THE Ti-C-N SYSTEM AND PROPERTIES OF Ti(C,N)

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Abstract

The hard constituents in *cermet* cutting tools are based on titanium carbonitrides. In order to gain more insight in the Ti-C-N system the phase diagram of the Ti-C-N system was established and single-phase samples of compact carbonitrides were prepared by hot pressing and various of their properties investigated.

Temperature conductivities of titanium carbonitrides were measured in the range 25 - 1400°C by the laser-flash method. Using the specific heats obtained by differential scanning calorimetry, the heat conductivities could be calculated. The nitrides generally had a higher heat conductivity than the carbides. In the region of solid solution between nitride and carbide the heat conductivity decreased steadily with increasing carbon content. Vickers microhardness values at a load of 0.98 N were measured and showed a positive deviation from the addition rule.

Diffusion couples $Ti(C_xN_{1-x})_{1.00}$/liquid Ni were prepared in order to study the interaction between titanium carbonitrides and liquid nickel. By EPMA measurements a quantification of this interaction was possible.

1 Introduction

Although Ti(C,N) is of substantial interest for technological applications in cermets [1] systematic experimental investigations necessary to establish a phase diagram of the Ti-C-N system have not been performed. Stone [2] investigated the metal-rich part of the system and constructed isothermal sections for temperatures between 800 and 1300°C. Teyssandier et al. [3] calculated a complete isothermal section for 1400°C. A number of studies have dealt with the investigation of the thermodynamic properties of $Ti(C_xN_{1-x})_{1.0}$ [4-7]. Generally, there is a lack of information on the physical properties of $Ti(C_xN_{1-x})$. The electrical conductivities have been investigated for several $Ti(C_xN_{1-x})_{1.0}$ compounds [8]. Existing microhardness data scatter considerably [9,10], and no studies on the thermal conductivity could be found in the literature. This study was performed performed in order to establish a phase diagram for the Ti-C-N system, to systematically investigate the

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properties of $Ti(C_xN_{1-x})_{1.0}$, and to reinvestigate properties for which the literature values are too scattered to be considered as reliable.

2 Experimental

TiC, TiN and Ti powders of various grain sizes were mixed and arc melted under Ar. They were then sealed in silica capsules under Ar, heat treated for two weeks at 1150°C and water quenched.

For the preparation of hot-pressed samples TiC, TiN and Ti powders were mixed in a planetary mill under cyclohexane, dried and filled into the graphite die of the hot press. Between sample powder and graphite a 25μm Zr foil was placed in order to impede carbon diffusion into the samples. After flushing the hot press with Ar the temperature and pressure were increased up to 2500°C and 55 MPa respectively. These conditions were kept constant for 5 minutes, and then the samples were cooled to room temperature. The zirconium carbide scale was completely removed from the samples by grinding with a diamond disc.

$Ti(C_xN_{1-x})_{1.0}$/liquid Ni diffusion couples were prepared by embedding hot-pressed carbonitride pieces in Ni powder in an alumina crucible. Coarse grained alumina was placed onto the bottom of the crucible in order to prevent the nickel melt from sticking to the crucible wall. The samples were heated to 1500°C within 15 minutes in a pure Ar atmosphere. The ramp time at this temperature was 20 min.

Compact hot-pressed carbonitride samples were chosen to make it easier to observe the interaction of molten nickel with the titanium carbonitride than is possible with fine-grained carbonitride and nickel powder mixtures used for cermet production. In addition, EPMA, an exceptionally most powerful quantitative microanalytical technique, can be applied to characterize this interaction. This is impossible when typical cermet starting materials are used [11] because of the restricted lateral resolution.

3 Sample Characterization

The samples were ground with a diamond disk (20μm) followed by SiC paper (2500 mesh). Polishing was performed first with 3μm diamond paste then with an aqueous silica suspension. The Vickers microhardness HV was measured at a load of 0.98 N. Usually about 10-15 indentations were made on each sample, and the mean value and the standard deviation were calculated. Density measurements were made by with $CHBr_3$ as an immersion liquid and a thin steel wire to a suspend the sample. XRD was performed with Ni-filtered Cu-K_α radiation or by use of a secondary graphite monochromator. Fine mortar-ground powders were used as well as compact samples, the latter being mounted on a rotating sample holder.

Chemical analysis was performed for nitrogen and carbon using Dumas gas-chromatography. V_2O_5 was used as a combustion booster. The obtained peak areas of the gas chromatograms were calibrated with standards. A detailed description of the setup and procedure is given in [12].

