

# DETERMINATION OF PHASE EQUILIBRIA OF Al-Ni-Ti SYSTEM AT 1 200 K<sup>①</sup>

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**ABSTRACT** An experimental determination was performed on the isothermal section of the Al-Ni-Ti system at 1 200 K by using a diffusion triple technique. Two kinds of alloys Ni51Al49 and TiAl<sub>3</sub> were used to make diffusion triples together with pure Ni and pure Ti, and samples were analysed by optical microscopy and electron probe microanalysis (EPMA) technique. Experimental results demonstrated that the technique of diffusion triple is feasible and powerful for the determination of isothermal section of ternary phase diagram.

**Key words** phase diagram ternary system nickel titanium aluminium

## 1 INTRODUCTION

Among the three relevant binary systems, the phase diagram of the Ni-Ti system<sup>[1]</sup> is relatively simple and certain, the remaining two are much more complicated. To ascertain them, a number of studies have been carried out on the system Al-Ni<sup>[2]</sup> and Al-Ti<sup>[3]</sup>. For the ternary system Al-Ni-Ti, many investigators have contributed to its experimental determination<sup>[4-10]</sup> and its evaluation<sup>[5]</sup>. According to literature, many studies mainly dealt with the Ni-rich corner<sup>[4, 6, 10]</sup>, Al-rich corner<sup>[7]</sup> and Ti-rich corner<sup>[11]</sup>. Four ternary compounds<sup>[8-10, 12]</sup> were found in the system, which are AlNi<sub>2</sub>Ti(H), AlNiTi( $\lambda$ ), Al<sub>2</sub>NiTi( $\mu$ ) and Al<sub>6.5</sub>NiTi<sub>2.5</sub>( $\pi$ ). The precise phase relationships of isothermal sections were not ascertained in detail, especially concerning the data on three-phase equilibria involving ternary compounds. The present work is aimed at exploiting diffusion triple technique<sup>[13]</sup> to determine the phase equilibria of the isothermal section at 1 200 K.

## 2 EXPERIMENTAL

The materials for making diffusion triples

included electrolytic Ni (99.98%), Ti bar (99.7%) and Al block (99.99%). The preparation of diffusion triple was completed in three steps.

(1) The preparation of alloy NiAl and TiAl<sub>3</sub>: under the protection of argon atmosphere, two kinds of alloy ingredients corresponding to Ni51Al49 and Ti25Al75 were molten respectively in water-cooled copper hearths in an arc-furnace with a magnetic stirring device, and then cooled down. The alloys were turned upside-down, and underwent the same melting process 4 times to reach homogenization. The above alloy buttons were cut into rectangular blocks (6 mm × 12 mm × 12 mm) by electrolytic cutting machine.

(2) Combination of Ni-Ti binary couple: the electrolytic Ni and Ti bar were cut into rectangular blocks (6 mm × 6 mm × 12 mm), ground, polished, cleaned, and swathed with tungsten wires, and then annealed under the same condition as triples' annealing process for 48 h to fulfill a good conjunction of Ni-Ti interface.

(3) Assembling of diffusion triple: the above Ni-Ti couple and a NiAl alloy block (or a TiAl<sub>3</sub> one) were ground, polished, cleaned and then swathed with tungsten wires. Fig. 1 illustr-

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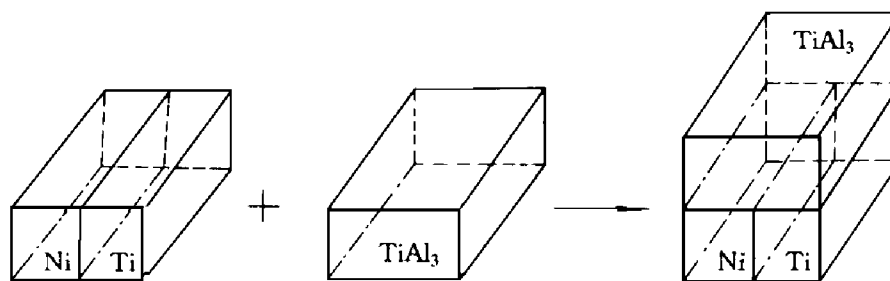


Fig. 1 Assembling process and configuration of diffusion triple

ates the assemblage and configuration of the diffusion triple.

