Journal of Alloys and Compounds, 177 (1991) 119–127
JAL 0037

The Ti–N–Ni system: investigations relevant for cermet sintering

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(Received June 1, 1991)

Abstract

The two-phase field δ-TiN$_{1-x}$ + γ-Ni$_x$Ti$_{1-x}$ was investigated. Sintered alloys were prepared from TiN, titanium and nickel powders. They were sealed in evacuated and argon-refilled silica tubes and equilibrated at 1100 °C. They were investigated by means of X-ray diffraction, metallography and specific saturation magnetization. The melting behaviour of TiN–Ni alloys was investigated by metallography and differential thermal analysis.

In equilibrium with the solid solution of titanium in f.c.c. γ-Ni, δ-TiN$_{1-x}$ remains nearly stoichiometric. In equilibrium with the Ni–Ti intermetallic phases, TiN becomes successively substoichiometric.

If a melting point minimum (pseudobinary eutectic) between nickel and TiN exists, it must be situated very close to the nickel corner.

1. Introduction

Because of their exceptional properties such as high hardness, high melting point and high thermal and electrical conductivities, the mononitrides of the group IVa metals are especially suitable for cutting tools and wear-resistant parts. During chip-forming operations TiC and particularly TiN show superior wear resistance compared to conventional WC–Co hard metals. This phenomenon seems to be partly the result of the high chemical stability of TiC and TiN and partly the result of diffusion barriers, probably consisting of titanium oxides formed between the tool material and the hot chips during the operation. Although Ti(C, N)-based cermets with an Ni–Mo binder have been known for some time, they have only recently been applied to a greater extent for high speed machining of chip-forming materials.

The phase diagram of the binary boundary system Ti–Ni is well established [1–4]. Titanium and nickel form three intermetallic compounds. TiNi$_3$, TiNi and Ti$_2$Ni. The maximum solubility of titanium in the nickel solid solution is 13.8 at.%. Nitrogen is only very slightly soluble in solid nickel [5]. The Ti–N binary boundary system was recently reinvestigated [6, 7] because several other proposals for the phase diagram had been reported [8], diverging in particular with respect to the area around 33 at.% N. Besides the mononitride δ-TiN$_{1-x}$ with an NaCl-type structure, four other compounds have been reported: ϵ-Ti$_2$N, δ'-TiN$_{0.5}$, η-Ti$_3$N$_{2-x}$ and ζ-Ti$_4$N$_{3-x}$. Nitrogen stabilizes the

0925-8388/91/$3.50

hexagonal α-Ti phase and forms an interstitial alloy resembling the subnitride phases T_2N (T, transition metal) in structure and composition. δ-TiN_{1-x} has a wide range of homogeneity.

Whereas the Ti–C–Ni system has already been reasonably well investigated, hardly any studies concerning the Ti–N–Ni system have been made. Fukuhara and Mitani reported a quasi-binary eutectic between a nickel solid solution and stoichiometric TiN [9]. The melting point of the eutectic was determined to be 1353 ± 4 °C, the eutectic composition about 11.4 at.% Ti, 6.3 at.% N and 82.3 at.% Ni. Further studies by the same researchers dealt with mechanisms of grain growth and denitrification during sintering of TiN–Ni alloys [10]. Schönberg described a ternary nitride $Ti_{0.7}Ni_{0.3}N$ which was prepared by passing oxygen-free dry ammonia over a finely powdered binary Ti–Ni alloy [11]. Thermodynamic calculations concerning the Ti–N–Ni system were carried out by Stomakhin and Polyakov [12]. They derived thermodynamic equations expressing the three-phase equilibria between TiN, nickel and N_2. Other researchers investigated the strength of several TiN–Ni materials [13] and the interaction of TiN with liquid nickel [14]. According to these studies, the strength of heterophase TiN–Ni materials depends mostly on the porosity and reaction between the components during sintering. The wetting of TiN by nickel begins above 1650 °C; the interaction results in nitrogen loss. Various Japanese patents describe the sintering of TiN–Ni cermets.

The present work deals mainly with that part of the Ti–N–Ni system which is of interest for the application of TiN and nickel in cermets, *i.e.* the two-phase field δ-TiN_{1-x} + γ-Ni_xTi_{1-x}.

