



# Reaction of compact carbonitrides with liquid binder metals

P. Wally<sup>1</sup>, S. Binder, P. Ettmayer, W. Lengauer

*Institute for Chemical Technology of Inorganic Materials, Vienna University of Technology, Getreidemarkt 9/161, A-1060 Vienna, Austria*

Received 7 April 1995

## Abstract

In order to gain insight into the metallurgical interactions between the carbonitrides of the transition metals and binder metals during the liquid phase sintering of cermet cutting tools, contact reactions of liquid nickel and also of nickel/cobalt with compact hot-pressed polycrystalline Ti(C,N), (Ti,Mo)(C,N), (Ti,W)(C,N) and (Ti,W,Mo,Ta,Nb)(C,N) samples were investigated. It was found that the carbide components of the carbonitride solid solutions are preferentially dissolved by the liquid metal, to the extent that the reacted zones of the carbonitride specimens contained significantly more nitrogen than the bulk carbonitride. This phenomenon is probably due to a dissolution and reprecipitation process. With the Mo and/or W containing samples higher reaction rates with the liquid metals were observed, presumably owing to enhanced interactions arising from the presence of readily soluble molybdenum and tungsten carbide in the carbonitride solid solution.

*Keywords:* Titanium carbonitride; Cermet; Binder phase; Interaction

## 1. Introduction

The interaction of titanium carbonitrides with liquid ferrous metals has not been investigated until recently. Ozturk [1] studied the thermodynamics of inclusion formation in Fe–Ti–C–N alloys and Binder et al. [2] have carried out contact reaction experiments on Ti(C<sub>x</sub>N<sub>1-x</sub>)/Ni (liq.) samples. On the other hand the boundary systems TiC–M (M = Fe, Co, Ni) are well known [3] and the system TiN–Ni was subjected recently to revision [4]. The Ti–C–M systems show binary eutectic reactions TiC + M, with eutectic temperatures located about 100–170°C below the melting point of the metal and the eutectic composition located at around 10 mol% TiC. At lower temperatures (with the exception of the system Fe–Ti–C) the monocarbide TiC<sub>1-x</sub> is in equilibrium with solid solutions of Ti (+C) in the ferrous metal within a significant part of its composition range and the solid solubility of Ti in the metal is a function of the carbon content in TiC<sub>1-x</sub>. Mo<sub>2</sub>C and WC are even more soluble than TiC<sub>1-x</sub> in nickel and cobalt melts. The

pseudobinary eutectic points are located at 32 mol% in the Mo<sub>2</sub>C–Ni and Mo<sub>2</sub>C–Co systems and at 13 and 20 mol% in the WC–Ni and WC–Co systems respectively [5]. Titanium nitride does not lower the melting point of nickel substantially, and a quasi-binary eutectic point liquid → Ni(ss) + TiN should be located at compositions very close to the nickel corner. On the basis of these boundary systems the results of Ozturk on the phase equilibria between the carbonitrides and liquid and solid iron can be extended to other systems, such as those involving Ni and Co. The ferrous metals Ni and Co, too, will be in equilibrium with Ti(C,N), whereby the composition of the carbonitride will determine the composition of the liquid metal phase together with the nitrogen partial pressure in the atmosphere at any given temperature.

In the experiments performed by Binder et al. [2], fully dense Ti(C,N) compacts were reacted with liquid nickel at a temperature of 1500°C. It was found that nickel reacted more intensively with Ti(C,N) of high carbon contents. As can be seen in Fig. 1, the nickel melt penetrated along the grain boundaries into the Ti(C,N) compact, and it dissolved preferentially the TiC component, leading to undissolved Ti(C,N) with a remarkably higher nitrogen content than the starting material. The reaction periods were kept short so that overall thermodynamical equilibrium was not reached.

<sup>1</sup>Present address: Advanced Technology Research Laboratories, Nippon Steel Corporation, 1618 Ida, Nakahara-ku, Kawasaki 211, Japan.