The well-prepared diffusion triples were sealed in a quartz capsule filled with high-purity argon, and annealed in a GK-2B type diffusion furnace at 1 200 K for 575 h. The temperature was controlled by a thyristor regulator, and turned out to be stable within  $\pm 1$  °C. After a given period of annealing, the capsule was taken out from the furnace and cooled down at room temperature to prevent the triples from cracking. The last samples were ground and polished parallel to the diffusion direction for electron probe microanalysis (EPMA). After EPMA, the samples were etched with a solution of 10%  $\text{H}_2\text{O}_2$ , 10% HF and 80%  $\text{H}_2\text{O}_2$  for 3~10 s, and then with a solution of 10%  $\text{H}_2\text{SO}_4$ , 20%  $\text{HNO}_3$  and 70%  $\text{H}_2\text{O}$  for 5~10 s.

### 3 RESULTS AND DISCUSSION

The optical micrographs and schematic diagrams of phase distribution are shown in Fig. 2, Table 1 exhibits the list of experimental data determined by EPMA on triple 1 (NiAl+ Ni-Ti) and triple 2 ( $\text{TiAl}_3$ + Ni-Ti). Most of the experimental values of tie-lines and tie-line triangles were determined by locating the separate points close to the phase boundaries, a few of them were obtained by extrapolating the composition-distance curves to the supposed positions of the phase interface<sup>[13]</sup>.

In terms of the experimental data given in Table 1, the isothermal section of the system Al-Ni-Ti at 1 200 K was constructed as Fig. 3. The equilibria unconfirmed experimentally were shown by dashed lines. As less attention was

paid to the determination of binary data, most of the binary data were introduced from well-known literatures.

