JOURNAL OF MATERIALS SCIENCE 17 (1982) 1303–1310

Morphological and crystallographic features of γ–γ' Ni–Al and Ni–Al–Ti two-phase bicrystals

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Several γ–γ'Ni–Al and Ni–Al–Ti two-phase bicrystals were made by the solid-state diffusion couple method. Each couple consisted of a γ'-phase single crystal and a pure-Ni polycrystal, and was annealed at 1473 K in an Ar gas atmosphere. Single crystal layers of γ-phase with uniform thickness always grow into the parent γ'-phase single crystals. The resultant γ/γ' interface has no voids or facets regardless of the orientation of interface and the chemical composition of the γ'-phase. Porosity formation due to the Kirkendall effect is observed in the diffused region. Concentration profiles exhibit nearly constant gradients in γ-phase. The orientation relationship between both phases is found to be $\langle 0\,0\,1\rangle_\gamma /\!/ \langle 0\,0\,1\rangle_{\gamma'}$, that is, the γ-phase grows epitaxially along the crystal orientation of γ'-phase.

1. Introduction

A two-phase bicrystal is defined as a macroscopic unit which consists of a single crystal of one phase joined to a single crystal of another phase. Several fundamental features of these crystals have been studied on α–β Cu–Zn [1–4] and α–β' Ag–Mg [5], made by the solid-state diffusion couple method. These bicrystals consist of a face-centered cubic (f c c) type crystal structure (α-phase) and a body-centered cubic (b c c) type structure (β-phase). In order to obtain further knowledge of the phase interface phenomena in practical duplex alloys, other types of two-phase bicrystals, which are constructed by other combinations of crystal structures, should be studied. Therefore, the present authors have made an attempt to produce two-phase bicrystals of Ni–Al and Ni–Al–Ti alloy systems, which consist of a f c c solid solution (γ-phase) and a f c c type ordered phase (γ'-phase), by again employing the solid-state diffusion couple method but with a minor modification. These bicrystals are thus said to consist of phases having similar crystal structures but differing in their chemical compositions.

These alloys are considered as fundamental systems for most commercial Ni–base superalloys which are usually strengthened by fine γ'-phase precipitates dispersed in the γ-phase matrix. It is well known that profitable high-temperature mechanical properties of superalloys depend on not only properties of the two consitituent phases but also particular properties of the phase interface between the two phases. Therefore, the experiments on these bicrystals provide fundamental knowledge on the role of the phase interface between γ'-precipitates and a γ-matrix.

2. Experimental procedure

Binary and ternary γ'-phase alloy ingots were produced by casting into a metal mould in a vacuum induction furnace using Ni of 99.9%, Al of 99.99% and Ti of 99.6% purities. Each ingot was remelted and grown into a single crystal in an alumina crucible in an Ar atmosphere using the Bridgman technique, then homogenized for 48 h at 1473 K in a vacuum furnace. The chemical compositions of each single crystal are specified in Table I. Disc plates of the desired

0022–2461/82/051303–08$03.46/0

TABLE I Specifications of the γ'-single crystals used for the diffusion couples

γ'-single crystal	Plate orientation*	Chemical composition (at %)		
		Ni	Al	Ti
B	nearly (0 1 1)	Balance	21.9	
T1	(0 0 1)	Balance	14.8	9.14
T1	(1 1 1)	Balance	14.8	9.14
T2	(1 1 5)	Balance	15.4	10.0
T2'	(0 1 1)	Balance	15.4	10.0

* For the exact orientation, see Fig. 10.

orientation, about 1 mm thick, were sectioned from these single crystals by a spark-cutting machine. The damaged layer due to cutting was removed first mechanically by fine emery paper then electrolytically in a phosphorous acid–water bath.

