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ESTIMATION OF THERMODYNAMIC PARAMETERS OF Ni-Si BASE ALLOYS USING THE SEMI-EMPIRICAL MIEDEMA MODEL

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Abstract: In this paper, we present a calculation method for evaluating the possibility of enhancing the thermal stability of nickel silicide by alloying with metals, which consists in determining the formation enthalpy (ΔH) of nickel silicide using the Miedema model. Changes in formation enthalpy (ΔH) were observed for nickel silicides that were alloyed with Mo, Pt, Pd, W, and Zr. The MAAT (Materials Analysis Applying Thermodynamics) software was used to calculate and plot the formation enthalpy of binary and ternary systems. Based on our calculations, we found that in binary systems, the optimum values to expand the formation enthalpy were ⍰51.28 and ⍰49.57 kJ/mol for nickel silicide alloys. For the ternary system, the results showed that adding Zr could increase monosilicide phase stability.

Keywords: *Miedema model, Formation enthalpy, Ni-Si alloys*

1. Introduction

Nickel monosilicide (NiSi) is a promising material for microelectronics, and it is mainly used due to its low resistivity (12–14 μOhm·cm), low formation temperature (T = 350–500°C), and compatibility with silicon and germanosilicide technologies (Chi et al., 2007). However, during high-temperature treatment (T ≥ 700°C), several problems arise, associated with the agglomeration of a thin film of nickel silicide and the phase transition to the highly resistive NiSi2 compound due to a sharp increase in the specific resistance of the material. The phase transformation of NiSi to NiSi2 leads to an increase in leakage currents and a deterioration in the morphology of the silicide/silicon interface.

To expand the application range for the nickel monosilicide phase in the nickel–silicon system, thermal stability should also be increased. Therefore, approaches to increasing the NiSi thermal stability compound have attracted much interest in the last decade. One possible solution is doping silicon single crystals with 〖BF〗_2^+ or F+ ions (Wong et al., 2002). The introduction of 〖BF〗_2^+ or F+ ions ensures the stable existence of the NiSi phase up to a temperature of T = 750°C, at which NiSi2 is usually formed. This effect is due to the segregation of fluorine at the silicide/silicon (001) interface and at the silicide grain boundaries, which slows down the growth of NiSi grains. Consequently, the presence of 〖BF〗_2^+ or F+ ions in the silicon substrate leads to an improvement in the uniformity of the monosilicide film and the formation of smaller grains. However, due to the possible ingrowth of silicon grains into the silicide layer and additional defects introduced by fluorite, this method cannot be considered an optimal way to increase thermal stability. The second method used to increase the morphological and phase stability of nickel silicide is doping nickel silicide with various metals or introducing a metal sublayer between nickel and silicon.

In particular, the studies (Huang et al., 2007; Shao et al., 2006; Gao et al., 2009) on the addition of the metals Pt, Pd, Ru, and Zr showed that such alloying has an influential effect on both the temperature stability and the morphological homogeneity of the surface and the NiSi/Si interface. The assessment of thermal stability was carried out based on the phase analysis of the Ni-Si system at different annealing temperatures using X-ray diffraction analysis and Raman spectroscopy (Gao et al., 2009; Skobelev et al., 2021).

This paper considers a calculation method for assessing the thermal stability of nickel silicide alloys with metals and the possibility of increasing it. This is achieved by using the Miedema model based on the determination of the formation enthalpy of nickel silicide (Steeneken & Houtgast, 1980). The analysis of changes in the thermal stability of nickel silicides doped with metals Mo, Pt, Pd, W, and Zr is carried out.

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2. Thermodynamic Analysis

Miedema Model

The two main parameters on which the formation enthalpy of a specific phase of metal alloys depends are the sign and the value. Therefore, we calculate the formation enthalpy for both binary and ternary systems according to the semi-empirical Miedema model (Steeneken & Houtgast, 1980; Wang et al., 2004).

