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MULTIPHASE DIFFUSION IN SOME RELATED TERNARY METAL SYSTEMS.

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Introduction

Recently the authors have published their results of investigations into multiphase diffusion phenomena in the systems Ti-Ni-Cu [1], Ti-Ni-Fe [2] and Ti-Ni-Co[3]. Especially the product layer morphology in those diffusion couples in which a $TiNi_3$-like phase was formed appeared to be very interesting. Therefore, a systematic investigation was started in order to compare the resulting morphologies in couples of the type $TiNi_xMe_{1-x}$ versus Ni_yMe_{1-y} in which $TiNi_3$-like phases are expected to occur (the symbol Me represents one of the elements Cu, Fe or Co). From a fundamental as well as from an experimental point of view it appeared to be advantageous to anneal the couples at one fixed temperature, i.e. 900°C. It was, therefore, necessary to determine the 900°C cross-section through the Ti-Ni-Cu phase diagram since in earlier investigations this was done by us only at 800 and 870°C [1].

The experimental procedure

For the determination of the 900°C isotherm of the Ti-Ni-Cu system as well as for the use as a terminal material in diffusion couples, alloys have been prepared by repeated argon arc melting. After melting they were homogenised for at least 100 hours at 900°C in sealed evacuated silica capsules. As reported by Zwicker et al. [4] the melting point of binary Ti-Cu alloys is very much influenced by traces of oxygen. Therefore, in order to prevent oxygen contamination as a result of direct contact between the alloy and the silica capsule some alloys were wrapped in titanium sheet.

Diffusion couples were made in a special furnace in which three slices of the terminal alloys were hot-pressed as a sandwich by means of a set of weights for 70 to 150 hours at 900°C in a vacuum better than 10^{-5} Torr. After diffusion annealing the couples were embedded, ground and polished parallel to the diffusion direction and, if necessary, etched with a mixture of 10% H_2O_2, 5%HF and 85% H_2O.

The alloys and couples were then investigated by optical microscopy using polarised light, by X-ray diffraction and by microprobe analysis using a Jeol Superprobe 733 [3].

The determination of the 900°C isotherm of the Ti-Ni-Cu phase diagram

In Table 1 a number of equilibrated alloys are given together with the phases which were found. The presence of a liquid phase in the $TiCu_2$-region made the determination of that part of the isotherm rather difficult. Our results are in line with the phase diagram of the binary Ti-Cu system as given by Moffat [5].

In fig. 1 the resulting isotherm is given.

Table 1.

Phases present in Ti-Ni-Cu alloys equilibrated at 900°C.
For the designation of the phases see Fig. 1.

Alloy composition	Phases present
$TiCu_4$, $TiCu_2$ and Ti_2Cu_3	Melting phenomena
$Ti_{25}Ni_{50}Cu_{25}$	C
$Ti_{31}Ni_8Cu_{61}$	E + "Ti_2Cu_7"
$Ti_{33}Ni_7Cu_{60}$	E
$Ti_{33}Ni_9Cu_{58}$	E
$Ti_{33}Ni_{11}Cu_{56}$	E+D
$Ti_{33}Ni_{13}Cu_{54}$	D
$Ti_{34}Ni_{11.5}Cu_{54.5}$	D+E+"Ti_2Cu_3"
$Ti_{34}Ni_{54.5}Cu_{11.5}$	D+$TiNi_3$+TiNi
$Ti_{38}Ni_8Cu_{54}$	D+"Ti_2Cu_3"+Ti_3Cu_4
$Ti_{39}Ni_4Cu_{57}$	E+"Ti_2Cu_3"
$Ti_{44}Ni_7Cu_{49}$	TiNi+Ti_3Cu_4
$Ti_{60}Ni_{23}Cu_{17}$	TiNi+Ti_2Ni+Ti_2Cu
$Ti_{75}Ni_{12.5}Cu_{12.5}$	β-Ti+Ti_2Ni+Ti_2Cu