EPMA was performed at the IFREMER Brest, France, with a CAMECA SX 50 microprobe, equipped with four wavelength-dispersive spectrometers. Samples of $Ti(C_xN_{1-x})_{1.0}$ and Ni-Ti alloys served as standards. Due to the coincidence of the Ti-L_l and the N-K_α lines nitrogen was determined as the balance of the concentrations of carbon, titanium and nickel.

From the hot-pressed samples discs 1mm thick and 5 or 10 mm in diameter were machined with a hollow diamond drill bit. The larger discs were used for thermal diffusivity measurements by the laser-flash method the smaller discs were used for heat capacity measurements by DSC.

4 Results and discussion

4.1 Phase equilibria

Fig.1 shows an isothermal section of the Ti-C-N system at 1150^{o}C based on the analysis of heat-treated arc-melted buttons and heat-treated hot-pressed samples. The phase diagram is consistent with the thermodynamic calculations of Teyssandier et al.[3].

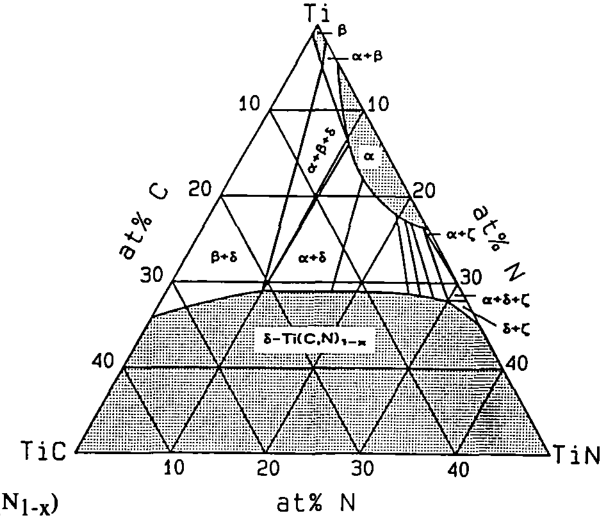

Fig.1
Phase diagram of the
Ti-C-N system (1150^{o}C)

4.2 Properties of δ-Ti(C_xN_{1-x})

4.2.1 Microhardness

The microhardness of Ti(C,N)$_{1.00}$ decreased in a nearly linear manner from TiC to TiN with a small positive deviation from an additive behavior (Fig.2). This positive deviation was also observed in substoichiometric samples Ti(C,N)$_{0.82}$. In the latter case the hardness curve is less steep due to the fact that the hardness decreases in δ-TiC$_{1-x}$ with decreasing C content [13,14] but increases in δ-TiN$_{1-x}$ with decreasing N content [15]. Apparently, the hardness of δ-Ti(C,N)$_{1-x}$ is an almost linear function of both the [C]/([C]+[N]) and the [Ti]/([C]+[N]) ratios.

4.2.2 Thermal diffusivity

Fig.3 shows the thermal diffusivities of stoichiometric Ti(C_xN_{1-x}). TiN had the highest thermal diffusivity and it can be seen that a 20% nitrogen replacement by carbon drastically reduced the thermal diffusivity. After this decrease the diffusivity decreased much less with increasing carbon content and the data are within the error limits (about 8%).

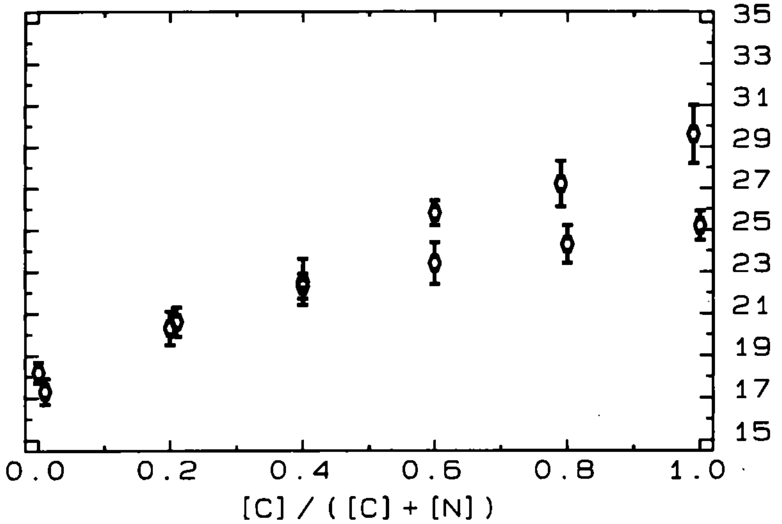

Fig.2
Microhardness $HV_{0.1}$ (load:0.98 N) of $Ti(C_xN_{1-x})_{1.00}$ and $Ti(C_xN_{1-x})_{0.82}$ as a function of the [C]/([C]+[N]) ratio.

