PHASE RELATIONS AND DIFFUSION PATHS IN THE Ti–Ni–Fe SYSTEM AT 900 $^\circ \! C$

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Summary

We investigated the 900 $^{\circ}$ C cross section through the ternary phase diagram Ti-Ni-Fe by means of the diffusion couple technique and by the investigation of equilibrated alloys. The course of a number of diffusion paths was established. Use was made of optical, microprobe and X-ray analyses. Some hitherto unaccountable results mentioned in the literature can now be explained.

1. Introduction

This investigation fits into a series of experimental work on multiphase ternary diffusion. In former publications on the systems Ti-Ni-Cu [1], Fe-Ni-Mo, Fe-Co-Mo and Ni-Co-Mo [2] we have emphasized the usefulness of the diffusion couple technique in obtaining reliable isothermal cross sections through phase diagrams.

In the literature we found for the Ti-Ni-Fe system only incomplete 700 and 1100 °C cross sections given by Vogel and Wallbaum [3], which have been slightly modified by Speich [4]. However, the experimental results of Speich, as well as recent work by Fournelle [5] on cellular precipitation in an austenitic Fe-30wt.%Ni-6wt.%Ti alloy, could not be explained by these cross sections.

Our 900 $^{\circ}$ C cross section for the Ti-Ni-Fe system agrees with the results of Speich and Fournelle. In comparison with the Ti-Ni-Cu system [1] the isotherm is simpler, although there are clear similarities. This makes it interesting to compare the diffusion paths of similar types of diffusion couples in both systems.

2. Experimental procedure

In this investigation we used Materials Research Corporation rods of titanium (99.97 wt.%), nickel (99.99 wt.%) and iron (99.95 wt.%).

The various binary and ternary alloys were prepared by repeated argon arc melting, after which they were homogenized at 900 $^{\circ}$ C for at least 1 week in sealed evacuated silica capsules.

Diffusion couples were made by solid state resistance welding of mechanically polished slices of pure metals or alloys in a modified argon arcmelting equipment. During this process no diffusion layers were formed. The couples were then heated in sealed evacuated silica capsules at 900 $^{\circ}$ C for 96 - 900 h and were quenched to room temperature.

In an alternative preparation method use was made of a special furnace in which slices of the starting materials were hot pressed in a vacuum (better than 10^{-6} Torr) using a set of weights. In this way the couples were annealed continuously at 900 °C for at least 96 h. Quenching was achieved by means of a sudden inlet of argon fully directed towards the specimen.

Both methods led to the same results.

After diffusion annealing the couple was embedded, was ground, was polished parallel to the diffusion direction and, if necessary, was etched with a mixture of 10 wt.% H_2O_2 , 5 wt.% HF and 85 wt.% H_2O .

The couples and alloys were then investigated using optical microscopy, microprobe analysis and X-ray diffraction. These techniques have been discussed in detail in a previous paper [1]. In the meantime a new microprobe (Jeol Superprobe 733) has become available which enables us to analyse three elements simultaneously. In order to transform the measured X-ray intensities into concentrations, use was made of the empirical Ziebold-Ogilvie [6] method as well as of the Magic-3B computer program by Colby [7]. Both methods led to the same results to within 1 at.%.

3. Experimental results

The types of couples together with the layers that developed are given in Table 1. Most of these layers were single phase and were bounded by planar interfaces. However, in those couples in which an Ni–Fe alloy was one of the constituents, a very peculiar interface between TiNi₃ and γ -(Ni,Fe) was found. Thin platelets of TiNi₃ protruded from the TiNi₃ layer into the γ matrix in a special crystallographically determined fashion (Fig. 1).