We present the calculation of the formation enthalpy of phases for both undoped and doped nickel silicides. Undoped nickel silicides are nickel silicides formed by the solid-phase reaction of a film of nickel and silicon, whereas doped nickel silicides are compounds formed by the solid-phase reaction of a nickel film containing an alloying addition, for example, a transition metal, and silicon. The concept of nickel silicides used in this work includes three phases: a nickel-rich phase (Ni2Si), a nickel monosilicide phase (NiSi), and a nickel disilicide phase (NiSi2).

Since the results of recent experimental work (Gao et al., 2009; Skobelev et al., 2021) predict the possibility of increasing the thermal stability of nickel silicides with the addition of several elements, we analyse and calculate the formation enthalpy of nickel silicides with different compositions.

The semi-empirical Miedema model (Steeneken & Houtgast, 1980; Chelikowsky, 1982) allows direct calculation of the formation enthalpy of liquid and solid alloys containing atoms of both transition and non-transition metals. In the Miedema model, each atom is described by two parameters: the chemical potential, ϕ*, and the averaged electron density over the surface of the Wigner–Seitz cell, n_WS^(1⁄3). The Miedema model assumes that there are two mechanisms that contribute to the formation enthalpy of binary alloy systems: the first is proportional to ϕ*2 and is associated with charge transfer between neighbouring cells due to attractive forces, and the second is proportional to n_WS^(2⁄3) and takes into account the repulsive forces due to surface tension.

Using the results of calculating the formation enthalpy of the binary system, obtained according to the Miedema model (Steeneken & Houtgast, 1980; Wang et al., 2004; Sharma & De Datta, 1986), we write the expression for the heat of formation:

$$\Delta H_{AB} = C_A^B X_A \Delta H_{A \text{ in } B} + C_B^A X_B \Delta H_{B \text{ in } A}) \quad (1)$$

The concentration functions C_A^B and C_B^A are given by

$$C_A^B = X_A^S \left[1 + \beta (X_A^S X_B^S)^2\right] \quad (2)$$

$$C_B^A = X_B^S \left[1 + \beta (X_A^S X_B^S)^2\right] \quad (3)$$

The factor β has different values, 0, 5, and 8, which refer to soli solution, metallic glasses, and intermetallic, respectively.

The surface concentrations by X_A^S and X_B^S are represented by

$$X_A^S = \frac{X_A V_A^{\frac{2}{3}}}{X_A V_A^{\frac{2}{3}} + X_B V_B^{\frac{2}{3}}} \quad (4)$$

$$X_B^S = \frac{X_B V_B^{\frac{2}{3}}}{X_A V_A^{\frac{2}{3}} + X_B V_B^{\frac{2}{3}}} \quad (5)$$

Also, the interfacial enthalpy $\Delta H_{A \text{ in } B}$ for mixing of A in B is described by

$$\Delta H_{A \text{ in } B} = \frac{P V_A^{2/3}}{(n_{\text{WS}}^{-1/3})_{av}} \times [-(\Delta \emptyset^*)^2 + {}^{Q}/_{P} \left(\Delta n_{\text{WS}}^{1/3}\right)^2 - {}^{R^*}/_{P}]$$

(6)

Here, the terms VA, Φ*, and nWS represent the molar volumes of A and B, the constituent element work function, and the density of electrons, respectively. P, Q, and R* are constants. Constant P has values of 14.2 and 10.7 (Alsaedi et al., 2020; Imani & Enayati, 2017; Li, 2014). The metal status of being transitioned or non-transitioned describes this difference in P values. In addition, P/Q has a value of 9.4. R* appears as an additional term for the enthalpy in Eq.6 for transition/non-transition metals.

Table 1. The values of the electron density at the boundary of the Wigner–Seitz cell, $n_{\text{WS}}^{1/3}$, experimentally obtained in [7], and the values of $n_{\text{CWS}}^{1/3}$ calculated in this study.