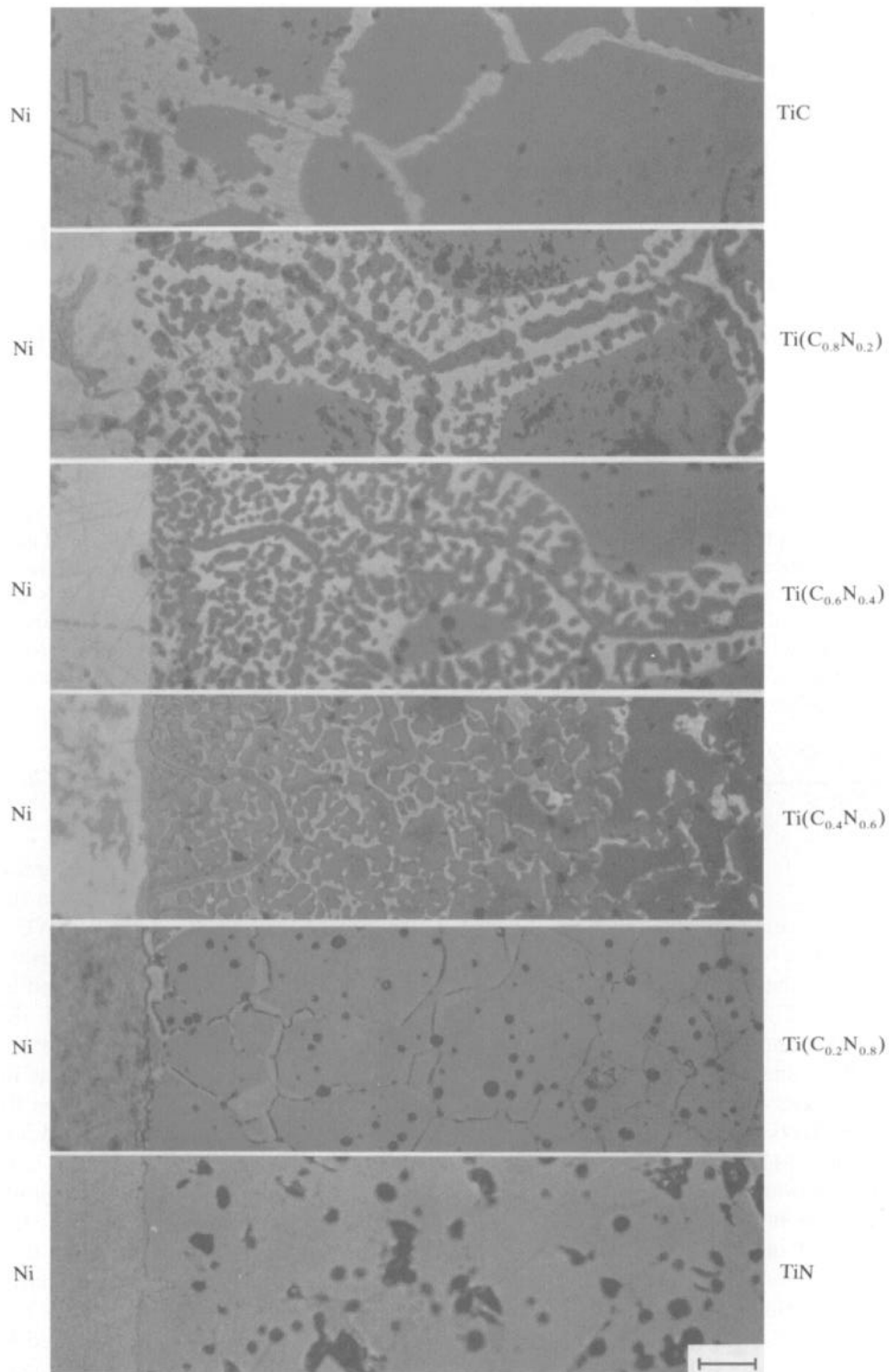


Fig. 1. Microstructure of the  $\text{Ti}(\text{C}_x\text{N}_{1-x})/\text{Ni}$  (liq.) contact reactions (the bar corresponds to  $20\ \mu\text{m}$ ).

It was possible to observe instead the onset of the reaction of the carbonitrides with the binder metals in order to obtain information about the reaction mechanisms in such composites.

