

Determination of the Critical Driving Force Associated with Phase Transformation from Fcc(γ) phase to Hcp(ϵ) phase observed in Co-Cr-Mo Alloy

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Abstract

In order to predict the thermodynamic properties for ternary systems from binary ones, using the Chou's model which is known as a new general solution model, Gibbs free energy and critical driving force associated with in fcc(γ) to hcp(ϵ) transformation observed in the Co-Cr-Mo ternary system containing very small nickel and carbon used widely in orthopedic implant materials such as hips and especially dental prosthesis in the human body are evaluated as a function of temperature. The Gibbs free energies and driving force and equilibrium temperature between the fcc and hcp phases are compared with those obtained from the experiments.

Keywords: Critical Driving Force, Phase Transformation, Fcc(γ) phase to Hcp(ϵ) phase, Co-Cr-Mo Alloy

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I. Introduction

Metallic materials present during long-term use compared to polymer materials and ceramics, because of the reliability, metallic materials have been used for load-bearing implants for along time. Among these materials, Co-Cr-Mo-based alloys are commonly used as orthopedic implant materials such as hips and especially dental prosthesis in the human body environment due to their excellent biocompatibility, corrosion resistance and good wear resistance [1, 2]. Dental prosthesis and hip implants are processed using conventional metallurgy and mechanical forming and in relation to this, there is yet rather limited information on the microstructural and thermodynamic properties of the evolution, particularly the phase transformations, which take place during the sintering of Co-Cr-Mo alloy powders [1]. Ni element has been reported as one of the most common contact allergens [3]. In order to improve their castability and workability in metallurgical processes, Co-Cr-Mo alloys contain Ni. Since the release of metal ions at the large interface between body fluid and metal gives rise to great concern and harmful to the body, the porous Co-Cr-Mo coating on the implants such as the substrate Co-Cr-Mo alloy, should not contain Ni. Co-base alloys fcc \leftrightarrow hcp martensitic phase change under (a) athermal, (b) isothermal or (c) a strain induced transformation (SIT) [4]. The ϵ phase is stable at lower temperatures for Co-(29-27)Cr-(5-6)Mo containing very small Ni and C. The ϵ phase is also produced by martensitic transformation upon cooling, but in Co-29.1 % wt Cr-5.83 % wt Mo ternary alloy phase transformation may occur in massive or thermal nature and the importance of the prediction of equilibrium and phase transformation temperatures observed in transformation fcc to hcp for the alloy in question, which has very importance in the dental applications, is increasing by day by. The prediction of these temperatures needs the Gibbs free energies of the both fcc and hcp phases. The stacking fault energy is one of the most important parameters in materials and is basically affected by composition (electron/atom ratio) and temperature. In order to determine the stacking fault energy the Gibbs free energy and interfacial free energy associated with the fcc(γ) to hcp(ϵ) transformation must be known.

The present work attempts to evaluate the Gibbs free energy of both the fcc and hcp phases in the Co-Cr-Mo ternary system containing very small nickel and carbon through an application of the model modified by Chou, which is known as a new general solution model, based on the binary thermodynamic properties in Co-Cr, Co-Mo, and Cr-Mo alloys. The equilibrium temperature between the fcc and hcp phases will be compared with those determined from the experimental results.

Determination of the Critical Driving Force by Chou's General Calculation Model

The Gibbs free energies of the FCC and HCP phases are described by the sub-regular solution model. The Gibbs free energy of the alloy is given by, so that ϕ denotes Fcc or Hcp phase,

$${}^mG^\varphi = x_1 {}^\circ G_1^\varphi + x_2 {}^\circ G_2^\varphi + x_3 {}^\circ G_3^\varphi + RT(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3) + {}^E G_m^\varphi + {}^{mag} G^\varphi \quad (1)$$

where ${}^\circ G_1^\varphi$, ${}^\circ G_2^\varphi$ and ${}^\circ G_3^\varphi$ are the Gibbs free energy of pure Co, Cr and Mo phases, respectively. x_1 , x_2 and x_3 denote the mole fraction of elements ternary alloy in question, respectively. The excess Gibbs free energy, ${}^E G_m^\varphi$, describing the deviation from the ideal behavior of solutions, is expressed by the Redlich-Kister description as [5-9]

$${}^E G^\varphi = \frac{x_1 x_2}{X_1^\varphi X_2^\varphi} {}^E G_{12}^\varphi + \frac{x_3 x_1}{X_3^\varphi X_1^\varphi} {}^E G_{31}^\varphi + \frac{x_2 x_3}{X_2^\varphi X_3^\varphi} {}^E G_{23}^\varphi \quad (2)$$

