A study of $\delta'$-TiN$_{1-x}$ formation in temperature gradient diffusion couples

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Abstract

The formation of $\delta'$-TiN$_{1-x}$ was studied by annealing diffusion couples in a temperature gradient for different lengths of time. From the microstructures of the diffusion couples the ordering transformation $\delta$-TiN$_{1-x} \rightarrow \delta'$-TiN$_{1-x}$ was characterized as a function of temperature and composition. The maximum temperature at which $\delta'$-TiN$_{1-x}$ could be observed was 1153 K. $\delta'$-TiN$_{1-x}$ appears to be a metastable phase which occurs within the transformation $\delta$-TiN$_{1-x} \rightarrow \delta'$-TiN$_{1-x} \rightarrow \epsilon$-Ti$_2$N (+ $\delta$-TiN$_{1-y}$ with $y < x$ if $x < 0.50$). The maximum composition range at which $\delta'$-TiN$_{1-x}$ forms from $\delta$-TiN$_{1-x}$ is 33.3–37.5 at.% N (0.50 ≥ $x$ ≥ 0.40) at $T < 1073$ K. A tentative $c$–$T$ diagram of this part of the Ti–N system is presented.

1. Introduction

The results reported in the literature concerning the phase character of $\delta'$-TiN$_{1-x}$ (whether it is metastable or not) are contradictory. According to refs. 1–3, the tetragonal $\delta'$-TiN$_{1-x}$ phase is formed by long-range ordering of nitrogen atoms in the f.c.c. compound $\delta$-TiN$_{1-x}$ within the composition region 33.3–37.9 at.% N (0.39 ≥ $x$ ≥ 0.50), concurring with a displacement of the titanium atoms. In several other studies [4–6] it was suggested that $\delta'$-TiN$_{1-x}$ is stable in the sense of the phase rule with a nitrogen content of 33.8 at.% N (x = 0.49) [4] or 37 at.% N (x = 0.41) [5] and hence phase diagrams with $\epsilon$-Ti$_2$N + $\delta'$-TiN$_{1-x}$ and $\delta$'-TiN$_{1-y}$ + $\delta$-TiN$_{1-y}$ (with $x > y$) two-phase regions were reported [4, 5] or compiled [6].

In contrast, annealing experiments [7, 8] as well as high temperature X-ray diffraction (XRD) measurements [8] clearly indicate the metastable character of $\delta'$-TiN$_{0.50}$. In a recent study [8] the highest temperature at which $\delta'$-TiN$_{0.50}$ starts to form from $\delta$-TiN$_{0.50}$ was observed to be time dependent (for short annealing times this temperature was 1144 ± 5 K). $\delta'$-TiN$_{0.50}$ that had developed from sintered powder compacts transformed upon extended annealing times into $\epsilon$-Ti$_2$N.

In order to obtain more insight into the reactions occurring at comparably low temperatures and to determine the phase character and composition range of $\delta'$-TiN$_{1-x}$, the present study was performed utilizing temperature
gradient diffusion couples (TGDCs), *i.e.* diffusion couples annealed in a temperature gradient which was perpendicular to the diffusion direction of nitrogen.

The potential of this technique to detect not only phase equilibria but order–disorder reactions as well was discussed recently [9]. With this technique it should in principle be possible to observe these transformations simultaneously as a function of temperature and composition. Suitable metallographic techniques that make the effects of transformation observable (polarized light, etching behaviour) are available. An additional variable, time, was introduced in the TGDC method in order to study the kinetics of transformation.

2. Experimental details

*In situ* TiN–Ti diffusion couples were prepared by reaction of titanium sheet 1 mm thick and nitrogen at 1593 K for 40 and 50 h. Cross-sectional studies show that under these conditions the sheet consists of $\delta$-TiN$_{1-x}$ with a small $\alpha$-Ti(N) core (after 40 h) or the complete cross-section has transformed to $\delta$-TiN$_{1-x}$ (after 50 h). This treatment leads to minimum nitrogen contents of $\delta$-TiN$_{1-x}$ at the $\delta$–$\alpha$ boundary (after 40 h) or in the centre of the sample (after 50 h) which are located between 31 and 32 at.% N. A surface concentration of 50 at.% N is achieved in either case. However, cooling to room temperature within about 2 min caused formation of $\epsilon$-Ti$_2$N in the centre (Fig. 1(a)). In order to re-establish and to "freeze in" the original state prevailing at high temperatures, the samples were reheated at 1573 K for 1 h in sealed silica tubes and water quenched (Fig. 1(b)). This procedure is necessary to avoid the formation of any phase nuclei that could adversely affect the transformation behaviour at low temperatures.

