Phase equilibria and interdiffusion in the cobalt-titanium system

Phase Equilibria and Interdiffusion in the Cobalt-Titanium System

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The Co-Ti equilibrium is investigated by means of a diffusion couple technique. The growth of solid solutions and intermetallic phases is studied with respect to time and temperature in various types of diffusion couples. From the determined boundary concentrations a modified phase diagram is proposed. Chemical diffusion coefficients and heats of activation are calculated for the various phases. From calculations of the ratio of the intrinsic diffusion coefficients for the Co_2Ti-phase Co appears to be by far the faster moving component at temperatures below 1000°C while at higher temperatures the mobility of Ti approaches that of Co.

Phasengleichgewichte und Diffusion im System Kobalt-Titan

Das Kobalt-Titan-Zustandsdiagramm wurde mittels der Diffusionspaartechnik untersucht. Das Wachstum von Mischkristallschichten und intermetallischen Phasen wurde in verschiedenen Diffusionspaaren als Funktion der Zeit und der Temperatur verfolgt. Aufgrund der gemessenen Phasengrenzenkonzentrationen wird ein abgeändertes Phasendiagramm vorgeschlagen. Die chemischen Diffusionskoeffizienten und Aktivierungsenergien für die verschiedenen Phasen wurden berechnet. Berechnungen der partiellen Diffusionskoeffizienten der Co_2Ti-Phase zeigen, daß unterhalb 1000°C Kobalt die bedeutend schneller diffundierende Komponente ist, während bei höheren Temperaturen Titan fast ebenso schnell diffundiert wie Kobalt.

Studies of the phase relationships in the titanium-cobalt system reported in the literature[1] to [10]) have established the existence of five intermetallic phases, denoted as: Co_3Ti (cubic-$AuCu_3$ type), Co_2Ti (hexagonal-$MgNi_2$ type), Co_2Ti (cubic-$MgCu_2$ type), CoTi (cubic-CsCl type) and $CoTi_2$ (cubic-Ti_2Ni type). Besides these intermetallic phases a solid solution of titanium in cobalt and one of cobalt in titanium are present. Recently Allen et al.[11]) reported two other stacking sequences for the Co_2Ti phase in addition to those mentioned above. It has turned out that the homogeneity regions of the various phases, as given by the mentioned authors, are not fully in agreement with each other. This is especially so for the solid solution of titanium in cobalt and for the Co_2Ti phases.

In order to establish the constitution of the Co-Ti phase diagram a technique is chosen in which diffusion couples consisting of combinations of the pure metals and intermetallic compounds are subjected to heat treatment at various temperatures and examined subsequently. It has turned out that this technique is a very suitable one for the determination of phase boundary concentrations as good results are achieved in our laboratory for e.g. the systems: Ti-Al[12]), Ti-Ni[13]), Mo-Ni[14]) and Ni-Al[15]). By using this technique it is possible to collect at the same time diffusion data, which govern the interdiffusion behaviour in the Co-Ti system.

Experimental procedure

Materials and preparation of alloys

For this investigation use was made of Ti-rod (99.97 wt.%) and Co-sheet (99.99 wt.%), both supplied by M.R.C. (U.S.A.). Alloys were prepared by repeated argon-arc melting. To achieve equilibrium the alloys were annealed in evacuated silica capsules during one week at 1100°C ($CoTi_2$ at 1000°C). The alloys appeared to be homogeneous.

Preparation and annealing of the diffusion couples.

Diffusion couples were prepared by solid state resistance welding of discs of the constituents. A good weld was obtained by clamping the couple constituents between two pieces of carbon rod and then passing an electric current through the assembly for some seconds. During this operation a vacuum better than 1×10^{-5} Torr was maintained. The constituents were either alloys or pure metals or combinations of both. Before welding the discs were ground on silicon carbide paper through 600 grit.