The thermal diffusivity of substoichiometric $Ti(C_xN_{1-x})$, i.e. $Ti(C_xN_{1-x})_{0.82}$, was much lower than that of the stoichiometric samples. At high temperatures (T = 500-1400°C) the thermal diffusivity decreased from $TiN_{0.82}$ to $TiC_{0.82}$. At low temperatures the sequence was reversed and $TiC_{0.82}$ had the highest thermal diffusivity.

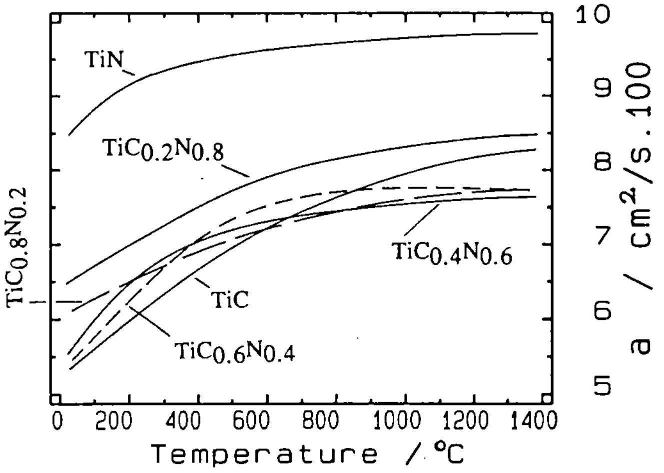

Fig.3
Thermal diffusivity of $Ti(C_xN_{1-x})_{1.0}$

4.2.3 Heat capacity

The molar heat capacity (Fig.4) increased slightly with increasing nitrogen content of $Ti(C_xN_{1-x})_{1.0}$. These samples showed a slightly higher heat capacity than samples with the composition $Ti(C_xN_{1-x})_{0.82}$. The latter showed a marked jump in C_p at 700-800°C which would be indicative of a phase transition in this temperature region. It should be investigated whether this phenomenon is reversible and/or repeatable. XRD patterns of the sample at room temperature did not give any indication of such a phase transition.

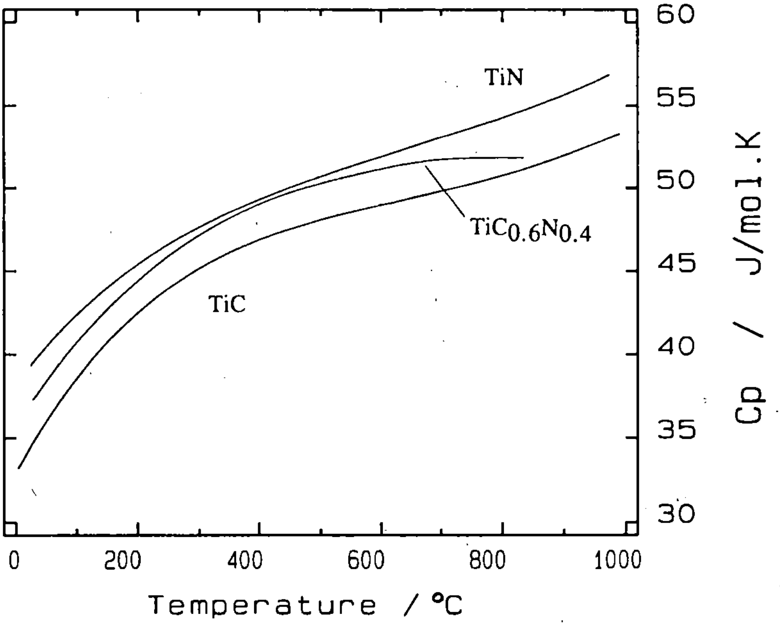

Fig.4
Molar heat capacity of TiC, TiN and $TiC_{0.6}N_{0.4}$

4.2.4 Heat conductivity

The data sets of thermal diffusivity and heat capacity were interpolated and used to calculate the thermal conductivity. It was assumed that in the $Ti(C_xN_{1-x})_{1.00}$ lattice the Ti and C+N sites were 100% occupied. Therefore X-ray densities were taken. The thermal expansion, which would cause a reduction in the density with increasing temperature, was neglected because the error is less than 3%. Fig.5 shows the heat conductivities of $Ti(C_xN_{1-x})_{1.00}$ and $Ti(C_xN_{1-x})_{0.82}$.