At first we were not sure whether this was a genuine diffusion-related phenomenon at 900 °C or a precipitation from a supersaturated solid solution (SS) of titanium in γ -(Ni,Fe) during the quenching procedure. Therefore, we investigated the alloy Ti_{8.5}Ni₃₇Fe_{54.5} (compositions are given in atomic per cent throughout this paper). This composition was chosen since it was a mean value of the two-phase TiNi₃- γ zone in, for example, diffusion couple (10). After heating the alloy at 1100 °C and quenching, single-phase γ was found. After reannealing this alloy at 900 °C and quenching, however, a number of crystallographically oriented plates of TiNi₃ were found in the γ matrix. The absence of TiNi₃ precipitates for the experiment at 1100 °C proves that no TiNi₃ is formed during the quenching procedure. Therefore

TABLE 1

<i>No</i> .	Type	Layer sequence
1	Ti–Ni	β -Ti; Ti ₂ Ni; TiNi; TiNi ₃ ; γ
2	Ti-Fe	β -Ti; TiFe; TiFe ₂ ; α -Fe
3	Ti–Ni ₆₀ Fe ₄₀	β -Ti; Ti ₂ Ni; Ti(Ni,Fe); TiFe ₂ ; TiNi ₃ ; TiNi ₃ + γ ; γ
4	Ti-Ni ₄₀ Fe ₆₀	β -Ti; Ti ₂ Ni; Ti(Ni,Fe); TiFe ₂ ; TiNi ₃ ; TiNi ₃ + γ ; γ
5	Ti ₈₅ Fe ₁₅ -TiFe	β-Ti; TiFe
6	Ti ₈₅ Fe ₁₃ Ni ₂ -TiFe	β -Ti; Ti ₂ Ni; TiFe
7	Ti ₂ Ni–Fe	Ti ₂ Ni; Ti(Ni,Fe); TiFe ₂ ; α-Fe
8	TiNi-"Ti ₅₈ Fe ₄₂ "	Ti(Ni,Fe); Ti(Ni,Fe) + Ti ₂ Ni; TiFe + β-Ti
9	TiNi-NigoFe20	$TiNi$; $TiNi_3$; $TiNi_3 + \gamma$; γ
10	TiNi-Ni ₅₀ Fe ₅₀	$TiNi$; $TiNi_3$; $TiFe_2$; $TiNi_3$; $TiNi_3 + \gamma$; γ
11	TiNi–Fe	Ti(Ni,Fe); TiFe ₂ ; α-Fe
12	TiFe–Ni	$TiFe; Ti_2Fe; TiNi_3; \gamma$
13	TiFe–Ni ₆₀ Fe ₄₀	$Ti(Fe,Ni)$; $TiFe_2$; $TiNi_3$; $TiNi_3 + \gamma$; γ
14	TiFe-Ni ₄₀ Fe ₆₀	$Ti(Fe,Ni)$; $TiFe_2$; $TiNi_3$; $TiNi_3 + \gamma$; γ
15	TiFe ₂ –Ni	$TiFe_2$; $TiNi_3 + \gamma$; $TiNi_3$; $TiNi_3 + \gamma$; γ

Types of couples and the layer sequence developed at 900 $^{\circ}C^{a}$

^aThe phases are denoted by their binary formulae, although most of them have of course a ternary composition.



Fig. 1. Diffusion couple (10) (TiNi- γ -Ni₅₀Fe₅₀) annealed for 140 h at 900 °C. The white bar indicates 10 μ m.

the two-phase interface structure in the couples is really developed during the diffusion annealing at 900 $^{\circ}$ C.

Another interesting point was a large apparent deviation from the stoichiometric composition which was sometimes found in the TiNi₃ phase in the presence of iron. In diffusion couples near the TiNi₃- γ interface, as well as in TiNi₃- γ two-phase alloys, a concentration of roughly 20 at.% Ti was found in TiNi₃. This deviation has also been reported in the literature [8] and has even been attributed to the existence of a separate phase, *e.g.*

 Ni_5Ti [4, 5]. However, we found exactly the same X-ray diffraction pattern as in stoichiometric TiNi₃.

The solution to this problem was found when we examined carefully polished sections nearly parallel to the TiNi₃- γ interface. As can be seen from Fig. 2, the TiNi₃ layer near that interface is in fact a very finely divided two-phase mixture of probably stoichiometric TiNi₃ and γ . This leads to too low a mean value for the titanium concentration. We believe that the TiNi₃ crystals in two-phase TiNi₃- γ alloys also consist of alternating lamellae of TiNi₃ and γ phase on such a fine scale that this structure is not readily recognized in scanning electron micrographs. In the next section this point will be discussed in more detail.