Fig. 1 illustrates the geometry of the diffusion couple together with schematical composition profiles, before and after diffusion annealing. Each γ'-plate has a pure-Ni layer about 0.3 mm thick electro-deposited on one side to ensure good contact. A pure-Ni polycrystal plate about 2 mm thick was then attached to the electro-deposited Ni layer to ensure a sufficient supply of the diffusive atoms. The various layers were clamped together with alumina plates in a graphite holder, then annealed at 1473 K in an Ar atmosphere. After the diffusion annealing, each couple was quenched in water to suppress the decomposition of the phases.

The microstructure of the cross-section of the couple was observed by optical microscopy. Crystallographic orientation relationships between the γ- and γ'-phases were measured by the usual Laue back-reflection method, exposing the surface of the transformed γ-phase by polishing out the pure Ni layer. Concentration profiles across the γ/γ' interface were measured by electron-probe microanalysis (EPMA) (using a JEOL JXA 50A) by monitoring Kα radiations of either Ni, Al or Ti with an accelerating voltage of 25 kV and a probe size of 5 to 6 μm.

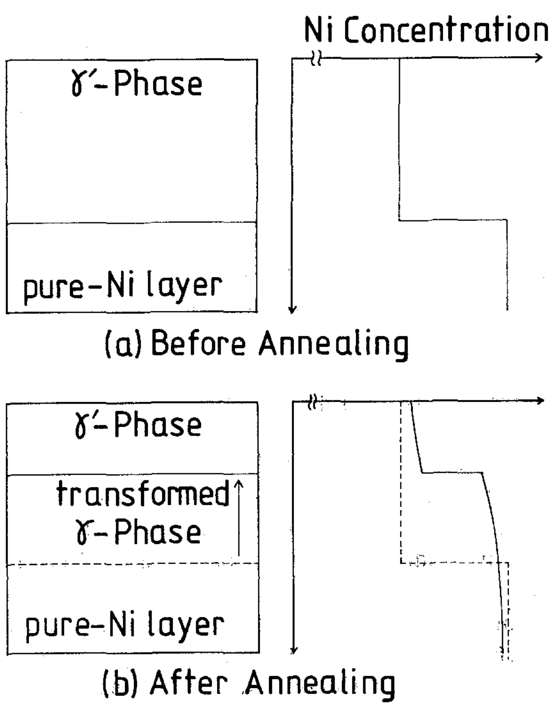

Figure 1 Schematic illustration of the geometry of the couple and the concentration profile (a) before and (b) after the diffusion annealing.

3. Results and discussion

3.1. Morphology of two-phase bicrystals

Figs 2, 3 and 4 show cross sections of the couples after diffusion annealing, each differing in the plate orientation of the ternary γ'-phase single crystal, which are (1 1 1), (0 1 1) and (0 0 1), respectively. As the thickness of the γ-phase is nearly constant across the cross-section in each couple, the orientation of resultant γ/γ' interface plane almost coincides with that of γ' crystal plate. Traces of the initial junction (which means that a contact plane existed between the γ'-single crystal plate and electro-deposited pure-Ni layer before diffusion annealing), is observable as a straight line sometimes accompanying a row of small voids. Therefore it is obvious that γ-phase transforms or grows into γ'-phase region.

The traces of the γ/γ' planes are quite straight, as shown in Fig. 2, or slightly wavy, as in Figs 3 and 4, in either couples having no voids or crystallographic facets. Moreover, there are no grain boundaries in the transformed γ-phase region although the traces resembling subgrain boundaries are visible in Fig. 2.