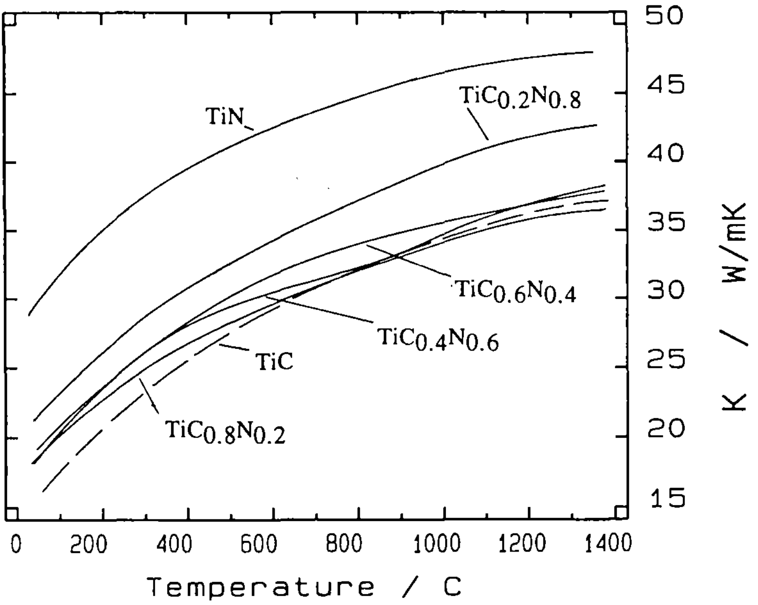

Fig.5
Heat conductivity of $Ti(C_xN_{1-x})_{1.0}$

4.2.5 Reaction of compact $Ti(C_xN_{1-x})_{1.0}$ with liquid nickel

Fig.6 shows the micrographs of the 6 different samples that were subjected to the action of liquid nickel. Liquid Ni penetrated along the grain boundaries of the carbonitride where the reaction proceeded to the center of the carbonitride grains. Carbon or TiC is preferentially dissolved by liquid Ni so that the reacted carbonitride contained significantly more nitrogen that the unreacted part. Interestingly, the original grain boundary structure of the carbonitride samples appeared to be retained in the microstructure of the reacted zone. The penetration depth of liquid Ni was the greater the higher the carbon content in the carbonitride. The original carbonitride grains were attacked by the nickel melt in such a way that the crystallites were broken up into smaller carbonitride grains which were significantly richer in nitrogen than the original hot-pressed carbonitride. Often the carbonitride formed via the liquid phase featured rectangular or triangular facetted crystallites. The more nitrogen the carbonitride contained the more globular were the precipitates.

Because Ni reacted more intensively with $Ti(C_xN_{1-x})_{1.0}$ with high carbon contents, the grain boundaries where Ni had penetrated the carbonitride changed structure as a function of the [N]/[C] ratio. At high carbon contents (see $TiC_{0.8}N_{0.2}$ and $TiC_{0.6}N_{0.2}$) the nickel canals were wide and the particles of the reacted carbonitride were located mainly within the nickel phase. The more nitrogen the carbonitride contained the narrower were the nickel intergrain canals and the original carbonitride grains appeared to have a rim with a higher nitrogen content. This was very pronounced in the $Ti(C_{0.2}N_{0.8})$ sample where the intergrain boundary consisted mainly of reacted $Ti(C_xN_{1-x})_{1.0}$ and only of very small Ni canals in comparison to $Ti(C_{0.8}N_{0.2})$, where a large Ni content was observed.