Fig. 2. The diffusion couple $\text{TiNi}-\gamma$ -Ni₈₀Fe₂₀ annealed for 456 h at 900 °C: (a) sample polished perpendicular to the original interface; (b) sample polished in a plane making only a small angle with the original interface. The white bar indicates 100 μ m; M indicates the Kirkendall interface.

In Table 2 the phases which are present in a number of equilibrated alloys according to optical, microprobe and X-ray diffraction analyses are given.

4. Evaluation of the experimental results

In Fig. 3 the resulting 900 $^{\circ}$ C isotherm through the Ti–Ni–Fe phase diagram is given. In Fig. 4 a number of diffusion paths are shown on this isotherm.

It is clear that the homogeneity region of the Ti_2Ni phase does not extend to the composition Ti_2Fe . The existence of a Ti_2Fe compound has been mentioned previously [9], but this must be a phase stabilized by an impurity component such as oxygen or nitrogen. In this respect the investi-

TABLE 2

No.	Alloy	Phases present at 900 °C
1	Ti ₇₈ Ni ₁₂ Fe ₁₀	$Ti(Ni,Fe) + \beta$ -Ti
2	$Ti_{66,7}Ni_4Fe_{29,3}$	$Ti(Ni, Fe) + \beta - Ti + Ti_2Ni$
3	Ti _{66.7} Ni ₂ Fe _{31.3}	$Ti(Ni,Fe) + \beta - Ti + Ti_2Ni$
4	Ti ₆₁ Ni ₈ Fe ₃₁	Ti(Ni,Fe) + Ti ₂ Ni
5	Ti42Ni10Fe48	$Ti(Ni,Fe) + TiFe_2$
6	Ti ₃₈ Ni ₃₀ Fe ₃₂	$Ti(Ni,Fe) + Ti_2Ni + TiNi_3$
7	Ti ₃₅ Ni ₅₆ Fe ₉	$Ti(Ni,Fe) + TiNi_3$
8	Ti27 Ni40 Fe33	$TiNi_3 + TiFe_2$
9	Ti25Ni68Fe7	TiNi ₃
10	Ti25 Ni62 Fe13	TiNi ₃
11	Ti ₂₅ Ni ₅₀ Fe ₂₅	$TiNi_3 + TiFe_2$
12	Ti21.5 Ni78.5	$TiNi_3 + \gamma - Ni$
13	Ti ₂₁ Ni ₇₄ Fe ₅	$TiNi_3 + \gamma$
14	Ti ₂₀ Ni ₇₀ Fe ₁₀	$TiNi_3 + \gamma$
15	$Ti_{21}Ni_{64}Fe_{15}$	$TiNi_3 + \gamma$
16	Ti ₁₅ Ni ₈₅	$TiNi_3 + \gamma - Ni$
17	$Ti_{15}Ni_{59}Fe_{26}$	$TiNi_3 + \gamma$
18	Ti15Ni25Fe60	$TiNi_3 + TiFe_2 + \gamma$
19	Ti ₁₅ Ni ₆ Fe ₇₉	$TiFe_2 + \gamma$
20	$Ti_{15}Ni_4Fe_{81}$	$TiFe_2 + \gamma + \alpha$
21	Ti ₁₅ Ni ₂ Fe ₈₃	$TiFe_2 + \alpha$
22	Ti ₁₀ Ni ₈₀ Fe ₁₀	$TiNi_3 + \gamma$
23	$Ti_{10}Ni_{65}Fe_{25}$	$TiNi_3 + \gamma$
24	Ti8 5Ni37Fe54 5	$TiNi_3 + \gamma$

Phases present in equilibrated alloys according to optical, microprobe and X-ray diffraction analyses^a

^aThe various phases are denoted by their binary formulae.



Fig. 3. The 900 °C isotherm through the Ti–Ni–Fe phase diagram according to our measurements: --, tie-lines; *, the alloy used by Speich [4] and Fournelle [5].