After this procedure the silica tubes were placed in a furnace with SiC heating elements in which the temperature distribution was appropriately

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Fig. 1. Titanium sheet nitrided for 50 h at 1593 K. (a) Microstructure of the sample as obtained after nitridation. The $\epsilon$-Ti$_2$N phase can be seen in the core. (b) Microstructure after re-annealing and quenching, confirming the presence of only $\delta$-TiN$_{1-x}$ at the nitridation temperature.
adjusted. An experimental set-up is given in ref. 9. Several different annealing times with the same temperature gradient were chosen in order to detect any time dependence of the $\delta'$ phase formation and decomposition. The temperature gradient was measured just before and just after sample annealing. The temperature $vs.$ distance functions differed by at most 4 K before and after annealing. Because of this slight change in temperature distribution of the SiC furnace during long annealing times, the temperature $vs.$ distance functions obtained just after quenching were taken as the true functions (Fig. 2).

Isothermal diffusion couples were prepared in generally the same way but in a furnace zone with a uniform temperature distribution.

The diffusion couples were embedded in cold-setting resin and diamond polished. For the measurement of the composition across the couples a Cameca Camebax SX 50 microprobe was used. The N Ka+Ti Li doublet as well as the Ti Kα line were measured and calibrated against external standards using a standardization routine described elsewhere [10]. A total of 16 line scans were recorded from the TGDCs, each corresponding to a single temperature. Approximately 200 data points were recorded within each scan in the step scan mode (5 μm step width) with a counting time of 10 s.

3. Results and discussion

3.1. XRD and microstructures

XRD measurements on an isothermal diffusion couple (10×8×1 mm$^3$ in size) annealed for 15 h at 990 K confirmed the presence of $\delta'$-TiN$_{1-x}$. Figure 3 shows the characteristic diffraction lines which appear when the nitrogen-rich $\delta$-TiN$_{1-x}$ diffusion layer is successively removed by abrasive grinding. The corresponding microstructure is shown in Fig. 4. Similar metallographic observations were made by Bars et al. [11]. The hatched appearance is characteristic for the transformation reaction of f.c.c. $\delta$-TiN$_{1-x}$ to tetragonal $\delta'$-TiN$_{1-x}$. It can be seen from Fig. 3 that within the hatched
area single-phase \( \delta'\text{-TiN}_{1-x} \) prevails (the small remaining \( \delta\text{-TiN}_{1-x} \) peak stems from the sample edges). Microstructures of nearly identical appearance develop in the system Nb–N, where the cubic-to-tetragonal transition \( \delta\text{-NbN}_{1-x} \rightarrow \delta\text{-NbN}_{3/2} \) was shown to be of second order [12, 13]. At the nitrogen-poor side of \( \delta'\text{-TiN}_{1-x} \), \( \epsilon\text{-Ti}_2\text{N} \) is formed upon low temperature annealing (Fig. 4).

When the diffusion couples were re-annealed in a temperature gradient, the temperature regions in which \( \delta\text{-TiN}_{1-x} \) transforms into \( \delta'\text{-TiN}_{1-x} \) could be read directly from the microstructures. Portions of the microstructure of a TGDC annealed for 3 h are shown in Figs. 5a–5d. The hatched structure is uniform in appearance in the entire temperature range in which \( \delta\text{-TiN}_{1-x} \) transforms into \( \delta'\text{-TiN}_{1-x} \). The maximum temperature at which \( \delta'\text{-TiN}_{1-x} \) was observed was 1153 K. It appears that the transformation temperature is somewhat lower for higher nitrogen content since the width of the hatched area becomes narrower with increasing temperature on the nitrogen-rich side.

At temperatures above the critical formation temperature of \( \delta'\text{-TiN}_{1-x} \) an \( \epsilon\text{-Ti}_2\text{N} \) phase is formed within \( \delta\text{-TiN}_{1-x} \). At compositions with more than 33.3 at.
\% N the reaction is \( \delta\text{-TiN}_{1-x} \rightarrow \epsilon\text{-Ti}_2\text{N} + \delta\text{-TiN}_{1-y} \), where \( y < x \). Because
Fig. 5. Microstructures of a portion of the temperature gradient diffusion couple annealed for 3 h (at selected temperatures).