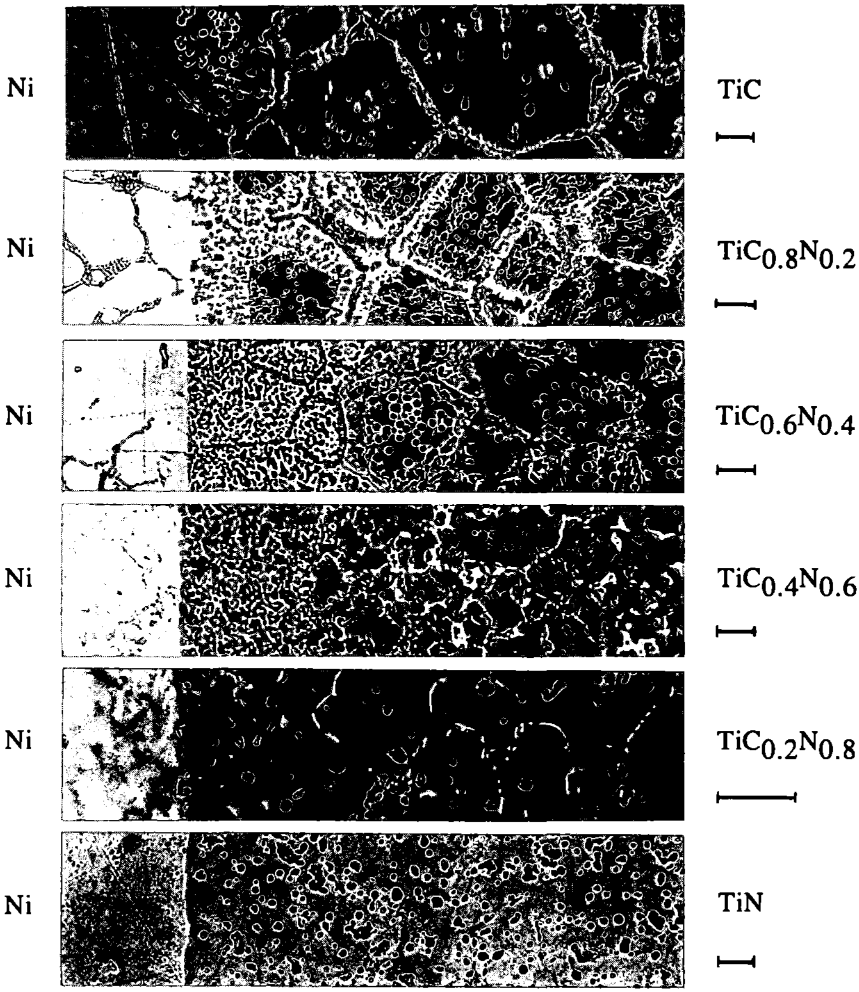

Fig.6
Microstructure of Ni/TiC_xN_{1-x} diffusion couples (the bar corresponds to 20μm).

As a first approach, for the nitrogen-rich carbonitride grades the color change as a function of the carbon/nitrogen ratio could well be used for an optical estimation of the [C]/([C]+[N]) shift upon reaction with Ni. Further quantitative information was obtained by EPMA. For all the investigated $Ni/Ti(C_xN_{1-x})_{1.0}$ diffusion couples the [N]/[C] ratio between the reacted and the unreacted carbonitride phase differed by a factor of 2-2.5. This is shown in Fig.7 for the sample $Ti(C_{0.2}N_{0.8})_{1.00}$.

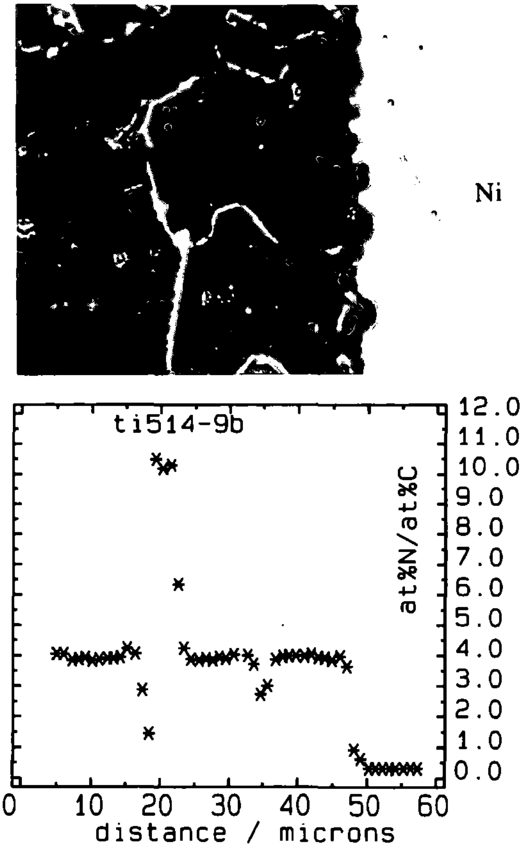

Fig.7
Microprobe scan across the interface of a Ni/$TiC_{0.2}N_{0.8}$ diffusion couple. The differences in composition between reacted and unreacted carbonitride can be seen.

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