Effect of alloying on the phase stability and elastic properties of $L1_2$ Pt_3Cu crystal structure

T. Mathibeng[1,3], H. Moller[1,2], M. Phasha[2], and A. Mwamba[2]

[1]University of Pretoria, South Africa
[2]Mintek, South Africa
[3]South African Diamond and Precious Metals Regulator, South Africa

The investigation on the effect of alloying on the phase stability and elastic properties of the ordered Pt_3Cu phase was carried out using density functional theory-based first-principles calculations. In this study, aluminium, zinc and chromium were considered as substitutional elements on the Cu site to form $L1_2$ $Pt_3Cu_{1-x}Y_x$ ternary alloys. The calculated heats of formation show that the thermodynamic stability was gradually enhanced with increasing contents of all three alloying elements, with Al being the most effective even at smaller compositions, while Cr was the least effective. However, despite low thermodynamic stability, the increase in Cr composition resulted into higher elastic properties such as tetragonal shear, and Young's moduli compared to the other two alloying elements. Current results reveal the alloying compositions that improve the thermodynamic stability of cubic ordered Pt_3Cu phase as well as satisfying the mechanical stability criteria. Therefore, a theoretical technique has been successfully employed to identify ternary $L1_2$ $Pt_3Cu_{1-x}Y_x$ compositions with potential to be used as cathode catalysts in proton-exchange membrane fuel cells.

Keywords: First-principles calculations, density functional theory (DFT), phase stability, elastic properties, $L1_2$ phase

INTRODUCTION

Fuel cells have emerged as a hopeful technology to supply clean energy in automobiles, portable and stationery applications (Ren *et al.,* 2020). Among the fuel cell types, the proton-exchange membrane fuel cells (PEMFCs) are generally considered one of the most promising solutions, especially when refuelled with hydrogen from renewable energy sources (Wang *et al.,* 2019; Zhang *et al.,* 2021, Mølmen *et al.,* 2021). Some of the key factors that offer PEMFCs a competitive advantage and render them attractive are zero emission, high efficiency, fast refuelling, and low upfront cost. These new niche technological applications hold promise for the quest to increase and diversify industrial uses of platinum group metals (PGMs). Moreover, face-centred-cubic (FCC) Pt-based alloys were found to have interesting chemical and mechanical properties, including high melting temperatures, thermal stability, and high corrosive resistance (Cornish *et al.,* 2007). However, some issues hindering commercial uptake and widespread adoption of PEMFCs is the use of expensive platinum (Pt) in its pure form as cathode electrocatalyst, which accounts for about 40% of the overall cost (Zhang *et al.,* 2021, Mølmen *et al.,* 2021), as well as the sluggish kinetics of the oxygen reduction reaction (ORR) on cathodes (Wang *et al.,* 2019a). Consequently, research and development efforts are underway around the globe, in quest to reduce cost and improve stability of the ORR catalysts without compromising catalytic performance. Alloying Pt with non-precious group metal (PGM) transition metals as one way of reducing the amount of Pt used has drawn much attention in the past few years (Ou 2014; Ren *et al.,* 2020).

Formation of the ordered (intermetallic) phase has been found to yield superior catalytic performance and phase stability in ORR (Zhao *et al.,* 2021; Kim and Joo, 2020; Saravanan *et al.,* 2016). Among the Pt_3TM cathode candidate alloys, Pt_3Co electrocatalyst has proved to be a viable option. However, the increased global demand of cobalt (Co) as an essential mineral used for magnets, hard metals, catalysts, superalloys, lithium-ion batteries in electric vehicles, computers, and mobile phones poses a huge supply risk and has escalated its cost significantly.

Due to this challenge, alternative Pt_3TM-based alloys are being considered as candidate cathode materials to be deployed in PEMFCs; among others, vital in supporting South African government hydrogen economy aspirations. Pt_3Cu alloy is among potential cathode materials (Saravanan *et al.,* 2016). However, as shown in Figure 1, this alloy composition which lies very close to the ordered rhombohedral $L1_1$ phase remains in FCC (A1) solid solution state at lower temperatures, slow or unlikely to order into $L1_2$ intermetallic phase. Despite copper (Cu) being readily available, the predicament mentioned above limits the chances of this alloy being used in the current form. As a result, this work paid attention on increasing thermodynamic and mechanical stability of ordered Pt_3Cu phase by means of introducing third alloying elements