As shown in Fig. 5, the couples using binary

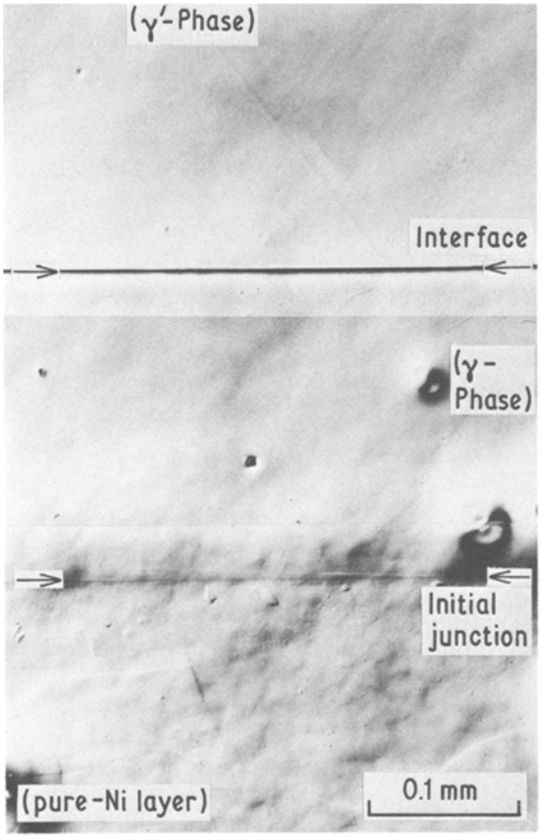

Figure 2 Optical micrograph showing the morphology in the couple using (111) oriented ternary γ'-phase single crystal plate (T1′ in Table I) annealed for 120 h at 1473 K. The meaning of "initial junction" is described in the text.

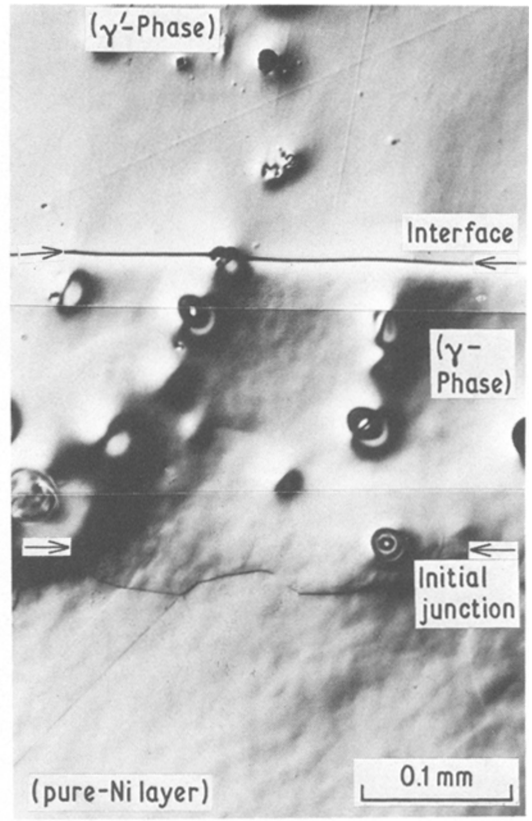

Figure 3 Morphology in the couple using a (011) oriented ternary γ' plate (T2′ in Table I) annealed for 120 h at 1473 K.

γ' single crystals exhibit similar morphological features to those in the couples using ternary γ' single crystals. However, in these couples, colonies of γ-phase pre-exist in the γ' single crystal, the chemical composition of which was chosen because of the reported difficulties in growing binary single crystals of γ' mono-phase [6]. As a result, the γ/γ' interface becomes wavy by a sort of tension force from these γ-phase colonies.

To investigate the morphology in detail, some replicas were taken on the same cross-section as in the optical micrographs, then observed by electron microscope. Fig. 6 shows the microstructure near the interface in the same couple as shown in Fig. 3. No crystallographic facets are observed in the interface trace even at such a high magnification. In the transformed γ-phase, however, precipitate-like patterns, 0.2 to 0.3 μm in size, are observed. These patterns almost disappear at a position 40 to 50 μm away from the interface. They resemble γ'-phase precipitates in the γ-phase matrix of commercial Ni-base superalloys [7] or the Ni–Al binary alloy system [8]. The patterns are cuboid in shape and uniformly distributed. Therefore, the patterns are thought to be the γ'-phase precipitates which are formed during cooling from annealing temperature, presumably due to the large heat content of the whole assembly of the couple.