The diffusion couples were annealed (with the exception of Co-Ti couples) in evacuated (0.1 Torr) silica capsules in a resistance furnace. Temperatures were measured with a Pt/Pt-10 Rh thermocouple. Annealing of the Co-Ti couples has to take place in a specially designed vacuum furnace[16]). In order to prevent warping of the diffusion couple an externally adjustable pressure was used. At the end of the annealing procedure the couples were rapidly cooled and embedded in mounting resin, ground and polished in a plane parallel to the diffusion direction and subsequently etched with a mixture consisting of 5% HF and 10% H_2O_2 in water.

Analysis of the diffusion couples.

Metallographic techniques were used to determine the number of phases formed and their layer thicknesses as a function of time and temperature. Concentration-penetration curves were recorded using an S.E.M. IIA electron probe microanalyzer (A.E.I., England). A detailed description of this procedure is given elsewhere[17]). The intensity measurements were performed by counting Ti-K_α pulses. The obtained X-ray intensity was corrected for background and divided by the net intensity of the pure Ti standard. The resulting value of the relative intensity K_{Ti} was related to the mol fraction N_{Ti} according to the Ziebold-Ogilvie[18]) expression:

$$\frac{1 - K_{Ti}}{K_{Ti}} = X_{Ti} \frac{1 - N_{Ti}}{N_{Ti}}$$

By means of a series of standard alloys the experimental constant X_{Ti} was found to be 1.18 ± 0.02 under the given circumstances (accelerating voltage 30 kV, probe current 0.2 μA). Penetration curves were recorded by taking point counts at intervals of 3 μm or larger along

the diffusion direction. For every recording the value of X_{Ti} was recalculated from the obtained intensities of a 50 at.-% Ti alloy.

From the concentration-penetration curves it is possible to construct the phase diagram and to calculate the chemical diffusion coefficient as a function of the concentration. In diffusion couples in which the marker interface is visible the relative mobilities of the diffusing species can be calculated.

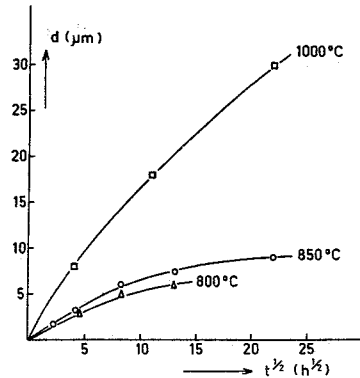X-ray analysis was used to establish the presence of the hexagonal and the cubic modification of Co_2Ti.

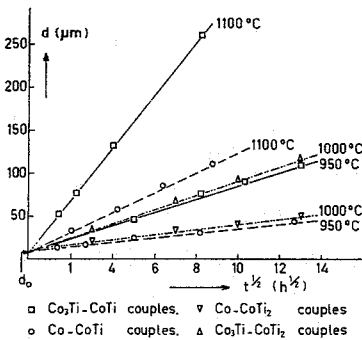Fig. 1. Plot of the layer width, d, of $CoTi_2$ in CoTi-Ti couples vs. the square root of time, t.

Fig. 2. Plot of the layer width, d, of Co_2Ti in Co_3Ti (22 at.-% Ti) — CoTi, Co-CoTi, Co_3Ti - $CoTi_2$ and Co - $CoTi_2$ couples vs. the square root of time, t.
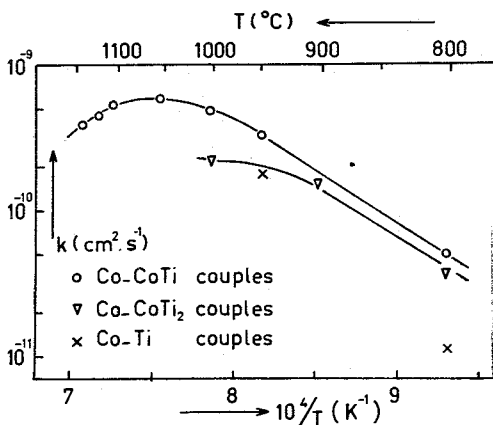

Fig. 3. Plot of log k vs. $1/T$ for the Co_2Ti layer in various types of couples.