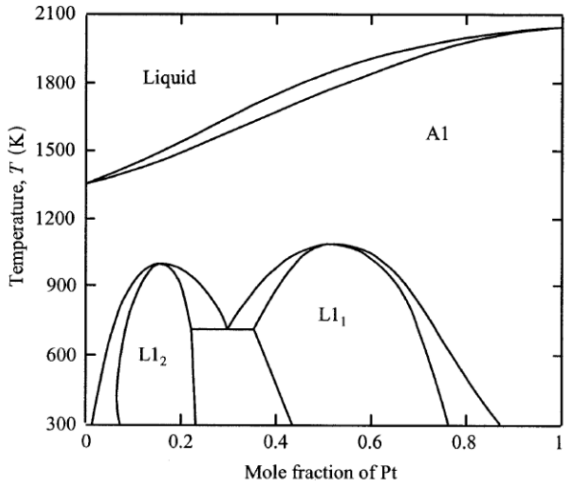

Figure 1. Cu-Pt phase diagram (Abe et al., 2006).

such as aluminum, zinc and chromium. The choice of third alloying element was on their ability to form stable $L1_2$ phase with Pt (i.e. Pt_3Y) as well as their cost viability.
In summary, the aim in this paper was to investigate the substitution effect of three alloying elements (Al, Zn and Cr) on the structure, thermodynamic phase stability and elastic properties of ordered Pt_3Cu phase. This systematic study was carried out using a first-principles approach.

METHODOLOGY

The calculations in this study were performed on 2x2x2 FCC supercell using density functional theory based on CASTEP code embedded in Materials Studio software package (Clark *et al.,* 2005). Robust Vanderbilt ultrasoft pseudopotentials (Vanderbilt, 1990) were used to describe the ion-electron interaction within the generalised gradient approximation (Perdew and Wang, 1992) of Perdew-Burke-Ernzerhof according to (Perdew *et al.,* 1997). A plane wave energy cutoff of 500 eV and k-points set of 6x6x6 were sufficient to converge the total energy of the considered systems.

Effects of alloying on the phase stability and elastic properties of $L1_2$ $Pt_3Cu_{1-x}Y_x$ (Y=Al, Zn, Cr) were determined from the ground-state structures optimised using the Brayden-Fletcher-Goldfarb-Shanno (BFGS) minimisation scheme. The convergence criterion of less than 1×10^{-5} eV/atom, the maximum residual forces of 0.03 eV/Å, maximum residual bulk stress of 0.05 GPa and maximum atomic displacement of 1×10^{-3}Å were utilised.

First-principles modelling of $L1_2$ Pt_3Cu and ternary compositions was conducted using FCC supercell based on space group #221(*Pm*-3*m*) consisting of 32 atoms. The ternary compositions considered were of stoichiometry $Pt_{24}Cu_7Y_1$, $Pt_{24}Cu_6Y_2$ representing 3.125 and 6.25 at.% of the alloying element.

Phase stability
Heats of formation were calculated from Equation 1 to determine thermodynamic stability (Phasha *et al.,* 2010).

$$H_f = \frac{1}{n}E_{Total}^{Pt3Cu1-xYx} - [(0.25\text{-}x)E_{Solid}^{Cu} + xE_{Solid}^{Y} + 0.75E_{Solid}^{Pt})] \text{---------- [1]}$$

where $E_{Total}^{Pt3Cu1-xYx}$ is the total energy of the alloy, E_{Solid}^{Pt}, E_{Solid}^{Cu} and E_{Solid}^{Y} are the total energies of the ground-state structures of elemental Pt, Cu and corresponding alloying elements, *x* and *0.25-x* refer to the fractional concentrations of the constituent elements, and the total number of atoms in the superstructure is represented by *n*.

Elasticity
The stress-strain relationship may be used to distinguish the elastic and plastic regimes of solid materials. The elastic moduli are the fundamental physical parameters which establish the stress-strain relationship in the elastic regime. For an isotropic polycrystalline solid, the two independent elastic parameters are the bulk modulus (*B*) and the shear modulus (*G*). The ratio of *B/G* predicts the brittleness of metals (ductile if above 1.75 and brittle if lower). For the cubic structures, only three elastic constants, corresponding to C_{11}, C_{12}, and C_{44}, are independent. The mechanical stability criteria of cubic crystals is given by expressions shown in Equation 2 (Nye, 1985).

