

# Thermodynamic Analysis of Solid Solution Formation in the Nanocrystalline W-Co-Si Ternary System by Mechanical Alloying

M. Zarezadeh Mehrizi\*, R. Beygi

Department of Materials Engineering and Metallurgy, Faculty of Engineering, Arak University, Arak 38156-8-8349, Iran.

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## ABSTRACT

Co<sub>3</sub>W<sub>2</sub>Si intermetallic compound was synthesized by mechanical alloying (MA) of W, Co and Si elemental powder mixtures. The phase composition of the milled products was evaluated by X-ray diffraction (XRD) analysis. Morphological evolutions were characterized by transmission electron microscopy (TEM). The results showed that high energy ball milling performed in the present work led to the formation of Co<sub>3</sub>W<sub>2</sub>Si intermetallic phase after 50h MA. A thermodynamic analysis of the process was then carried out using Miedema model. The thermodynamic results showed that there exists a positive thermodynamic driving force in W-Si and Co-Si binary systems and W-Co-Si ternary system to form a solid solution at all compositions but Gibbs free energy change in Co-W binary system is positive for solid solution formation. So that there is no thermodynamic force to form a solid solution in Co-W system. In Co-W-Si ternary system, the addition of elemental W to Co<sub>3</sub>Si compound decreases Gibbs free energy change and a more stable structure is formed.

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## 1-Introduction

Nowadays, there is a growing interest in the production of intermetallic compounds because of their excellent physical and mechanical properties [1]. Among them, the alloys based on transitional-metal- Si (e.g., Ni-Si, Mo-Si, Ti-Si, W-Si and Nb-Si binaries and their multicomponent alloys such as Mo-Ni-Si, W-Ni-Si, etc.) represent the largest family of intermetallic compounds and exhibit attractive mechanical and chemical properties at high temperatures. As such, they are well recognized as a new family of ultrahigh-temperature candidate structural materials, because of their excellent combinations of high melting point, [9]. Mechanical alloying is a process that yields solid solution, amorphous or crystalline

low density, high elastic modulus, and excellent oxidation resistance [2-7]. The major barriers to the use of these compounds as structural materials are their low toughness and ductility at ambient temperature [2,3]. A further improvement of mechanical properties can be achieved by decreasing the grain size to the nanometer scale. One of practical processing methods for the synthesis of nanometer scale compounds and nanocomposites by the direct producing is mechanical alloying (MA) [1, 8-10]. Since 1966, many kinds of alloys and composites were produced by mechanical alloying. Here, reactive milling as well as alloying at the atomic level can be performed (nanocrystalline) structures but studies show that the primary phase in MA is the most stable

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\* Corresponding author:

E-mail address: m-zarezadeh@araku.ac.ir

phase [9, 11].

Recently, much attention has been given to the evaluation of ternary systems by mechanical alloying. As for ternary alloy system (like Co–W–Si system), only a very few systems have been studied. In our previous work [10], the formation of a (Co, W, Si) solid solution with a layered nanocrystalline structure was investigated. Although MA of Co–W–Si system has been investigated in the literature [10], many problems such as the thermodynamic aspects of formation need to be solved.

Recently, much attention has been paid to the investigation of ternary systems by mechanical alloying, but a few systems have been studied (e.g., Ni–Fe–Al and Fe–Ti–Al)[1, 12]. These studies showed that the most stable phase is intermetallic compound at all compositions. The thermodynamic aspects of Co–W–Si intermetallic compound formation have not been analyzed in the literature yet. Therefore, a thermodynamic analysis is necessary to compare the relative stabilities of phases in Co–W–Si system. However, it is expensive and time-consuming to measure it experimentally, especially for ternary and n-component alloy systems for which  $n > 3$ . It is established that during the synthesis processes, the phase with the most negative Gibbs free energy amongst competing phases at the considered composition is formed. So, thermodynamic analysis can be used to predict the MA product [13]. Usually, formation energies are obtained by basic experimental measurements.

Miedema et al. developed a widely used thermodynamic theory for calculating the formation energies of binary transition metal alloy systems [14]. This model is useful only for binary systems. Hence, a simple but effective method has been proposed to extend the Miedema theory to ternary and n-component alloy systems [15-17]. The Miedema model is built upon the “macroscopic atom” picture. The basic assumption, in this case, is that the reference can be chosen as atoms embedded in a metal, instead of free atoms. The essence of the model lies in estimating quantitatively the effects of the change in the Wigner–Seitz cell boundary electron density. Dissimilar cells, in contact with each other, would tend to shift their electron densities such as to remove the cell boundary discontinuities in order to form the alloy. Elimination of such discontinuities is expected to require energy; hence, the electron density difference  $\Delta n_{ws}$  accounts for a positive contribution to the interface energies [18].

