive researches covering both experimental and theoretical aspects are urgently required. Here, we provide theoretical study on structural and mechanical properties of various nickel-based alloys based on first-principles, density functional theory (DFT) technique. First, we evaluate the accuracy of several exchange-correlation functionals (LDA-PZ, GGA-PBE, GGA-PBEsol) by comparing the calculated lattice constants for each system with the known experimental results. Based on the best functional, we analyze structural changes caused by the mixture of different atom to the principal element of nickel. Finally, we derived the related mechanical properties for all systems based on the calculated elastic constants. Furthermore, the elastic constants can also be used to predict the stability of alloy structure.

Keywords: DFT; Ni-alloy; LDA; GGA; Elastic constants

Introduction

With the well-known large reserves of laterite nickel, it is important for Indonesia to optimize its capabilities to utilize the nickel (Ni) ore for various applications. One of the main applications for nickel is its ability (and stability) to be mixed/bonded with different metallic elements of Cr, Cu, Mo producing Ni-Cr, Ni-Cu, and Ni-Mo alloy structure respectively. This alloying process is very useful to achieve additional and/or strengthening properties, such as corrosion (Guyader, 2007). and high-temperature resistance (Petrushin, 1984). Based on its compositions, the higher limits for alloying elements of Cr and Mo are 35-40 wt. %, and 20 wt. % (Takeuchi, 2005) respectively. For Ni-Cu alloy, it is known to have a complete solid solubility, meaning that both Ni and Cu can be fully utilized as alloying element (Kunimine, 2019).

Due to its importance on various applications, a clear understanding on phase stability, structural and mechanical properties on Ni-alloy systems are required. While experimental approaches can be done to fully characterize the alloy structure, it is usually involving a destructive test to obtain the alloy performance under various environmental conditions. Hence, different method to obtain mechanical properties are still required to provide different perspective on alloy properties in general.

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In this study, we report the structural and mechanical properties of Ni-Cr, Ni-Cu, and Ni-Mo alloy (Ni composition is determined to be 75 wt. %, while alloying elements of Cr, Cu, and Mo are determined to be 25 wt. %) that obtained from the computational method known as density functional theory (DFT) technique element (Kohn, 1965). Since its first application on metallic element (Perdew, 1986), DFT has been known to provide great accuracy on predicted structural, electrical, and mechanical properties of various systems. Aside from its accuracy, DFT method also known for its flexibility in which one can determine the accuracy level without compromising much with the obtained results.

Currently, DFT level of accuracy can be explained based on the Jacob's ladder (Perdew, 2001), in which the accuracy can be divided into 5 categories (in terms of chosen exchange-correlation functional): local density approximation (LDA); generalized gradient approximation (GGA); meta-generalized gradient approximation (meta-GGA); exact exchange and compatible correlation; and exact exchange and exact partial correlation. In this study, only LDA and GGA functionals are considered due to its cheaper computational cost compared to the rest of DFT functionals.

Research Methods

All DFT calculations are performed using Quantum Espresso (QE) v7.0 software. For LDA level of accuracy, we chose the Perdew-Zunger version of LDA functional (Perdew, 1981), while for the GGA level of accuracy, we chose two different functionals. First is the Perdew-Burke-Ernzerhof (PBE) functional and second is the PBE further modification for solid systems, PBEsol (Perdew, 1996; Perdew, 2008).

To obtain the best functional for our targeted system, we compare the calculated lattice parameter from three different functionals (LDA-PZ, GGA-PBE, GGA-PBEsol) with the known experimental observation of pure Ni system. Pure nickel system in its cubic form is shown in Figure 1(a), while three variation of Ni-alloy structures accommodating a fraction of Cu, Cr, and Mo elements are shown in Figure 1(b-d). Softer and darker blue balls show Cu and Cr atom, while purple ball indicates Mo atom.

The structure is drawn by using VESTA software (Momma, 2011). With each unit cell consisting of 4 Ni atoms, producing 75-25 wt. % of Ni-alloy requires a single Ni atom to be replaced with the alloying elements of Cu, Cr, and Mo. The middle area of the crystal structure is chosen as the replacement sites to reduce a possible spurious interaction caused by the alloying elements to the boundary of the supercell structure.