Fig. 4. The 900 $^{\circ}$ C isotherm through the Ti–Ni–Fe phase diagram together with the diffusion paths of some couples. The numbers correspond to those in Table 1. gation of the diffusion couple TiNi-Ti₅₈Fe₄₂ was very interesting. As can be seen from the schematic diagram in Fig. 5(a), the original two-phase mixture of TiFe and β -Ti(SS) in Ti₅₈Fe₄₂ changes into a two-phase mixture of Ti(Ni,Fe) and Ti₂(Ni,Fe) during the interdiffusion process. In fact the system consists of two interwoven diffusion couples, namely TiNi-TiFe and TiNi- β -Ti(SS). This gives rise to various interactions, and the analysis of the couple results in a number of tie-lines and in the exact location of the three-phase triangle Ti(Ni,Fe)-Ti₂(Ni,Fe)- β -Ti(SS) (Fig. 5(b)).

In fact, the use of two-phase terminal materials in diffusion couples has great advantages over the normal type of couple; however, great care must be taken in view of the steep concentration gradients which sometimes exist in all directions and not just in the gross diffusion direction.

From the isotherm in Fig. 3 it is clear that the alloy $Ti_{7.6}Ni_{27.2}Fe_{65.2}$ is indeed a two-phase mixture of $TiNi_3$ and γ as found by Speich [4] and Fournelle [5]. Vogel and Wallbaum [3] have erroneously situated this composition in the $TiFe_2-\gamma$ two-phase field. The most intriguing problem is the peculiar two-phase character of the $TiNi_3-\gamma$ boundary in diffusion couples. The more iron that is present in the terminal alloy, the more prominent are the $TiNi_3$ platelets protruding into the alloy (see Figs. 1 and 2) and the lower is the measured apparent titanium concentration in the adjacent $TiNi_3$ layer. The two-phase morphology is present only on the γ side of the Kirkendall interface (Fig. 2). On the opposite side of this interface the $TiNi_3$ layer consists of large crystals with an exact stoichiometric composition.

In the binary Ni–Ti system [10], as well as in some comparable couples in the closely related Ti–Ni–Cu system [1], this phenomenon does not occur. In Fig. 6(a) the couple TiNi– γ -Ni₅₀Cu₅₀ annealed at 900 °C is shown; the diffusion path is given in Fig. 6(b). Large differences can be seen when these results are compared with the morphology in the couple TiNi– γ -Ni₅₀Fe₅₀ (Fig. 1) and its diffusion path (Fig. 4, path 10).

We investigated whether there is a relation between this two-phase morphology and the excellent fitting of the crystal lattices of TiNi₃ and γ .



Fig. 5. (a) A schematic diagram of the diffusion zone in the couple $TiNi-Ti_{58}Fe_{42}$ annealed for 500 h at 900 °C. The concentration measurements at the positions (1), (2) and (3) lead to the corresponding tie-lines in Fig. 5(b), whereas measurements at the three-phase regions (4) lead to the three-phase triangle β -Ti-Ti₂Ni-TiFe in Fig. 5(b).





As has already been mentioned by other investigators [4, 5, 11], an orientation relation exists between hexagonal TiNi₃ and the f.c.c. γ phase in such a way that

 $\{111\}\gamma//\{0001\}\text{TiNi}_3 \\ \langle 110\rangle\gamma//\langle 11\bar{2}0\rangle\text{TiNi}_3$

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Lattice parameters of the coexisting γ and TiNi₃ phases in the Ti–Ni, Ti–Ni–Fe and Ti–Ni–Cu systems together with the values of the respective misfits^a