Metal	Atomic radius (nm)	$n_{\text{ws}}^{1/3}$ (d. u)$^{1/3}$	$\emptyset^*$(V)	$V_m^{2/3}$ (cm)^2
Si	0.118	1.50	4.70	4.20
Ni	0.124	1.75	5.20	3.50
Mo	0.140	1.77	4.65	4.40
W	0.141	1.81	4.80	4.50
Zr	0.160	1.39	3.40	5.80
Pd	0.137	1.67	5.45	4.30
Pt	0.139	1.78	5.65	4.40

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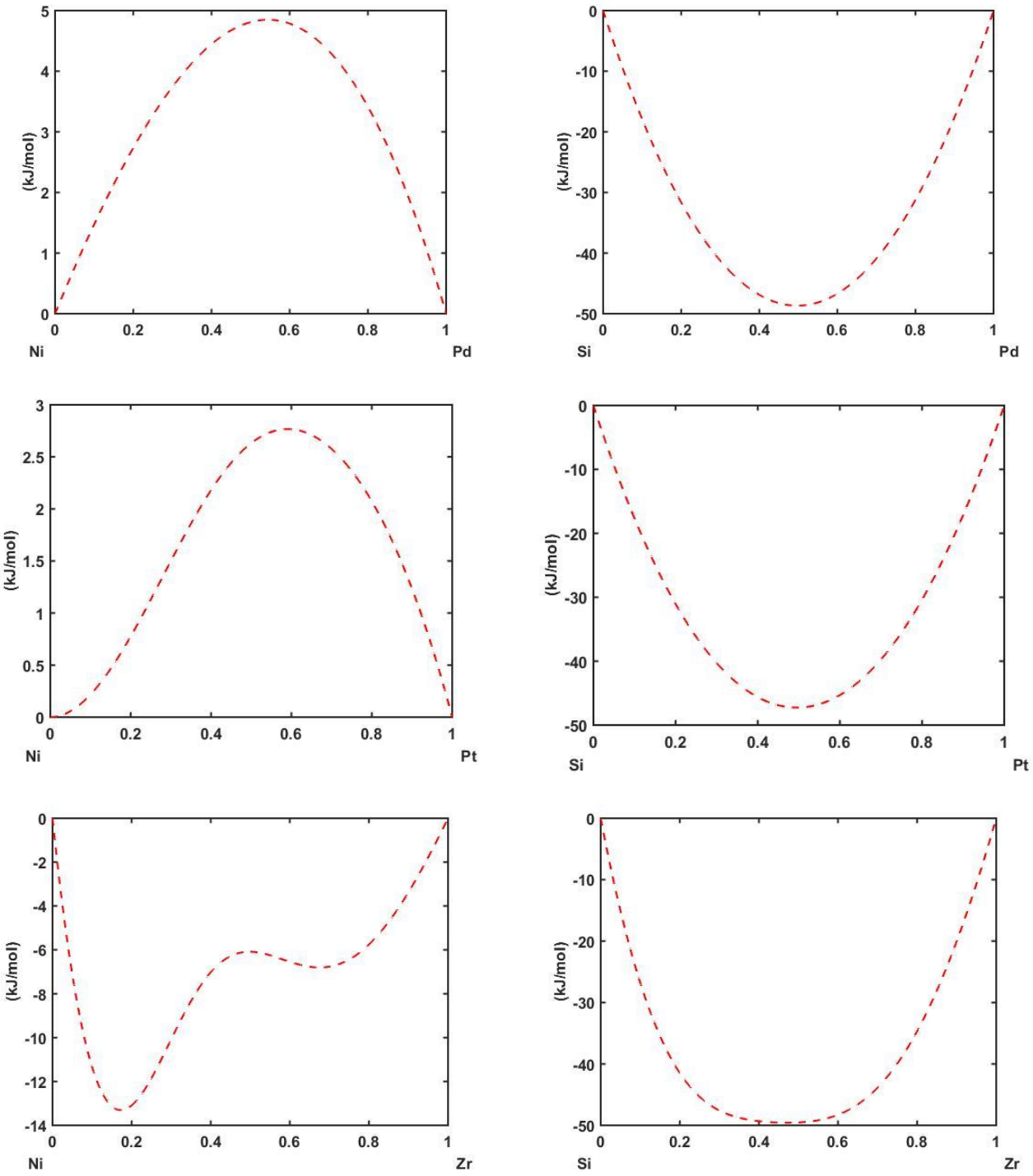
3. Results and Discussion