To obtain the optimized structure for each system, kinetic energy cut-off of 100 Rydberg (Ry) are chosen to accommodate denser fast Fourier transform (FFT) grids that is required for mechanical properties estimation. Aside from those reasoning, the initial DFT calculation also shows that 100 Ry produce convergent total energy as shown in Fig. 2. Brillouin zone of the systems is examined by $10 \times 10 \times 5$ k-point grids that is automatically generated from QE software. The electronic and structural optimizations are conducted based on the convergence criteria of 1×10^{-6} Ry, 1×10^{-5} Ry/Bohr, 5×10^{-1} kbar for total energy, force per-atomic units, and pressure respectively.

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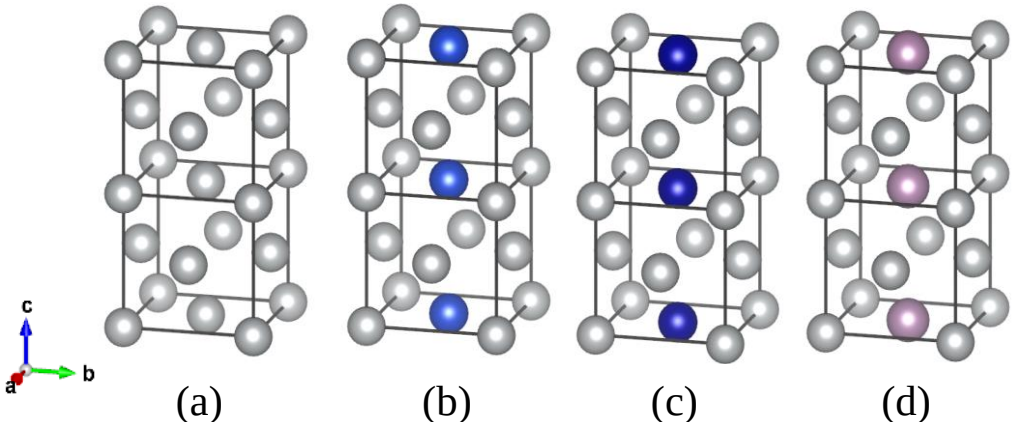

Figure 1. Supercell structure of (a) Pure Ni (b) Ni-25Cu (c) Ni-25Cr (d) Ni-

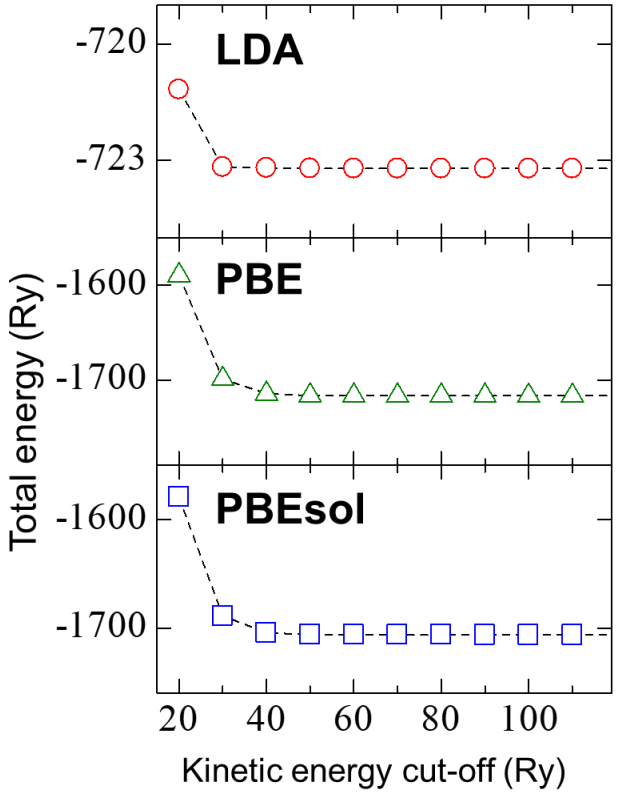

Figure 2. The calculated total energy of pure Ni system in respect to the utilized kinetic cut-off energy. Dashed lines are guides to the eye.

Mechanical properties bulk (B), Young (E) and shear (G) moduli) of all considered systems are determined based on the calculated elastic constants from the Voigt-Reuss-Hill model that is implemented in thermo_pw v.1.6.0. package. For this step,

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we increase the kinetic cut-off energy from 100 to 120 Ry, to obtain finer grids required for mechanical properties estimation. For all of our system, only the optimized structures are considered to calculate the elastic constants. The simple flowchart for our calculation method is shown in Figure 3.