		Samples quench	ed to room tem	perature		Samples at the a	nnealing tempera	ture	
		a (Å)	c (Å)	Misfit (%) <110> ₇ °	$\substack{\textit{Misfit (\%)}\\ \langle 111\rangle_{\gamma}}^{\textit{Misfit (\%)}}$	a (Å)	c (Å)	Misfit (%) <110> _γ °	$\substack{\textit{Misfit (\%)}_{\langle III \rangle_{\gamma}}^{d}}$
Ti ₁₅ Ni85 90 h, 870 °C	٢	3.565 ± 0.004				3.612 ± 0.004			
TiNi ₃ + γ-Ni90.5Ti9.5	TiNi ₃	5.094 ± 0.005	8.300 ± 0.008	1.0 ± 0.2	0.8 ± 0.2	5.155 ± 0.005	8.418 ± 0.008	0.9 ± 0.2	0.9 ± 0.2
Ti 20 Ni 70.5 Feg. 5 48 h, 900 °C	۲ ر	3.590 ± 0.010				3.652 ± 0.004			
$Ti_{24}Ni_{72}Fe_4 + \gamma - Ni_{63}Fe_{31}Ti_6$	TiNi	5 103 + 0 005	8 390 + 0 008	0.5 ± 0.4	0.4 ± 0.4	5 170 ± 0 005	8 468 + 0 008	0.1 ± 0.2	0.4 ± 0.2
Ti ₂₁ Ni ₆₉ Cu ₁₀ 48 h. 870 °C	γ	3.592 ± 0.004				3.641 ± 0.004			
$Ti_{24}Ni_{72}Cu_4 + \gamma Ni_{49}Cu_{49}Ti_2^b$	TiNi ₃	5.118 ± 0.005	8.349 ± 0.008	0.8 ± 0.2	0.6 ± 0.2	5.165 ± 0.005	8.439 ± 0.008	0.3 ± 0.2	0.4 ± 0.2

 a Measurements were performed on alloys at the annealing temperature as well as on samples quenched to room temperature (Cu K α

Tradiation; $39^{\circ} < 2\theta < 54^{\circ}$). b Concentration values were estimated from the phase diagram since direct microprobe measurements were very inaccurate because of the small size of the γ precipitates. c Misfit given by $\left(\frac{1}{2}a_{\text{TiNi}_3} - \frac{\sqrt{2}}{2}a_{\gamma}\right)\left(\frac{\sqrt{2}}{2}a_{\gamma}\right)^{-1} \times 100\%$.

^d Misfit given by $\left(\frac{1}{4}c_{\mathrm{TiNi}_3} - \frac{\sqrt{3}}{3}a_{\gamma}\right) \left(\frac{\sqrt{3}}{3}a_{\gamma}\right)^{-1} \times 100\%.$

We found that the interplanar spacings in these directions given by

$$\Big(\frac{1}{4}c_{\mathrm{TiNi}_{3}}-\frac{\sqrt{3}}{3}a_{\gamma}\Big)\Big(\frac{\sqrt{3}}{3}a_{\gamma}\Big)^{-1}$$

and

$$\Big(rac{1}{2}a_{\mathrm{TiNi}_3} - rac{\sqrt{2}}{2}a_{\gamma}\Big)\Big(rac{\sqrt{2}}{2}a_{\gamma}\Big)^{-1}$$

match to within 1% for pure nickel and TiNi₃ and are even closer when iron is introduced (see Table 3). Data were obtained from X-ray diffractograms of polished sections of two-phase TiNi₃- γ alloys quenched to room temperature as well as from high temperature diffractograms of these alloys. In fact the latter data are the more relevant since they give information about the lattice parameters at the reaction temperature.

It is clear that this close matching of both lattices is responsible for the sometimes very fine alternating lamellae of both phases in the two-phase TiNi₃- γ mixtures and that the apparently low titanium concentration is caused by quasi-single-phase TiNi₃. However, the close matching cannot be the only factor which accounts for the two-phase character of the TiNi₃- γ boundary. This can be seen from the lattice parameter values and their misfit in the Ti-Ni-Cu system, also given in Table 3. The misfit in this system is roughly the same as that in the Ti-Ni-Fe system (better than 0.5% at the annealing temperature); nevertheless, the two-phase character at the TiNi₃- γ boundary is absent in, for example, the TiNi- γ -Ni₅₀Cu₅₀ diffusion couple, in contrast with the TiNi- γ -Ni₅₀Fe₅₀ couple.

At present we are trying to obtain more information about this phenomenon by investigating various diffusion couples in the Ti-Ni-Fe, Ti-Ni-Cu and possibly other related systems.

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