Following the development of Miedema’s model, a number of research teams tried to use this model for a variety of metallurgical problems ranging from glass formation to lattice defects [1, 12, 13, 18, 19].

In this work, the formation of solid solution in three binary systems W–Co, W–Si and Co–Si and a ternary system Co–W–Si during MA was analyzed and confirmed by experimental data. To the best of our knowledge, there is no study to evaluate these systems thermodynamically.

## 2- Experimental

The raw materials used in this study were powders of W (-50 $\mu$ m, 99.5% purity), Co(-50 $\mu$ m, 98% purity) and Si(-50 $\mu$ m, 99.99% purity). Mechanical alloying was performed in a Retsch PM100 type ball mill (Retsch GmbH, Haan, Germany). The milling media consisted of 21.6 mm diameter balls, confined in a 527.7 mL volume vial. The ball and bowl materials were made of hardened chromium steel. In all milling runs, the ball/powder weight ratio was 20:1, and the vial rotation speed was 300 revmin<sup>-1</sup>. A total of 15 g powder was milled under argon atmosphere to avoid oxidation. The phase changes during ball milling were detected by X-ray diffraction analysis using a Philips X’PERT multipurpose X-ray diffractometer (Philips Analytical BV, Almelo, The Netherlands) with Cu-K $\alpha$  radiation ( $\lambda=0.15405$  nm). The crystallite size and internal strain of phases were calculated by analyzing XRD peak broadening using the Williamson–Hall method. Enthalpy of mixing was calculated by Miedema model for binary systems and extended Miedema model for the ternary system. The morphology and particle size of powder particles of the milled specimens were analyzed using a transmission electron microscope (Philips EM208S).

## 3-Thermodynamic analyses for the formation of solid solution alloys

### 3-1- Binary W–Co, W–Si, and Co–Si solid solution alloys

The formation of disordered A(B) solid solution from a mixture of pure elements A and B, the free-energy change can be calculated as follows when the original pure elements are taken in the standard state:

$$\Delta G^S = \Delta H_m^S + RT(X_A \ln X_A + X_B \ln X_B) \quad (1)$$

Where  $X_A$  and  $X_B$  are the molar fraction of elements A and B in solid solution, respectively,

so,  $X_A + X_B = 1$ . R is the universal gas constant. T is the temperature at which a solid solution is formed by mechanical alloying, which in this case takes the value of T=298 K.

$\Delta H_m^S$  is the enthalpy of mixing, which comprises three items as shown below [20, 21]:

$$\Delta H_m^S = \Delta H_C + \Delta H_E + \Delta H_S \quad (2)$$

where  $\Delta H_C$  is the chemical contribution, which is the same for liquid and solid solutions,  $\Delta H_E$  represents the elastic mismatch energy in the solid solutions, and  $\Delta H_S$  represents the lattice stability energy. The three terms in the expression are determined as follows:

According to extended Miedema model [14], the complete form of  $\Delta H_{Chem}$  in A-B binary alloy system, which can extend in a similar system, is as follows:

$$\Delta H_C = \frac{2Pf(X^S)(X_A V_A^{2/3} + X_B V_B^{2/3})}{(n_{ws}^A)^{-1/3} + (n_{ws}^B)^{-1/3}} \times \left[ -(\Delta\Phi^*)^2 + \frac{Q}{P}(\Delta n_{ws}^{1/3})^2 - \frac{R}{P} \right] \quad (3)$$

where  $X_A$  and  $X_B$  are the mole fractions of elements A and B;  $V_A$  and  $V_B$  are the molar volumes of atoms A and B, respectively;  $\Phi^*$  is the work function of constituent elements;  $n_{ws}$

is the electron density; and P, Q, and R are constants related to constituent elements. Eq.(3) has an additional enthalpy term, R, for transition metal/non-transition metal alloys due to filling of the Brillouin zones of a particular crystal structure [14, 22],  $f(X^S)$  is the concentration function that is given by Eq. (4) for solid solution. In this equation,  $\gamma$  may be 0, 5 and 8 for solid solutions, amorphous alloys and ordered crystalline alloys, respectively.

$$f(C_A^S) = X_A^S X_B^S [1 + \gamma(X_A^S X_B^S)] \quad (4)$$

$$X_A^S = \frac{x_A V_A^{2/3}}{x_A V_A^{2/3} + x_B V_B^{2/3}} \quad \text{and}$$

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

According to references [1, 14], Table 1 represents the Miedema parameters P, Q, and R for different elements.

According to relationships presented above, Table 2 and Table 3 represent the Miedema parameters and parameters to calculate free energy changes for W-Co, W-Si and Co-Si systems, respectively.