Experimental results

Growth of the various phases

In various types of diffusion couples the layer growth has been studied with respect to time and temperature. It turned out that all phases, mentioned in the introduction, were present. In figs. 1 and 2 the width of the $CoTi_2$ and Co_2Ti layers, resp., in different couples is plotted as a function of the square root of time. Except for the $CoTi_2$ phase (fig. 1) the growth of the intermetallic phases was according to the parabolic law $d^2 = k \cdot t$ (d = layer width, t = time). The layer width of both Co_2Ti phases was measured together for reasons which will be explained further on. In the early stages of the diffusion process ($t < 2$ h) the growth of the Co_2Ti phases was faster than according to the parabolic law and the growth could be expressed by $(d - d_o)^2 = kt$. The value of d_o, obtained by extrapolating the straight line towards $t = 0$, appeared to be approximately 10 μm (fig. 2).

The temperature dependence of the penetration constant, k, can be given by $k = k_o \exp(-A/RT)$ for both the solid solutions and for the CoTi and Co_2Ti phases. In figs. 3 and 4 the logarithm of the penetration

Table 1: Numeric values of k_o and A in the expression $k = k_o \exp(-A/RT)$ for various phases grown in different types of diffusion couples. Values of k_o and A are calculated with least square methods.

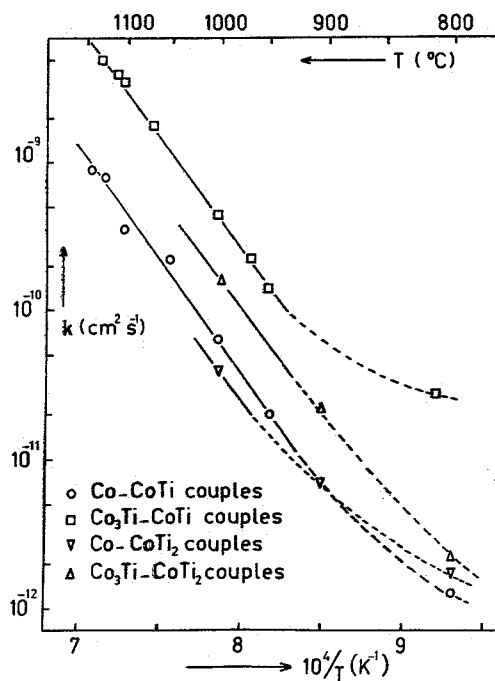| Phase	Couple	T in °C	k_o in $cm^2 \cdot s^{-1}$	A in $kcal \cdot mole^{-1}$
Co_{ss}	Co-CoTi	800 - 1140	1.53×10^4	86.6
Co_2Ti	Co-CoTi	950 - 1140	6.81×10^1	70.0
	Co_3Ti-CoTi	950 - 1140	3.67×10^2	69.1
CoTi	Co_3Ti-$CoTi_2$	800 - 1000	1.50×10^{-4}	37.4
β-Ti	CoTi-Ti	700 - 850	2.67×10^2	52.7
	Co_3Ti-Ti	700 - 850	5.17×10^1	49.7
	Co-Ti	700 - 850	2.92×10^1	48.9

Fig. 4. Plot of log k vs. $1/T$ for the Co_3Ti layer in various types of couples.

constant for the Co_2Ti and Co_3Ti phase is plotted vs. the reciprocal of the absolute temperature. The plot for the Co_3Ti phase yields no straight line at higher temperatures. A maximum occurs at approximately 1050°C for the Co-CoTi diffusion couples. For those phases for which the growth is parabolic with respect to time and for which the log k vs. $10^4/T$ plot yields a straight line numeric values for k_o and A are presented in table 1.