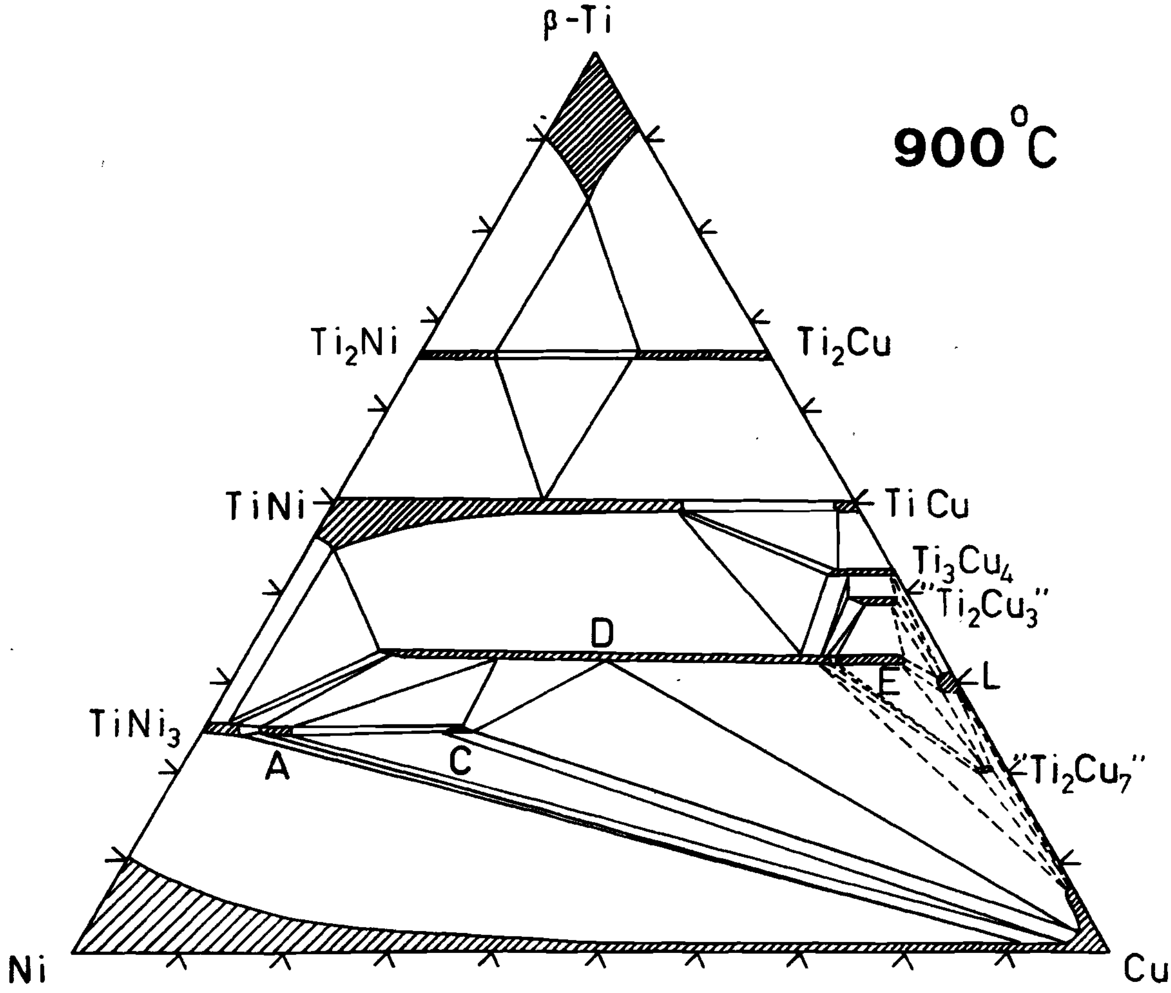

Fig. 1. The 900°C isotherm of the Ti-Ni-Cu phase diagram.

Results of the diffusion couple experiments

In figs. 2, 3 and 4 our results on diffusion couples are shown in a qualitative way. The thicknesses of the product layers are normalised for an annealing time of 100 hours by multiplying the actual thicknesses by a factor $(^{100}/t)^{\frac{1}{2}}$, where t = annealing time in hours. For a number of couples the parabolic growth behaviour has been verified.