3.2. Porosity formation

There are porosity-like patterns in the transformed γ-phase region and sometimes also in γ'-phase, as seen in Figs 2 to 5. Their occurence has not been understood systematically, because their distribution is changed from specimen to specimen. Nevertheless they should be related to the porosities formed in diffusion couples exhibiting the Kirkendell effect [9].

In general, the Kirkendall effect forms porosities at the higher concentration side of the more diffusive element against the marker interface (the

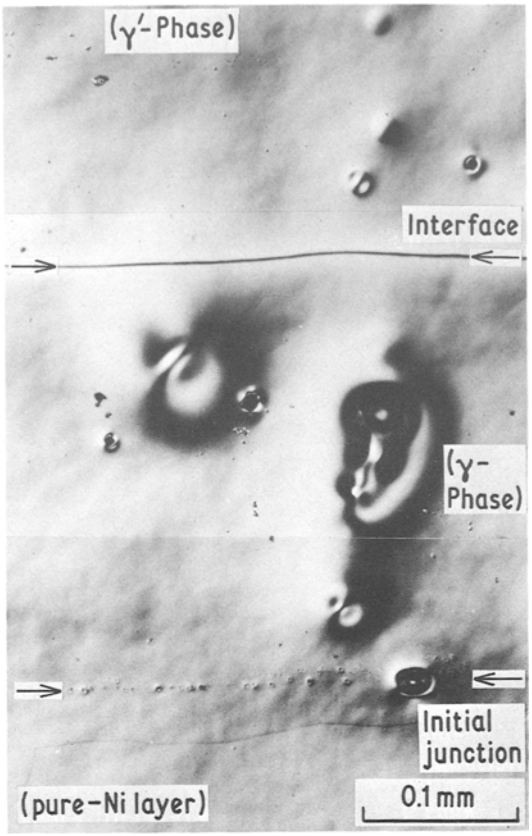

Figure 4 Morphology in the couple using (001) oriented ternary γ' plate (Ti in Table I) annealed for 222 h at 1473 K.

initial junction plane) and also makes the marker interface migrate toward the side of higher concentration of the more diffusive element. Therefore, in the case of α–β brass diffusion couples, the porosities are expected to form in the β phase in front of the migrating marker interface because the intrinsic diffusion coefficient of Zn, D_{Zn}, is higher than that of Cu, D_{Cu}. Indeed, Hashimoto *et al.* [3] observed the porosities in the original β plate layer in front of migrating marker interface.

Returning to the present couples, since porosities are located in only one side of the initial junction, that is, only in the γ- and/or γ'-phases and not in the pure Ni, the intrinsic diffusion coefficient of Al, D_{Al}, should be higher than that of Ni, D_{Ni}, as far as the couples using binary γ'-phase are concerned. Porosity formation described above is schematically illustrated in Fig. 7.

According to the research work by Janssen [10] on the growth kinetics in the couples consisting of pure Ni- and γ'-polycrystals, the porosities are formed only in the newly appearing γ phase, suggesting the ratio of each intrinsic diffusion coefficient, D_{Al}/D_{Ni} is > 1.

3.3. Growth behaviour

In any couple, the movement of the initial junction was not detectable. Accordingly the thickness of the γ-phase corresponds to the migration