Fig. 6. Tentative TTT diagram valid for 33.3 at.% N (x = 0.50, y = 0.46, z = 0.54) showing the transformation of $\delta'$-TiN$_{1-x}$ (solid line) as observed by TGDCs (compact samples). The broken lines reflect the transitions only qualitatively.

of the intergrowth of $\epsilon$-Ti$_2$N and $\delta$-TiN$_{1-x}$, this $\epsilon$-Ti$_2$N has an acicular texture (Fig. 5a) as opposed to the $\epsilon$-Ti$_2$N formed in the core of the sample. If the temperature is low enough for the $\delta'$-TiN$_{1-x}$ phase to form, then no $\epsilon$-Ti$_2$N phase can be observed within the $\delta$-TiN$_{1-x}$ phase and the core $\epsilon$-$\delta'$ boundary
remains straight without any detectable acicular ε-Ti₂N (Figs. 5b–5d). Obviously the direct formation of ε-Ti₂N from δ'-TiN₁₋ₓ (δ-TiN₀.₅₀ → ε-Ti₂N or δ-TiN₁₋ₓ → ε-Ti₂N + δ-TiN₁₋ₙ for x < 0.50) does not take place when the concentration and temperature are such that δ'-TiN₁₋ₓ is formed. This fits excellently into the previously observed [7, 8] phase formation sequence δ-TiN₀.₅₀ → δ'-TiN₀.₅₀ → ε-Ti₂N at 973 K, where the second step sets in only after the entire sample has been transformed into δ'-TiN₀.₅₀ [8]. In other words, below the critical temperature of about 1153 K the transformation δ-TiN₀.₅₀ → ε-Ti₂N proceeds via δ'-TiN₁₋ₓ and above this temperature directly, without formation of the δ' phase.

When the annealing time was increased, δ'-TiN₁₋ₓ transformed into ε-Ti₂N + δ-TiN₁₋ₙ (or into ε-Ti₂N for x = 0.50) with a corresponding decrease in the maximum temperature of appearance. This confirms the metastable character of δ'-TiN₁₋ₓ. The values of the decomposition of δ'-TiN₁₋ₓ obtained by applying different annealing times for the TGDCs were introduced in the TTT diagram shown in Fig. 6.

3.2. Electron probe microanalysis (EPMA)

Since TGDCs make possible a direct relationship between the concentration (or activity) of the diffusion species on the one axis and the temperature on the other perpendicular to it, by using EPMA a direct conversion of the TGDC microstructures into a phase diagram is possible. Two representative EPMA scans across the layers at the corresponding temperatures are shown in Fig. 7. Above the occurrence region of δ'-TiN₁₋ₓ the nitrogen profile shows a certain amount of scatter (Fig. 7(a)) in the region where acicular ε-Ti₂N is observed in the microstructure (the distinct α-Ti(N)–ε-Ti₂N discontinuity in the core, which is also visible, plays no role here). This scatter is due to the presence of an ε-Ti₂N–δ-TiN₁₋ₓ mixture in this region, which is created by a first-order phase reaction (leading to a concentration discontinuity). In contrast, for temperatures at which δ'-TiN₁₋ₓ occurs, a smooth nitrogen profile without any discontinuity or scatter could be observed (Fig. 7(b)). It is clear that the usual concentration discontinuities (a single clear “jump”) observed in diffusion couples (see e.g. ref. 14) may not necessarily be observed here even for a first-order reaction, since a sample reflecting a high temperature state (with δ-TiN₁₋ₓ existing down to approximately 31 at.% N) is re-annealed at comparably very low temperatures, where several phases may form within what was previously δ-TiN₁₋ₓ. However, as the EPMA data scatter for the ε-Ti₂N–δ-TiN₁₋ₓ region show, at least a deviation from a smooth profile should be observed due to the precipitation of one phase into the other, even in the present case of very low nitrogen diffusivity. However, neither scatter nor any deviation from a smooth profile was observed for either side of the δ'-TiN₁₋ₓ phase region at any temperature, which is thus further evidence that δ'-TiN₁₋ₓ is not formed by a first-order phase reaction. This conclusion is supported by the fact that the metallographic appearance of δ'-TiN₁₋ₓ is uniform at the nitrogen-poor and nitrogen-rich boundaries without perceptible precipitation structure.
Fig. 7. EPMA scans of a temperature gradient diffusion couple. (a) Above the formation temperature of $\delta'$-TiN$_{1-x}$ (sample contained an $\alpha$-Ti(N) core). $\epsilon$-Ti$_2$N--$\delta$-TiN$_{1-x}$ precipitates formed in a first-order reaction scattered the EPMA data (concentration differences). (b) Below the formation temperature of $\delta'$-TiN$_{1-x}$ (sample contained no $\alpha$-Ti(N) core). No discontinuity or scatter in the nitrogen profiles could be observed. No significant differences between the profiles measured at different temperatures were observed.

Fig. 8. $c$--$T$ diagram showing the region of the $\delta$-TiN$_{1-x}$$\rightarrow$$\delta'$-TiN$_{1-x}$ transition for three different annealing times. Phase fields with stable phases are encircled. At the lower left the error bar of the concentration width for $\delta'$-TiN$_{1-x}$ is given.