In fig. 2, for instance, a schematic presentation is given of the

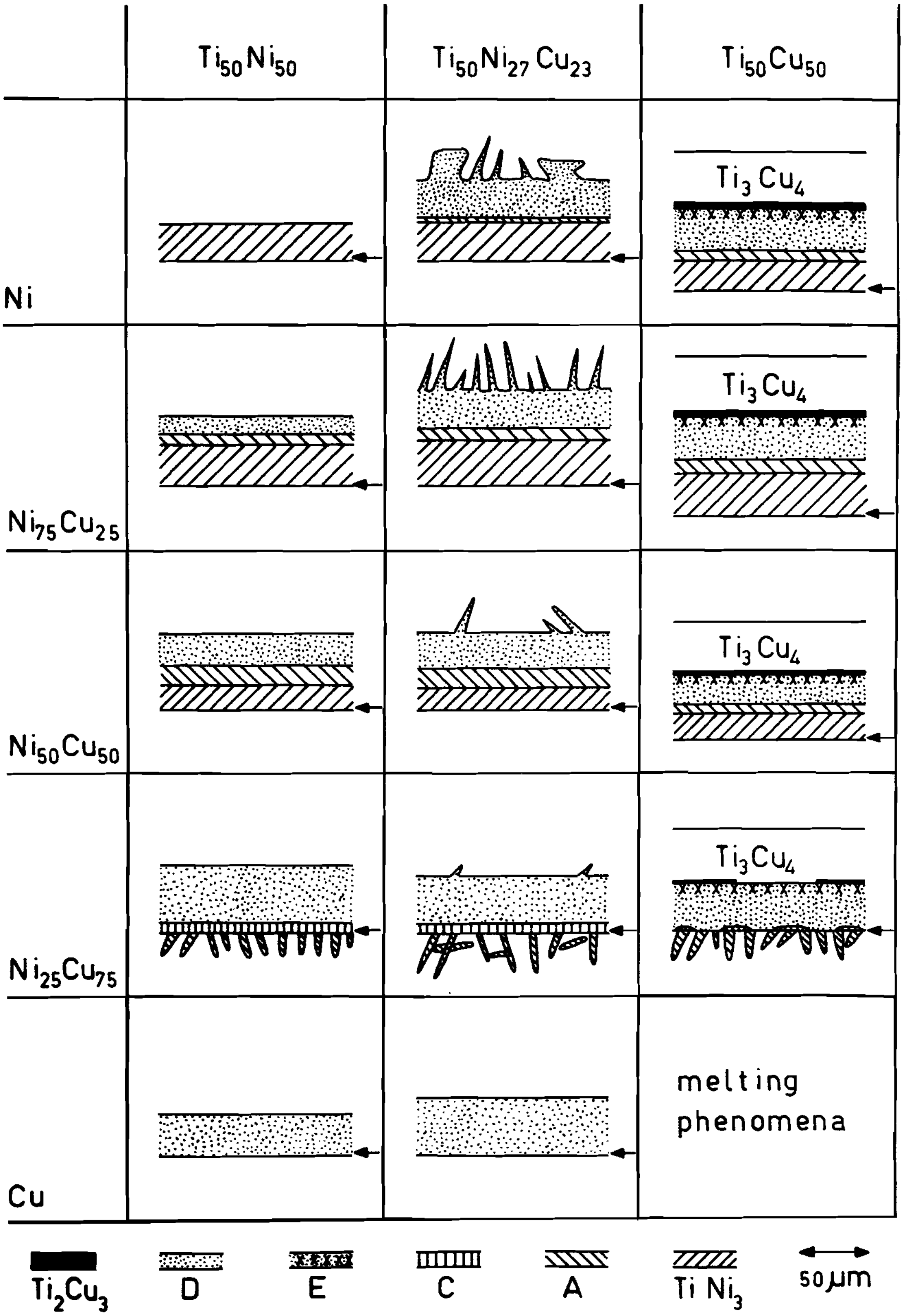

Fig. 2. Survey of the morphologies and thicknesses of the reaction layers in Ti-Ni-Cu diffusion couples after annealing 100 hours at 900°C

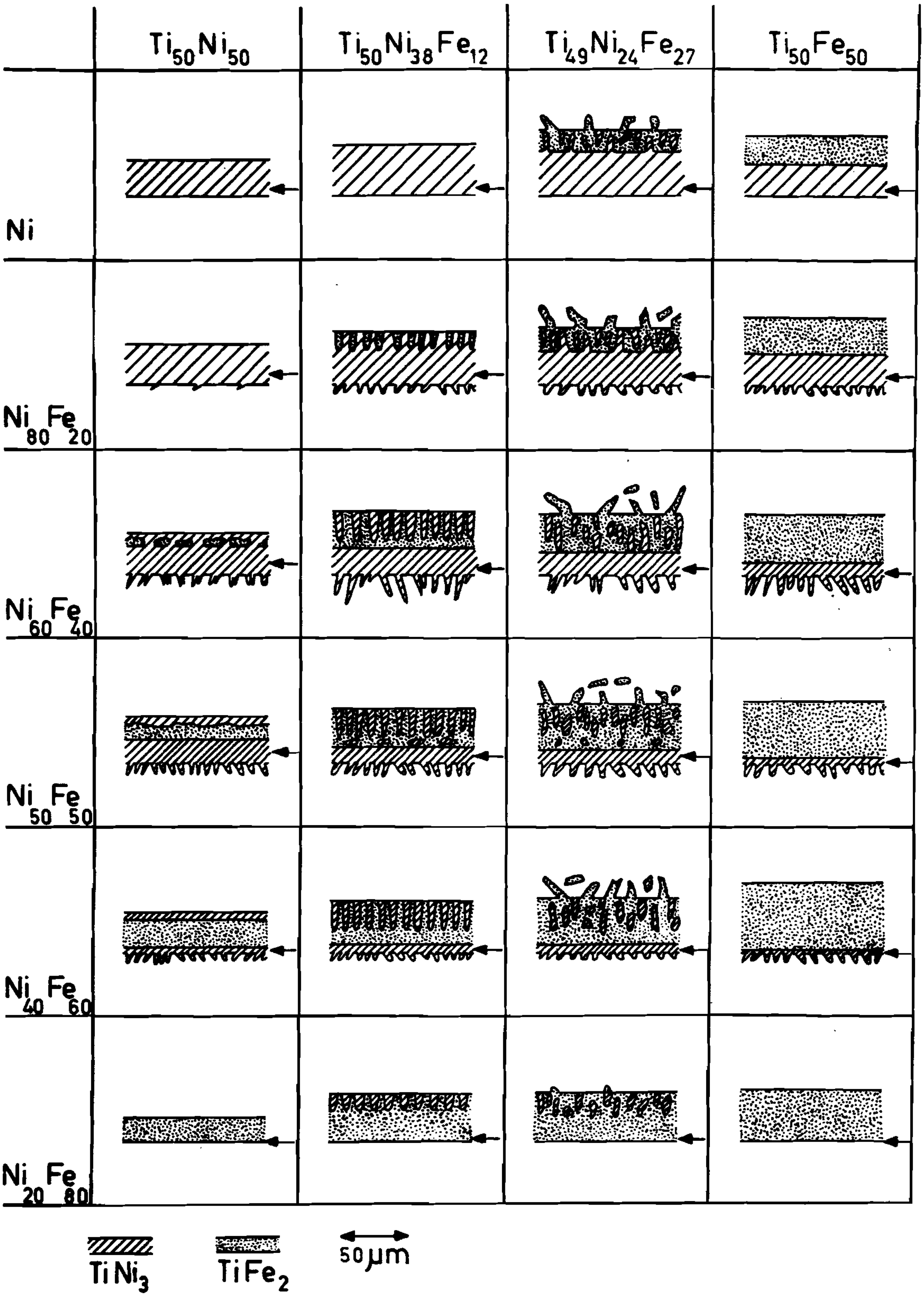

Fig. 3. Survey of the morphologies and thicknesses of the reaction layers in Ti-Ni-Fe diffusion couples after annealing 100 hours at 900°C.