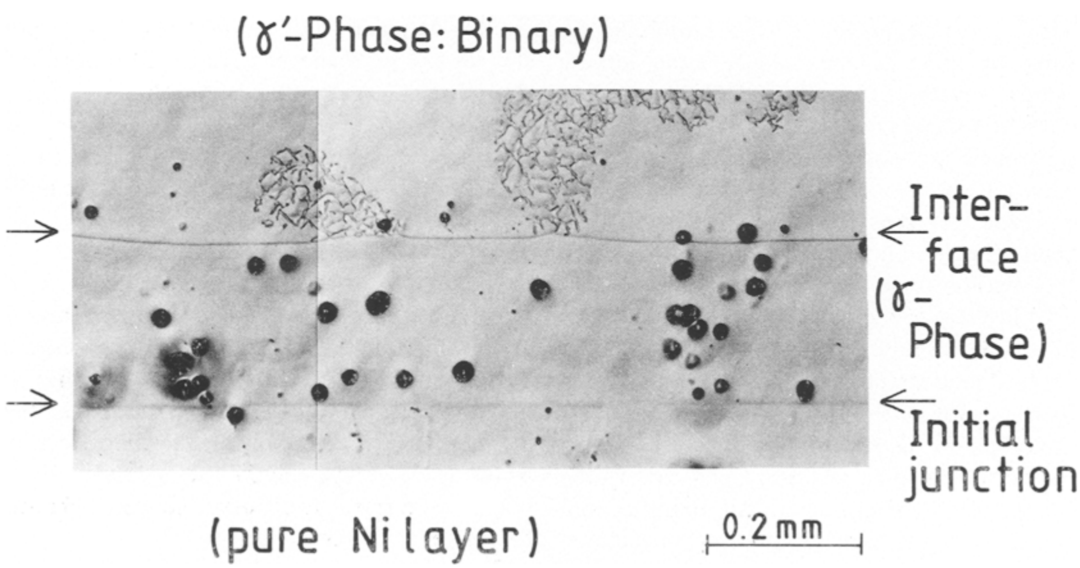

Figure 5 Morphology in the couple using a nearly (0 1 1) oriented binary γ' plate (B in Table I) annealed for 24 h at 1473 K. The patterns observed in the γ'-phase are the pre-existing γ-phase colonies.

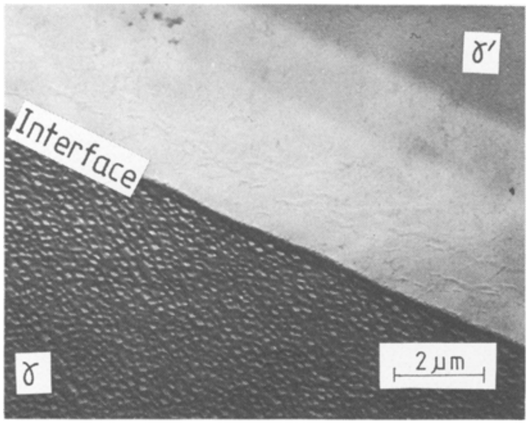

Figure 6 A replica electron micrograph taken on the same cross-section as shown in Fig. 3.

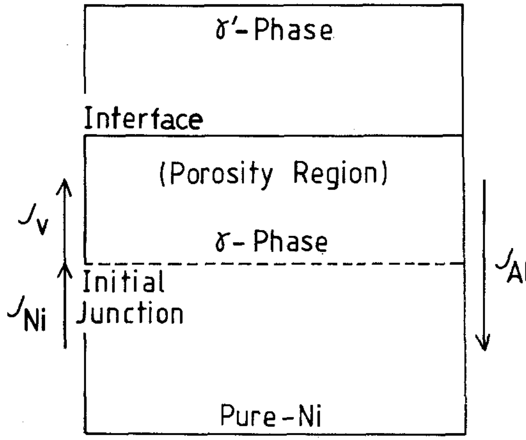

Figure 7 Schematic illustration of the porosity formation process in the couple consisting of pure Ni and binary γ′-phase. J_{Al}, J_{Ni} and J_V are the diffusion fluxes of Al, Ni and vacancies respectively.

distance of the γ/γ' interface. Fig. 8 summarizes the variation of migration distance with the square root of diffusion annealing time. In couples using either a binary γ'-phase single crystal or a ternary one, the well-known parabolic law seems to hold. This fact indicates that the growth of γ-phase is controlled by volume diffusion as in the Janssen study [10]. Deviations from this law in shorter-time annealing are thought to result from the non-isothermal diffusion during heating from room temperature up to the annealing temperature. It should be noted that the diffusion rate in the couples using ternary γ'-phase is lower than that in those with binary one. This indicates that the addition of Ti to Ni–Al binary system would retard the growth of γ'-phase precipitates from the super-saturated γ-matrix.