$C_{11} > 0,\ C_{44} > 0,\ C_{11} - C_{12} > 0,\ C_{11} + 2C_{12} > 0$ ----------[2]

$B_V = B_R = \frac{1}{3}(C_{11} + 2C_{12}),\ C' = \frac{C_{11}-C_{12}}{2},\ G_H = \frac{G_V - G_R}{2},\ E = \frac{9B_H G_H}{3B_H + G_H}$ and

$v = 0.5\left(\frac{3B_H - 2G_H}{3B_H + G_H}\right)$ ---------- [3]

RESULTS AND DISCUSSION

Phase stability
The calculated lattice constants and formation energies of binary $L1_2$ Pt_3Cu and $Pt_3Cu_{1-x}Y_x$ ternary compositions are presented in Figure 2 (a) and (b), respectively. As shown in Figure 2(a), the lattice constant increased with addition of Zn and Al, due to their larger atomic sizes than Cu (Callister and Rethwisch, 2011), but decreased with increasing Cr composition. Although the introduction of each of the three considered alloying elements led to more negative formation energies, Al was found to be the most effective in increasing the thermodynamic stability of $L1_2$ Pt_3Cu, as shown in Figure 2 (b). A phase is more thermodynamically stable when the value of formation energy is more negative. The structural properties of binary alloy were calculated to benchmark the ternary alloys in order to determine the effect of alloying elements.

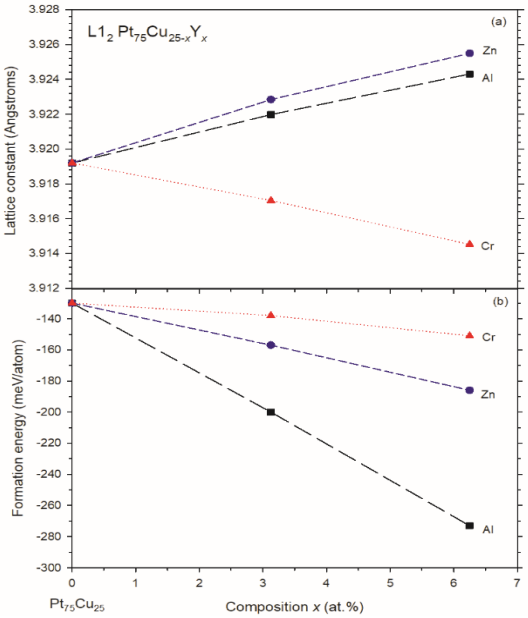

Figure 2. Calculated properties (a) lattice parameters and (b) formation energies of $L1_2$ $Pt_3Cu_{1-x}Y_x$.

Elastic properties

Figure 3 presents the predicted elastic constants C_{11}, C_{12}, and C_{44} of $L1_2$ $Pt_3Cu_{1-x}Y_x$ plotted against composition of the respective alloying element Al, Zn and Cr in (a), (b) and (c), respectively. Although the change of elastic constants due to alloying is minimal, their effect on elastic properties is significant, as shown in Figure 4. It follows from Figure 4 (a) that addition of Cr linearly increases with tetragonal shear modulus (C') whilst it first dips at 3.125 at. % and increases thereafter for Al and Zn addition. Figures 3 (a), (b), (c) and 4 (a) are an indicative that the mechanical stability criterion for cubic crystals as outlined in Equation 2 is satisfied and it increases as the difference between C_{11} and C_{12} elastic constants widens with higher alloying content.

Current results predict Cr to be the most effective in promoting mechanical stability of $L1_2$ Pt_3Cu phase. On the other hand, the increase in shear strength correlates with a decrease in ductility on alloying with Cr. The opposite trend is strongly observed for Al whereas it is weak for Zn. As a result, Zn addition results in the most ductile alloy, followed by Al while Cr yields the least. This behaviour is informed by mechanical property results shown in Table I, wherein highest bulk modulus (B) corresponds with lowest G_H in the case of Zn. Furthermore, it is interesting to note a combination of higher mechanical stability (C') in Figure 4 (a) which corresponds with highest Young's (E) and shear modulus (G_H) as well as lowest values of Poisson's ratio in Table I.