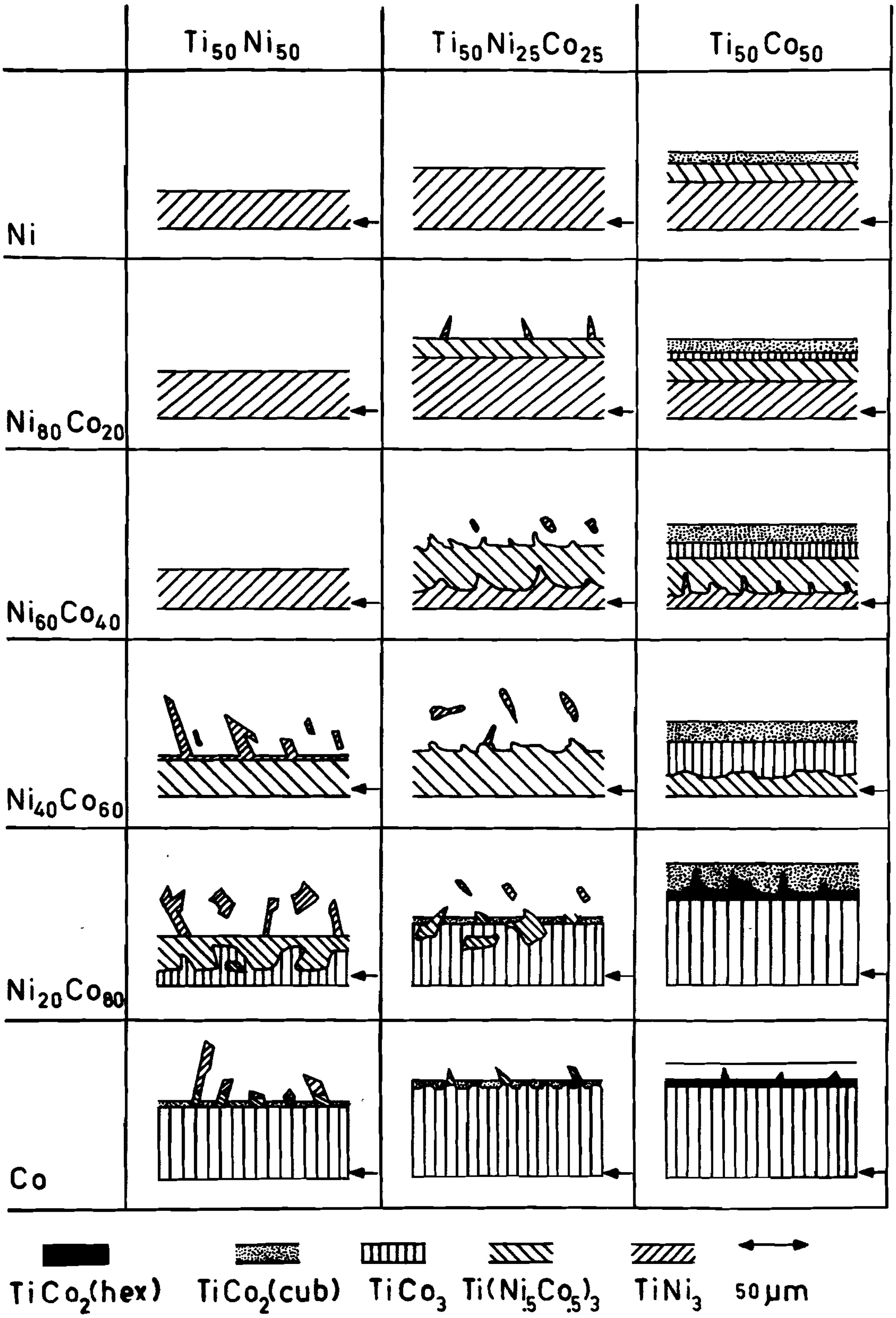

Fig. 4. Survey of the morphologies and thicknesses of the reaction layers in Ti-Ni-Co diffusion couples after annealing 100 hours at 900°C.

product morphology in each of the 15 diffusion couples investigated in the Ti-Ni-Cu system. The $TiNi_xCu_{1-x}$ terminal alloy is always the upper part, whereas Ni_yCu_{1-y} is the bottom part in each drawing. In these schemes no information can be found concerning the concentration gradients existing in the various phases. In all couples these have been determined by microprobe analysis, but in the framework of this article only two examples are shown in Fig. 5,a and b. Especially in the TiNi terminal alloy a large zone is found in which the concentration of the various elements gradually change, in contradiction to the always steep concentration gradients in all other terminal alloys. Typical for these systems is the maximum in the Ti concentration profile in the NiCu terminal alloy, and the maximum in the Ni concentration profile in the TiNi terminal alloy in couples of the type $TiNi-Ni_yFe_{1-y}$ and $TiNi-Ni_yCo_{1-y}$.

In the Figs. 6, 7 and 8 a number of diffusion paths is presented on the respective isotherms.

In all types of couples the original welding interface (Kirkendall interface) was found near the Ni_yMe_{1-y} terminal alloy as indicated by the arrow in Figs. 2, 3 and 4.

Evaluation of the experimental results

In each vertical column in Figs. 2, 3 and 4 a clear relation can be found concerning the various morphologies and thicknesses of the product layers. In the horizontal rows this relation is also present although less pronounced.

The most interesting point for us is the question why in certain couples one or more interfaces are no longer straight and become serrated. In all three systems this phenomenon occurs, but clearly not in the same way. The kind of perturbation is also different: the needles of the $TiNi_3$ phase protruding into Ni_yFe_{1-y}, for example, are clearly much more regular than the needles of $TiFe_2$ protruding into $Ti_{49}Ni_{24}Fe_{27}$. In the first case an orientation relation exists between the relevant phases, leading to parallel needles or fixed angles between the needles. Between $TiFe_2$ and $Ti_{49}Ni_{24}Fe_{27}$ such a relation has not been established up to now. Besides, in this case the situation is