Concentration profiles normal to interface were measured by EMPA on the same cross-section as in the optical observations. Fig. 9 shows examples of the concentrations profiles, which have not been corrected quantitatively. It is found that there are nearly-constant concentration gradients of each constituent element from the interface to the pure-Ni layer through the γ-phase range.

Hashimoto *et al.* [11] reported a refined technique for preparing α–β brass two-phase bicrystals with nearly uniform and nearly thermodynamic equilibrium chemical compositions by the same method. Also in this study, a couple, which consisted of γ'-phase (nominal composition Ni–24 at % Al) and γ-phase (Ni–9 at % Al), in place of the pure Ni electro-deposited layer, was diffusion-annealed, to obtain a specimen having minimized concentration gradients in the transformed γ-phase. However, such a trial resulted in the non-uniform growth of the γ-phase, meaning that a good contact is essential for the uniform growth of γ-phase.

Also, from these profiles, the occurence of γ'-phase precipitation in the γ-phase during the cooling described in Section 3.1. might also correspond to the local enrichment of the γ'-phase forming elements of Al and Ti. Further inquiry is necessary on details of the concentration profiles near the interface.

3.4. Orientation relationship

Table II lists the couples used for measuring the orientation relationship between γ- and γ'-phase. Fig. 10 summarizes the measured {001} planes of the transformed γ-phase on the standard stereographic (001) projection of the parent γ'-phase. Each {001} plane of the γ-phase coincides

TABLE II Bicrystals used to measure the orientation relationship between the γ- and γ'-phases.

Specimen number	γ'-plate	Annealing time (h)
1	B	24
2	B	67
3	B	240
4	T1	222
5	T1′	120
6	T2	66
7	T2	222
8	T2′	120

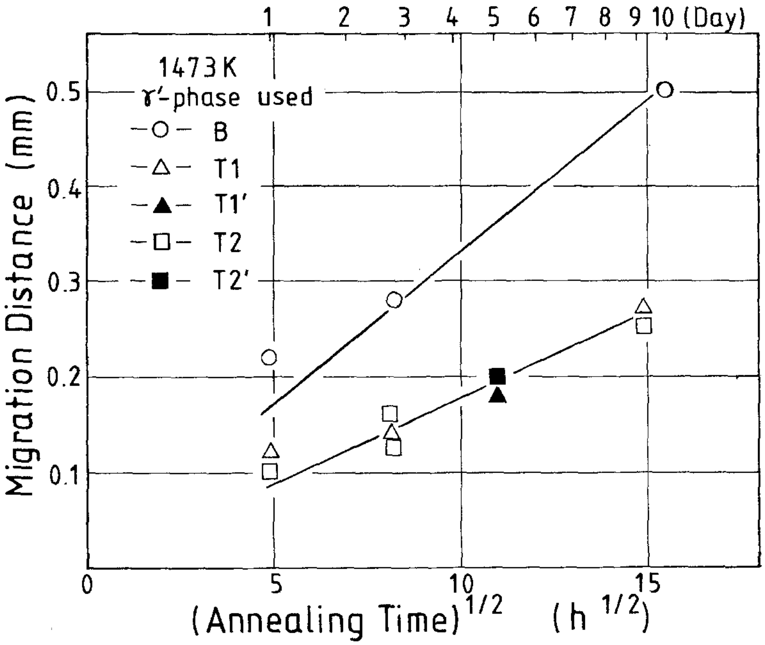

Figure 8 Variation of the migration distance of γ/γ' interface with the square root of diffusion annealing time at 1473 K.

with that of the γ'-phase to within several degrees. Therefore it is clear that γ-phase grows "epitaxially" along the crystal orientation of γ'-phase, that is, such a relationship as $\langle 001 \rangle \ /\!/ \ \langle 001 \rangle_{\gamma'}$ holds.