Phase boundary concentrations

In order to obtain the equilibrium phase diagram at temperatures at which solid-solid equilibrium exists phase boundary concentrations must be determined from the concentration-penetration curves. For various reasons these concentrations cannot be determined within 2 μm of the phase boundary. However, when the phase in question has a reasonable layer width the phase boundary concentration can be determined by extrapolation towards the phase boundary. Problems arise when the concentration gradient is steep near the phase boundary. This is especially the case for the Co-solid solution at temperatures lower than 1000°C. In order to overcome this problem long annealing times, up to 4 weeks, are necessary. More satisfactory results are achieved for this phase when diffusion couples of the Co-Co_3Ti (22 at.% Ti) type are used, although at temperatures below 1000°C a too low value of the maximum solubility of titanium in cobalt may still be found. Attempts to investigate the Co-solid solution boundary by means of an equilibrated two phase alloy (18 at.-% Ti) annealed for 4 weeks at respectively 700, 800 and 900°C failed. The obtained precipitates were too small to determine phase boundary concentrations. In fig. 8 the $Co_{ss}/(Co_{ss}+Co_3Ti)$ phase boundary has been drawn while taking account of the mentioned restrictions.

morphology changes from a needle-like structure at the titanium rich side to an equiaxed structure at the cobalt-rich side. Concentration-penetration curves (fig. 6) showed sometimes the presence of a concentration gap of less than 0.6 at.% Ti, but in many cases a distinct gap could not be determined. If this gap truly exists then it is apparently too small to be measured. The shape of the determined Co_2Ti field in the phase diagram is presented in fig. 7.

Concerning the other intermetallic phases no problems about the determination of the boundary concentrations were encountered. The type of diffusion couple (except for the Co_{ss} boundary) seems to be irrelevant in determining phase boundary concentrations. The results of our investigation concerning the equilibrium phase diagram are compared in table 2 with data from
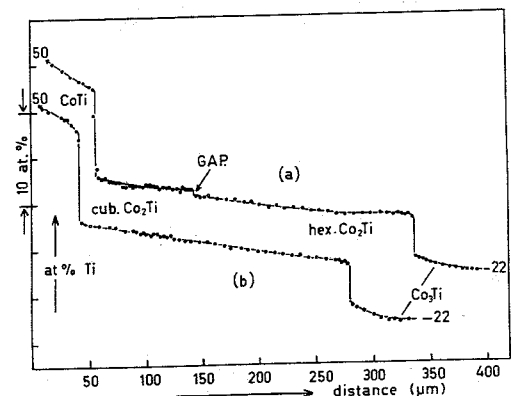
Fig. 6. Concentration-penetration curves of two Co_3Ti-CoTi couples. (a) 79 h at 1100°C, (b) 58 h at 1100°C.

Fig. 5. Optical micrograph of a Co-CoTi couple annealed 2 weeks at 1100°C
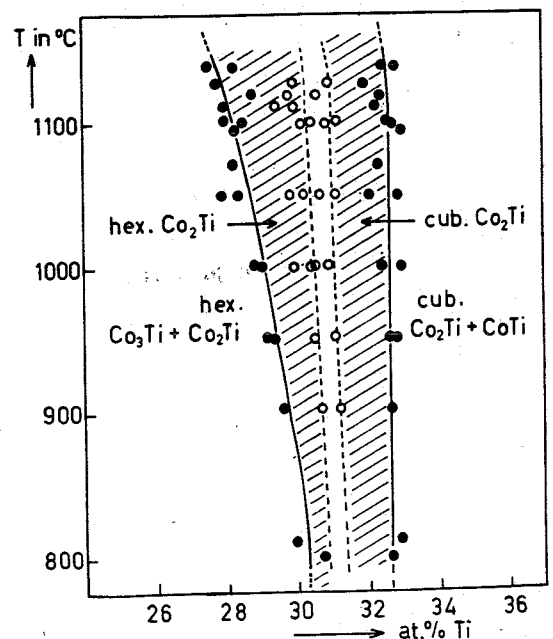
Fig. 7. Composition range of Co_2Ti phases as determined from Co-CoTi and Co_3Ti-CoTi couples.