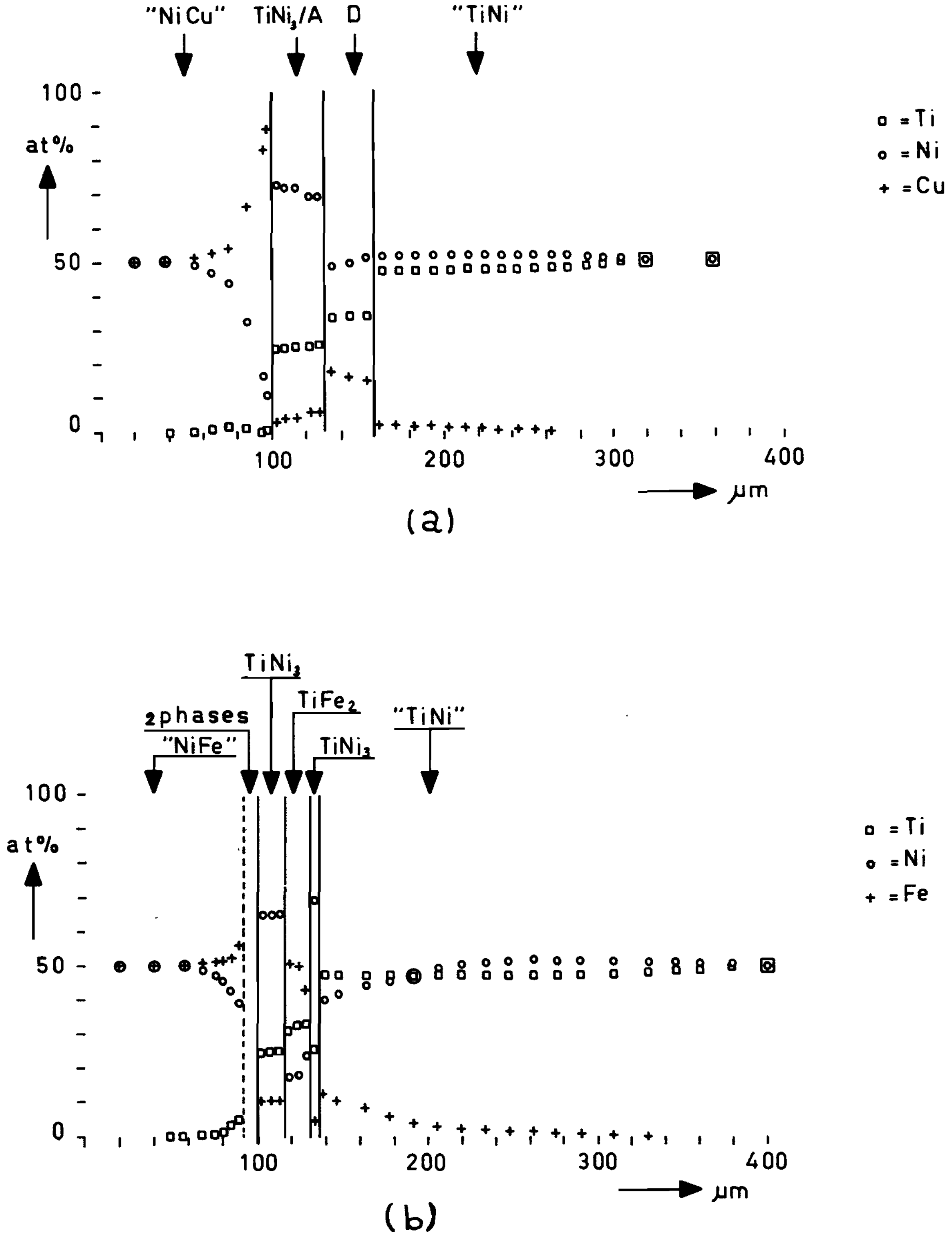

Fig. 5. Concentration profiles in the diffusion couples TiNi-NiCu (a) and TiNi-NiFe (b), both annealed 100 hours at 900°C.