2. Experimental details

2.1. *Preparation of sintered samples*

The sintered samples were prepared from nickel (FSSS grain size 5 μm, less than 200 ppm O and 50 ppm C), titanium (FSSS grain size 22.4–25.0 μm, maximum of 0.120% O and 0.024% N) and TiN (FSSS grain size 2–5 μm, 0.1% C, 2.0% O) powders. The sintering was carried out under vacuum (3 Pa) in an induction furnace in vacuum for 3 h. A graphite tube served as susceptor. The samples were placed on small Al_2O_3 plates. Temperatures ranging from 1300 to 1360 °C for specimens with high TiN concentrations (20–50 mol.%) and from 1200 to 1250 °C for samples containing less than 4.5 mol.% TiN were applied. After sintering, the samples were put into cylinders of molybdenum foil, sealed in silica tubes under argon at 30 kPa and subjected to heat treatments at 1100 °C for 10 days. Afterwards the tubes were quenched in water.

The specific saturation magnetization was measured with a Sermag sigmameter. Each sample was inserted into the magnetic field of a permanent magnet (12 400 G), which was sufficient to magnetically saturate the sample. Rapidly moving the sample out of the magnetic field induced electric current in the two coils on either side of the gap. This current was measured with a ballistic galvanometer. The specific saturation magnetization can be calculated from the deflection of the galvanometer and the weight of the sample.

The lattice parameters of δ-TiN and γ-Ni_xTi_{1-x} were determined by X-ray diffraction with nickel-filtered Cu Kα radiation. There is a linear relationship between the lattice parameters of δ-TiN_{1-x} and the [Ti]:[N] ratio; hence the compositions of the TiN phase in equilibrium with Ni–Ti alloys could be determined using the equation [15]

$$a\ (\mathrm{nm}) = 0.00593(1-x) + 0.41847$$

The samples could not be pulverized because of their high ductility. Small fragments of specimens were investigated by the Debye–Scherrer technique. Larger fragments were cut and ground to obtain a flat surface and diffractograms were taken. If a sample contained too little TiN, the nickel phase was selectively dissolved in hot HCl (1:1) and the insoluble TiN residue was used for X-ray diffraction.

2.2. *Samples for differential thermal analysis*

In order to investigate the melting behaviour of TiN–Ni alloys and to verify the reported existence [9] of a quasi-binary eutectic, various samples for differential thermal analysis (DTA) were prepared.

(a) An alloy of 10 at.% Ti and 90 at.% Ni was melted and nitrided in an Al_2O_3 crucible in an autoclave with nitrogen at a pressure of 400–500 kPa. The specific saturation magnetization of this alloy was 53 μT m^3 kg^{-1}, which indicated that about 2.5 at.% Ti was still dissolved in the nickel solid solution. Part of the specimen was used for DTA.

(b) A pressed powder pellet containing 11 at.% Ti, 7 at.% N and 82 at.% Ni, corresponding approximately to the eutectic composition reported by Fukuhara and Mitani [9], was sintered in an Al_2O_3 crucible in argon at 1450 °C for 30 min. Part of the sample was used for DTA.

(c) Powder mixtures of 50 wt.% TiN + 50 wt.% Ni (33 at.% Ti, 33 at.% N, 34 at.% Ni) and of 11.6 wt.% TiN + 88.4 wt.% Ni (10 at.% Ti, 10 at.% N, 80 at.% Ni) as well as a mixture of the latter composition containing about 0.02 at.% C were subjected to DTA. Graphite was added to remove the thin films of titanium oxide surrounding the TiN particles in order to improve their wettability with respect to the molten nickel.

(d) A small TiN rod, which had been cut from a completely nitrided titanium sheet, together with a small cutting from a compact electrolytic nickel sheet were placed in the Al_2O_3 crucible for DTA. The sample was heated to a temperature slightly above the melting point of nickel and held there for about 1 h. This was done to ensure equilibration and saturation of the nickel melt with TiN. After cooling, the ingot was sectioned and metallographically investigated.

(e) In order to re-examine the results concerning the eutectic structure reported by Fukuhara and Mitani [9], an alloy of 60 wt.% TiN and 40 wt.% Ni was sintered at 1500 °C for 1 h as described in their paper. Another sample of the same composition containing about 0.02 at.% C to enhance the TiN–Ni wettability was sintered under the same conditions. Another sample of the same starting composition, 60 wt.% TiN + 40 wt.% Ni, was sintered at 1600 °C for 1 h.

The DTA runs were performed by heating and cooling in argon at atmospheric pressure. The heating and cooling rates were generally 10 °C $\min^{-1}$ and sometimes 5 °C $\min^{-1}$. Two to three cycles were necessary to obtain DTA curves which could be clearly interpreted.

