From Figure 34, it can be seen that lattice parameter increases as Cr concentration increases, the increase however does not follow the Vegard's law as there is no linear relationship between the lattice parameter and Cr concentration

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The use of DFT first principles and FactSage simulation methods to predict phase stability of FCC Ni-Cr-Al alloys in attempt to improve metal dusting resistance in the petrochemical industry

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INTRODUCTION & AIM

Corrosion is a chemical or electrochemical change of the material when it interacts with the environment. The major problem experienced with corrosion is that complete elimination of corrosion is impossible, but it can only be controlled.

In particular, due to high temperatures and gaseous operating conditions in the oil and gas industry, infrastructure experiences a high rate of metal dusting (MD) corrosion. This MD causes material deterioration that leads to unplanned shutdowns or even catastrophic failure. So far, it is difficult to eliminate metal dusting, but it can be controlled. High temperature operations result in metal pitting that occurs in carbon supersaturated gaseous environments at temperatures ranging from 400 to 850°C.

This project aimed to assist with controlling metal dusting in the oil and gas industry. Ni-based alloys are effective metal-dusting-resistant materials at high temperatures and have been used successfully in the oil and gas industry [1]. However, to increase oil and gas production, the environment becomes more aggressive, which increases the rate of metal dusting due to higher operating temperature and pressure, as well as higher levels of carbon dioxide (CO_2). Thus, requiring more robust corrosion-resistant Ni-based alloys to mitigate the problem.

In response to this challenge, this work explored the use of density functional theory (DFT) first principles and FactSage simulations to predict suitable Ni-Cr-Al alloy compositions that can be used in the petrochemical industry. This involved simulating phase diagrams of Ni-Cr, Ni-Al and Ni-Cr-Al alloys. CASTEP simulation was used to calculate structural and mechanical properties of Ni-Cr-Al alloys using the supercell approach. The calculations are aimed at finding a suitable alloying composition range for Cr and Al. In addition, FactSage simulations were used to mimic the industry to see the response of the alloys towards metal dusting-enhancing environments such as CO and CO-H_2O-H_2 at 525 and 650°C. After exposure, the amounts of possible metal oxides formed were predicted. In this project, the thermodynamics, phase stability, structural and mechanical properties, as well as metal dusting at high temperatures, were taken into consideration during the design of the alloys.

METHOD

Thermo-Calc calculations:

Thermo-calc data was used to calculate Ni-Cr-Al alloys phase diagrams and thermodynamic results. This assesses the stable phases in the Ni-Cr and Ni-Cr-Al phases. For the systems SSOL4 thermodynamics database was used, and the calculations were performed at 525 and 650°C. The following will be determined using Thermo-Calc:

- Binary phase diagrams
- Ternary phase diagrams

FactSage simulations for metal dusting:

- Thermochemical simulations of the Ni-Cr-Al alloy using FactSage™ 8.0 software to deduce the best metal dusting resistance system.
- 'Equilib' module equipped with 'FactPS', 'FToxid', and 'SGTE' chemical thermodynamic databases was used to complete the calculations
- Metal dusting tests were conducted under CO and CO-H_2O-H_2

CASTEP simulations:

Build possible crystal structure for Ni – Cr, Cr – Ni, Ni-Al and Cr-al using supercell approach and calibrate it (using lattice parameter information from literature) → The use of supercell approach is to help in determining which approach is more suitable to calculate Ni-Cr-Al alloys → Geometry optimisation (this task allows one to determine the most stable structure by refining the geometry of a 3D periodic system) → Elastic constants calculation (to evaluate all the mechanical properties) → Structural stability (such as enthalpy and stability)