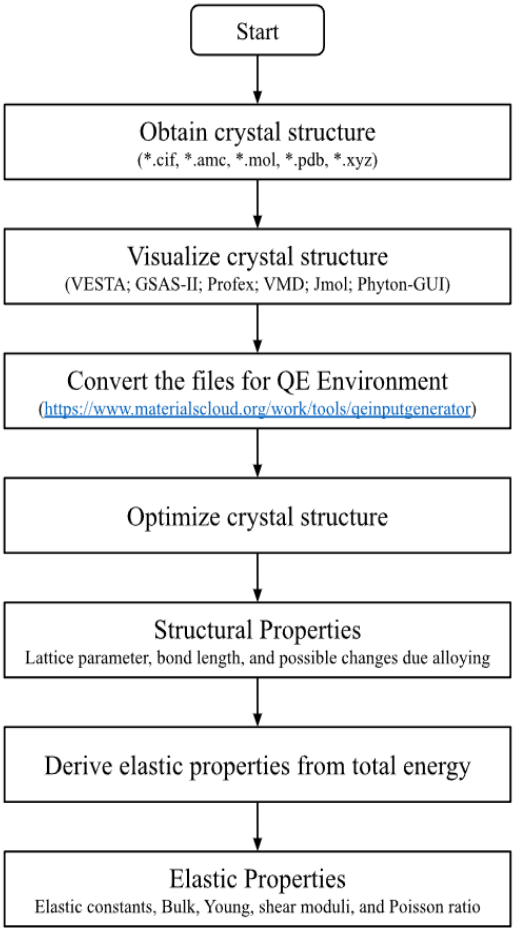

Figure 3. Flowchart of the research

Result and Discussion

Table 1 show the calculated lattice constant of pure Ni system based on LDA-PZ, GGA-PBE, and GGA-PBEsol functional. For the sake of simplicity, we call those three functionals as PZ, PBE, and PBEsol respectively. Based on our calculation's condition, the initial lattice parameter (a_{in}) of 3.4751 Å is optimized (a_{opt}) to 3.4237 Å for PZ functional, 3.5090 Å for PBE functional, and 3.4570 Å for PBEsol functional. All calculated lattice values show slight differences (< 5 %) compared to the known low-temperature lattice parameter of Ni system (3.5155 Å), with the least error is ~ 0.2 % for the PBE functional, 2.6 % for the PZ functional and 1.6% for the PBEsol functional. It is interesting to see that PBEsol functional fails to give significant improvement over the PBE functional, and only slightly more accurate compared to PZ functional. It is known

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from the report by Zhang et al (2018), that Ni solid is one of the exceptions where the PBEsol functional fails to predict accurate lattice parameter compared to PBE functional. Hence, for the rest of discussion in this study, only PBE functional is considered as the chosen exchange-correlation functional.

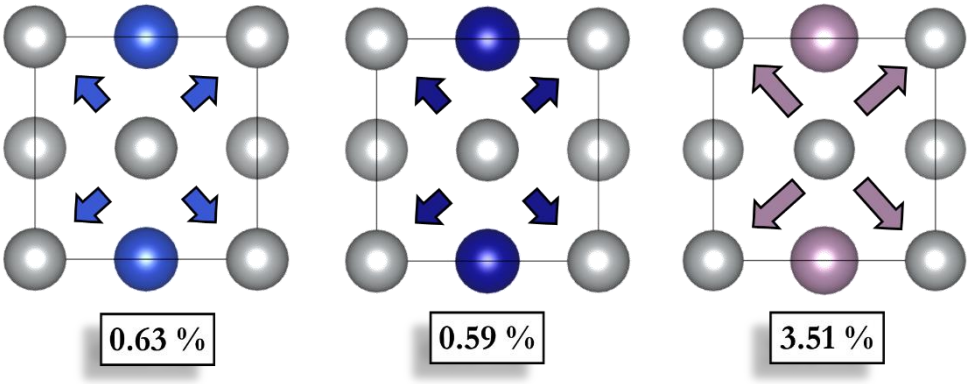

Figure 4. Lattice parameter expansion due to substitutional atom of (a) Cu (b) Cr (c) Mo.