In several samples the titanium content in the nickel solid solution was measured with a CAMEBAX SX 50 microprobe. The accelerating voltage was 15 kV, the measuring time 10 s per step. An arc-melted nickel alloy containing 5 at.% Ti, which had been homogenized at 900 °C for 10 days, was used as a standard.

3. Results and discussion

3.1. γ-Ni_xTi_{1-x}–δ-TiN_{1-x} *phase equilibria at 1100 °C*

Figure 1 shows the composition of the sintered samples, which were prepared as described in Section 2.1, and gives the tentative phase relationships in a part of an isothermic section at 1100 °C of the ternary system Ti–N–Ni.

Most of the samples were located in the nickel-rich corner. Titanium in the nickel solid solution increases the lattice parameter of the γ phase [3, 4]. The present measurements were consistent with literature data. Nitrogen

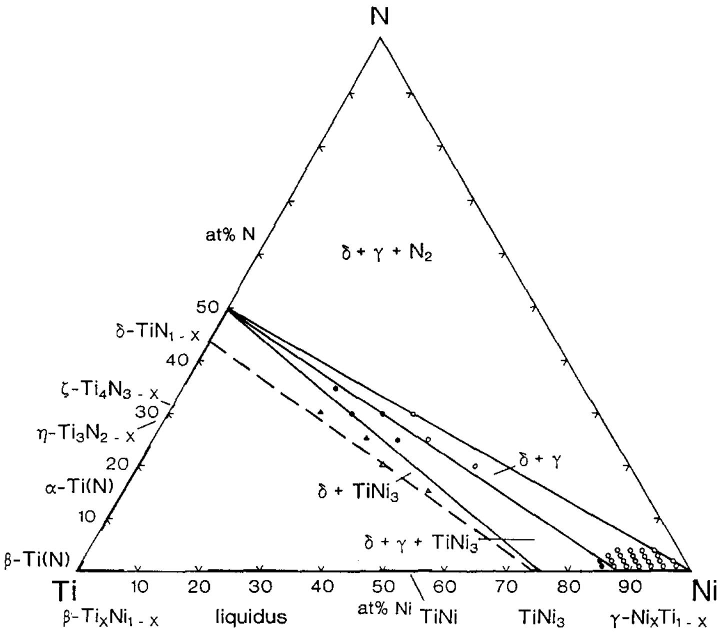

Fig. 1. Tentative phase relationships in the investigated part of the Ti–N–Ni system (1100 °C, $p(N_2) \leq 100$ kPa): ○, $\delta+\gamma$; ●, $\delta+\gamma+TiNi_3$; △, $\delta+TiNi_3$.

reacted with titanium in the solid solution to form TiN, thus removing the titanium from the γ phase. In alloys containing more than 12 at.% Ti, TiNi$_3$ was formed and the lattice parameters were about 0.3565–0.3570 nm. The diffraction lines of the nickel solid solution became broader with increasing titanium content; diffraction lines of samples containing more than 6 at.% Ti showed no resolved Cu Kα_1–α_2 doublet.

The specific saturation magnetization of the nickel solid solution decreased nearly linearly with increasing titanium content. In order to check the influence of dissolved nitrogen, ternary Ni–Ti–N alloys were prepared. Apparently nitrogen is soluble only to a negligible extent. Any nitrogen present in the ternary alloys combined with titanium to form TiN, which precipitated from the solid solution. Therefore the specific saturation magnetization was determined solely by the titanium content of the resulting Ni–Ti solid solution in equilibrium with the precipitated TiN. In Fig. 2 the data points for the various nominal nitrogen contents of the ternary alloys were corrected by taking into account the removal of titanium from the solid solution via TiN precipitation and by checking the residual titanium content in the solid solution based on the linear relationship between the lattice parameter and the titanium content of the nickel solid solution.

The δ-TiN$_{1-x}$ lattice parameters of samples in the two-phase $\delta+\gamma$ field scattered around 0.424 25(13) nm, characteristic for 50 at.% N. No significant influence of the titanium content in the nickel solid solution on the TiN lattice parameters could be detected. Hence within the accuracy of the results only stoichiometric TiN is in equilibrium with the nickel solid solution.

