

Interdiffusion in Co-Mn Alloys

YOSHIAKI IJIMA, OSAMU TAGUCHI, AND KEN-ICHI HIRANO

Interdiffusion coefficient (\tilde{D}) in cobalt-manganese alloys has been determined by Matano's method in the temperature range between 1133 and 1423 K on (pure Co)-(Co-30.28 at. pct Mn alloy) and (pure Co)-(Co-51.76 at. pct Mn alloy) couples. This, \tilde{D} , has been found to increase with the increase of manganese content. However, the activation energy (\tilde{Q}) and frequency factor (\tilde{D}_0) show a maximum at about 10 at. pct Mn. The concentration dependence of \tilde{D} and \tilde{Q} has been discussed taking into account the thermodynamic properties of the alloy. The difference in \tilde{Q} between the ferro- and paramagnetic phases in Co-5 at. pct Mn alloy has been found to be 24 kJ/mol, which is larger than that for the diffusion of Mn⁵⁴ in this alloy. Further it has been found that the Kirkendall marker moves toward manganese-rich side, showing that manganese atoms diffuse faster than cobalt atoms. From the marker shift, the intrinsic diffusion coefficients, D_{Co} and D_{Mn} , at 33 at. pct Mn have been determined as follows:

$$D_{Co} = 0.22 \times 10^{-4} \exp(-263 \text{ kJ mol}^{-1}/RT) \text{ m}^2/\text{s},$$

and

$$D_{Mn} = 0.98 \times 10^{-4} \exp(-229 \text{ kJ mol}^{-1}/RT) \text{ m}^2/\text{s}.$$

IN the past few decades, much efforts have been made on the theoretical and experimental studies on diffusion in pure metals and dilute alloys.¹ Although a few studies on atomic mechanism of diffusion in concentrated alloys have been carried out, they are limited to either completely random or completely ordered alloys.² It may be interesting to study the diffusion particularly in concentrated alloys to examine the relationships between the diffusion parameters and their physical or thermodynamical properties. The activation energy and frequency factor for interdiffusion determined by the Arrhenius relationship are related not only to the self-diffusion of both components in the alloy but also to the temperature dependence of the thermodynamic factor in Darken's relation.³ Further the effect of magnetic transformation on the self-diffusion and impurity diffusion has been studied fairly well in α -iron⁴⁻¹³ and cobalt.^{14,15}

Though, the present authors have studied interdiffusion in a series of cobalt alloys, such as Co-Ni,¹⁶ Co-Pd¹⁷ and Co-Fe¹⁸ alloys, now Co-Mn system has been chosen for the investigation, since Co-Mn alloys appear to be suitable for studying both the temperature and concentration dependence of interdiffusion coefficient and the effect of magnetic transformation on interdiffusion. This has been facilitated since cobalt and manganese form a solid solution over a wide range of temperature and composition¹⁹ (the maximum solubility of manganese is about 58 pct* at

*Composition of alloys is expressed always in at. pct unless otherwise stated.

1433 K) and the magnetic transformation takes place in an appropriate temperature range for diffusion experiments.

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In the present work, an attempt is also made to examine the Arrhenius relationships as cited above, in some concentrated Co-Mn alloys. The interdiffusion experiments on (pure Co)-(Co-30.28 pct Mn alloy) and (pure Co)-(Co-51.76 pct Mn alloy) couples have been carried out in the temperature range between 1133 and 1423 K. The data on the diffusion of Mn⁵⁴ in cobalt, in Co-5.22 and in 10.24 pct Mn alloys¹⁵ and the thermodynamic data²⁰ have been used to interpret the results.

EXPERIMENTAL PROCEDURE

Pure cobalt discs, 8.7 mm in diameter and 7 mm thick, were machined from the cobalt bar which was obtained by vacuum-melting electrolytic cobalt. Chemical analysis showed the impurities to be Ni: 0.02, Fe: 0.02, C: 0.005, Cu: 0.003 and Mn: <0.0001 wt pct. Co-30.28 pct Mn and Co-51.76 pct Mn alloys were made by melting the electrolytic cobalt and electrolytic manganese (99.94 wt pct purity) in an argon gas atmosphere. The alloy discs were machined to make the same dimension as the pure cobalt discs. After the annealing for grain growth at the temperatures about 100 K lower than the melting point for 3 or 4 days in a stream of purified hydrogen gas, the average grain size was 4 to 5 mm in pure cobalt and 2 to 3 mm in alloys. Analysis of the alloy specimens by an electron probe micro-analyzer showed that during the annealing the surface was depleted in Mn to a depth of about 0.5 mm as a result of evaporation. The depleted surface layer was therefore removed by a precision cutting machine. Flat faces of each specimen were then carefully ground on emery papers and polished on a lap with fine alumina paste. Sandwich type diffusion couple consisted of three discs, two outer cobalt discs and a central alloy disc, was put in a stainless steel holder with screws, and pressed by the screws and diffusion-welded by heating at 1173 K for 2 h in