Although the phase denoted as Co_2Ti was obtained in thick layers in Co-CoTi and Co_3Ti-CoTi diffusion couples it appeared to be impossible to produce a distinct boundary between the reported hexagonal and cubic modifications by etching. From fig. 5 it is clear that the

literature. Values reported by references[9] [23] and [24] for the CoTi phase at 1000°C show no strong deviations from our results. In fig. 8 the complete phase diagram as determined by means of diffusion couples is presented.

Table 2: Boundary concentration in at. % Ti determined from diffusion couples and the results given by the references.

T in °C	Co_ss				Co_3Ti			
	couples	ref. 6)	ref. 3)	ref. 2)	couples	ref. 6)	ref. 3)	ref. 4)
1140	-14.0	-12.0	-13.7		20.0 - 22.8	17.5 - 22.0	20.0 - 23.6	
1100	-13.3	- 9.0	-12.8	-12.5	20.0 - 23.8	18.0 - 24.0	20.8 - 24.0	
1000	-11.7	- 6.6		-10.0	20.0 - 24.2	19.3 - 25.0		20.5 - 25.0
900	-10.5	- 5.0	-11.4	-10.0	20.5 - 24.6	19.5 - 25.0	22.5 - 25.5	
800	- 9.7	- 3.9		- 9.8	22.0 - 24.9	19.5 - 25.0		
700	- 9.2	- 3.0		- 9.6	22.5 - 25.0	19.5 - 25.0		

T in °C	hexagonal Co_2Ti			cubic Co_2Ti		
	couples	ref. 3)	ref. 8)	couples	ref. 3)	ref. 7)
1140	27.8 - 30.3*)	31.0 - 31.5		30.9*) - 32.5	34.0 - 34.3	
1100	28.2 - 30.4*)	31.0 - 31.5		31.0*) - 32.6	34.0 - 34.3	
1000	28.9 - 30.5*)	31.0 - 31.5	29.0 - 31.3	31.1*) - 32.7	34.0 - 34.3	32.8 - 33.4
900	29.5 - 30.7*)	31.0 - 31.5		31.3*) - 32.7	34.0 - 34.3	
800	30.4 - ?	31.0 - 31.5		? - 32.7	34.0 - 34.3	

T in °C	CoTi			CoTi_2		β-Ti	
	couples	ref. 3)	ref. 1)	couples	ref. 10)	couples	ref. 5)
1140	41.8 -	46.0 - 51.7	45.5 -				
1100	42.2 -	46.5 - 51.7	45.5 -				
1000	43.9 - 51.0	47.0 - 51.7	45.5 - 52.0	66.3 - 66.8	67.0	85.5 - 100	86.5 - 100
900	45.8 - 51.0	47.0 - 51.7	45.5 - 51.7			88.2 - 100	90.0 - 100
800	47.0 - 51.0	47.0 - 51.7	45.5 - 51.5	66.1 - 66.5		89.5 - 95.0	91.5 - 95.7
700						91.0 - 92.0	91.8 - 92.3
650					66.7		

*) Less certain values.

The deviations between our results and the reported references[1] to [10]) might partly be caused by the use of not completely equilibrated alloys for X-ray investigation by the referred authors. In their study concerning the solubility limits of the CoTi compound Iannucci et al.[1]) mentioned an uncertainty regarding this point. By