Figure 1 shows the formation enthalpy (ΔH) of the binary systems Ni-Pd, Si-Pd, Ni-Pt, Si-Pt, Ni-Zr, Si-Zr, Ni-Mo, Si-Mo, Ni-W, Si-W, and Ni-Si. Furthermore, Figure 1 reveals that the binary systems Ni-Si, Si-Pd, Si-Pt, Ni-Zr, Si-Zr, Si-Mo, and Si-W are more stable because the values of the formation enthalpy are negative for all composition values. The highest negative value was found in the binary system Si-Zr (−49.57 kJ/mol), and the lowest negative value was observed in Ni-Zr (−13.31 kJ/mol). The curve has two minimal points near xNi ~ 0.2 and x ~ 0.7. This indicates that in a binary system, the formation of these phases results from the stored energy released by a thermodynamic force.

The ΔH values of binary systems Ni-Mo, Ni-Pd, Ni-Pt, and Ni-W were positive for all composition values. This indicates that the formation of these binary systems is impossible under standard conditions, demonstrating that there is no strong interaction between the atoms. The reason for this behaviour could be the small differences between the electron negativities, atomic volumes, and electron densities of the atoms, as shown in Table 1.



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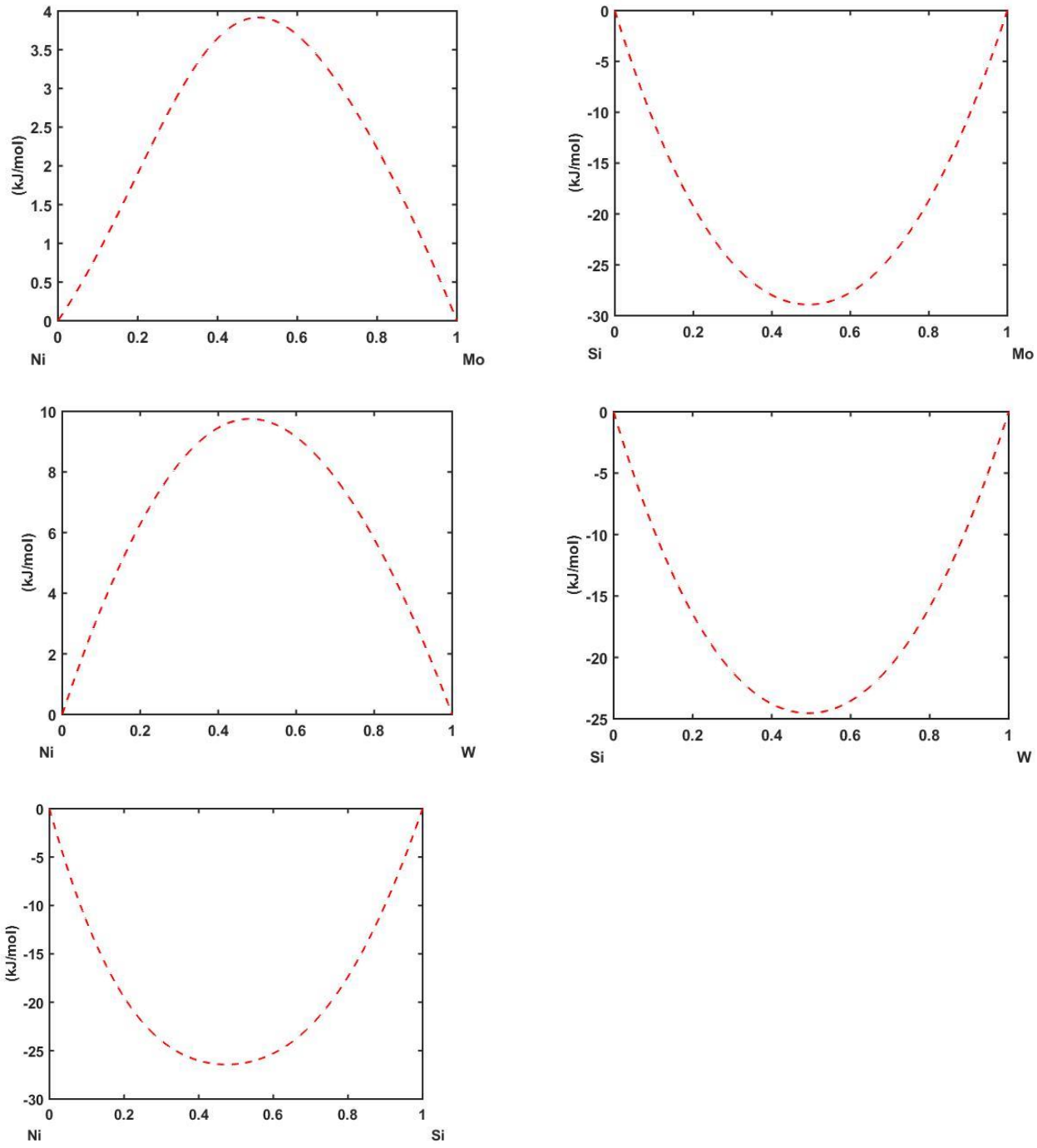