**Table1.** Miedema parameters P, Q and R for different elements [18].

| A-B element type                | R(kJ.cm <sup>-1</sup> ) | P(kJ.V <sup>-2</sup> .cm <sup>-1</sup> ) | Q(kJ.V <sup>-1</sup> ) |
|---------------------------------|-------------------------|--|------------------------|
| Transitional-Ttransitional      | =0                      | 14.1                                     | 132.54                 |
| Transitional-Nontransitional    | ≠0                      | 12.3                                     | 115.62                 |
| Nontransitional-Nontransitional | =0                      | 10.6                                     | 99.64                  |

**Table 2.** Miedema parameters for W-Co, W-Si and Co-Si systems [14].

| System | P (kJ.V <sup>-2</sup> .cm <sup>-1</sup> ) | Q (kJ.V <sup>-1</sup> ) | R (kJ.cm <sup>-1</sup> ) |
|--------|---|-------------------------|--------------------------|
| W-Co   | 14.1                                      | 132.54                  | 0                        |
| W-Si   | 12.3                                      | 115.62                  | 25.83                    |
| Co-Si  | 12.3                                      | 115.62                  | 25.83                    |

**Table 3.** Parameters for free-energy changes calculation.

| Element | G(GPa) | K(GPa) | $V_m^{2/3}$ (cm <sup>3</sup> .mol <sup>-1</sup> )[14] | $n_{ws}^{1/3}$ ((d.u) <sup>1/3</sup> ) [14] | $\Phi$ (V) [14] |
|---------|--------|--------|---|---|-----------------|
| W       | 161    | 310    | 4.50  | 1.81  | 4.80            |
| Co      | 175    | 180    | 3.55  | 1.75  | 5.10            |
| Si      | 65     | 100    | 5.27  | 1.49  | 4.70            |

The second item,  $\Delta H_E$ , i.e. elastic mismatch energy in solid solution, is determined by the following formula [23]:

$$\Delta H_E = X_A X_B (X_A \Delta E_{A \text{ in } B} + X_B \Delta E_{B \text{ in } A}) \quad (6)$$

where  $\Delta E_{A \text{ in } B}$  and  $\Delta E_{B \text{ in } A}$  are the elastic energy caused by dissolution of A in B and B in A, respectively and can be estimated by Eq. (7) [20]:

$$\Delta E_{A \text{ in } B} = \frac{2K_A u_B (V_B - V_A)^2}{3K_A V_B + 4u_B V_A} \quad \text{and} \quad (7)$$

$$\Delta E_{B \text{ in } A} = \frac{2K_B u_A (V_A - V_B)^2}{3K_B V_A + 4u_A V_B}$$

where K and u are the elastic modulus and shear modulus per unit volume for relevant constituent elements, respectively.

The third item,  $\Delta H_S$ , i.e. the structure contribution, based on Miedema theory is related to the number of valence electrons per atom Z and reflects that transition metals show preference to crystallize in one of the three simple crystallographic phases bcc, fcc, and hcp, depending on the number of valence electrons Z (summation of s and d electrons) [24]. This rule is applicable to only binary solid solutions of transitional–transitional elements in which there are common d bonds [19], such as the W–Co system. So, in these solid solutions, structural enthalpy will vary systematically with the average number of valence electrons (z) that is written as [20]:

$$\bar{z} = x_A z_A + x_B z_B \quad (8)$$

Where  $z_A$  and  $z_B$  are the valence electrons of A and B atoms, respectively. Based on an empirical curve of the variation in the enthalpy of three main crystal structures with respect to z [19, 20], structural enthalpy change of transitional metals in a ternary system is calculated from the following equation:

$$\Delta H(\text{structure}) = E^{str}(\bar{z}) - E^{ref}(\bar{z}) \quad (9)$$

Where  $E^{str}(\bar{z})$  is structural solid solution enthalpy,  $E^{ref}(\bar{z})$  is reference enthalpy of the binary system.

Reference enthalpy of a ternary system is obtained by:

$$H^{ref}(z_A) = X_A H(z_A) + X_B H(z_B) + X_C H(z_C) \quad (10)$$

where  $H(z_A)$ ,  $H(z_B)$  and  $H(z_C)$  are the structural enthalpies of A, B, and C pure elements. The empirical curves of structural enthalpy versus

valence electrons in bcc, fcc and hcp crystal structures were obtained from experimental data and equation 14, as can be seen in Fig. 1 [19].