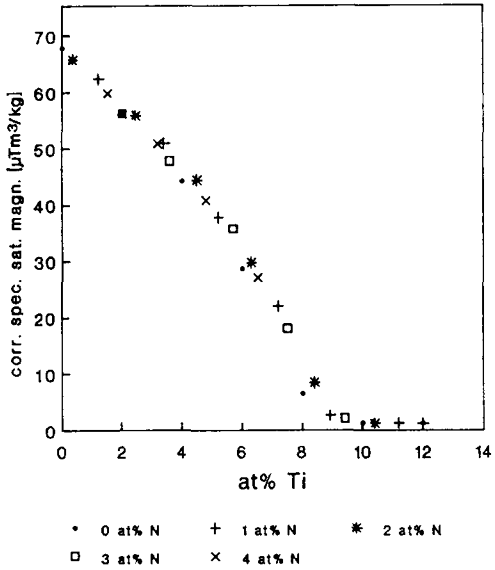

Fig. 2. "Corrected" specific saturation magnetization of γ-Ni$_x$Ti$_{1-x}$ for various nitrogen contents. Nitrogen combines with titanium to form TiN; the residual titanium contents in the γ phase were determined on the basis of lattice parameter measurements.

Only when δ-TiN$_{1-x}$ coexists with TiNi$_3$ does its composition appear to be nitrogen deficient. The δ-TiN$_{1-x}$ lattice parameters of samples in the two-phase δ+TiNi$_3$ field were between 0.423 49 and 0.424 26 nm, corresponding to compositions of TiN$_{0.85}$–TiN$_{0.98}$ (45.9–49.5 at.%).

3.2. Investigation of the TiN–Ni quasi-binary eutectic

The samples described in Section 2.2 were used for DTA.

Sample 2.2(a) started to melt at 1390 °C. Its specific saturation magnetization after the experiment was 40 μT m^3 kg^{-1}, corresponding to 4–5 at.% Ti dissolved in the nickel solid solution. Microprobe analysis of the nickel phase gave a titanium content of 3.7 at.%. The starting Ti–N–Ni alloy had a specific saturation magnetization of 53 μT m^3 kg^{-1}; obviously there was less titanium dissolved in the nickel solid solution before than after DTA. Most probably nitrogen escaped from the samples during the repeated heating and cooling cycles.

Sample 2.2(b) started to melt at 1382 °C. The specific saturation magnetization was 33 μT m^3 kg^{-1}, which indicated that a little more than 5 at.% Ti was dissolved in the nickel. A little less than 5 at.% Ti ($\sigma_s = 39$ μT m^3 kg^{-1}) was dissolved in the sample containing 10 at.% Ti, 10 at.% N and 80 at% Ni (2.2(c)), which started to melt at 1387 °C. Microprobe analysis showed almost the same result: 4.2 at.% Ti in the nickel solid solution. Since this sample had originally consisted of only TiN and nickel powder, it must have lost nitrogen during DTA. The sample of the same starting composition but with 0.02 at.% C started to melt at 1375 °C. For the last of the samples described in Section 2.2(c) (50 wt.% TiN, 50 wt.% Ni) no clear DTA signals were obtained. The peaks were too small and too vague to be interpreted unambiguously.

Metallographic investigation revealed no eutectic structures, not even in those samples that had been prepared (see 2.2(e)) according to the Japanese work on the TiN–Ni eutectic [9]. TiN particles, which apparently remained undissolved at sintering temperatures, were embedded in nickel binder without any traces of a eutectic structure resembling the microstructure shown in Fukuhara and Mitani's paper. Even when compact TiN was equilibrated with nickel (Section 2.2(d)), no eutectic structures could be detected. The existence of a persistent diffusion barrier, such as titanium oxides on the surface of the compact TiN rod which would impede equilibration between TiN and nickel melt, can be ruled out. The TiN–Ni microsection showed an excellent wetting of TiN by nickel and in some areas molten nickel had penetrated along the grain boundaries of TiN (Fig. 3(a)). This is due to the very clean and oxygen-free compact TiN as compared to powdered TiN. The titanium contents in the nickel solid solution were measured after DTA. They were nearly the same throughout the entire sample, with an average of 0.92 at.% Ti. Figure 3(b) shows the concentration profile of titanium dissolved in nickel, starting from the TiN–Ni interface.