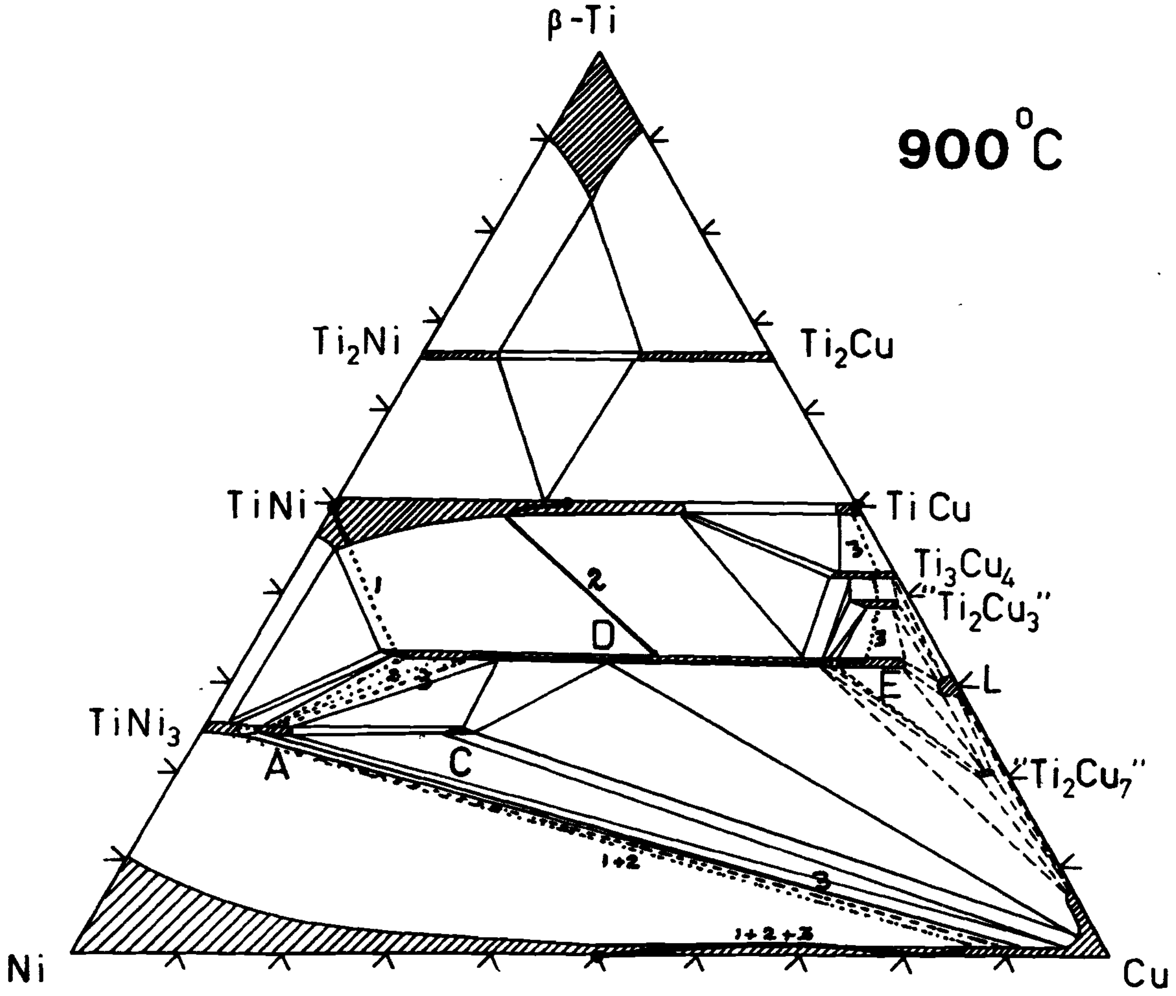

Fig. 6. Some diffusion paths on the 900°C isotherm of the Ti-Ni-Cu phase diagram.

complicated by the fact that also in some grain boundaries in this alloy the $TiFe_2$ phase is formed.

The possibility of the presence of an orientation relation is, in any case, not sufficient in order to create interface perturbations, since then the effect had to be seen in more couples. We believe, therefore, that the diffusion mechanism plays an important role. It is a well-known fact that in single phase ternary alloys it already takes four independent diffusion coefficients in order to describe the

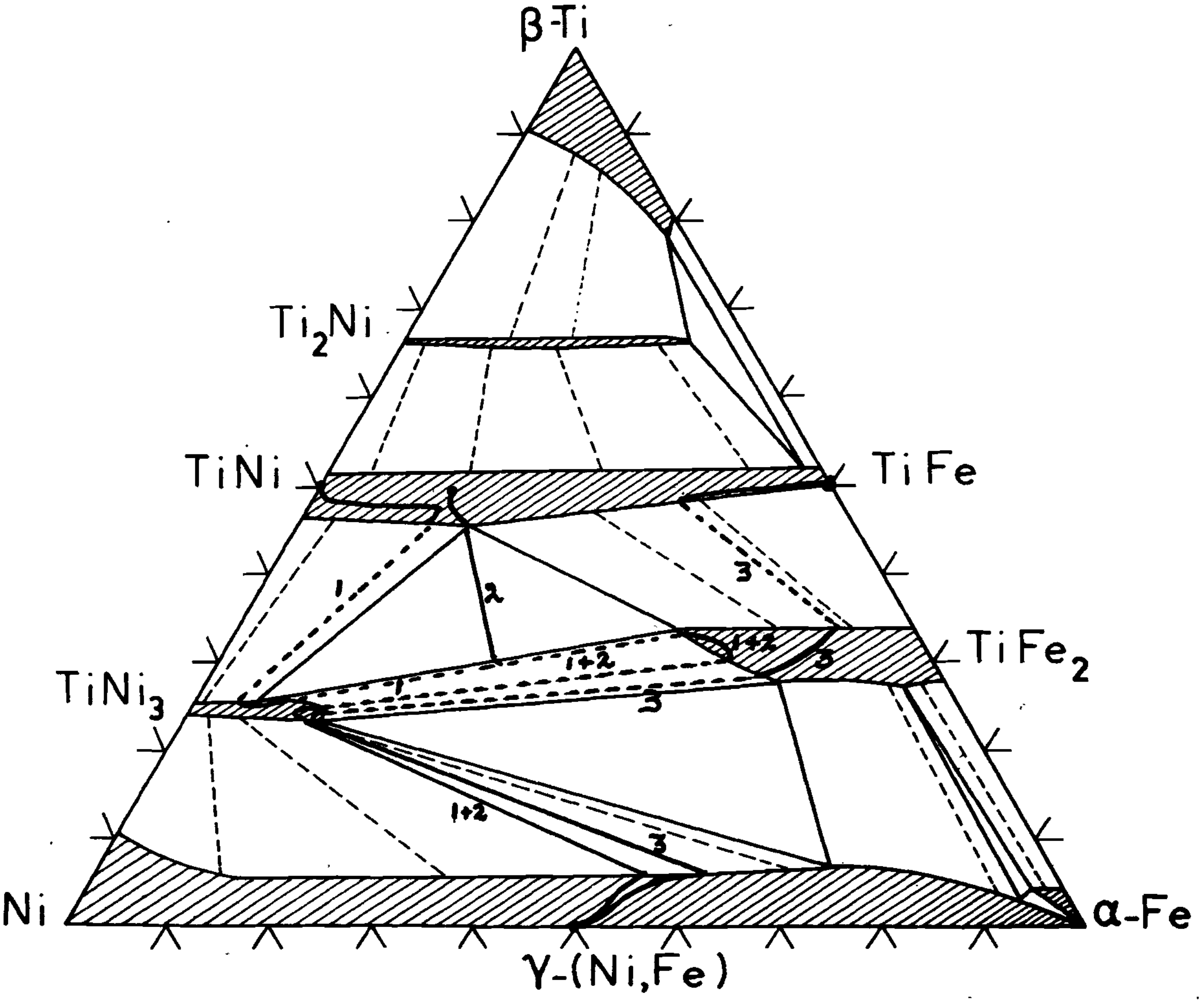

Fig. 7. Some diffusion paths on the 900°C isotherm of the Ti-Ni-Fe phase diagram.