a stream of purified hydrogen gas. The diffusion width by this treatment was about 10 μm which was negligible compared with that by the actual diffusion annealing. A very small amount of fine chromium oxide powder was put in the welding interface of the couple as the Kirkendall marker. The diffusion couple was sealed in a quartz tube with argon gas and annealed in electric resistance furnaces in the temperature range between 1133 and 1423 K. The furnace temperature was controlled within ± 2 K during the diffusion. After the diffusion anneal, the couple was cut parallel to the diffusion direction, and the cut surface was ground on emery papers and finally polished on a lap with fine alumina paste.

An electron probe microanalyzer (Shimadzu-ARL-Type II) was used to determine the concentration distribution in the diffused specimen. The analysis conditions of the microanalyzer were as follows: accelerating voltage, 30 kV; take-off angle of radiation, 52.2 deg; specimen current for pure cobalt, 0.008 μA ; scanning speed, 8 $\mu\text{m}/\text{min}$ or 24 $\mu\text{m}/\text{min}$. The relative intensities of the X-ray radiations ($\text{Co-K}\alpha$ and $\text{Mn-K}\alpha$) were converted into concentrations using the calibration curves shown in Fig. 1 which was obtained by the standard specimens.

The interdiffusion coefficient was determined as a function of concentration by Matano's method.²¹ It was shown that the molar volume of Co-Mn alloy was proportional to the mole fraction of manganese up to about 52 pct Mn,²² therefore the partial molar volume of each component in the alloy was constant independent of concentration and the mole of manganese per cubic centimeter could be used as the unit of concentration without any correction for the variation of volume with composition.²³ Numerical calculations for Matano's analysis were made using NEAC 2200 Model 700 Electronic Computer in Tohoku University.

RESULTS AND DISCUSSION

1. Concentration and Temperature Dependence of Interdiffusion Coefficient

Fig. 2 shows the concentration dependence of the interdiffusion coefficient (\bar{D}) determined by using

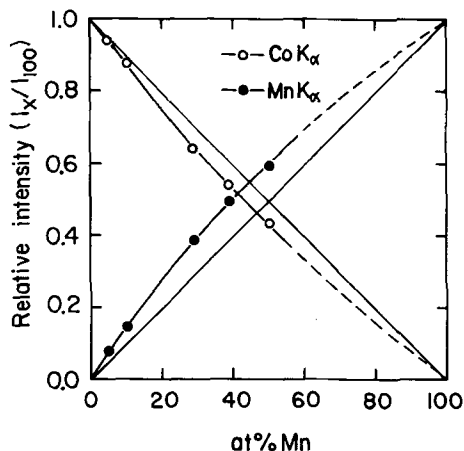


Fig. 1—Standard calibration curves for electron probe microanalysis of Co-Mn alloys.

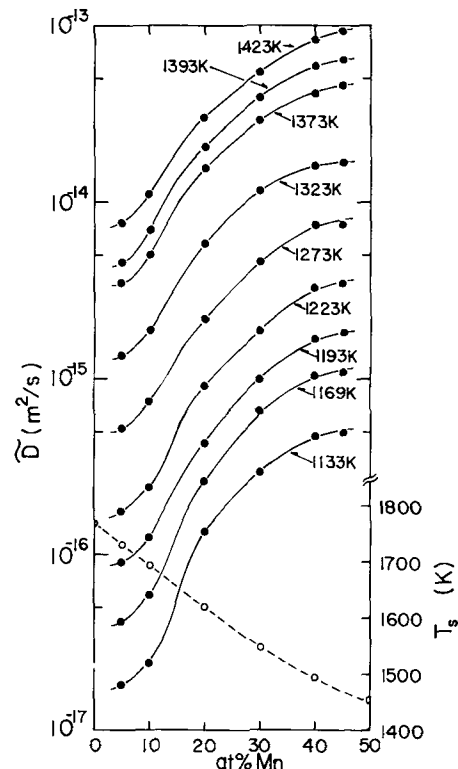


Fig. 2—Concentration dependence of interdiffusion coefficient (\bar{D}) and solidus temperature (T_s) in Co-Mn alloys.