This relationship accounts for the entire absence of grain boundaries in the transformed γ-phase region. Additional diffusion-annealing experiments performed on a couple using a binary γ'-phase polycrystal indicates that the transformed γ-phase grows in a polycrystal whose grain boundaries

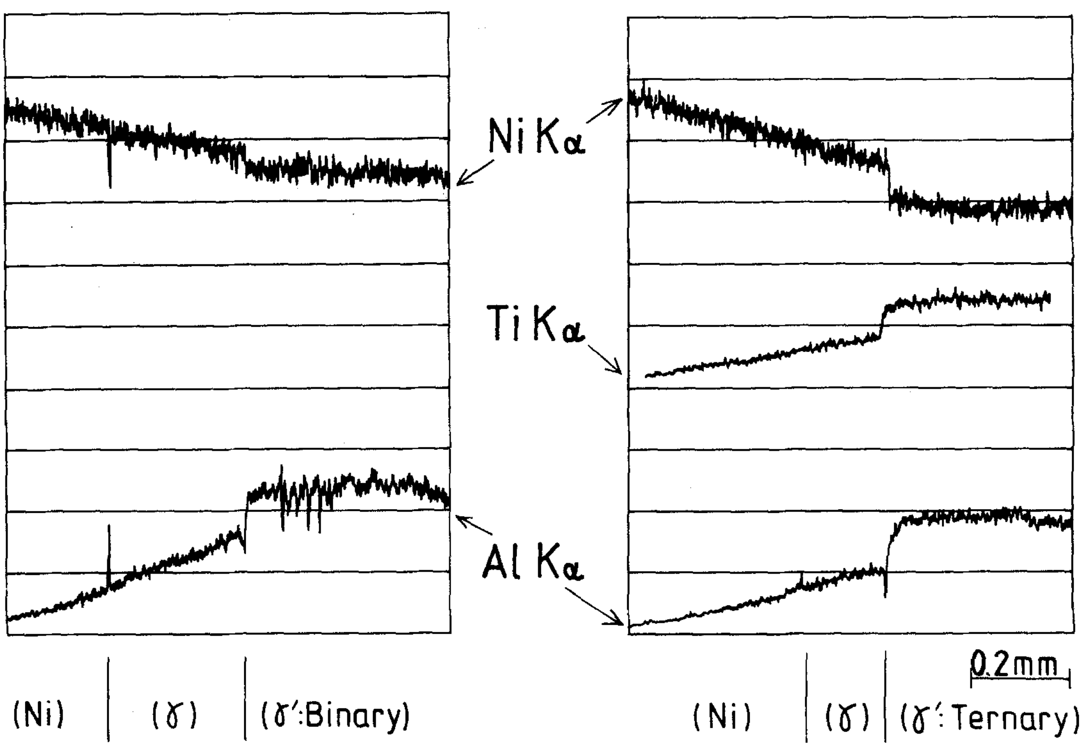

Figure 9 Copies of the charts recording the profiles of the intensity of each Kα radiation in the couple using (a) binary and (b) ternary γ'-phase.