${}^E G_{12}^\varphi$, ${}^E G_{31}^\varphi$ and ${}^E G_{23}^\varphi$ represent the excess Gibbs energy in Co-Cr, Mo-Co and Cr-Mo binaries, respectively. On the other hand, the binary compositions in Equation (2) are connected with x according to the following relationships:

$$X_1^\varphi = x_1 + x_3 e_{12}^\varphi, \quad X_2^\varphi = x_2 + x_1 e_{23}^\varphi \quad \text{and} \quad X_3^\varphi = x_3 + x_2 e_{13}^\varphi \quad (3)$$

X_1^φ indicates mole fraction of component of Co in Co-Cr or Co-Mo binary solutions, X_2^φ of component Cr in Co-Cr or Cr-Mo binaries, X_3^φ of component Mo in Co-Mo or Cr-Mo binaries, respectively [10]. e_{12}^φ , e_{13}^φ and e_{23}^φ , which are called as similarity coefficients, in Equation (3) are expressed as the following equation:

$$e_{12}^\varphi = \frac{\eta_1^\varphi}{\eta_1^\varphi + \eta_2^\varphi}, \quad e_{13}^\varphi = \frac{\eta_3^\varphi}{\eta_1^\varphi + \eta_3^\varphi} \quad \text{and} \quad e_{23}^\varphi = \frac{\eta_2^\varphi}{\eta_2^\varphi + \eta_3^\varphi} \quad (4)$$

where η , which are called as deviation sum of squares, can be expressed as

$$\eta_1^\varphi = \int_0^1 ({}^E G_{12}^\varphi - {}^E G_{13}^\varphi)^2 dX_1, \quad \eta_2^\varphi = \int_0^1 ({}^E G_{12}^\varphi - {}^E G_{23}^\varphi)^2 dX_2 \quad \text{and} \quad \eta_3^\varphi = \int_0^1 ({}^E G_{13}^\varphi - {}^E G_{23}^\varphi)^2 dX_3 \quad (5)$$

The binary Gibbs excess energy terms in Eq (5) are given by

$${}^E G_{ij}^\varphi = X_i^\varphi X_j^\varphi [{}^{(0)}L_{ij}^\varphi + {}^{(1)}L_{ij}^\varphi (X_i^\varphi - X_j^\varphi) + {}^{(2)}L_{ij}^\varphi (X_i^\varphi - X_j^\varphi)^2] \quad (6)$$

The term ${}^{mag}G^\varphi$ in Eq. (1) is a magnetic contribution to the Gibbs free energy, which is expressed by the following equation [10, 11]

$${}^{mag}G^\varphi = RTf(\tau) \ln(\beta + 1) \quad (7)$$

where β is the Bohr magneton number and the function $f(t)$ is represented by the following polynomial with the normalized temperature τ as

$$f(\tau) = 1 - \left[\frac{79\tau^{-1}}{140p} + \frac{474}{479} \left(\frac{1}{p} - 1 \right) \right] \left[\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right] / D \quad \text{for } \tau < 1$$

and

$$f(\tau) = - \left[\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right] / D \quad \text{for } \tau > 1 \quad (8)$$

where $D = \frac{515}{1125} + \frac{11692}{15975} \frac{1}{p} \left(\frac{1}{p} - 1 \right)$ and p is the constant given by 0.28 for FCC and HCP metals and 0.4 for BCC metals. The value of τ is defined as $\tau = T/T_C$, where T_C is the Curie temperature for materials and is given by

$$T_c^\varphi = x_1 {}^\circ T_{c1}^\varphi + x_2 {}^\circ T_{c2}^\varphi + x_3 {}^\circ T_{c3}^\varphi + x_1 x_2 T_{c12}^\varphi + x_1 x_3 T_{c13}^\varphi + x_2 x_3 T_{c23}^\varphi$$