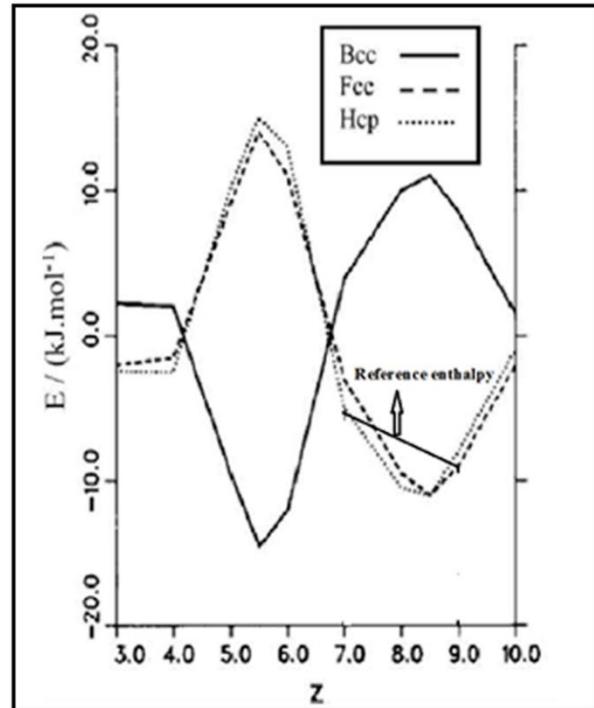


Fig. 1. Lattice stability as a function of the number of valence electrons for the three main types of crystal structure: bcc (solid curve), fcc (dashed curve) and hcp (dotted curve) [24].

### 3-2-Ternary W–Co-Si solid solution alloys

The free-energy change for ternary solid solution alloys can be calculated as follows when the original pure elements are taken as the standard state:

$$\Delta G_{ABC} = \Delta H_{ABC} + RT(X_A \ln X_A + X_B \ln X_B + X_C \ln X_C) \quad (11)$$

Based on extended Miedema model for ternary systems the formation enthalpy change of a solid solution including A, B and C constituents ( $\Delta H_{ABC}$ ) is calculated by the following relationship:

$$\Delta H_{ABC} = \Delta H_{ABC}^C + \Delta H_{ABC}^E + \Delta H_{ABC}^S \quad (12)$$

where  $\Delta H_{ABC}^C$  is:

$$\Delta H_{ABC}^C = \Delta H_{AB}^C + \Delta H_{AC}^C + \Delta H_{BC}^C \quad (13)$$

and  $\Delta H_{ABC}^E$  is:

$$\Delta H_{ABC}^E = \Delta H_{AB}^E + \Delta H_{AC}^E + \Delta H_{BC}^E \quad (14)$$

But  $\Delta H_{ABC}^S$  is represented by Eq. (9) which z changes according to Eq. (15):

$$\bar{z} = x_A z_A + x_B z_B + x_C z_C \quad (15)$$

## 4- Results and discussion

### 4-1- Phase transition during MA

The XRD patterns of the powder mixtures after various milling times are shown in Fig. 2(a). The milling sequence runs from the bottom to the top of the figure. As expected, the pattern of the powder mixture at time 0 shows only sharp peaks corresponding to the starting metal mixture: Co, W, and Si. A mixture of different crystalline structures, the cubic phase of W (PDF#004-0806, bcc), two allotropic structures of Co, (PDF #15-0806, fcc) and (PDF #05-0727, hcp) and, the cubic phase of Si (PDF# 027-1402, bcc) were found. As can be seen, the diffraction pattern shows strong W peaks because W has high mass absorption coefficient.

With increasing the milling time up to 3h, the intensity of W, Co, and Si diffraction peaks decreases and their width increases progressively with increasing the milling time during MA. The reflections of silicon completely disappear after 5 h of milling. Also, the intensity of W peaks decreases with increasing the milling time and it can be suggested that Si and W have been dissolved in Co with increasing the milling time. At this

time, the Co peaks become slightly shifted towards lower angles, which indicates that the lattice parameter of Co has increased and confirmed the solid solution (Co, W, and Si) formation as previously explained. According to Fig. 2(b) and Fig. 2(c), it can be suggested that (Co, W, Si) solid solutions have been formed with increasing the milling time. At this time, the Co and W peaks become slightly shifted towards higher angles, indicating that the lattice parameters of Co and W have decreased. Since Si has a smaller radius than Co and W, the lattice parameters of Co and W decrease with the substitutional dissolution of Si into Co and W lattices. Also, W and Co have almost equal radii, so that dissolution of W and Co together has a little effect on their lattice parameters.

Further milling up to 10 h led to the disappearance of the Co(fcc) peaks and only the peaks of Co(hcp) are observed. According to other authors [8], there is an allotropic and reversible transformation, Co(fcc) to Co(hcp), depending on the milling parameters, which is not usual in equilibrium conditions [25]. By this transformation, dissolution of W and Si in Co increases.