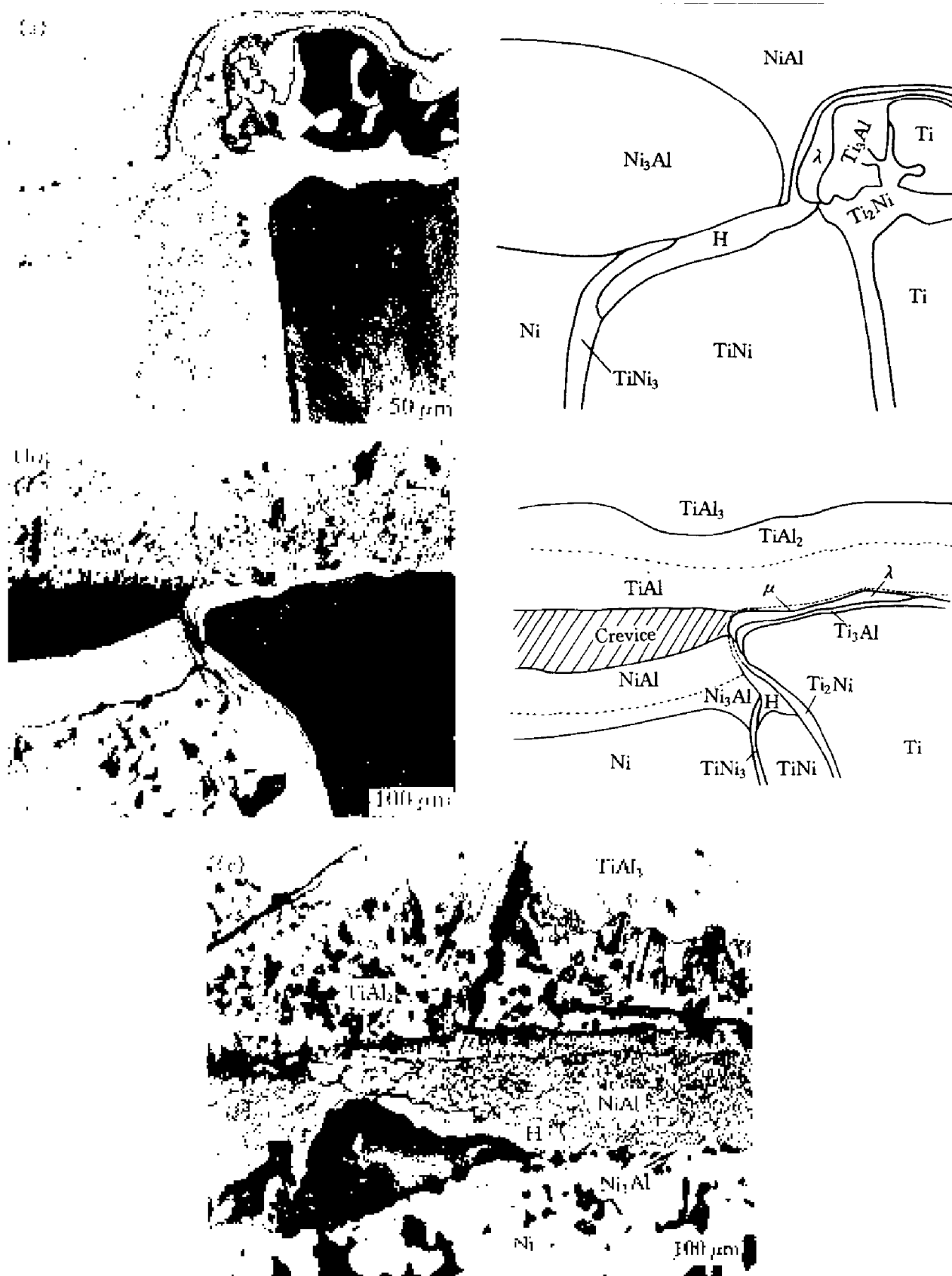
The phase relationships in the present work as shown in Fig. 3 were in good agreement with previous experimental results by other investigators<sup>[4, 9]</sup>. The ternary compound  $\text{Al}_{6.5}\text{NiTi}_{2.5}$  ( $\pi$ ) didn't turn up in our experimental samples. Compared with [9], there existed some discrepancies. Their experimental temperature was 1 173 K, ours was 1 200 K, the temperature difference is relatively small, but the phase zones of ( $\alpha\text{Ti}$ ), ( $\beta\text{Ti}$ ),  $\text{Ti}_3\text{Al}$  and  $\mu$  for our experimental results were remarkably larger than theirs, especially concerning ( $\beta\text{Ti}$ ),  $\text{Ti}_3\text{Al}$  and  $\mu$ .

We used two kinds of alloys NiAl and  $\text{TiAl}_3$  in the preparation of diffusion triples. In the Ni-Ti-NiAl triple after annealing, there appeared two ternary compounds which are  $\lambda$  and H. If we further look into the configuration and sequence of the phases' distribution in the NiAl-Ti side in Fig. 2(a), we would find that there is a diffusion path proceeding from NiAl phase, through H,  $\lambda$ ,  $\text{Ti}_3\text{Al}$ , ( $\alpha\text{Ti}$ ), and up to ( $\beta\text{Ti}$ ) phase in the NiAl-Ti side. There turned up three ternary compounds  $\lambda$ ,  $\mu$  and H in the Ni-Ti- $\text{TiAl}_3$  diffusion triple. Just the same, there is a diffusion path which is  $\text{TiAl}_3 \rightarrow \text{TiAl}_2 \rightarrow \mu \rightarrow \text{NiAl} \rightarrow \text{Ni}_3\text{Al} \rightarrow (\text{Ni})$  in the Ni-Ti- $\text{TiAl}_3$  side (referring to Fig. 2(c)).