(pure Co)–(Co-51.76 pct Mn alloy) couple, in comparison with that of the solidus temperature (T_s). To examine the concentration dependence of \bar{D} on the cobalt-rich side in detail, the couple of (pure Co)–(Co-30.28 pct Mn alloy) has also been diffused at the temperatures of 1223, 1323 and 1423 K. It has been found that the result of (pure Co)–(Co-30.28 pct Mn alloy) couple is in agreement with that of (pure Co)–(Co-51.76 pct Mn alloy) couple within experimental errors. It is clear from Fig. 2 that in the range of 5 to 45 pct Mn the interdiffusion coefficient (\bar{D}) increases about tenfold with decrease of the solidus temperature (T_s), as has been generally recognized in many binary alloys.²⁴

The values of $\ln \bar{D}/T_s$ for the two temperatures, 1323 and 1423 K, along with the activation energy and frequency factor for all the compositions studied in this investigation are listed in Table I. It can be seen from this that the values of $\ln \bar{D}/T_s$ for 1323 and 1423 K are nearly independent of composition. This can also become clear by expressing the Arrhenius equation as

$$\frac{\ln \bar{D}}{T_s} = \frac{1}{T_s} \left(\ln \bar{D}_0 - \frac{\tilde{Q}}{RT} \right) \quad [1]$$

From the above, since both \tilde{Q}/T_s and \bar{D}_0 are nearly independent of composition excepting at 10 pct Mn, $\ln \bar{D}/T_s$ is constant at these two temperatures.

2. Concentration Dependence of Activation Energy and Frequency Factor

Fig. 3 shows the Arrhenius plot of the interdiffusion coefficient for each concentration. From this

Table I. Activation Energy (\tilde{Q}) and Frequency Factor (\tilde{D}_0) for Interdiffusion in Co-Mn Alloys. \tilde{Q}/T_s and $\ln \tilde{D}/T_s$ Are Also Listed.

| Composition (At. Pct Mn) | \tilde{Q} (kJ/mol) | \tilde{D}_0 (10^{-4} m ² /s) | \tilde{Q}/T_s (J/mol K) | $\frac{\ln \tilde{D}_{1323\text{K}}}{T_s}$ | $\frac{\ln \tilde{D}_{1423\text{K}}}{T_s}$ |
|-----------------------------|-------------------------|---|------------------------------|--|--|
| 5 (ferro) | 296 | 7.79 | 171 | — | — |
| 5 (para) | 273 | 0.781 | 157 | -1.97×10^{-2} | -1.87×10^{-2} |
| 10 | 284 | 3.07 | 167 | -2.00×10^{-2} | -1.88×10^{-2} |
| 20 | 257 | 0.700 | 159 | -2.04×10^{-2} | -1.92×10^{-2} |
| 30 | 248 | 0.721 | 160 | -2.07×10^{-2} | -1.97×10^{-2} |
| 40 | 241 | 0.627 | 161 | -2.12×10^{-2} | -2.02×10^{-2} |

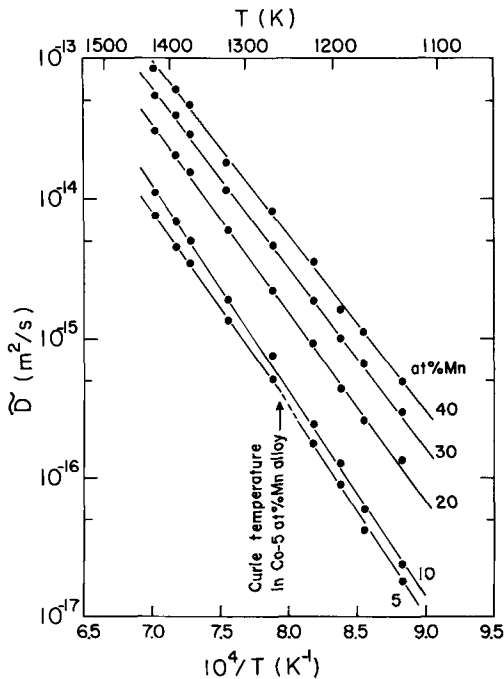


Fig. 3—Temperature dependence of interdiffusion coefficient in Co-Mn alloys.