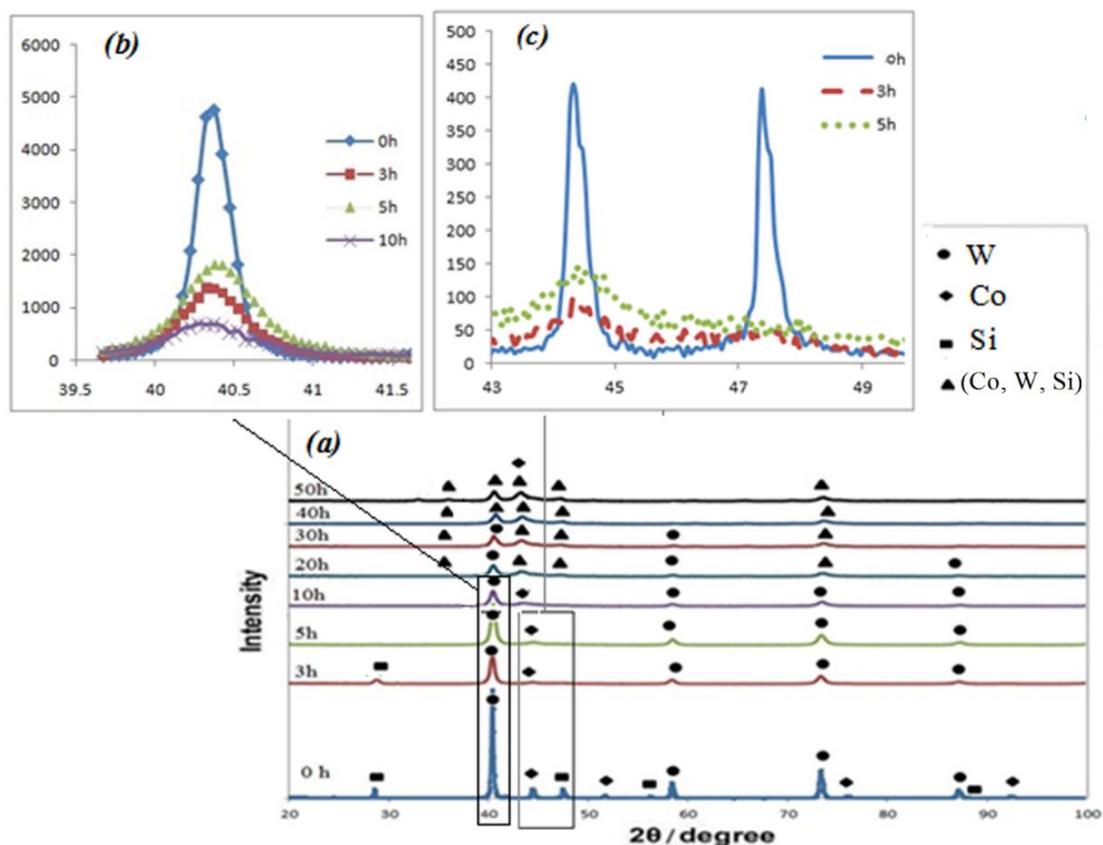
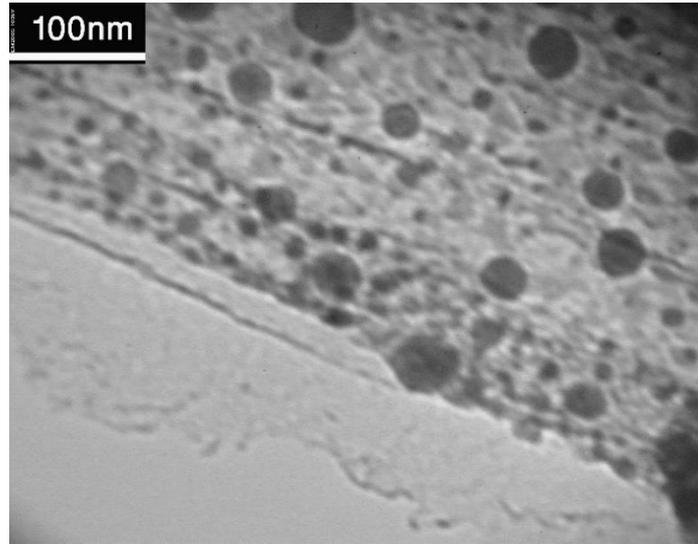


Fig.2. X-ray diffraction results of powders milled at different periods.