Calculation of the chemical diffusion coefficient D^v

For the calculation of diffusion coefficients it is necessary that the parabolic law is obeyed. This rules out the possibility to perform calculations for the CoTi_2 phase in CoTi-Ti couples. The fact that the diffusion coefficient
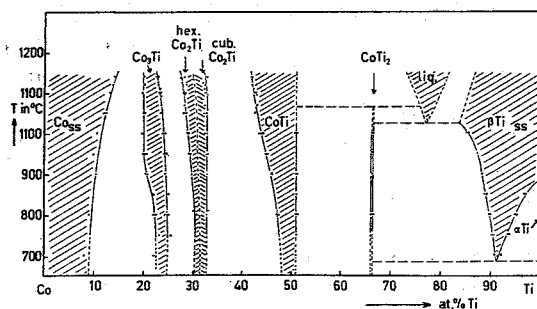

Fig. 8. Phase diagram of the Co-Ti system as determined by means of the diffusion couple technique in the present investigation.

Fig. 9. The molar volume for the various phases as calculated from lattice parameter data.

using the diffusion couple technique we have the advantage that the phases are growing in equilibrium with each other, which can be verified by recording the penetration curves after various annealing times. Values of an equilibrated two phase alloy (25 at.% Ti) annealed for 4 weeks at 900, 1000 and 1200°C are in good agreement (better than 0.2 at.% Ti) with the values obtained from diffusion couples.

for a certain phase can be calculated from different types of diffusion couples offers the possibility to verify the results. When volume diffusion is rate controlling the same results should be found.

Calculations are performed with a computing program designed by Heijwegen and Visser[19]). The program operates with the equation derived by Sauer and Freise[20]) and by Wagner[21]). This equation has been de-

rived for the case that changes in volume occur during diffusion. The molar volumes of the phases are calculated from lattice parameters given in literature[3] to [5], [7] to [10]). In fig. 9 the molar volumed for the various phases is plotted against concentration. In different types of diffusion couples chemical diffusion coefficients are calculated for the occurring phases as a function of concentration. Except for the Co_3Ti phase no distinct concentration dependence of D^v within a certain phase was found. The chemical diffusion coefficient for Co_2Ti tends to increase with increasing Ti content.

Table 3: Numeric values of frequency factor D_0^v and heat of activation Q in the expression $D^v = D_0^v \exp(- Q/RT)$ in which D^v is the chemical diffusion coefficient. Values are calculated with least square method.

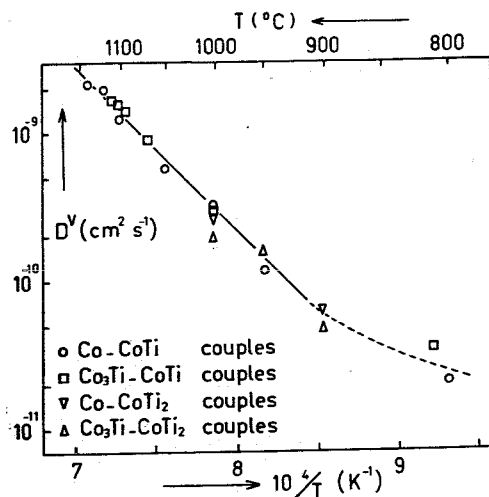| Phase	at.% Ti	T in °C	D_0^v in cm²s⁻¹	Q in kcal · mole⁻¹
Co_{ss}	4 - 8	900 - 1140	1.5×10^1	67.0 ± 4.5
Co_3Ti	21	900 - 1140	5.3×10^{-2}	40.0 ± 6.0
Co_2Ti	30 - 32	900 - 1140	2.8×10^{-1}	52.0 ± 4.0
$CoTi$	46 - 50	900 - 1140	4.4×10^{-4}	41.4 ± 3.5
β-Ti	90 - 95	700 - 850	6.7×10^1	49.5 ± 5.5

Fig. 10. The logarithm of the chemical diffusion coefficient of Co_2Ti vs. $1/T$ for various types of diffusion couples.

The temperature dependence of D^v can be written as $D^v = D_0^v \exp(- Q/RT)$, in which Q is the heat of activation. In Fig. 10 log D^v is plotted vs. $10^4/T$ for the Co_2Ti phase. Numeric values for D_0^v and Q are presented in table 3. The values for Co_3Ti are given at 21 at.% Ti. The values for higher Ti contents are not inserted because the spreading in the measurement makes them rather irrelevant.