## 2. Experimental

$\text{Ti}(\text{C}_x\text{N}_{1-x})$  compacts with compositions  $x = 0, 0.2, 0.4, 0.6, 0.8$  and  $1$  were prepared by hot pressing

Table 1  
Composition of the samples in the contact reactions

Sample	Composition of hard materials	Recting metal melt
GA	$(\text{Ti}_{0.85}\text{Mo}_{0.15})(\text{C}_{0.62}\text{N}_{0.38})_{1.003}$	Ni
GB	$(\text{Ti}_{0.8}\text{Mo}_{0.2})(\text{C}_{0.79}\text{N}_{0.21})_{0.989}$	Ni
GX	$(\text{Ti}_{0.8}\text{Mo}_{0.2})(\text{C}_{0.83}\text{N}_{0.17})_{0.975}$	Ni
LB	$(\text{Ti}_{0.8}\text{Mo}_{0.2})(\text{C}_{0.71}\text{N}_{0.29})_{0.967}$	Ni
HP2	$(\text{Ti}_{0.8}\text{Mo}_{0.2})(\text{C}_{0.55}\text{N}_{0.45})_{0.926}$	Ni
HP3	$(\text{Ti}_{0.8}\text{Mo}_{0.2})(\text{C}_{0.32}\text{N}_{0.78})_{0.861}$	Ni
HP4A	$(\text{Ti}_{0.8}\text{Mo}_{0.2})\text{C}_{0.945}$	Ni
HP4B	$(\text{Ti}_{0.8}\text{Mo}_{0.2})\text{C}_{0.975}$	Ni
HP6	$(\text{Ti}_{0.91}\text{W}_{0.09})(\text{C}_{0.62}\text{N}_{0.38})_{1.002}$	Ni
HP15	$(\text{Ti}_{0.79}\text{W}_{0.09}\text{Mo}_{0.07}\text{Ta}_{0.04}\text{Nb}_{0.01})(\text{C}_{0.76}\text{N}_{0.24})_{0.972}$	Ni/Co(40/60)
HP25	$(\text{Ti}_{0.85}\text{W}_{0.10}\text{Ta}_{0.04}\text{Nb}_{0.01})(\text{C}_{0.60}\text{N}_{0.40})_{1.011}$	Ni/Co(50/50)

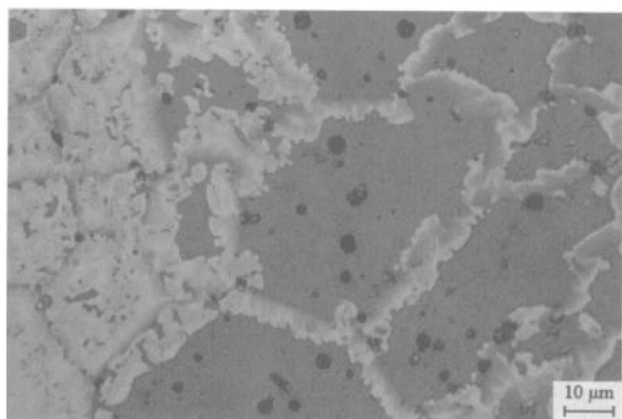


Fig. 2. Penetration of Ni in the contact reaction  $\text{Ti}(\text{C}_{0.4}\text{N}_{0.6})/\text{Ni}$  showing the irregular faceted appearance of the N-rich precipitates at the grain boundaries.

TiC + TiN mixtures at  $\sim 2400^\circ\text{C}$ . Quaternary  $(\text{Ti},\text{Mo})(\text{C},\text{N})$  and  $(\text{Ti},\text{W})(\text{C},\text{N})$  compacts were prepared from pre-alloyed powders supplied by H.C. Starck, Germany, by hot pressing at  $\sim 2000^\circ\text{C}$  and the  $(\text{Ti},\text{W},(\text{Mo}),(\text{Ta}),(\text{Nb}))(\text{C},\text{N})$  samples were prepared from the respective carbides plus titanium nitride and graphite under the same conditions. A piece of each sample was embedded in nickel powder (or a nickel–cobalt mixture; see Table 1) contained in an alumina crucible and heated to  $1500^\circ\text{C}$  with a heating rate of  $25^\circ\text{C min}^{-1}$  in an Ar atmosphere. After reaching the vertex temperature a ramp time of 20 min was set. It was observed that all the samples containing Mo and/or W had reacted completely after 20 min, making the investigation of the reaction zone between melt and carbonitride impossible. Therefore, after having reached  $1500^\circ\text{C}$  the samples were immediately cooled down, which led to satisfactory results. Sections of the samples were investigated by optical and electron microscopy, and energy dispersive spectrometry (EDS) was used to determine the metal contents in the

carbonitrides and the solidified metal melt. In the  $\text{Ti}(\text{C},\text{N})\text{--Ni}$  samples wavelength-dispersive analysis by electron probe microanalysis (EPMA) was additionally used to determine the  $[\text{N}]/[\text{C}]$  ratio across the interface.