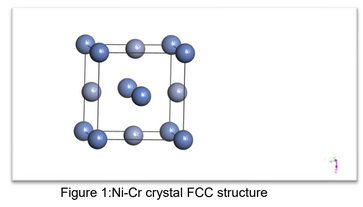

Figure 1:Ni-Cr crystal FCC structure

RESULTS & DISCUSSION

Thermo-Calc results

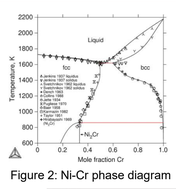

Figure 2: Ni-Cr phase diagram

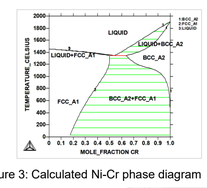

Figure 3: Calculated Ni-Cr phase diagram

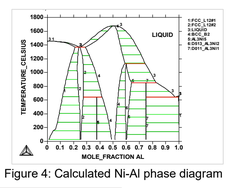

Figure 4: Calculated Ni-Al phase diagram

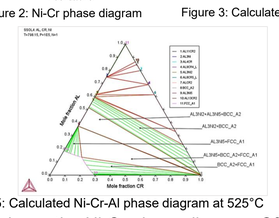

Figure 5: Calculated Ni-Cr-Al phase diagram at 525°C

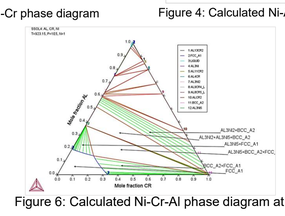

Figure 6: Calculated Ni-Cr-Al phase diagram at 650°C

- Figure 2 shows the Ni-Cr phase diagram. Of importance from the phase diagram is the Ni_2Cr phase, which is not desirable for metal dusting, as it is brittle.
- The calculated phase diagrams of Ni-Cr and Ni-Al (Figures 3 and 4) alloys showed that the stable phases were found to be BCC and FCC. According to the phase diagrams, stable phases are BCC and FCC, with BCC being Cr dominate and FCC being Ni-dominant. The Gibbs energy of the alloys shows that the alloys are thermodynamically stable at 650°C. This is in agreement with the binary phase diagrams that were calculated and published by Chan et al. (2006) [2] .
- In ternary phase diagrams (Figures 5 and 6) of Ni-Cr-Al, intermetallics compete with the FCC solid solution of Ni-Cr-Al. The present intermetallics are Ni-Al intermetallics, which are more dominant at high Al concentrations.

CASTEP simulation results

Ni-Cr binary alloy

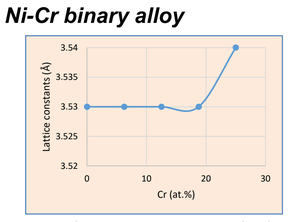

Figure 7:Calculated lattice constants of Ni-Cr alloys

Voigt and Reuss methods:

$G_V = 1/5(C_{11} - C_{12} + 3C_{44})$

$G_R = 5(C_{11} - C_{12})\, C_{44} / [4C_{44} + 3(C_{11} - C_{12})]$

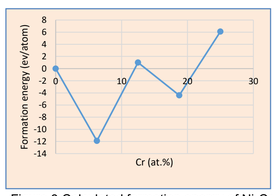

Figure 8:Calculated formation energy of Ni-Cr alloys

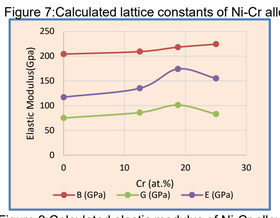

Figure 9:Calculated elastic modulus of Ni-Cr alloys

Bulk modulus

$B = 1/3(C_{11}+2C_{12})$

Shear modulus

$G = 1/2(G_v + G_R)$

Young's modulus

$E = 9BG/(3B+G)$

Pugh's ratio

Pugh's ratio = B/G

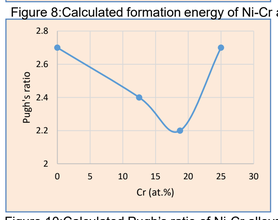

Figure 10:Calculated Pugh's ratio of Ni-Cr alloys

- From Figure 7, it can be seen that the lattice parameter is nearly constant until Cr content is above 20 at.%. The equations to calculate elastic modulus from elastic constants are also shown
- Figure 8 shows the relationship between formation energy and Cr content. 6.25 and 18.75 at.% Cr. This shows the thermodynamic stability of FCC solid solution at lower Cr content.
- The shear modulus represents the plastic deformation of the material while bulk modulus represents the compressibility resistance or resistance to volume change by applied pressure. While the Young's modulus shows the material's stiffness, which is associated with strength
- The bulk modulus decreases between 0 and 12.4 at.% Cr followed an increase in the bulk modulus as Cr concentration increases. Shear modulus and Young's modulus have the same tread with the highest peak at 18.75 at.% Cr. The highest values of shear modulus and Young's modulus are 101 and 174 at.% Cr, respectively. There is a decrease in the shear modulus and Young's modulus between 18.75 and 25 at.% Cr. This is shown in Figure 9
- The ductility or brittleness of the material also plays an important role when looking at the properties of the coating. When the coating is exposed to different shocks, it should be able to withstand the shocks without introducing cracks or failures. A ductile material is preferred (B/G>1.75)
- 18.75 at.% Cr is the least ductile composition. Given that brittle Ni_2Cr is not preferred, the predicted suitable working Cr content should be between 18.75 and 25 at.%.