figure, one can see a deviation from the linearity for Co-5 pct Mn. As this is not so remarkable, it has been attempted to determine the activation energy and frequency factor, separately from this plot in the ferro- and paramagnetic phases. It can be seen from Table I that the difference in the activation energy, $\Delta\tilde{Q}_{\text{mag}}$, between the two phases in Co-5 pct Mn alloy is 24 kJ/mol which is larger than that (12 kJ/mol) for the diffusion of Mn⁵⁴ in Co-5.22 pct Mn alloy.¹⁵ This result is in contrast to the case of Co-Pd alloys¹⁷ where the influence of magnetic transformation on interdiffusion is smaller than that on the self-diffusion in these alloys. This difference between the two systems may be attributed to the difference in the effects of magnetic transformation on their temperature dependence of the thermodynamic factor. Corresponding to this difference in the activation energy at this composition, the frequency factor in the ferromagnetic phase is as large as tenfold that in the paramagnetic phase. The activation energies and frequency factors at 10 to 40 pct Mn alloys are determined only in the paramagnetic phase, because diffusion temperatures in the present work are beyond the Curie temperatures in these compositions.

From Fig. 4, it can be seen that the activation

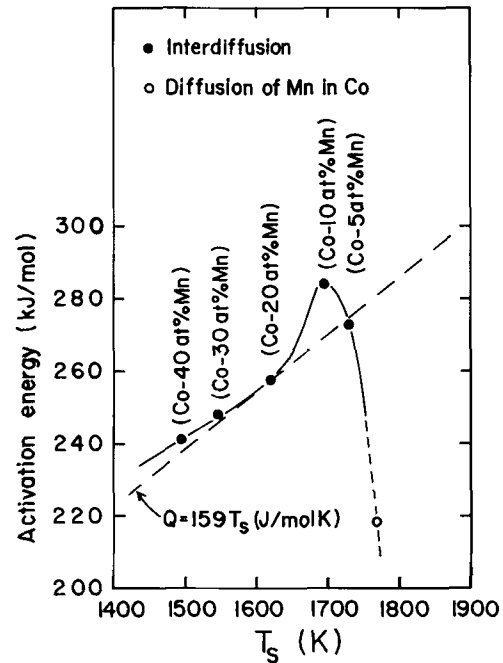


Fig. 4—Relationship between activation energy for interdiffusion and solidus temperature in Co-Mn alloys.

energy is proportional to T_s , except for a peak at 10 pct Mn. All the activation energies including the value for the impurity diffusion of Mn in pure Co are the values for the paramagnetic phase. The ratio of \tilde{Q} to T_s is about 134 (J/mol K), which is close to 159 (J/mol K) for the self-diffusion in pure fcc metals.²⁵

According to Darken²⁶ and Manning,²⁷ the interdiffusion coefficient (\tilde{D}) is represented by

$$\tilde{D} = (N_2 D_1^* + N_1 D_2^*) m S \quad [2]$$

where N_1 and N_2 are the mole fractions, D_1^* and D_2^* are the self-diffusion coefficients of components 1 and 2 in the alloy, m the thermodynamic factor, and S is the factor which arises from vacancy flow²⁷ in the interdiffusion couple. Then, the apparent activation energy for interdiffusion \tilde{Q} can be written as a sum of three parts corresponding to the temperature dependence of $(N_2 D_1^* + N_1 D_2^*)$, m and S :

$$\tilde{Q} = Q^* + Q_T + Q_S. \quad [3]$$

According to Hilliard,³

$$Q^* = p Q_1^* + (1 - p) Q_2^* \quad [4]$$

where

$$p = 1/[1 + (N_1 D_{01}^*/N_2 D_{02}^*) \exp(Q_T^* - Q_C^*)/RT]. \quad [5]$$

D_{01}^* and D_{02}^* are the frequency factors for self-diffusion of components 1 and 2 in the alloy.

Q_T is calculated by

$$Q_T = -R d(\ln m)/d(1/T) \quad [6]$$

where

$$m = 1 + d(\ln \gamma_1)/d(\ln N_1) \quad [7]$$

and γ_1 is the activity coefficient of the component 1 in the alloy of concentration N_1 .