**Fig. 3.** TEM micrographs of Co–W–Si powder mixtures after 50 h-milling.

With increasing the milling time to 20 h, new peaks related to  $\text{Co}_3\text{W}_2\text{Si}$  appeared. Also, broadening of W peaks and decreasing of its intensity are seen. Further increasing of the milling time led to the dissolution of W in  $\text{Co}_3\text{W}_2\text{Si}$ . Lack of superlattice diffraction peaks for  $\text{Co}_3\text{W}_2\text{Si}$  phase formed during MA suggests that the crystalline  $\text{Co}_3\text{W}_2\text{Si}$  phase has disordered structure. The crystallite size and internal strain of  $\text{Co}_3\text{W}_2\text{Si}$  phase for the 50 h milled sample were calculated by analyzing XRD peak broadening using the Williamson–Hall method [26]. The average crystallite size and internal strains were  $\sim 55$  nm and  $\sim 2\%$ , respectively. Fig. 3 shows the TEM image of 50h milled powder specimens with smallest particle size. It is evident that the synthesized powders produced nanosized particles in the range of 40–60 nm.

#### 4-2- Thermodynamic analysis of solid solution formation in binary systems

The total enthalpy change for W-Si consists of chemical and elastic parts and there is not structural enthalpy in this system. Thermodynamic calculations for this system are as follows:

$$\Delta H_{W-Si}^{Chem} = \frac{-553.48 X_W \cdot X_{Si}}{4.5 X_W + 5.27 X_{Si}} \quad (kJ.mole^{-1}) \quad (16)$$

$$\Delta H_{W-Si}^{Ela} = X_W \cdot X_{Si} \cdot [19.96 X_W + 19.38 X_{Si}] \quad (kJ.mole^{-1}) \quad (17)$$

$$\Delta S_{W-Si} = -8.314 \cdot [X_W \ln X_W + X_{Si} \ln X_{Si}] \quad (kJ.mole^{-1}) \quad (18)$$

Also, for the Co-Si system, like W-Si system,

total enthalpy has no structural enthalpy part, so

$$\Delta H_{Co-Si}^{Chem} = \frac{-607.49 X_{Co} \cdot X_{Si}}{3.55 X_{Co} + 5.27 X_{Si}} \quad (kJ.mole^{-1}) \quad (19)$$

that:

$$\Delta H_{Co-Si}^{Ela} = X_{Co} \cdot X_{Si} \cdot [97.38 X_W + 82.45 X_{Si}] \quad (kJ.mole^{-1}) \quad (20)$$

$$\Delta S_{Co-Si} = -8.314 \cdot [X_{Co} \ln X_{Co} + X_{Si} \ln X_{Si}] \quad (J.K^{-1}.mol^{-1}) \quad (21)$$

For the Co-W binary system, total enthalpy change has chemical, elastic and structural parts.

The chemical and elastic parts of enthalpy are calculated as follows:

$$\Delta H_{Co-W}^{Chem} = \frac{-22.60 X_{Co} \cdot X_{Si}}{3.55 X_{Co} + 4.5 X_{Si}} \quad (kJ.mole^{-1}) \quad (22)$$

$$\Delta H_{Co-W}^{Ela} = X_{Co} \cdot X_W \cdot [67.35 X_W + 46.6 X_{Co}] \quad (kJ.mole^{-1}) \quad (23)$$

$$\Delta S_{Co-W} = -8.314 \cdot [X_{Co} \ln X_{Co} + X_W \ln X_W] \quad (J.K^{-1}.mol^{-1}) \quad (24)$$

In this system, the structural enthalpy should be considered. The reference enthalpy line is plotted by considering valence electrons in W ( $z=7$ ) and Co ( $z=9$ ) and using Eq. 9 (Fig. 1).

The structural enthalpy changes of solid solution for W-Co system as a function of valence electrons numbers are calculated using Fig. 1 (shown in Fig. 4).