Ni-Al binary

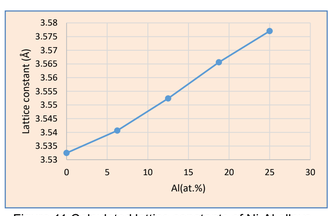

Figure 11:Calculated lattice constants of Ni-Al alloys

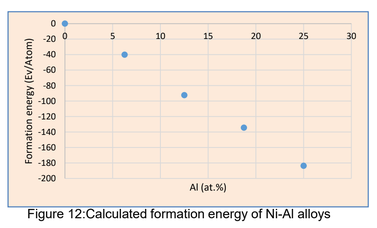

Figure 12:Calculated formation energy of Ni-Al alloys

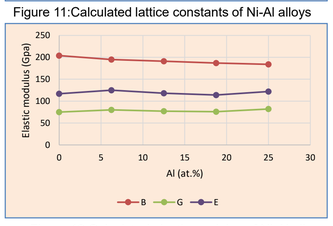

Figure 13:Calculated elastic modulus of Ni-Al alloys

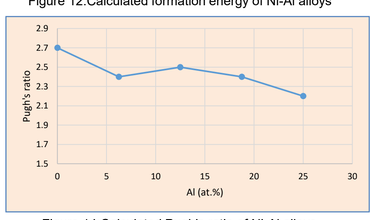

Figure 14:Calculated Pugh's ratio of Ni-Al alloys

- Lattice parameter increases as Al concentration increases and it follow the Vegard's law as there is a linear relationship between the lattice parameter and Al concentration. This is shown in Figure 11
- Heat of formation for all Ni-Al compositions are negative, indicating favourable thermodynamically stability. This is shown in Figure 12
- Mechanical properties are not changing by increasing the Al content
- Bulk modulus slightly decreases from 204 to 184 GPa as Al concentration increases
- For the Shear modulus and Young's modulus, increase between 0 and 6.25 at.% Al, which is then followed by a decrease between 6.25 and 18.75 at.% Al. This is shown in Figure 13
- The highest strength is at 6.25 at.% Al and the highest shear modulus is at 25 at.% Al
- The ductility of the binary alloy decreases as the Al content increases, 25 at.% Al is the least ductile. This is shown in Figure 14

Ni-Cr-Al ternary

Table 1: Calculated lattice parameter and heat of formation of Ni- Cr-Al alloys

	Lattice parameter (Å)	Heat of formation (KJ/mol)
$Ni_{24}Cr_7Al_1$	a=3.545	-8.2
$Ni_{24}Cr_6Al_2$	a=3.549	-40.2

Table 2: Calculated mechanical properties of Ni-Cr-Al alloys

	B	E	G	B/G
$Ni_{24}Cr_7Al_1$	212	164	89	2.4
$Ni_{24}Cr_6Al_2$	205	171	96	2.1

- Table 1 and 2 shows the calculated lattice parameter, heat of formation and the mechanical properties of Ni-Cr-Al ternary
- The lattice parameter of FCC Ni-Cr increases with Al content
- Heat of formation for Ni-Cr increases with Al, as shown in Table 1, $Ni_{24}Cr_6Al_2$ is more thermodynamically stable
- $Ni_{24}Cr_6Al_2$ exhibit higher shear and Young's modulus compared to $Ni_{24}Cr_7Al_1$, and the result is the opposite for bulk modulus
- Table 2 shows the Pugh's ratio, and it can be noted that all the alloys are ductile as the B/G ratios are larger than 1.75

CASTEP data to be used as input in FactSage simulations:

- Cr content will be between 18.25 at.% and 25 at.% Cr to avoid formation of Ni_2Cr
- The alloys of interest for metal dusting tests using FactSage will be:
  1. Alloy 1- Ni 69.33 at.% - Cr 30.67 at.%
  2. Alloy 2- Ni 75 at.% - Cr 25 at.%
  3. Alloy 3- Ni - Cr 30.67 at.% - 6.25 at.% Al
  4. Alloy 4- Ni - Cr 18.75 at.% - 6.25 at.% Al

FactSage results

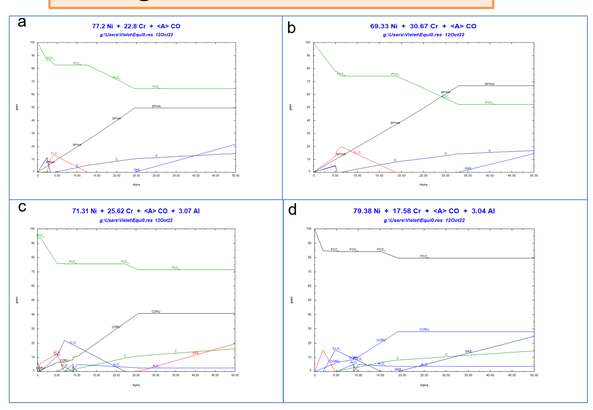

Figure 15: Stable phases for alloy 1(a), 2(b), 3(c) and 4(d) when exposed to CO 525°C