These results indicate the existence of a very shallow melting point minimum near the nickel corner between TiN and nickel. The question arises

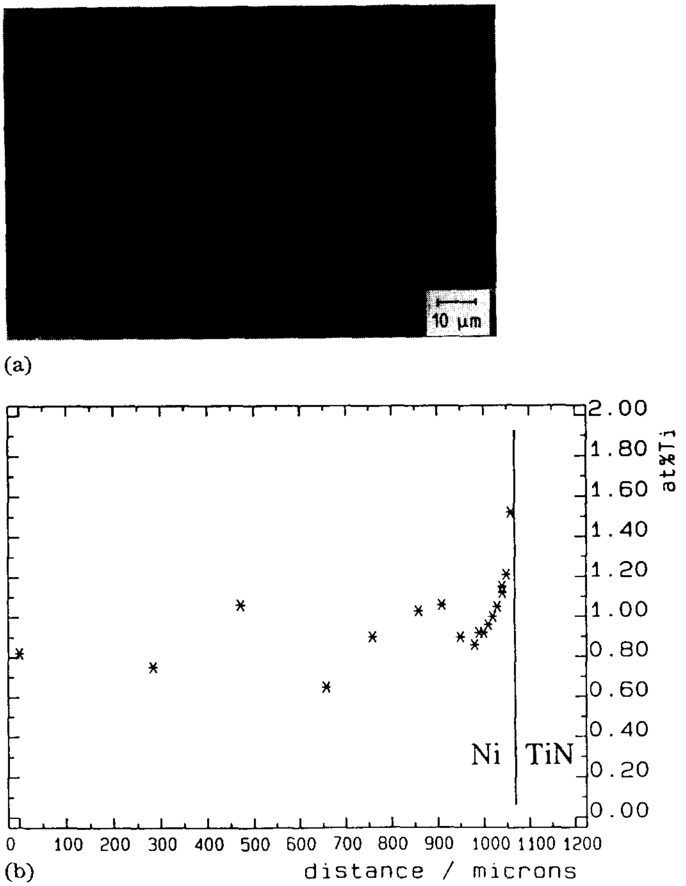

Fig. 3. (a) Microsection of compact TiN which had been heated in molten nickel for 1 h. Excellent wetting of TiN by nickel was observed. (b) Titanium concentration profile in the nickel solid solution determined by microprobe analysis of the sample shown in (a). The titanium contents were nearly the same throughout the entire sample.

as to the reasons for the different melting behaviour in the Ti–N–Ni system as compared to the otherwise very similar Ti–C–Ni system.

For one thing, at a pressure of 1 bar the solubility of nitrogen in solid and liquid nickel is much lower than the solubility of carbon. This is reflected by nitrogen's ΔG, the free energy of solution [16]:

$$\tfrac{1}{2}N_2 \rightleftharpoons N\ (\text{in Ni(l)}), \qquad \Delta G = 44800 + 57.3T \quad (\text{J (g atom)}^{-1})$$

as compared to the less positive ΔG for graphite in nickel [17]:

$$\tfrac{1}{2}C \rightleftharpoons C\ (\text{in Ni(l)}), \qquad \Delta G = 17200 + 8.8T \quad (\text{J (g atom)}^{-1})$$

ΔG for the solid solution of nitrogen in nickel is not known but can safely be supposed to be more positive than the free energy of solution in liquid nickel.

The combination of the thermodynamic data for the solution of graphite in solid [18] and liquid nickel leads to a eutectic temperature in the Ni–C system of 1340 °C and 9.5 at.% C, which is consistent with the experimental data in ref. 1.

Taking into account the low solubility of nitrogen in liquid nickel, which is only 0.004 at.% N at 1455 °C and which will not be increased dramatically by the addition of an equimolar amount of titanium to the melt, the melting point depression due to dissolved TiN in the nickel melt should be rather low. Hence the pseudobinary eutectic composition must be situated very close to the nickel corner of the composition triangle, which is also consistent with the present measurements. From the rather shallow saddle point between TiN and nickel a melting trough develops which probably proceeds into the region of titanium-rich compositions. Probably another melting trough, which has its source in the saddle point between $TiNi_3$ and TiN, joins the melting trough representing the monovariant reaction TiN + Ni. From their intersection onwards the melting trough represents the monovariant reaction liquidus $\rightleftharpoons Ni_3Ti + \gamma\text{-}Ni_xTi_{1-x}N_y$ solid solution and proceeds to the binary eutectic in the Ni–Ti system at 1287 °C and 80.8 at.% Ni [1].

Acknowledgments

The authors express their gratitude to Professor Dr. J. Debuigne and his team as well as to M. Bohn for his assistance during the microprobe measurements at the Centre de la Microsonde de l'Ouest, IFREMER, Brest (France). Thanks are further due to Mrs. C. Jelinek's editing work. Financial support via the French–Austrian research contract, project A 16, is also gratefully acknowledged.

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