where

$$T_c^{fcc} = 1396 x_1 - 1109 x_2 - 3700 x_1 x_3 \quad (9)$$

and

$$T_c^{hcp} = 1396 x_1 - 1109 x_2 - 1000 x_1 x_3$$

The same phenomenological expression is applied to the Bohr magneton number according to the following relationship:

$$\beta_c^\varphi = x_1 {}^\circ \beta_{c1}^\varphi + x_2 {}^\circ \beta_{c2}^\varphi + x_3 {}^\circ \beta_{c3}^\varphi + x_1 x_2 \beta_{c12}^\varphi + x_1 x_3 \beta_{c13}^\varphi + x_2 x_3 \beta_{c23}^\varphi$$

where

$$\beta_c^{fcc} = 1.35 x_1 - 2.46 x_2 - 3.578 x_1 x_3$$

and

$$\beta_c^{hcp} = 1.35 x_1 - 2.46 x_2 \quad (10)$$

Equations (9) and (10), ${}^\circ T_1$, ${}^\circ T_2$ and ${}^\circ T_3$ are the magnetic transition temperatures of pure Co, Cr and Mo. The coefficients of the magnetic contribution were also adopted from the previous works [8, 12,13].

II. Results and Discussion

Since ternary systems such as Co-Cr-Mo are difficult to study experimentally, it will be significant to study a Co-29.1 % wt Cr-5.83 % wt Mo ternary system with a theoretical model. In the present study, since this method provided recently by Chou [5-9, 13] has been proved to be the most reasonable one in all aspects among other geometrical models, the integral molar Gibbs energy and molar excess Gibbs energy of mixing for Co-Cr-Mo ternary system as a function of temperature are predicted by using Chou's general solution model [10].

For simplicity, 1, 2 and 3 have been used to denote Co, Cr and Mo elements, respectively. Based on this table, total 6 η and 6 ϵ have been calculated in terms of Equations (4) and (5). It is possible to calculate the similarity coefficients and deviation sum of squares too. As a function of the temperature, similarity coefficients for the two phases are calculated as:

$$\begin{aligned}
 e_{12}^{fcc} &= \left(1 + \frac{0.902 \times 10^8 - 0.570 \times 10^5 T + 9.302 T^2}{0.0393 \times 10^8 - 0.05174 \times 10^5 T + 3.815 T^2}\right)^{-1} \\
 e_{13}^{fcc} &= \left(1 + \frac{0.0393 \times 10^8 - 0.05174 \times 10^5 T + 3.815 T^2}{1.24 \times 10^8 - 0.77747 \times 10^5 T + 13.434 T^2}\right)^{-1} \\
 e_{23}^{fcc} &= \left(1 + \frac{1.24 \times 10^8 - 0.77747 \times 10^5 T + 13.434 T^2}{0.902 \times 10^8 - 0.57068 \times 10^5 T + 9.302 T^2}\right)^{-1} \\
 e_{12}^{hcp} &= \left(1 + \frac{0.976 \times 10^8 - 0.759 \times 10^5 T + 14.787 T^2}{0.0672 \times 10^8 - 0.05828 \times 10^5 T + 3.875 T^2}\right)^{-1} \\
 e_{13}^{hcp} &= \left(1 + \frac{0.0393 \times 10^8 - 0.05174 \times 10^5 T + 3.815 T^2}{1.057 \times 10^8 - 1.15845 \times 10^5 T + 33.575 T^2}\right)^{-1} \\
 e_{23}^{hcp} &= \left(1 + \frac{1.057 \times 10^8 - 1.15845 \times 10^5 T + 33.575 T^2}{0.9022 \times 10^8 - 0.57068 \times 10^5 T + 9.302 T^2}\right)^{-1}
 \end{aligned}
 \tag{11}$$

To verify the results of some parameters, Equation (12) must be proved:

$$e_{1,2}^{fcc} e_{2,3}^{fcc} e_{1,3}^{fcc} = (1 - e_{1,2}^{fcc})(1 - e_{2,3}^{fcc})(1 - e_{1,3}^{fcc}) \quad \text{and} \quad e_{1,2}^{hcp} e_{2,3}^{hcp} e_{1,3}^{hcp} = (1 - e_{1,2}^{hcp})(1 - e_{2,3}^{hcp})(1 - e_{1,3}^{hcp})$$