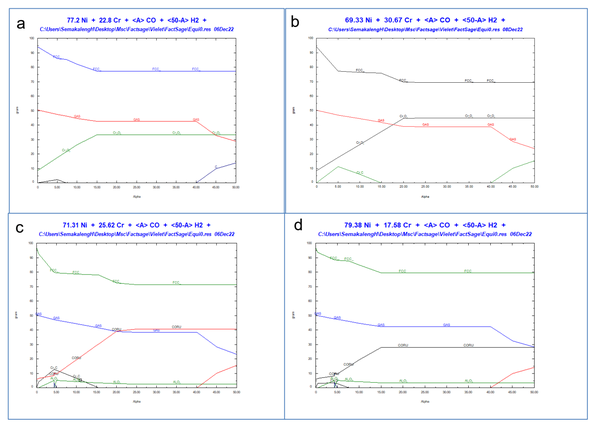

Figure 15: Stable phases for alloy 1(a), 2(b), 3(c) and 4(d) when exposed to CO-H_2O-H_2 525°C

- Figures 15 and 16 show the stable phases that are present during metal dusting corrosion under CO and CO-H_2O-H_2 environments at 525°C, the same calculations were done at 650°C, but not presented
- Metal dusting occurs in a highly carburising atmosphere. In the phase diagrams, metal dusting will be assumed to have occurred when there is high saturated carbon phase.
- During the metal dusting process, the interaction of carbon species with the alloys led to the reaction of the carbon with the alloy, leading to carbides [3]. As shown in Figures 15 and 16 of the alloys, it can be noted that all the alloys had a Cr-carbide phase present. This shows that there is metal dusting corrosion at low CO and CO-H_2O-H_2 exposures.

Table 3: Calculated oxide layer when alloy exposed to CO

alloy	Cr oxide layer (g)		Al oxide layer (g)	
	525°C	650°C	525°C	650°C
1	0	0	0	0
2	0	0	0	0
3	3.4244	3.7445	5.1322	5.8007
4	3.3909	0	5.0821	2.557

Table 4: Calculated oxide layer when alloy exposed to CO-H_2O-H_2

alloy	Cr oxide layer (g)		Al oxide layer (g)	
	525°C	650°C	525°C	650°C
1	4.4826	4.4826	0	0
2	3.3323	3.3323	0	0
3	3.4244	0	5.1322	2.5785
4	3.3909	0	5.0821	3.2976

- The oxide layers that are formed in all alloys are shown in Tables 3 and 4.
- It can be concluded that alloy 3 performs better as a metal dusting resistance alloy, and also the best working temperature is 650°C when exposed to CO, and when the alloys are exposed to CO-H_2O-H_2, the best performing alloy is alloy 3 at 525°C.
- The addition of Al to the alloys does improve the metal dusting resistance, as supported by the oxide layers that are formed in alloys 3 and 4 compared to those formed in alloys 1 and 2.

CONCLUSIONS

- The simulated phase diagrams of Ni-Cr, Ni-Al and Ni-Cr-Al alloys showed that the stable phases were found to be BCC and FCC. BCC being chromium (Cr) dominant, and FCC being nickel (Ni) dominant. The Gibbs free energy of the alloys shows that the alloys are thermodynamically stable at 650°C. CASTEP simulation was used to calculate the structural and mechanical properties of Ni-Cr-Al alloys using the supercell approach. From the calculations, the suitable working range for Cr is between 18.25 and 25 at.%, and with Al 6.25 at.% showed to be the best alloying concentration for the ternary alloy. The metal dusting results showed that with CO exposure, the alloys experience carbon attack at low CO exposure, due to minimum amount of oxide layer that is present. With the exposure of CO-H_2-H_2O, all alloys had oxide layers that were formed. It can be concluded that Ni - 30.67 at.% Cr - 6.25 at.% Al performed better as metal dusting resistance alloy when exposed to CO and CO-H_2-H_2O at 525 and at 650°C.

FUTURE WORK/ REFERENCES/ACKNOWLEDGMENT

Future work

For future work, the alloys will be cast and tested for metal dusting using a metal dusting simulator at Mintek.

Reference

1. Saaedi, J., Coyle, T. W., Mirdamadi, S., Arabi, H., & Mostaghimi, J. (2008). Phase formation in a Ni-50Cr HVOF coating. Surface and Coatings Technology, 202, 5804-5811
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3. Guo, X., Vullum, P. E., & Venvik, H. J. (2021). Inhibition of metal dusting corrosion on Fe-based alloy by combined near-surface severe plastic deformation (NS-SPD) and thermochemical treatment. Corrosion Science(190), 1-12

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