### 3. Results and discussion

The reaction of Ni with  $\text{Ti}(\text{C},\text{N})$  is shown in Fig. 1. The metal melt penetrated along the grain boundaries, separating the crystallites. The extent of this reaction can be observed to be greater the higher the carbon content of the carbonitride. Apparently, TiC is preferentially dissolved from the crystallite periphery, leading to a nitrogen-enriched rim around the unreacted bulk. This rim can be distinguished in optical microscopy because of the typical yellow color of TiN, appearing as a darker border in Fig. 2. Because of the particular microstructural feature of this nitrogen-rich rim, the nitrogen-enrichment is presumed to proceed in two steps: the carbonitride is dissolved by the liquid nickel, forming a solution supersaturated with respect to TiN and hence, because of the low solubility of TiN, a nitrogen-rich carbonitride  $\text{Ti}(\text{C},\text{N})$  precipitates around adjacent crystallites that serve as nuclei. Evidence of this can be observed by the faceted appearance of the TiN-rich rim. The reprecipitation of  $\text{Ti}(\text{C},\text{N})$  is triggered apparently by locally favorable conditions such as interfacial tension or contamination, and thus apparently forms only on one side of the nickel melt that had been penetrated between two  $\text{Ti}(\text{C},\text{N})$  grains.

Because of the higher reaction rate of liquid Ni with carbon-rich  $\text{Ti}(\text{C},\text{N})$  samples, the nickel melt reacts not only by penetrating into the carbonitride along the grain boundaries, but also by attacking the crystallites. Thus the crystallites are broken up into smaller carbonitride grains, which were significantly richer in nitrogen than the original hot-pressed carbonitride.

Fig. 3 shows an EPMA scan across a nitrogen-enriched crystallite of a Ti(C,N) sample. The color difference between bulk and precipitates is in agreement with the measurement of the  $[N]/[C]$  ratio (TiN: gold color  $\rightarrow$  Ti(C<sub>0.2</sub>N<sub>0.8</sub>): violet color  $\rightarrow$  Ti(C<sub>0.4</sub>N<sub>0.6</sub>): grey color) [6].

The reaction of (Ti,Mo)(C,N)<sub>1-x</sub>, (Ti,W)(C,N)<sub>1-x</sub> and (Ti,W,(Mo),(Ta),(Nb))(C,N)<sub>1-x</sub> samples with liquid Ni (or Ni/Co) was studied, as listed in Table 1.

The complex carbonitrides react with liquid Ni in the same manner as Ti(C,N), i.e. the carbide com-

ponents are preferentially dissolved so that the reacted carbonitride contained significantly more nitrogen than the unreacted part. A remarkably higher rate of the reaction was observed, so that in order to retain a microstructurally observable reaction zone, cooling down immediately after reaching the vertex temperature was necessary. In spite of this, the reaction proceeded to a large extent, leading to the aforementioned breaking up of the original crystallites of the compact carbonitrides into nitrogen-rich ones, in this case resulting in very fine precipitates, with compositions close to Ti(C,N) because of the dissolution of other metallic components in the melt. A thin nitrogen-enriched rim can also be found, as shown in Fig. 4(a–c).