Figure 1. The formation enthalpy of the binary systems Ni-Pd, Si-Pd, Ni-Pt, Si-Pt, Ni-Zr, Si-Zr, Ni-Mo, Si-Mo, Ni-W, Si-W, and Ni-Si.

Figure 2 shows the formation enthalpy of the ternary system of nickel silicides doped with Pd, Pt, Zr, Mo, and W, and it shows that the addition of Zr, Pd, and Pt in the composition of the nickel film leads to the most negative values of the formation enthalpy of doped nickel silicide (⍰49.62, ⍰48.67, ⍰46.80 kJ/mol for Zr, Pd, and Pt, respectively). This means that for the conversion of nickel monosilicide into nickel disilicide, it will be necessary to spend more energy and, consequently, heat, which will lead to an increase in the process temperature.

The more negative the value of the formation enthalpy, the more stable the connection and the stronger the bond between silicon and metal atoms. As a result, it is more difficult to break it for the formation of a disilicide. As can be seen, it is precisely the more negative value of the formation enthalpy of nickel silicide due to the addition of an alloy element to the composition of the compound that leads to an improvement in its thermal stability.

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The data in Figure 2 show that the addition of elements such as Mo and W leads to less negative values of the formation enthalpy of nickel disilicide than the formation enthalpy of pure nickel disilicide (−26.43 and −25.97 kJ/mol for Mo and W, respectively). However, the experimental data (Huang et al., 2007; Shao et al., 2006) indicate that the addition of these elements, albeit insignificantly, increases the thermal stability of nickel monosilicide, which might be due to the influence of other factors, for example, an improvement in the morphology of the interface and a slowdown in the growth of grains in the NiSi2 phase.