According to the determined isothermal section of the Al-Ni-Ti system and literatures, we can sketch out the stability diagram of the Al-Ni-Ti system at 1 200 K as Fig. 4, i. e., the diagram of chemical potential of aluminium  $\mu_{\text{Al}}$  vs.  $Y_{\text{Ni}}$ , where  $Y_{\text{Ni}} = X_{\text{Ni}} / (X_{\text{Ni}} + X_{\text{Ti}})$ , and  $X$  is

**Table 1 Tie-lines and three-phase equilibrium data determined by EPMA in Al-Ni-Ti diffusion triples**

|                    |       |                   |       | (balance, Aluminium) |       |                    |       |
|--------------------|-------|-------------------|-------|----------------------|-------|--------------------|-------|
| Ti <sub>3</sub> Al |       | (αTi)             |       | H                    |       | Ni <sub>3</sub> Al |       |
| Ni                 | Ti    | Ni                | Ti    | Ni                   | Ti    | Ni                 | Ti    |
| 1.27               | 76.93 | 2.59              | 80.43 | 52.51                | 23.92 | 72.05              | 15.58 |
| 1.92               | 77.05 | 3.12              | 80.08 | H                    |       | λ                  |       |
| 4.20               | 76.67 | 5.60              | 77.33 | Ni                   | Ti    | Ni                 | Ti    |
| (αTi)              |       | (βTi)             |       | 47.14                | 27.64 | 29.50              | 43.45 |
| Ni                 | Ti    | Ni                | Ti    | 47.69                | 27.50 | 30.29              | 44.30 |
| 6.67               | 83.74 | 9.52              | 83.88 | H                    |       | NiAl               |       |
| 9.93               | 79.51 | 13.80             | 77.72 | Ni                   | Ti    | Ni                 | Ti    |
| 10.47              | 78.03 | 16.68             | 73.88 | 51.01                | 16.15 | 51.55              | 12.40 |
| 10.68              | 75.31 | 19.90             | 70.45 | 47.46                | 17.32 | 48.80              | 8.50  |
| (βTi)              |       | NiTi <sub>2</sub> |       | NiAl                 |       | Ni <sub>3</sub> Al |       |
| Ni                 | Ti    | Ni                | Ti    | Ni                   | Ti    | Ni                 | Ti    |
| 21.01              | 70.37 | 30.84             | 63.67 | 59.60                | 4.43  | 62.57              | 7.02  |
| 20.60              | 71.85 | 30.63             | 64.80 | 60.70                | 1.16  | 72.68              | 1.52  |
| 20.82              | 72.54 | 30.37             | 65.42 | NiAl                 |       | μ                  |       |
| λ                  |       | NiTi <sub>2</sub> |       | Ni                   | Ti    | Ni                 | Ti    |
| Ni                 | Ti    | Ni                | Ti    | 47.10                | 6.12  | 26.54              | 21.05 |
| 28.14              | 52.44 | 30.43             | 54.36 | 44.76                | 4.40  | 25.38              | 19.54 |
| NiTi <sub>2</sub>  |       | NiTi              |       | μ                    |       | TiAl <sub>2</sub>  |       |
| Ni                 | Ti    | Ni                | Ti    | Ni                   | Ti    | Ni                 | Ti    |
| 32.73              | 59.25 | 45.80             | 49.05 | 15.61                | 33.89 | 1.66               | 34.72 |
| 33.40              | 62.58 | 42.02             | 50.37 | 15.71                | 32.21 | 2.17               | 33.50 |
| Ti <sub>3</sub> Al |       | NiTi <sub>2</sub> |       | TiAl                 |       | Ti <sub>3</sub> Al |       |
| Ni                 | Ti    | Ni                | Ti    | Ni                   | Ti    | Ni                 | Ti    |
| 5.83               | 73.07 | 30.60             | 58.08 | 1.35                 | 53.06 | 1.17               | 63.61 |
| Ti <sub>3</sub> Al |       | λ                 |       | Ti <sub>3</sub> Al   |       | λ                  |       |
| Ni                 | Ti    | Ni                | Ti    | Ni                   | Ti    | Ni                 | Ti    |
| 5.33               | 71.15 | 26.57             | 51.40 | 4.90                 | 73.02 | 26.70              | 53.09 |
| 5.07               | 68.83 | 27.34             | 46.95 | Ti <sub>3</sub> Al   |       | (αTi)              |       |
| H                  |       | NiTi              |       | Ni                   | Ti    | Ni                 | Ti    |
| Ni                 | Ti    | Ni                | Ti    | 6.02                 | 74.21 | 9.73               | 74.85 |
| 49.66              | 31.53 | 48.91             | 44.40 | λ                    |       | H                  |       |
| 51.47              | 31.05 | 50.41             | 42.06 | Ni                   | Ti    | Ni                 | Ti    |
| NiTi <sub>2</sub>  |       | H                 |       | 29.52                | 50.10 | 48.74              | 26.62 |
| Ni                 | Ti    | Ni                | Ti    | NiTi <sub>2</sub>    |       | H                  |       |
| 32.60              | 58.09 | 48.33             | 31.56 | Ni                   | Ti    | Ni                 | Ti    |
| H                  |       | NiTi              |       | 52.50                | 25.87 | 73.15              | 17.58 |
| Ni                 | Ti    | Ni                | Ti    | H                    |       | NiAl               |       |
| 53.25              | 29.25 | 53.21             | 41.53 | Ni                   | Ti    | Ni                 | Ti    |
|                    |       |                   |       | 52.28                | 19.45 | 56.42              | 9.20  |
|                    |       |                   |       |                      |       | Ni <sub>3</sub> Al |       |
|                    |       |                   |       |                      |       | Ni                 | Ti    |
|                    |       |                   |       |                      |       | 71.62              | 14.27 |