diffusion kinetics. In an actual multiphase diffusion couple in which e.g. two phases are formed this leads to 16 independent diffusion coefficients which can all be concentration dependent. We do not believe, however, that the question of interface instability can be solved by analysing the diffusion mechanism along these lines, apart from the experimental difficulties.

In a qualitative way, on the other hand, it might be possible to find keys to a solution of the problem in a similar way as shown in a former study on the Mo-Si-C system [6] and which follows essentially

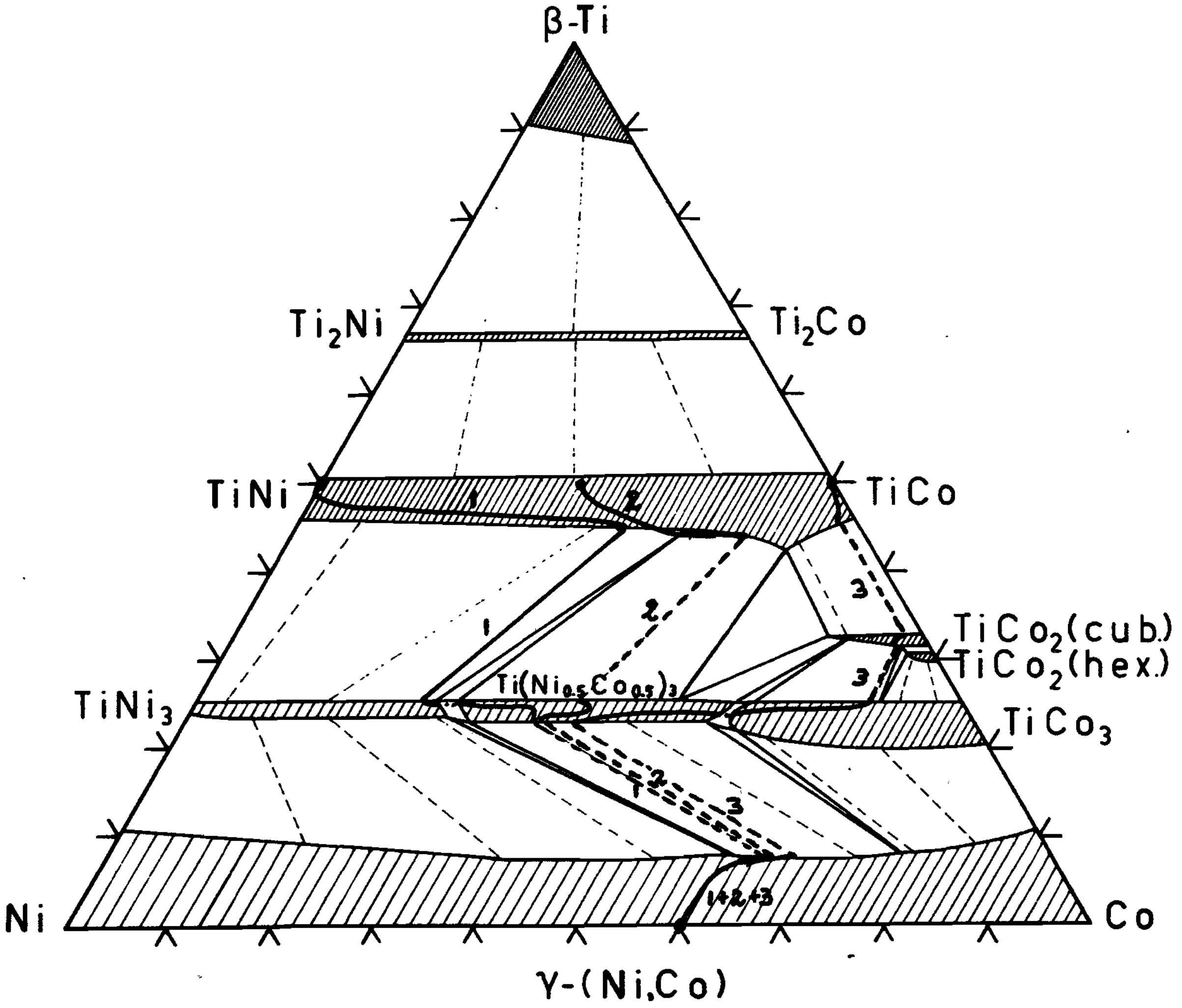

Fig. 8. Some diffusion paths on the 900°C isotherm of the Ti-Ni-Co phase diagram.

a line given by Wagner [7] for oxidation processes. Compare, for instance, in Fig. 9 the couples TiNi-NiFe and TiNi-NiCu and let us concentrate on the interface $TiNi_3$-NiMe.