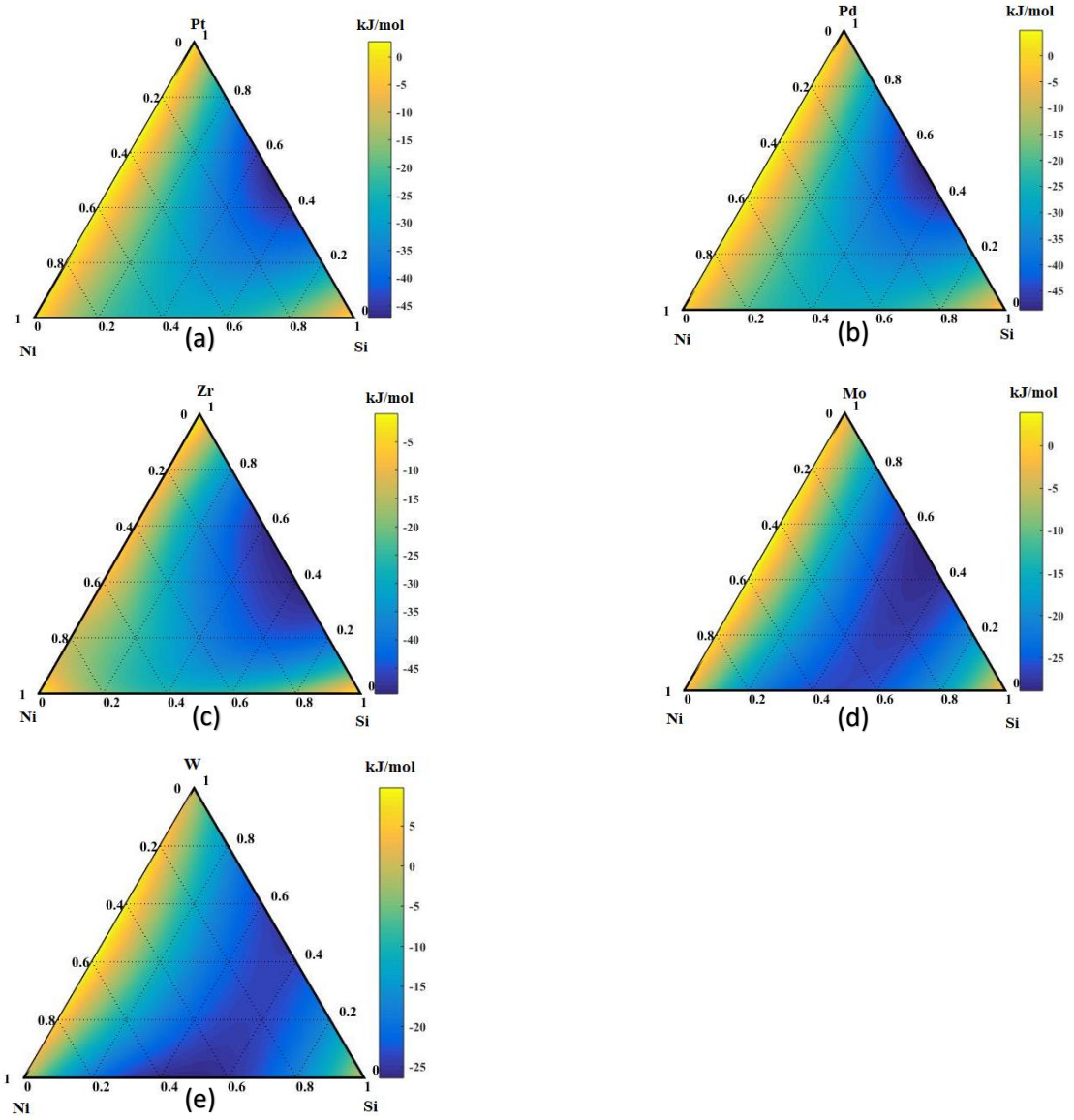

Figure 2. Formation enthalpy of ternary systems: (a) Ni-Pd-Si, (b) Ni-Pt-Si, (c) Ni-Zr-Si, (d) Ni-Mo-Si, and (e) Ni-W-Si.

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4. Conclusions

The semi-empirical Miedema model is a good approach to calculating the thermodynamic properties of solid solution and amorphous binary and ternary systems. In this work, the MAAT software was used to calculate and plot the formation enthalpy of binary and ternary systems. A preliminary assessment was made to investigate the effectiveness of adding certain types of elements to increase the thermal stability of nickel monosilicide based on the calculations of the formation enthalpy of the Ni-Si phase for doped nickel silicides. The values of the formation enthalpy of the nickel monosilicide phase with the addition of the alloy elements Pd, Pt, Zr, Mo, and W were calculated based on the use of the semi-empirical Miedema model. Here, the most negative value of the formation enthalpy of doped nickel silicide was found to be (-49.67 kJ/mol), which is 2 kJ/mol more than the formation enthalpy of undoped nickel silicide.

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