The data shown in Table 2 only displays the e_{12} , e_{13} and e_{23} data for fcc and hcp phases. Substituting these data into Equation (3), the six binary compositions are obtained. If the values of the six binary compositions, ${}^{\circ}G_1^{\phi}$, ${}^{\circ}G_2^{\phi}$, ${}^{\circ}G_3^{\phi}$, ${}^E G_{12}^{\phi}$, ${}^E G_{31}^{\phi}$ and ${}^E G_{23}^{\phi}$ and ${}^{\text{mag}}G^{\phi}$ are substituted into Equation (1), the Gibbs free energies of both fcc and hcp phases in Co-29.1 % wt Cr-5.83 % wt Mo ternary alloy are evaluated and plotted in Figure 1. The value of equilibrium temperature between fcc and hcp phases from the data on which Figure 1 or Figure 2 is based, is evaluated as nearly 1430 K for Co-29.1 % wt Cr-5.83 % wt Mo ternary alloy. The value of equilibrium temperature is found as quite efficiently between 1373 K and 1473 K for Co-Cr-Mo powder alloy of milled 6 h, which is heat treated at 1473 K. This temperature is in agreement with that of obtained from the Figure 1 or Figure 2. It is found from the same figure that the value of the Gibbs free energy corresponding to the equilibrium temperature is nearly -8×10^4 J / mol. It can also be determined from the same figure that the calculated critical driving force corresponding to the phase transition temperature (1273 K), which is found experimentally [2], is calculated by 200 J / mol. The result calculated in the present study for the equilibrium temperature is in agreement with those obtained from the references [14, 15]. It is found in fcc to hcp transformation of cobalt and its alloys that the difference in the Gibbs free energy between the two phases is small. Therefore, the driving force for transformation due to supercooling is small and martensite transformation temperature is affected sensitively by small differences in transformation conditions. Hence, the transformation temperature range is very wide and both austenite and martensite transformation temperatures are difficult to determine with precision. So, in this study, the value of the only equilibrium temperature is calculated and compared with experimental values. In the calculation carried out in the present study, using the values of the curie temperature and magnetic moment $T_c = 450.11$ K, $\beta^c = -0.01446$ and $T_c = 139.08$ K, $\beta^c = 0.06705$ for fcc and hcp phases respectively, in the temperature interval of 950 K-1373 K, the mean contribution of the magnetic energy to the Gibbs energy becomes very small for fcc phase (the only by 0.3 J / mol) and for hcp phase (the only by -0.0034 J / mol) can be ignored in comparison with nonmagnetic free energies such as the molar Gibbs energy and excess energies.

Cosequently, alloys based on the Cr-Co-Mo systems are of great practical interest in the production of Ni-based super alloys, surgical implants, heat-resistant and corrosion-resistant protective coatings. In spite of this fact, while there are a lot of articles dealing with the thermodynamics of the constituent binary systems, thermodynamic studies of such three-component systems have not yet been completely reported in the literature.

Recently the work of just one of the free energy related to the excess energy in Cr-Co-Mo system can be found in the ref. [16]. In addition to this, it is known that there are many difficulties in making the experimental stage. In order to perform experiments is much more difficult, especially, at high temperatures. It is anticipated that most of the thermodynamic data of ternary and multicomponent systems will come from theoretical calculations rather than from direct experimentation. In the present study, considering this situation, the integral Gibbs energy of Co-Cr-Mo ternary system as a function of temperature are predicted by using Chou's general solution model. It is shown that this model is applicable successfully to this type ternary alloys where there are no much works in the literature. These calculations may be used to provide a thermodynamic base for design of surgical implant alloys, such as Co-Cr-Mo ternary systems.

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Table 1. Redlich-Kister parameters associated with Fcc and Hcp phases for Co-Cr, Co-Mo and Cr-Mo binaries [8, 9].