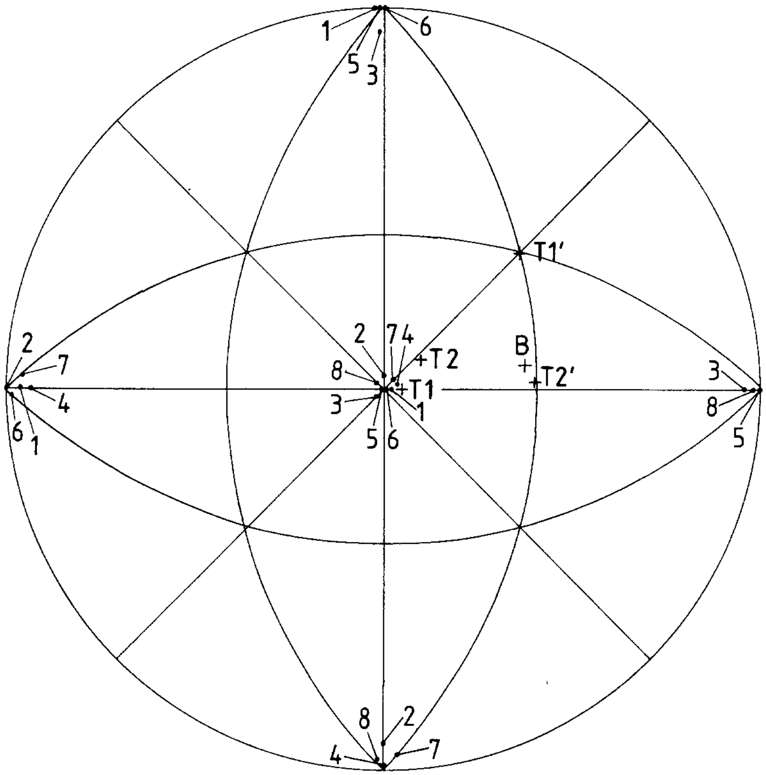

Figure 10 Plots of the measured (0 0 1) planes of the transformed γ-phase on the standard stereographic (0 0 1) prejection of the parent γ'-phase. Crosses indicate the γ'-phase plate orientation which appear in Table I.

inherit the grain boundaries in the γ'-phase. This orientation relationship is believed to be identical with that between the γ'-precipitates and the γ-matrix in most Ni-base superalloys [7]. The γ'-phase always precipitates coherently from supersaturated γ-matrix in the initial stage of precipitation. Such an agreement of the orientation relationship in the present couples and in the pratical alloys is attributed to the common interface crystal structure and the same diffusion-controlled growth process in solid-state, though differing a growing phase, γ-phase in the former while γ'-phase in the latter.

It has been shown [12, 13] that coherency between the γ'-precipitate and the γ-matrix is lost by the introduction of a dislocation network at the interface, for the relaxation of lattice mismatch when the growth of γ'-precipitates occurs. Hence the γ/γ' interface structure in the present bicrystal is expected to have misfit dislocations as can be seen in the microstructure of pratical Ni-base superalloys. This will be clarified by direct observation by transmission electron microscopy on thin foil.

3.5. General discussion

The present study showed that γ–γ' two phase bicrystals which have macroscopically simple geometry are easily obtained by the aid of the crystallographic restriction as the orientation relationship equals $\langle 0 0 1\rangle_\gamma /\!/ \langle 0 0 1\rangle_{\gamma'}$. However, these bicrystals have two structural faults; the porosity due to the Kirkendall effect in the diffused region and the supersaturation of chemical composition in the γ phase near the interface, resulting in fine γ'-precipitates. Therefore it should be noted that these diffusion-induced faults would inevitably have some influence on the mechanical properties of bicrystal specimen in use for mechanical testings.

4. Conclusions

(a) Present two-phase bicrystals have single crystal layers consisting of the uniformly transformed γ-phase and untransformed γ'-phase and defectless γ/γ' interface.

(b) The growth rate of γ-phase obeys the parabolic law.

(c) The orientation relationship of $\langle 0 0 1\rangle_\gamma /\!/ \langle 0 0 1\rangle_{\gamma'}$ is found between both phases within several degrees regardless of interface orientation.

(d) Present bicrystals have two structural faults; the porosities due to the Kirkendall effect and the concentration gradient in the transformed γ-phase.

Acknowledgements
We are indebted to Drs S. Hanada and K. Aoki for their help in the chemical analysis of ingots and specimen preparation, to Mr R. Kamata for the preparation of ingots, and also to the Faculties of Mechanical Engineering in Yonago Technical College for their technical support in manufacturing a vacuum furnace.

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Received 26 August
and accepted 18 September 1981