According to Manning,²⁷

$$S = 1 + \frac{2N_1 N_2 (D_1^* - D_2^*)^2}{M_0 (N_1 D_2^* + N_2 D_1^*) (N_1 D_1^* + N_2 D_2^*)} \quad [8]$$

where M_0 is the constant, equal to 7.15 for the fcc alloys. Then,

$$Q_S = -R d(\ln S)/d(1/T) \quad [9]$$

$$= (Q_1^* - Q_2^*) \left(1 - \frac{1}{S}\right) \left[\frac{2}{1 - (D_2^*/D_1^*)} - \frac{1}{1 + (N_1 D_2^*/N_2 D_1^*)} - \frac{1}{1 + (N_2 D_2^*/N_1 D_1^*)} \right]. \quad [10]$$

Eremenko, Lukashenko and Sidorko¹⁹ have measured the activity of manganese in Co-Mn alloys for seven compositions (9.5, 15.2, 20.0, 30.3, 38.4, 49.6 and 53.3 pct Mn) in the temperature range between 950 and 1150 K. They have found that in cobalt-rich solid solution the activity of manganese is smaller than that in the ideal solution. The activity data of the ferromagnetic phase have been obtained only in 9.5 pct Mn alloy. Q_T estimated by Eqs. [6] and [7] using their results in the composition range from 15 to 50 pct Mn is negligibly small compared with Q^* . However, owing to the positive temperature dependence of m at 9.5 pct Mn, Q_T in Co-5 pct Mn and 10 pct Mn alloys appears to be a relatively large positive value though the exact value can not be determined, due to the lack of the activity data in more cobalt-rich alloys.

If (D_{Mn}^*/D_{Co}^*) and $(Q_{Mn}^* - Q_{Co}^*)$ in Co-Mn alloys are nearly the same as those in pure cobalt,^{14,15} Q_S estimated by Eq. [10] should be negligibly small compared with Q^* .

Although the self-diffusion coefficients of manganese in this system has been studied by the present authors,¹⁵ the same measurement for cobalt has not yet been made. However, with the present experimental results on D_{01}^* and Q_{Co}^* (for the self-diffusion of manganese in the alloy) and Q , the values of D_{02}^* and Q_C^* (for the self-diffusion of cobalt in the alloy) and Q_T can be estimated as follows: When we assume

$D_{Mn}^* > D_{Co}^*$ and $Q_{Mn}^* < Q_{Co}^*$ as in pure cobalt in Eq. [5], the value p is nearly equal to one at the temperature 1273 K which is representative in the present experiment. From Eq. [4], Q^* is near Q_{Mn}^* and then Q_T can be estimated appropriately from Eq. [3]. When D_{Mn}^*/D_{Co}^* is not so large as two, D_{Co}^* and Q_{Co}^* can be estimated from Eqs. [4] and [5]. The results are displayed in Table II.

A peak of the mixing enthalpy in Co-Mn alloy at about 10 pct Mn observed by Eremenko, Lukashenko and Sidorko¹⁹ may be related to the peak of Q at the same composition. Though, at present it is not possible to give a detailed mechanism to explain these results, it appears that the alloy is more rigid around that composition.

3. Kirkendall Effect

The Kirkendall effect has been observed in (pure Co)-(Co-51.76 pct Mn alloy) couples diffused at 1323, 1373, and 1423 K. The concentration of manganese at the marker position has been confirmed to be constant (33 pct Mn) and independent of diffusion time and temperature. Also, the marker movement toward the manganese-rich side has been observed. In Fig. 5, the linear relationship between marker shift and square root of diffusion time shows that marker velocity is constant at each temperature.

From Darken's relation²⁶ and the observed marker velocity, the intrinsic diffusion coefficients of both the components are calculated in Co-33 pct Mn alloy. Also, the temperature dependence of the intrinsic diffusion coefficients in this alloy is obtained as follows:

$$D_{Co} = 0.22 \times 10^{-4} \exp(-263 \text{ kJ mol}^{-1}/RT) \text{ m}^2/\text{s} \quad [11]$$

and

$$D_{Mn} = 0.98 \times 10^{-4} \exp(-229 \text{ kJ mol}^{-1}/RT) \text{ m}^2/\text{s}. \quad [12]$$

The above values are listed in Table III. It is evident

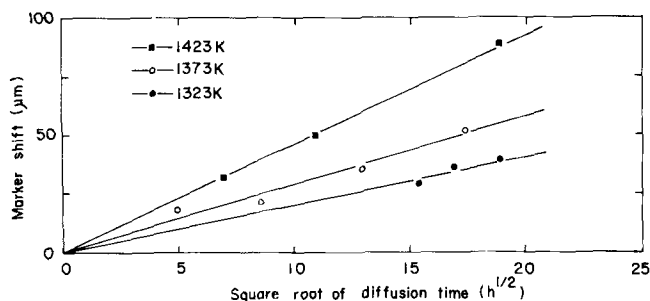


Fig. 5—Relationship between Kirkendall marker shift and square root of diffusion time for interdiffusion in Co-Mn alloys.