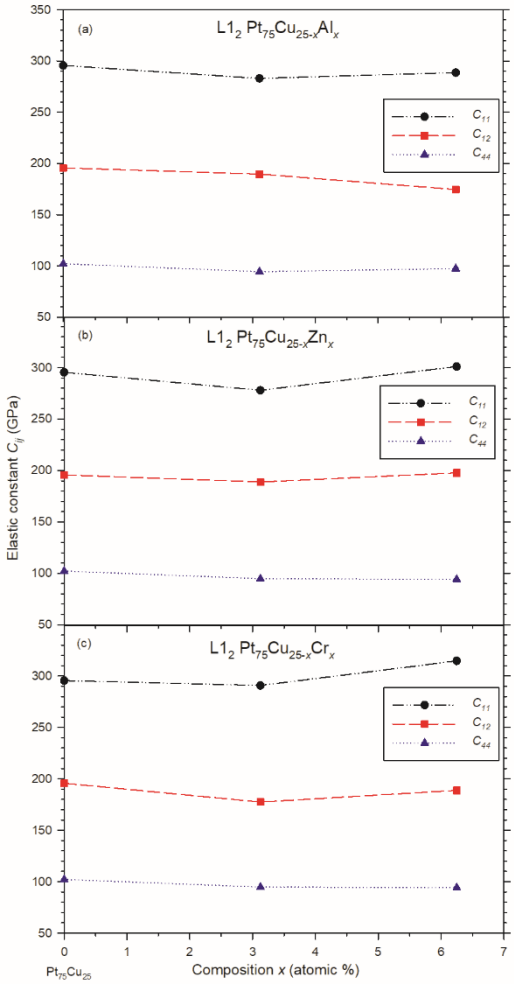

Figure 3. Predicted elastic constants of (a) Al, (b) Zn, and (c) Cr alloyed $L1_2$ $Pt_3Cu_{1-x}Y_x$.

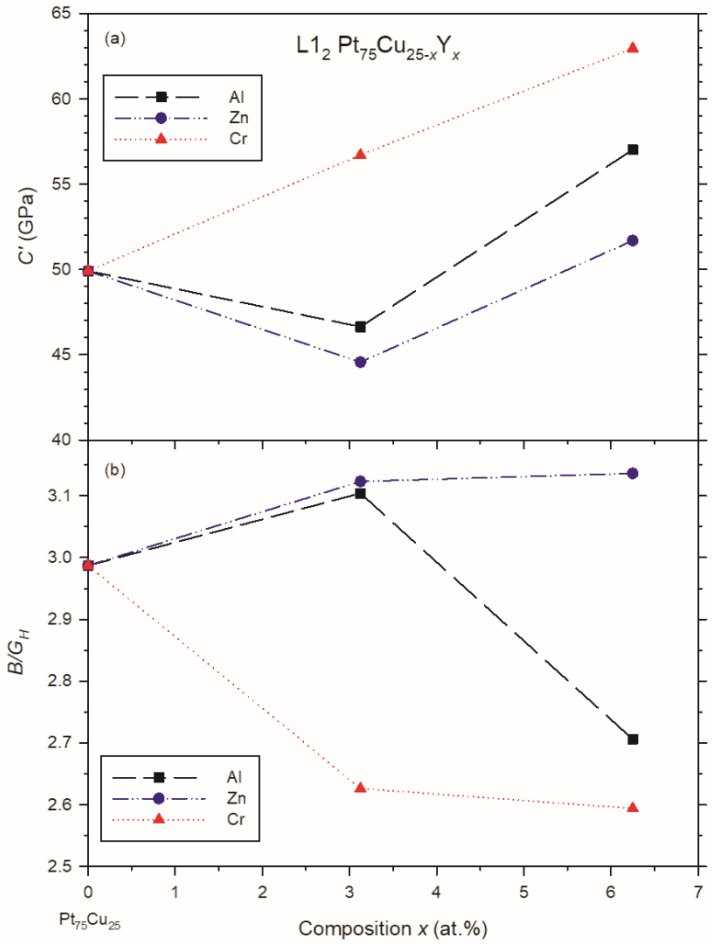

Figure 4. Predicted elastic moduli (a) C′ and ratio B/G_H of L1$_2$ $Pt_3Cu_{1-x}Y_x$.