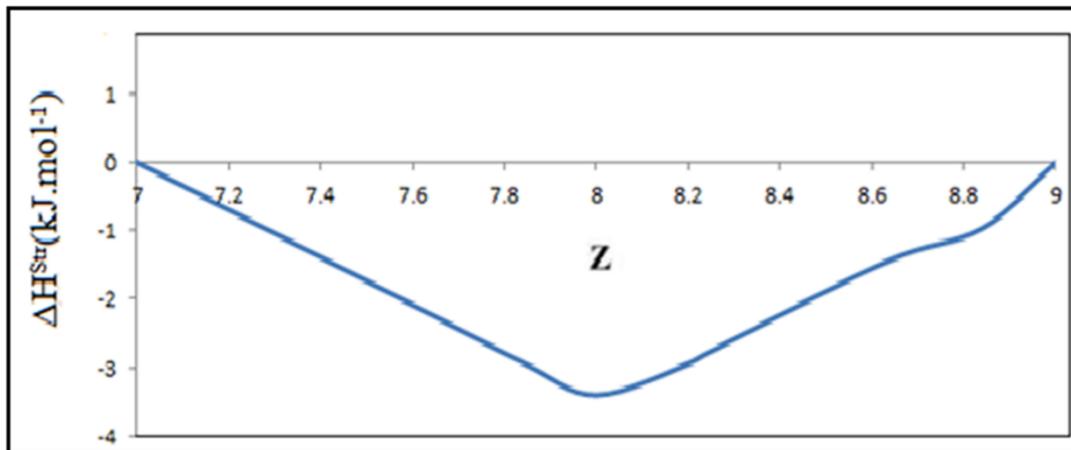


Fig.4. The structural enthalpy changes with z for W-Co binary system.

Fig. 5 represents enthalpy, entropy and Gibbs free energy changes for these binary systems. It can be seen that in none of the compositions of W-Si and Co-Si systems, Gibbs free energy change is negative. So, for solid solution formation, there is a thermodynamic driving force in these systems within all composition ranges. The free energy change calculated for the W-Co alloy system to form a solid solution is positive across the entire range of Co content, which means that there is no thermodynamic driving force for the system to form a solid solution. As a result, the diffusion of atoms should be considered during alloying. During the early stage of MA, powder particles may experience severe plastic deformation, resulting

in repeated cold working, shearing and fracturing, and rewelding. This process can lead to the formation of lamellar structures of alternate layers. The hard and brittle powder particles can be broken and embedded in the lamellar soft matrix. Further milling leads to the decrease of the interlamellar spacing. As the milling time is prolonged, the crystalline sizes of powders will decrease, and a mixed nanocrystalline structure is formed uniformly in the mechanically alloyed powder. Meanwhile, interdiffusion may take place across the interfaces due to the reduced diffusion distances and increased diffusivity, as aided by the creation of lattice defects and formation possibility of new compounds increase during MA[21].

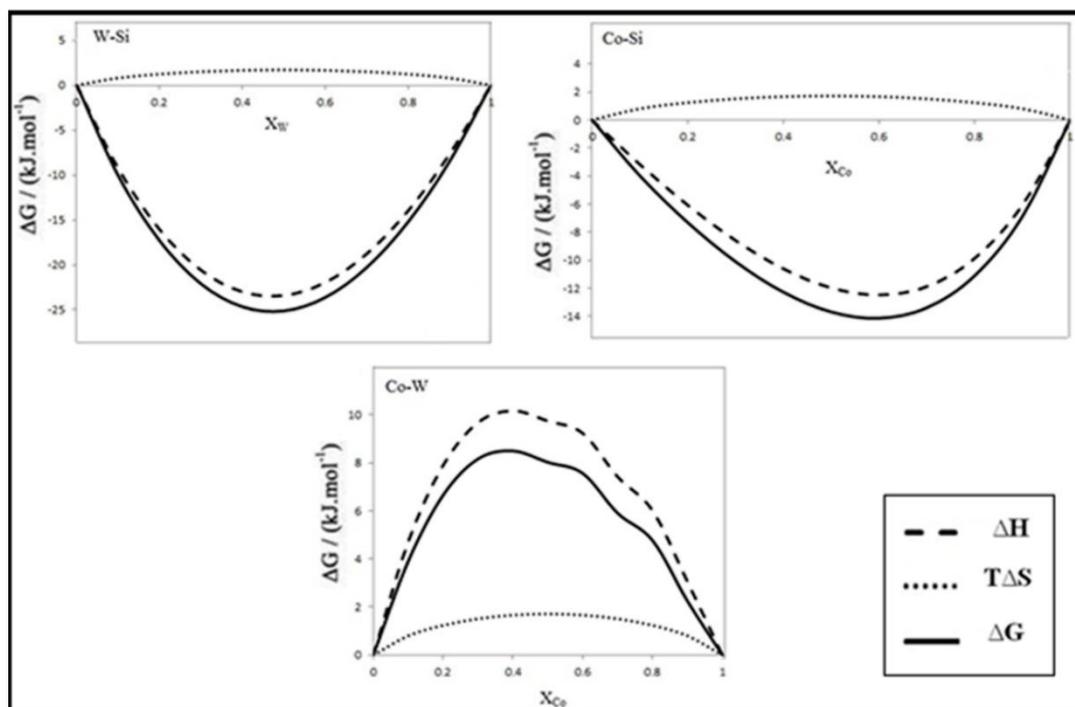


Fig. 5. Enthalpy, entropy and Gibbs free energy changes for W-Si, Co-Si and W-Co binary systems.