Table 1. Lattice parameter of Ni (Å)

	a_{in}	a_{opt}	exp.
PZ		3.4237	
PBE	3.4751	3.5090	3.5155[a]
PBEsol		3.4570	3.5235[b]

[a]Bandyopadhyay, 1977 (T = 0 K)
[a]Bandyopadhyay, 1977 (T = 300 K)

Table 2. Calculated elastic parameters (GPa)

	C_{11}	C_{12}	C_{44}	B	E	G	G/B
Ni	269.93	175.81	121.99	207.18	220.25	83.36	0.40
Ni-Cu	254.28	163.58	117.74	193.81	211.46	80.32	0.41
Ni-Cr	298.80	182.35	114.42	221.17	231.25	87.25	0.39
Ni-Mo	294.37	195.70	60.25	228.59	154.34	55.62	0.24

The existence of substitutional inside Ni cubic structure increase the lattice parameter due to the difference of atomic size of Ni (1.24 Å) with Cu (1.28 Å), Cr (1.30 Å), and Mo (1.39 Å). With the substitution of those atoms, the lattice parameter will be increased by 0.63, 0.59, and 3.51 % for Ni-Cu, Ni-Cr, and Ni-Mo respectively as described visually by Figure 4. Comparing to the known experimental results, Gubicza et al., reported that the replacement of 25% Cu to Ni will expand the lattice parameter by 0.45 % (Gubicza, 2018). Thus, our calculated results show consistent trend with the known experimental observation albeit with higher expansion. This is very likely due to

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the error introduced by our functional and can be corrected further by using a more accurate functional such as meta-GGA, SCAN functional.

Finally, we determine the mechanical properties of bulk, Young and shear moduli from the calculated elastic constants as listed in Table 2. Stability of the structure can be estimated based on Born stability criteria (Born, 1940). For a cubic structure the following criteria are required:

$$C_{11} - C_{12} > 0 \quad (1)$$
$$C_{11} + 2C_{12} > 0 \quad (2)$$
$$C_{44} > 0 \quad (3)$$

whereas all of our considered systems are succeeded to pass all of the criteria, suggesting that all structure have high mechanical stability. Compared to the pure Ni system, we observe that the bulk modulus for Ni-Cr and Ni-Mo are higher while Ni-Cu system exhibits lower bulk moduli with the highest bulk modulus is observed for Ni-Mo at 228.59 GPa. For the Young and shear moduli, we observe similar trend where Ni-Cr alloy show largest values compared to Ni-Cu, Ni-Mo and pure Ni systems.

First, we discuss the effect of Cu alloying element to the Ni system, where the general strength of the Ni-Cu alloy is decreased compared to the pure Ni system. This is also known experimentally where the commercial Ni-Cu alloy of CDA715 with 70 wt. % Cu and 30 wt. % Ni have larger tensile strength (517 MPa vs 414 MPa), Young (150 GPa vs 140 GPa) and shear moduli (57 GPa vs 52 GPa) compared to CDA706 with 90 wt. % Cu and 10 wt. % Ni. Increased general strength for Ni-Cr and Ni-Mo compared to the pure Ni are also known experimentally. For Ni-Mo alloy it has been observed that the alloy with the addition of Mo as one of the alloying elements improves the tensile strength by ~30% (Konca, 2017). For Ni-Cr alloy, we observed that both Young and shear moduli of this system are the largest compared to other systems, suggesting that the Ni-Cr alloy provide the most improvement over pure Ni system.

To estimate the ductility and the brittleness parameters for our structure, the ratio of shear and bulk moduli can be utilized, where the system with the G/B ratio larger than 0.57 can be categorized as ductile material (Pugh, 1957). All of our considered structure can be considered as ductile system with the lowest value are observed for Ni-Mo alloys. The increase of ductility (based on the decrease values of G/B ratio), can be attributed to the fact that the stacking fault energy for Ni-Mo alloy is lower compared to the Ni-Cr alloy system (Mehta, 2015).

Conclusions

The theoretical approach based on DFT method to estimate the mechanical properties of Ni, Ni-Cu, Ni-Cr, and Ni-Mo alloy have been conducted. Based on the calculated lattice parameter, we determine that the GGA-PBE functional is the best choice to calculate Ni-alloy structure compared to the LDA-PZ and GGA-PBEsol functionals. The existence of alloying elements (Cu, Cr, Mo) are found to expand the bond length with the largest expansion is observed for Ni-Mo alloy. From the calculated elastic constants, bulk, Young, and shear moduli can be estimated, where all of our calculated results show similar trend with what is observed experimentally.