The current results depict for the first time a correlation between thermodynamic stability (formation energy) and mechanical strength. As it has been experimentally reported that formation of the ordered (intermetallic) phase yielded superior catalytic performance and phase stability in ORR in fuel cells (Zhao *et al.,* 2021; Kim and Joo, 2020; Saravanan *et al.,* 2016), this correlation emanating from this work could be responsible for stability and enhanced performance. The Al and Cr at around 6 at. % could be promising L1$_2$ $Pt_3Cu_{1-x}Y_x$ ternary alloys with potential to be used as catalysts in oxygen reduction reactions of proton-exchange membrane fuel cells.

Table I. Calculated mechanical properties of L1$_2$ $Pt_3Cu_{1-x}Y_x$

Composition	**Bulk Modulus *B* (GPa)**	**Young' Modulus *E* (GPa)**	**Shear Modulus G_H (GPa)**	**Poisson's ratio μ (GPa)**
$Pt_{24}Cu_8$	228.96	139.59	76.65	0.398
$Pt_{24}Cu_7Al_1$	220.71	130.70	71.10	0.401
$Pt_{24}Cu_6Al_2$	212.55	157.01	78.55	0.377
$Pt_{24}Cu_7Zn_1$	218.51	125.18	69.97	0.404
$Pt_{24}Cu_6Zn_2$	232.15	144.34	74.03	0.396
$Pt_{24}Cu_7Cr_1$	215.20	156.39	81.96	0.379
$Pt_{24}Cu_6Cr_2$	230.79	173.12	88.97	0.375

CONCLUSIONS

Using first-principles modelling on the $L1_2$ $Pt_3Cu_{1-x}Y_x$ compositions, the calculated heats of formation showed that the thermodynamic stability was gradually enhanced with increasing content of all three alloying elements, with Al being the most effective even at smaller compositions while Cr was the least. However, despite low thermodynamic stability, the increase in Cr composition resulted in higher elastic properties such as tetragonal shear and Young's moduli compared to the other two alloying elements, implying higher strength.

The current results reveal the alloying compositions that improved the thermodynamic stability of cubic ordered Pt_3Cu phase as well as satisfied the mechanical stability criteria. Therefore, a theoretical technique has been successfully employed to identify ternary $L1_2$ $Pt_3Cu_{1-x}Y_x$ compositions with potential to be used as cathode catalysts in proton-exchange membrane fuel cells.

ACKNOWLEDGEMENTS

This work was mostly conducted at Mintek's computer laboratory and was supported by Mintek, University of Pretoria and the South African Diamond and Precious Metals Regulator.

REFERENCES

Abe, T., Sundman, B., and Onodera, H., 2006. Thermodynamic Assessment of the Cu-Pt System. *Journal of Phase Equilibria and Diffusion*, vol. 27, no. 1, pp.5-13. https://doi.org/10.1361/105497196X92736

Callister W.D., and Rethwisch D.G., 2011. Materials Science and Engineering, 8th edition, John Wiley & Sons.

Clark, S., Segall, M.D., Pickard, C.J., Hasnip P.J., Probert M.I.J., Refson, K., and Payne, M.C., 2005. First Principles Methods Using CASTEP. Zeitschrift fuer Kristallographie, vol. 220, pp. 567-570. https://doi.org/10.1524/zkri.220.5.567.65075

Cornish, L.A., Süss, R., Völkl, R., Wenderoth, M., Vorberg, S., Fischer, B., Glatzel, U., Douglas, A., Chown, L.H., Murakumo, T., Preussner, J., Lupton, D., Glaner, L., Maledi, N.B., Potgieter, J.H., Sephton, M., and Williams, G., 2007. Overview of the Development of New Pt-based Alloys for High Temperature Application in Aggressive Environments. *Journal of South African Institute of Mining and Metallurgy*, vol. 107, pp. 697-711.

Kim, H.Y., and Joo, S.H., 2020. Recent advances in nanostructured intermetallic electrocatalysts for renewable energy conversion reactions. *Journal of Materials Chemistry A*, vol. 8, pp. 8195-8217. https://doi.org/10.1039/D0TA01809K

Mølmen, L., K. Eiler, K., Fast, L., Leisner, P., and Pellicer, E., 2021. Recent advances in catalyst materials for proton exchange membrane fuel cells. *APL Materials*, vol. 9, pp.040702 (1-24). https://doi.org/10.1063/5.0045801

Nye, J.F., 1985. Physical properties of crystals. Oxford: Oxford University Press.

