This supplementary material is a detailed introduction of calculating the enthalpy of formation of a ternary solid solution.

According to Miedema's model and Alonso's method (F. R. De Boer, R. Boom, W. C. Mattens, A. R. Miedema and A. K. Niessen, *Cohesion in Metals: Transition Metal Alloys*, North-Holland, Amsterdam, 1988; L. J. Gallego, J. A. Somoza and J. A. Alonso, *J. Phys: Condens Mat.* 1990, **2** 6245), the enthalpy of formation of a ternary solid solution of transition metals *A*, *B* and *C* is given by

$$\Delta H_{\mathrm{ABC}}^{\mathrm{S.S}} = \Delta H_{ABC}^{c} + \Delta H_{ABC}^{e} + \Delta H_{ABC}^{s} \qquad (1)$$

where ΔH_{ABC}^{c}, ΔH_{ABC}^{e} and ΔH_{ABC}^{s} are the chemical, elastic and structural contributions, respectively.

The chemical term ΔH_{ABC}^{c} is closely related to the electron redistribution generated at surface of contact between dissimilar atomic cells when alloying. In order to calculate this term, it could be divided into three binary subsystems, thus the chemical term ΔH_{ABC}^{c} is given by

$$\Delta H_{ABC}^{c} = \Delta H_{AB}^{c} + \Delta H_{AC}^{c} + \Delta H_{BC}^{c} \qquad (2)$$

In equation (2), ΔH_{AB}^{c}, ΔH_{AC}^{c} and ΔH_{BC}^{c} are the chemical terms of the three binary subsystems. The concentrations of A, B and C in each subsystems is the same as the ternary system. For the binary subsystem with constituents of A and B, the chemical term ΔH_{AB}^{c} is given by

$$\Delta H_{AB}^{c} = c_{\mathrm{A}} c_{\mathrm{B}} [c_{\mathrm{B}} \Delta \bar{H}_{\mathrm{A\ in\ B}}^{\mathrm{inter}} + c_{\mathrm{A}} \Delta \bar{H}_{\mathrm{B\ in\ A}}^{\mathrm{inter}}] \qquad (3)$$

In equation (3), c_A and c_B are the atomic concentrations of metals A and B, $\Delta\overline{H}^{\text{inter}}_{\text{A in B}}$ and $\Delta\overline{H}^{\text{inter}}_{\text{B in A}}$ are the electron redistribution contribution to the enthalpies of A solved in B and that of B solved in A. Similarly, the chemical terms of another two subsystems, i.e., ΔH^c_{AC} and ΔH^c_{BC}, could also be calculated. Consider the chemical short range order of the alloy phases, the right-hand side of equation (3) should be multiplied by a factor

$$f = 1 + \gamma(c^s_A c^s_B)^2 \qquad (4)$$

In the factor, c^s_A and c^s_B are the cell surface concentrations, which could be calculated by $c^s_A = \frac{c_A V_A^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}}$, and $c^s_B = 1 - c^s_A$. The parameter γ in equation (4) is an empirical constant which is used to describe the short range order of different alloys. For solid solution, glass phase and intermetallic compound, it is usually take 0, 5 and 8, respectively. Since the chemical term of each binary subsystem could be calculated by equation (3), the chemical term ΔH^c_{ABC} could be easily obtained by equation (2).

The elastic term ΔH^e_{ABC} is an atomic size mismatch contribution, and could also be divided into three terms of binary subsystems:

$$\Delta H^e_{ABC} = \Delta H^e_{AB} + \Delta H^e_{AC} + \Delta H^e_{BC} \qquad (5)$$

In equation (5), ΔH^e_{AB}, ΔH^e_{AC} and ΔH^e_{BC} are the elastic terms of the three binary subsystems. The concentrations of *A*, *B* and *C* in each subsystems is also the same as

the ternary system. For the binary subsystem with constituents of *A* and *B*, the elastic term ΔH^{e}_{AB} is given by

$$\Delta H^{e}_{AB} = c_{\mathrm{A}} c_{\mathrm{B}} [c_{\mathrm{B}} \Delta \overline{H}^{\mathrm{elastic}}_{\mathrm{A\ in\ B}} + c_{\mathrm{A}} \Delta \overline{H}^{\mathrm{elastic}}_{\mathrm{B\ in\ A}}] \qquad (6)$$

In equation (6), c_A and c_B are the atomic concentrations of metals *A* and *B*, $\Delta \overline{H}^{\mathrm{elastic}}_{\mathrm{A\ in\ B}}$ and $\Delta \overline{H}^{\mathrm{elastic}}_{\mathrm{B\ in\ A}}$ are the elastic contribution to the enthalpies of *A* solved in *B* and that of B solved in A. After the elastic terms of each binary subsystem were obtained, the elastic term (ΔH^{e}_{ABC}) of the ternary system could be calculated by equation (5).

The structural contribution, ΔH^{s}_{ABC}, reflects the correlation between the number of valence electrons and the crystal structure of transition metals. It can be deduced from the lattice stability $E_{\sigma}(\overline{Z})$ of each crystal structure σ (σ=*bcc*, *fcc* or *hcp*) as a function of the number of valence electrons *Z* of the metal,

$$\Delta H^{s}_{ABC} = E_{\sigma}(\overline{Z}) - [c_A E_{\sigma}(Z_A) + c_B E_{\sigma}(Z_B) + c_C E_{\sigma}(Z_C)] \qquad (7)$$

In the equation, c_A, c_B and c_C are the atomic concentrations of metals *A*, *B* and *C*, $\overline{Z}$, Z_A, Z_B and Z_C are the mean valence electrons of alloy phase and numbers of valence electrons of pure metals *A*, *B* and *C*, $E_{\sigma}(\overline{Z})$, $E_{\sigma}(Z_A)$, $E_{\sigma}(Z_B)$ and $E_{\sigma}(Z_C)$ are the lattice stability parameters of the alloy phase and the pure *A*, *B* and *C*, respectively.