In both cases Ti will be the less mobile component in the $TiNi_3$ phase in view of the location of the Kirkendall interface, and Ni is preferently withdrawn from the NiMe alloy. If the arrival of Ni atoms at the interface is rate-determining for the growth of the $TiNi_3$ phase, then this layer grows faster at point 1 than at point 2, so an accidental perturbation will grow. If the supply of Ti is rate-

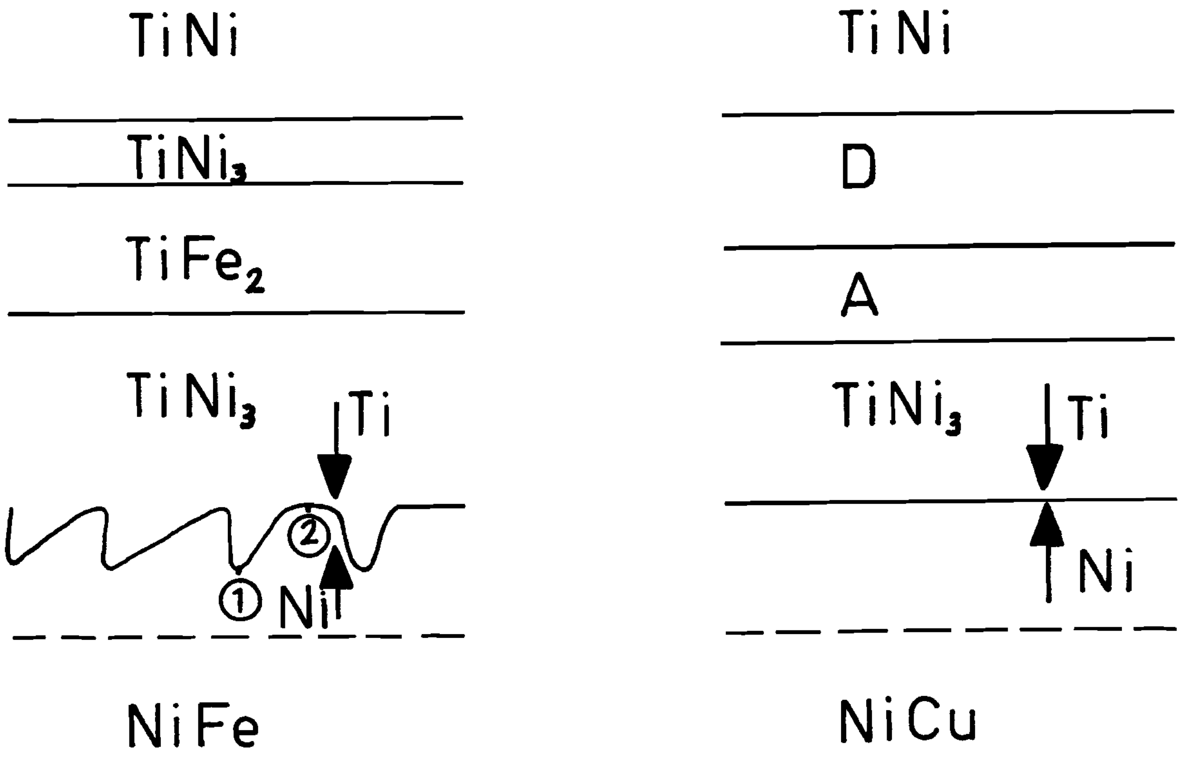

Fig. 9. Schematic representation of the diffusion layers in the couples TiNi-NiFe and TiNi-NiCu.

determining, then the layer will grow faster at point 2 than at point 1 and the interface will stay straight.

Since the diffusion rate of Ti in $TiNi_3$ can be expected to be roughly the same for the Ti-Ni-Fe and Ti-Ni-Cu system, the difference between both systems should then be the faster diffusion of Ni in a NiCu alloy than in a NiFe alloy. This is indeed reported in the literature [8] and has been verified by us in diffusion experiments on the couples NiFe-Fe and NiCu-Cu. As a consequence, the product layer in the Ti-Ni-Cu system should be thicker than in the Ti-Ni-Fe system which is indeed the case. The perturbation effect must become more pronounced if the supply of Ni gets less, i.e. when using alloys poorer in Ni. This is indeed true as can be seen from Figs. 2 and 3 where at the end even in the Ti-Ni-Cu system the interface is not straight anymore.

Semi-quantitatively our results satisfy Wagners condition, which states that straight interfaces occur if the quantity $Q > 1$, whereas serrated boundaries may occur if $Q < 1$, where Q is a function of the relevant diffusion coefficients and concentrations [7].

We believe that these relatively simple considerations will be very useful in predicting the occurrence of perturbations in reaction interfaces in ternary diffusion couples. This may be of technological importance in view of the adherence of e.g. coatings on substrates.

References

1. F.J.J. van Loo, G.F. Bastin and A.J.H. Leenen, J. Less-Common Met., 57 (1978) 111.
2. F.J.J. van Loo, J.W.G.A. Vrolijk and G.F. Bastin, J. Less-Common Met., 77 (1981) 121.
3. F.J.J. van Loo and G.F. Bastin, J. Less-Common Met., 81 (1981) 61.
4. U. Zwicker, E. Kalsch, T. Nishimura, D. Ott and H. Seilstorfer, Metall 20 (1966) 1252.
5. W.G. Moffat, The Handbook of Binary Phase Diagrams, General Electric Company, Schenectady, N.Y., 1978.
6. F.J.J. van Loo, F.M. Smet, G.D. Rieck and G. Verspui, Proc. Plansee-Seminar 1981, Vol. 1, p. 141.
7. C. Wagner, J. Electrochem. Soc., 103 (1956) 571.
8. Y. Adda and J. Philibert, La Diffusion dan les Solides, Tome II, Presses Universitaires de France, Paris 1966.