As given in Table 2, the width of the reaction zone of the (Ti<sub>0.8</sub>Mo<sub>0.2</sub>)(C,N)<sub>1-x</sub> compact increases with increasing N contents. This behavior is opposite to the observations for Ti(C,N). Although other factors may influence the increase of width of the reaction zone, such as stoichiometry, homogeneity and grain size, there is a clear tendency that gives evidence of this. This phenomenon is thus due to the presence of Mo (and/or W) and could be explained as follows: because of the low chemical affinity between the N and Mo atoms, a decrease of the C content within the carbonitride will give rise to an increase of the Mo activity, leading to an accelerated dissolution of Mo (or Mo<sub>2</sub>C) in the Ni melt. At the same time with a decrease of the N contents in the carbonitride compact, the nickel melt will become rather more rapidly saturated with Ti-rich (Ti,Mo)C, because there is more Ti available in the form of soluble TiC as compared to carbon-poorer compositions. As a result of this more Mo remains undissolved in (Ti,Mo)(C,N) and the reaction is more retarded the higher the C content. Another factor that might favor the rapid dissolution of TiC and Mo<sub>2</sub>C carbide is the better wettability of carbonitrides by the nickel melt in the presence of Mo.

The same is true for the interaction of W containing carbonitride. W also has a low chemical affinity to N and a high solubility of its carbides in nickel and cobalt melts. All these observations are consistent with the results listed in Table 2.

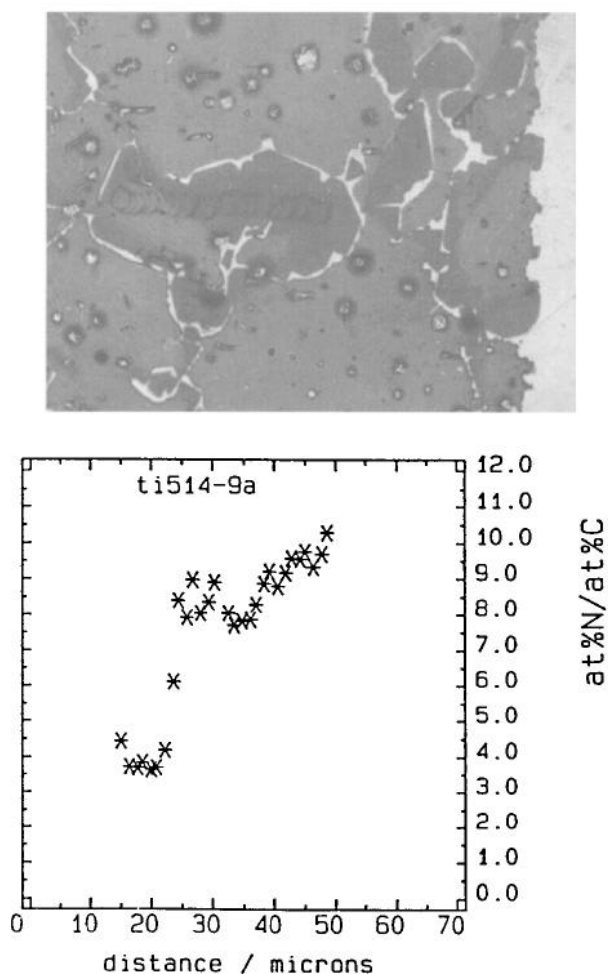


Fig. 3. EPMA scan across a Ti(C<sub>0.2</sub>N<sub>0.8</sub>) particle after reaction with liquid Ni.

Table 2

Width of the reaction zone carbonitride–liquid nickel in samples with a ratio 4:1 between titanium and molybdenum contents (at.%)

Sample	Composition	Width of the reaction zone
HP4B	(Ti <sub>0.8</sub> Mo <sub>0.2</sub> )C <sub>0.975</sub>	140 μm
GX	(Ti <sub>0.8</sub> Mo <sub>0.2</sub> )(C <sub>0.83</sub> N <sub>0.17</sub> ) <sub>0.975</sub>	88 μm
GB	(Ti <sub>0.8</sub> Mo <sub>0.2</sub> )(C <sub>0.79</sub> N <sub>0.21</sub> ) <sub>0.989</sub>	229 μm
LB	(Ti <sub>0.8</sub> Mo <sub>0.2</sub> )(C <sub>0.71</sub> N <sub>0.29</sub> ) <sub>0.967</sub>	258 μm
HP2	(Ti <sub>0.8</sub> Mo <sub>0.2</sub> )(C <sub>0.55</sub> N <sub>0.45</sub> ) <sub>0.926</sub>	reacted completely

#### 4. Conclusions

The mechanism of the contact reaction between liquid Ni and Ti(C,N) as well as Ti(C,N)-based complex carbonitrides of the transition metals is a process in which a dissolution and reprecipitation of the carbonitrides leads to a gradual enrichment in N of the precipitates. The Ti(C,N)-based Mo and/or W-containing complex carbonitrides react with liquid Ni at a