**Fig. 2 Phase distribution and configuration of Ni-Ti-Al diffusion triples annealed at 1 200 K for 575 h**

(a) —optical micrograph and schematic diagram of (Ni-Ti+ NiAl) triple; (b) —optical micrograph and schematic diagram of (Ni-Ti+ TiAl<sub>3</sub>) triple at ternary juncture; (c) —optical micrograph on TiAl<sub>3</sub>-Ni side of (Ni-Ti+ TiAl<sub>3</sub>) triple

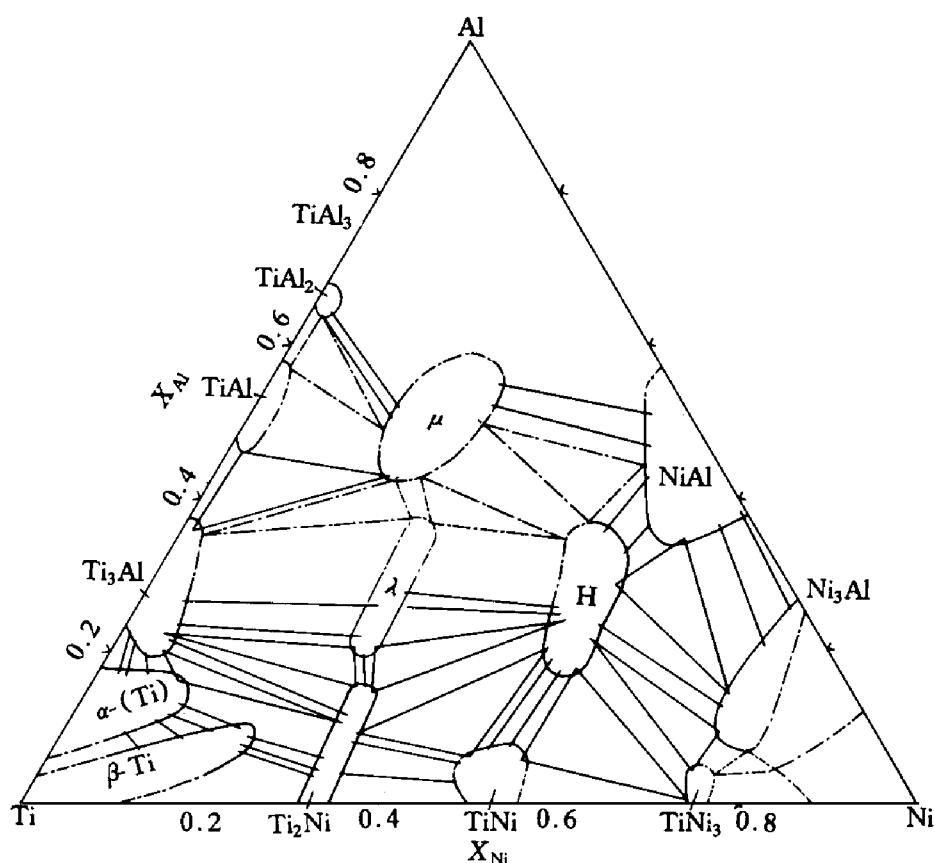


Fig. 3 Phase diagram of Al-Ni-Ti system at 1200 K

mole fraction. The above-mentioned two diffusion paths are also shown in Fig. 4. From the stability diagram, we can elicit a deduction. For instance, we analyse two of the three-phase equilibria in Fig. 4, one for  $\lambda$ ,  $\mu$  and  $\text{Ti}_3\text{Al}$ , and another for  $\lambda$ ,  $\mu$  and  $\text{H}$ , where  $X_{\text{Ni}(1)}$  and  $X_{\text{Ni}(2)}$  are the Ni mole fractions of three-phase equilibrium point 1 and 2 in the phase  $\mu$ ,  $X_{\text{Ni}(3)}$  and  $X_{\text{Ni}(4)}$  are the ones of three-phase equilibrium point 3 and 4 in the phase  $\lambda$  respectively. If  $Y_{\text{Ni}(3)} > Y_{\text{Ni}(1)}$ , then there is