Co-Cr-Mo alloy	Binary alloys	⁰ L	¹ L	² L
Fcc phase	Co-Cr	-23080 + 8.34 T	12370 -12.08 T	0
	Co-Mo	-29557.1 + 10.953 T	-1382.2 + 15.371 T	-18135.4
	Cr- Mo	28890 - 7.962 T	5974 – 2.428 T	0
Hcp phase	Co-Cr	-25149 + 13 T	1719 -3 T	0
	Co-Mo	-29315.7 + 23.775 T	-27975.9 -1.936 T	+24698.3
	Cr- Mo	28890 - 7.962 T	5974 – 2.428 T	0

Table 2. The calculated similarity coefficients for Co-Cr-Mo ternary alloy in 1450 K.

	e_{12}	e_{13}	e_{23}
Fcc phase	0.141599	0.899925	0.402676
Hcp phase	0.256632	0.650863	0.764809

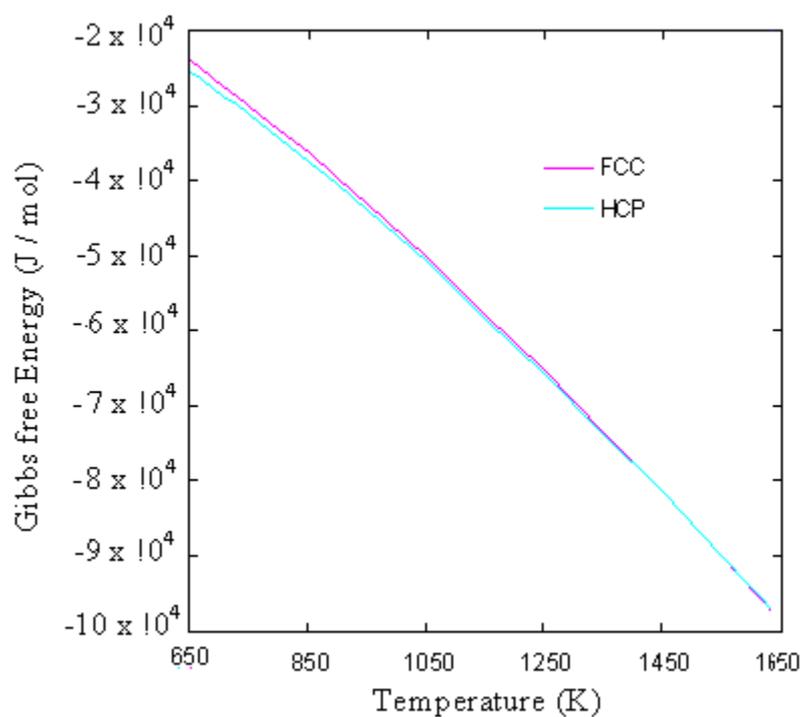


Figure 1. The calculated Gibbs energies as a function of the temperature for both fcc and hcp phases in Co-29.1 % wt Cr-5.83 % wt Mo ternary alloy.

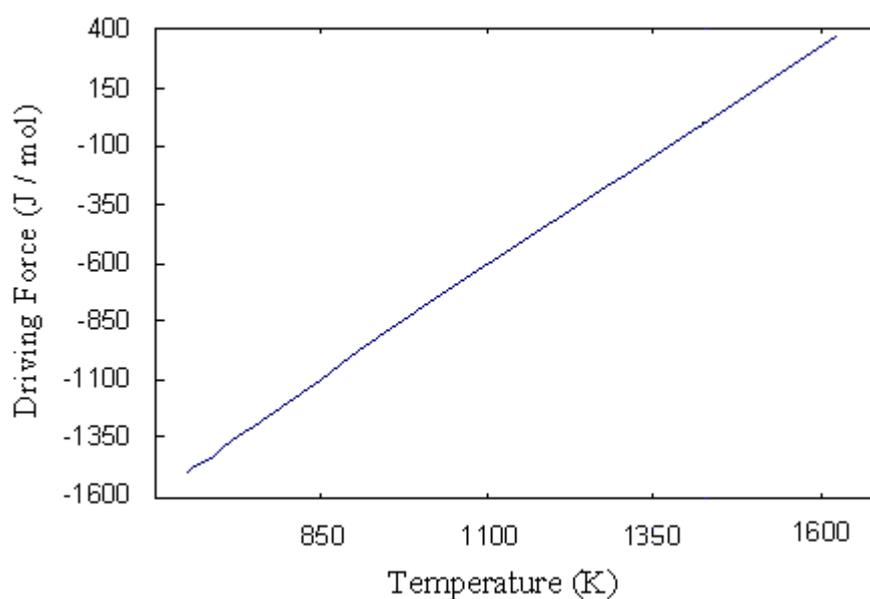


Figure 2. The calculated driving force as a function of the temperature in Co-29.1 % wt Cr-5.83 % wt Mo ternary alloy.

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