#### 4-3-Thermodynamic analysis of solid solution formation in W-Co-Si ternary system

Fig. 6 also shows Gibbs free energy change at 298 K. As it is observed, the change of Gibbs free energy is negative at all compositions. Therefore, there is a thermodynamic driving force in W-Co-Si system to form alloys at a wide composition. As mentioned in section 4.2, Gibbs free energy change of W-Co binary system is positive in all compositions, but by Si addition to this system, the value of Gibbs free energy change becomes negative.

Furthermore, in W-Co-Si ternary system, the minimal thermodynamic driving force to form these compounds is in the corners where the concentration of W or Co or Si is higher than 90%. Also, maximum Gibbs free energy change for solid solution formation is about  $-32\text{kJ}\cdot\text{mol}^{-1}$  for equiatomic compositions. With increasing the Co content Gibbs free energy change decreases down to stoichiometric point corresponding to the disordered  $\text{Co}_3\text{W}_2\text{Si}$  compound. For this compound, Gibbs free energy change is  $-20.2\text{kJ}\cdot\text{mol}^{-1}$  whereas Gibbs free energy change for disordered  $\text{Co}_3\text{Si}$  compound (solid solution) is about  $-12\text{kJ}\cdot\text{mol}^{-1}$ . Gibbs free energy change for both compounds

is negative and, therefore, the formation of these compounds is possible at ambient temperature. Addition of W to  $\text{Co}_3\text{Si}$  compound makes the Gibbs free energy change become more negative. So, the  $\text{Co}_3\text{W}_2\text{Si}$  compound is more stable than the  $\text{Co}_3\text{Si}$  compound and the  $\text{Co}_3\text{W}_2\text{Si}$  compound is favored to form. According to Fig. 2, the XRD results indicate that MA of W, Co, and Si powder mixture leads to the formation of the  $\text{Co}_3\text{W}_2\text{Si}$  intermetallic compound and no traces of other phases (such as  $\text{Co}_3\text{Si}$ ) were observed at all stages of MA.

#### 5- Conclusion

The following conclusions can be made from the present research:

- $\text{Co}_3\text{W}_2\text{Si}$  compound can be produced by mechanical alloying. Thermodynamic analysis for binary systems shows that there is a thermodynamic driving force for W-Si, Co-Si systems to form solid solution for all compositions but Gibbs free energy change for W-Co system is positive for all compositions and there is no thermodynamic force to form a solid solution.

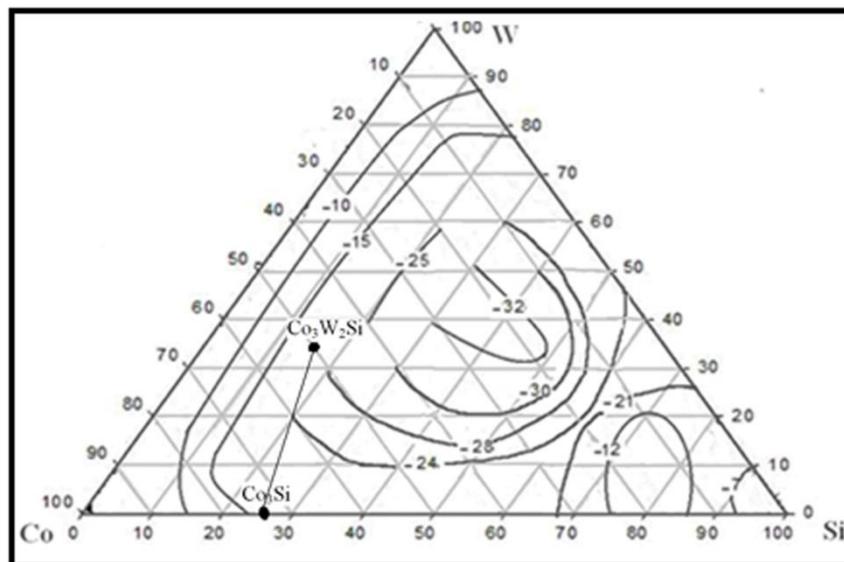


Fig. 6. Iso Gibbs free energy change lines for W-Co-Si ternary system

- Thermodynamic analysis for W-Co-Si ternary system indicated that Gibbs free energy change for all compositions is negative; therefore, there is a thermodynamic driving force to form solid solution for all compositions.
- Gibbs free energy change for the

formation of  $\text{Co}_3\text{Si}$  compound is negative but the addition of W to this compound makes this value become more negative. Therefore, the  $\text{Co}_3\text{W}_2\text{Si}$  compound is more stable than  $\text{Co}_3\text{Si}$  compound and  $\text{Co}_3\text{W}_2\text{Si}$  is favored to form.

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