The data of the EPMA scans where $\delta'$-TiN$_{1-x}$ was present were fitted by a second-order polynomial equation (after excluding the data points of the $\alpha$-Ti(N) core, where present) to yield the nitrogen concentration vs. position of the occurring phases at a corresponding temperature. The $R$ factor 100(at.% $N_{\text{obs}}$)/(at.% $N_{\text{calc}}$)/at.% $N_{\text{obs}}$, indicative of the goodness of fit, was always less than 2% and in most cases less than 1.5%. The absolute accuracy is about $\pm$ 1 at.% N and the accuracy of the width of the occurrence region of $\delta'$-TiN$_{1-x}$ is better than $\pm$ 0.5 at.% N. Within these limits the nitrogen profiles for the temperatures at which $\delta'$-TiN$_{1-x}$ was observed were identical.

The diagram in Fig. 8 shows the regions of (co)existence of the stable phases $\epsilon$-Ti$_2$N and $\delta$-TiN$_{1-x}$ and the occurrence of $\delta'$-TiN$_{1-x}$ from $\delta$-TiN$_{1-x}$ for three different annealing times. $\delta'$-TiN$_{1-x}$ occurs immediately in the two-phase field $\epsilon$-Ti$_2$N and $\delta$-TiN$_{1-x}$. The diagram was constructed on the assumption that the $\epsilon$-Ti$_2$N structure can accommodate a maximum occupancy of 33.3 at.% N (the EPMA data were scattered around this value).
3.3. In situ diffusion process

A further way to decide whether the formation of $\delta'$-TiN$_{1-x}$ is a first-order reaction by concentration measurements would be to prepare the $\delta'$-TiN$_{1-x}$ phase via a diffusion process at a temperature at which it would be expected to form. $\epsilon$-Ti$_2$N, $\delta'$-TiN$_{1-x}$ and $\delta$-TiN$_{1-x}$ should then be separated by a concentration step if the phase reaction were of first order. However, several peculiarities make the investigation of such diffusion couples difficult: (1) the nitrogen diffusivity at these temperatures is so low that the microstructures of the diffusion layers would be difficult to observe in light optical microscopes; (2) EPMA is not applicable for such thin layers; (3) $\delta'$-TiN$_{1-x}$ is metastable and probably ceases to exist long before appropriate layer thicknesses are achieved.

In order to obtain experimental information concerning these points, two isothermal diffusion experiments were carried out by reacting titanium sheets at 1023 K with 7.5 bar N$_2$ for 330 and 1464 h. Figure 9 shows that although the annealing time was extensive, the layers formed in this diffusion couple are very thin. The $\delta$ phase could be made visible metallographically in the microstructure only by a 30° inclined cut, but the layers were much too thin to be able to observe any substructure (hatchings) in polarized light. XRD measurements from the as-reacted surface showed the presence of $\epsilon$-Ti$_2$N and $\delta$-TiN$_{1-x}$ only but no $\delta'$-TiN$_{1-x}$, thus confirming the metastable character in an independent experiment. These diffusion couples were not suited for investigation with EPMA. This result is also valid for higher temperatures (where $\delta'$-TiN$_{1-x}$ still exists), since the increase in thickness of $\delta$-TiN$_{1-x}$ when going from 1073 to 1173 K is less than 5% [15].

As the present results show, $\delta'$-TiN$_{1-x}$ is not formed at low temperatures. The occurrence of this phase is obviously causally connected with the presence of $\delta$-TiN$_{1-x}$ having a composition of 33.3–37.5 at.% N (0.50 $\geq$ $x$ $\geq$ 0.40) and not from a phase reaction $\epsilon$-Ti$_2$N + $\delta$-TiN$_{1-x} \rightarrow \delta'$-TiN$_{1-x}$ as the literature [4, 6] suggests.

Fig. 9. Microstructure of an in situ diffusion couple prepared at 1023 K for 1424 h. Only $\alpha$-Ti(N), $\epsilon$-Ti$_2$N and $\delta$-TiN$_{1-x}$ could be observed (confirmed by XRD).
4. Conclusions

It has been shown that the TGDC technique has significant potential as an efficient method for the otherwise time-consuming investigation of the ordering reaction within a compound as a function of both temperature and composition. By applying different annealing times, it was also possible to determine a time dependence of the reaction $\delta'-\text{TiN}_{1-x} \rightarrow \epsilon-\text{Ti}_2\text{N}$. The microstructural appearance and the absence of concentration discontinuities or scatter at either side of the $\delta'$-TiN$_{1-x}$ region suggest that the formation of $\delta'$-TiN$_{1-x}$ is not first order.

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