certainly a relationship  $Y_{\text{Ni}(4)} > Y_{\text{Ni}(2)}$ . That is to say, the two three-phase equilibria, in which two common phases are involved, shouldn't be the same reaction type in the stability diagram, or it violates phase law. This point is very significant for phase diagram construction and experimental assessment of ternary systems.

#### 4 SUMMARY

The isothermal section of the Al-Ni-Ti system at 1200 K was determined by using diffusion

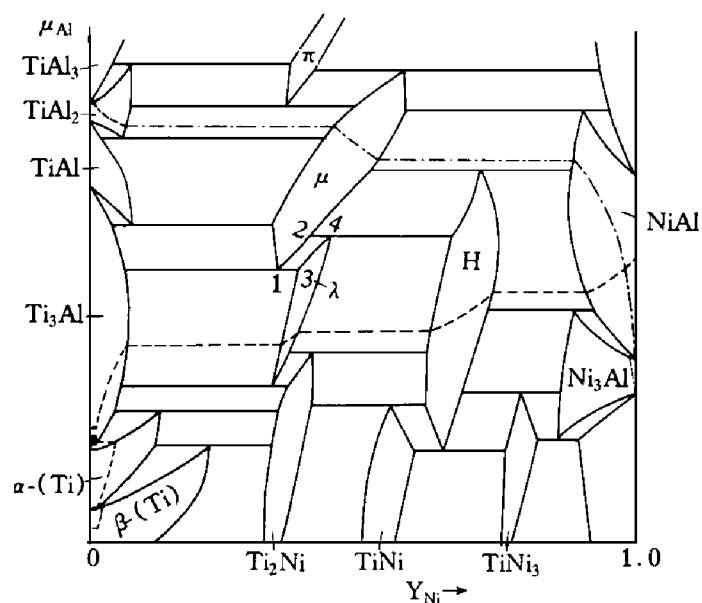


Fig. 4 Stability diagram  $\mu_{\text{Al}}-Y_{\text{Ni}}$  of Al-Ni-Ti system at 1200 K

triple technique, optical microscopy and EPMA technique, and presented in Fig. 3. By means of two kinds of alloys NiAl and  $\text{TiAl}_3$ , the diffusion

triples for the Al-Ni-Ti system were made to circumvent the low melting point of metal Al. Experimental results demonstrated that the present method is a feasible and powerful approach to the determination of ternary phase diagram, especially under the condition of encountering the low melting point metals such as Al.

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