Calculation of the ratio of the intrinsic diffusion coefficients

Using the equation derived by van Loo[22] and following a quite similar procedure as the one used by Bastin[13] the ratio of the intrinsic diffusion coefficients is calculated at different temperatures for Co_2Ti in Co_3Ti-$CoTi$ couples. The ratio of the partial molar volumes of Co and Ti in Co_2Ti as calculated from lattice parameter data is 0.76 for hexagonal Co_2Ti and 0.36 for cubic Co_2Ti. A value of 0.56 is used when calculating the ratio of the intrinsic diffusion coefficients since we are not sure in which lattice the marker interface is situated.

Calculations are performed with the mentioned computing program. The ratio of the intrinsic diffusion coefficients appears to be very sensitive to slight variations in the position of the marker interface. In table 4 D_{Co}/D_{Ti} is given for various temperatures together with the titanium content at the marker interface. From table 4 it is clear that for temperatures below 1000°C diffusion occurs almost exclusively by the motion of Co atoms, whereas at higher temperatures the mobility of Ti increases and approximates closely that of Co.

Table 4: The ratio of the intrinsic diffusion coefficients for Co_2Ti in Co_3Ti-$CoTi$ couples at different temperatures.

Temperature in °C	Ti concentration at marker interface in at.%	D_{Co}/D_{Ti}
810	31.8	$+ \infty$
950	31.4	17.4
1000	30.9	42.4
1050	31.0	2.4
1070	31.1	1.0
1095	31.2	2.5
1100	31.2	1.0
1110	31.2	1.8
1140	31.1	1.2

Results of the X-ray investigation

As has been mentioned already a distinct concentration gap between the hexagonal and cubic Co_2Ti phases could not always be measured. Therefore we have investigated the occurring phases with X-ray diffraction. After grinding the Co_2Ti diffusion layer parallel to the original contact interface the surfaces throughout the entire Co_2Ti layer are exposed to Co-K_α X-ray radiation. From the observed diffraction patterns it was clear that the Co_2Ti phase exhibits a hexagonal structure at the Co-rich side and a cubic structure at the Ti-rich side. A sudden change-over from one modification into the other could not be found in the Co_2Ti layer. Experimental difficulties might be the cause since Co_2Ti is extremely brittle and partial crumbling of the Co_2Ti layer took place very often.

The observed relative X-ray intensities obtained from the ground Co_2Ti exhibit strong deviations from the calculated and recorded values[7][8] for a random-orientated Co_2Ti powder samples. Probably a preferred orientation is present in both Co_2Ti phases. A study of this phenomenon, possibly related to an orientation relationship between the hexagonal and cubic modification of the Co_2Ti phases, is still in progress.

Conclusions

1. All phases which could be expected on the basis of the Co-Ti equilibrium phase diagram are present in the diffusion zones of all types of diffusion couples.

2. From the measured phase boundary concentrations a modified Co-Ti phase diagram is proposed for temperatures at which solid-solid equilibrium exists. The composition ranges determined for the two Co_2Ti phases are contradictory with those reported in literature. Evidence has been found for the existence of a concentration gap of 0.6 at.% Ti between the hexagonal and the cubic Co_2Ti modification. The maximum solubility of

Co in CoTi appears to be larger (58.2 at.% Co, 1140°C) than according to Pet'kov et al. and Iannucci et al. (54.0 resp. 54.5 at.% Co, 1140°C).

3. The layer growth obeys the parabolic law in all phases except $CoTi_2$.

4. Chemical diffusion coefficients are calculated for those phases which obey the parabolic law. From calculations of D_{Co}/D_{Ti} in Co_2Ti it appears that at temperatures below 1000°C Co is by far the faster moving component while at higher temperatures the mobility of Ti approaches that of Co.

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