Table II. Estimation of Q_T , Q^* , D_{0Co}^* and Q_{Co}^* in Co-5 Pct Mn and Co-10 Pct Mn Alloys

| Composition (At. Pct Mn) | Experimental | | | | | Estimated | | | | |
|-----------------------------|-----------------------|---|------------------------|---|------------------------|-------------------|-------------------|---|------------------------|--|
| | \bar{Q} (kJ/mol) | D_{0Mn}^* ($10^{-4} \text{ m}^2/\text{s}$) | Q_{Mn}^* (kJ/mol) | D_{0Co}^* ($10^{-4} \text{ m}^2/\text{s}$) | Q_{Co}^* (kJ/mol) | Q_T (kJ/mol) | Q^* (kJ/mol) | D^* ($10^{-4} \text{ m}^2/\text{s}$) | Q_{Co}^* (kJ/mol) | |
| 0 | — | 0.011 | 218 | 0.17 | 260 | — | — | — | — | |
| 5 | 273 | 0.501 | 257 | — | — | 15 | 258 | 6 | 285 | |
| 10 | 284 | 1.36 | 263 | — | — | 19 | 265 | 19 | 293 | |

Table III. Interdiffusion Coefficient (\tilde{D}) and Intrinsic Diffusion Coefficients (D_{Mn} and D_{Co}) in Co-33 Pct Mn Alloy. Ratio of D_{Mn} to D_{Co} is Also Shown

| Temperature, K | \tilde{D} (10^{-14} m ² /s) | D_{Mn} (10^{-14} m ² /s) | D_{Co} (10^{-14} m ² /s) | D_{Mn}/D_{Co} |
|----------------|--|---|---|-----------------|
| 1423 | 6.58 | 8.78 | 2.11 | 4.16 |
| 1373 | 3.40 | 4.55 | 1.06 | 4.29 |
| 1323 | 1.38 | 1.92 | 0.294 | 6.51 |

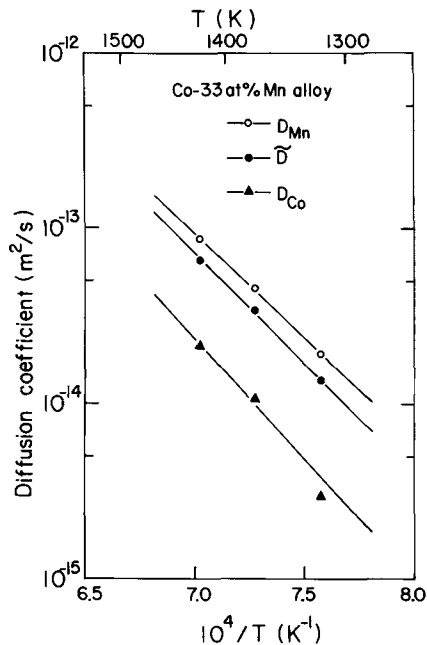


Fig. 6—Temperature dependence of intrinsic diffusion coefficient of Co and Mn atoms and interdiffusion coefficient in Co-33 pct Mn alloy.

from this that manganese atoms diffuse faster than cobalt atoms in this alloy. Fig. 6 shows plot of these values together with the interdiffusion coefficient. The Kirkendall void has not been observed.

CONCLUSIONS

Experimental results on the interdiffusion in Co-Mn alloys are summarized as follows:

1) The interdiffusion coefficient in the range of 5 to 45 at. pct Mn increases about tenfold with decrease of the solidus temperature from 1768 to 1453 K.

2) The activation energy \tilde{Q} and the frequency factor for the interdiffusion show a maximum at about 10 at. pct Mn.

3) The difference in \tilde{Q} between the ferro- and paramagnetic phases in Co-5 at. pct Mn alloy has been found to be 24 kJ/mol.

4) Kirkendall marker moves toward manganese-rich side, showing that manganese atom diffuses faster than cobalt atom in this system.

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