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References

Bandyopadhyay, J., & Gupta, K.P. (1977). Low temperature lattice parameter of nickel and some nickel-cobalt alloys and Grüneisen parameter of nickel. Cryogenics, 17, 345-347. https://doi.org/10.1016/0011-2275(77)90130-8

Born, M. (1940). On the stability of crystal lattices. Mathematical proceedings of the Cambridge Philosophical Society, 36(2), 160-172. https://doi.org/10.1017/S0305004100017138

Gubicza, J., Jenei, P., Nam, K., Kadar, C., Jo, H., & Choe, H. (2018). Compressive behavior of Cu-Ni alloy foams: Effects of grain size, porosity, pore directionality, and chemical composition. Material Science and Engineering: A, 725, 160-170. https://doi.org/10.1016/j.msea.2018.04.018

Guyader, H., Grolleau, A., Lemieux, E., Lucas, K., & Wolejsza, T. (2007). Corrosion Behaviour and Protection of Copper and Aluminium Alloys in Seawater. European Federation of Corrosion (EFC) Series, 95-115. https://doi.org/10.1533/9781845693084.2.95

Kohn, W. & Sham, J. (1965). Self-Consistent Equations Including Exchange and Correlation Effects. Physical Review, 140, A1133. https://doi.org/10.1103/PhysRev.140.A1133

Konca, E., Tur, K., & Koç, E. (2017). Effect of Alloying Elements (Mo, Ni, and Cu) on the Austemperability of GGG-60 Ductile Cast Iron. Metals, 7(8), 320. https://doi.org/10.3390/met7080320

Kunimine, T., & Watanabe, M. (2019). A Comparative Study of Hardness in Nanostructured Cu–Zn, Cu–Si and Cu–Ni Solid-Solution Alloys Processed by Severe Plastic Deformation. Materials Transactions, 60(8), 1484-1488. https://doi.org/10.2320/matertrans.MF201944

Mehta, K.K., Mukhopadhyay, P., Mandal, R.K., & Singh, A.K. (2015). Microstructure, texture, and orientation-dependent flow behaviour of binary Ni-16Cr and Ni-16Mo solid solution alloys. Metallurgical and Materials Transactions A, 46(8), 3656-3669. https://doi.org/10.1007/s11661-015-2947-8

Momma, K. & Izumi, F. (2011). VESTA 3 for three-dimensional visualization of crystal, volumetric, and morphology data. Journal of Applied Crystallography, 44, 1272-1276. https://doi.org/10.1107/S0021889811038970

Perdew, J.P. & Zunger, A. (1981). Self-interaction correction to density-functional approximations for many-electron systems. Physical Review B, 23, 5048. https://doi.org/10.1103/PhysRevB.23.5048

Perdew, J.P. (1986). Density-functional approximation for the correlation energy of the inhomogeneous electron gas. Physical Review B, 33, 8822(R). https://doi.org/10.1103/PhysRevB.33.8822

Perdew, J.P., Burke, K & Ernzerhof, M. (1996). Generalized Gradient Approximation Made Simple. Physical Review Letters, 77, 3865. https://doi.org/10.1103/PhysRevLett.77.3865

Perdew, J.P. & Schmidt, K. (2001). Jacob's ladder of density functional approximations for the exchange-correlation energy. AIP Conference Proceeding, 577, 1-20. https://doi.org/10.1063/1.1390175

Perdew, J.P., Ruzsinszky, A., Csonka, G.I., Vydrov, O.A., Scuseria, G.E., Constantin, L.A., Zhou, X. & Burke, K. (2008). Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces. Physical Review Letters, 102, 039902. https://doi.org/10.1103/PhysRevLett.100.136406

Petrushin, N.V., Lagunov, A.V., & Gorin, V.A. (1984). Structural stability of heat-resistant nickel alloys at high temperature. Metal Science and Heat Treatment, 26, 361-364. https://doi.org/10.1007/BF00707410

Pugh, S.F. (1954). Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 45(367), 823-843. https://doi.org/10.1080/14786440808520496

Takeuchi, A., & Inoue, A. (2005). Classification of Bulk Metallic Glasses by Atomic Size Difference, Heat of Mixing and Period of Constituent Elements and Its Application to Characterization of the Main Alloying Element. Materials Transactions, 46(12), 2817-2829. https://doi.org/10.2320/matertrans.46.2817

Zhang, G.X., Reilly, A.M., Tkatchenko, A., & Scheffler, M. (2018). Performance of various density-functional approximations for cohesive properties of 64 bulk solids. New Journal of Physics, 20, 053020. https://doi.org/10.1088/1367-2630/aac7f0