Ou, L., 2014. The origin of enhanced electrocatalytic activity of Pt-M (M = Fe, Co, Ni, Cu and W) alloys in PEM fuel cell cathodes: A DFT computational study. *Computational and Theoretical Chemistry*, vol. 1048, pp. 69-76. https://doi.org/10.1016/j.comptc.2014.09.017

Perdew, J.P., and Wang, Y., 1992. Accurate and simple analytic representation of the electron-gas correlation energy. *Physical Review B*, vol. 45, pp. 13244-13249. https://doi.org/10.1103/PhysRevB.45.13244

Perdew, J.P., Kieron Burke, K., and Ernzerhof, M., 1997. Generalized Gradient Approximation Made Simple. *Physical Review Letters*, vol. 77, pp. 3865-3868. https://doi.org/10.1103/PhysRevLett.77.3865

Phasha, M.J., Ngoepe P.E., Chauke H.R., Pettifor D.G., and Nguyen-Mann D., 2010. Link between structural and mechanical stability of fcc- and bcc-based ordered Mg-Li alloys. *Intermetallics*, vol. 18, pp. 2083-2089.

Ren, X., Lv, Q., Liu, L., Liu, B., Wang, Y., Liu, A., and Wu, G., 2020. Current progress of Pt and Pt-based electrocatalysts used for fuel cells. *Sustainable Energy Fuels*, vol. 4, pp. 15-30. https://doi.org/10.1039/C9SE00460B

Saravanan, G., Khobragade, R., Nagar, L.C., and Labhsetwar, N., 2016. Ordered intermetallic Pt–Cu nanoparticles for the catalytic CO oxidation reaction. *RSC Advances*, vol. 6, pp. 85634-85642. https://doi.org/10.1039/C6RA19602K

Vanderbilt, D., 1990. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Physical Review B, vol. 41, pp. 7892–7895. https://doi.org/10.1103/PhysRevB.41.7892

Wang, X.X., Swihart, M.T., and Wu, G., 2019. Achievements, challenges and perspectives on cathode catalysts in proton exchange membrane fuel cells for transportation. *Nature Catalysis*, vol. 2, pp. 578-589. https://doi.org/10.1038/s41929-019-0304-9

Wang, X., Li, Z., Qu, Y., Yuan, T., Wang, W., Wu, Y., and Li, Y., 2019a. Review of Metal Catalysts for Oxygen Reduction Reaction: From Nanoscale Engineering to Atomic Design. Chem, vol. 5, issue 6, pp. 1486-1511. https://doi.org/10.1016/j.chempr.2019.03.002

Zhao, X., Cheng, H., Song, L., Han, L., Zhang, R., Kwon, G., Ma, L., Ehrlich, S.N., Frenkel A.I., Yang, J., Sasaki, K., and Xin, H.L., 2021. Rhombohedral Ordered Intermetallic Nanocatalyst Boosts the Oxygen Reduction Reaction. *ACS Catalysis*, vol. 11, no. 1, pp. 184–192. https://doi.org/10.1021/acscatal.0c04021

Tiny Mathibeng

Inspectorate Manager
South African Diamond and Precious Metals Regulator

Currently Managing the Inspectorate Division at the South African Diamond and Precious Metals Regulator.
Positions Held previously – Technician in training (2003) Direct Reduction Arcelor Mittal, Junior Metallurgist (2004-2006), and Shift Metallurgist (2007) in Highveld Steel and Vanadium

The very first precious metals inspector appointed in the country under section 3. (2)(c) of the Precious Metals Act, with 14 years' experience working as precious metals Inspector and Transformation Officer. Responsible for ensuring compliance and promotion of local beneficiation of the diamonds and precious metals through enterprise development project in collaboration with industry and created SMME's owned by HDP and skill development in the Jewellery manufacturing and diamond cutting and polishing. Also acquired various certificates: Jewellery manufacturing techniques, rough diamond evaluation, import and exports procedure, environmental law (NEMA), ISO management systems for quality and environmental, 3D jewellery computational design (Rhino course), BEE for transformation. Tiny Mathibeng holds a BSc(hons) Degree in Metallurgy and currently studying MSc degree in Metallurgy at the University of Pretoria.