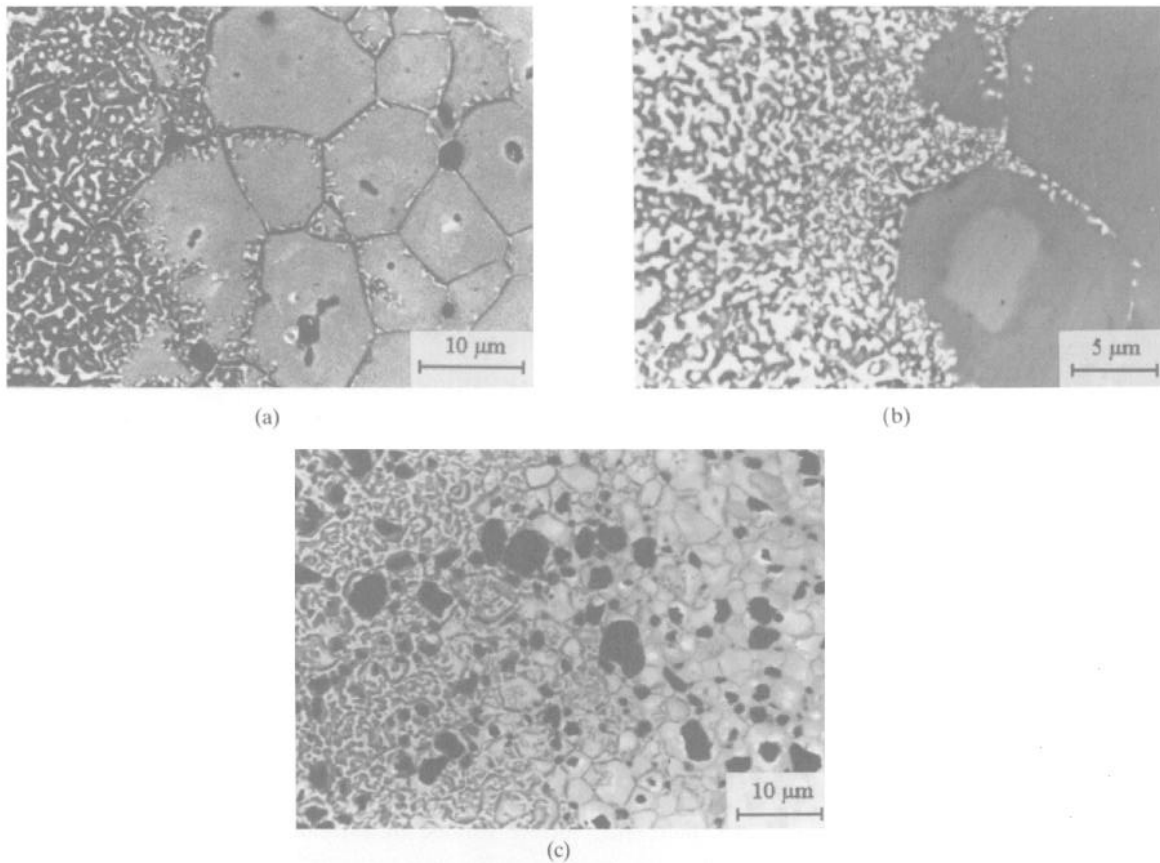


Fig. 4. (a) BSE micrograph showing the contact reaction HP6–Ni (see composition in Table 1). Bright zone, Ni; light grey, unreacted carbonitride; dark grey, reacted, Ti and N-richer carbonitride. The black spots are Ti(C,N) inhomogeneities. (b) BSE micrograph showing the contact reaction GX–Ni (see composition in Table 1). Bright zone, Ni; light grey, unreacted carbonitride; dark grey, reacted, Ti and N-richer carbonitride. (c) BSE micrograph showing the contact reaction HP25–Ni (see composition in Table 1). Bright zone, Ni/Co; light grey, unreacted carbonitride; dark grey, reacted, Ti and N-richer carbonitride. The black spots are Ti(C,N) inhomogeneities.

higher rate than Ti(C,N), mainly because of enhanced metallurgical interactions due to the presence of Mo or W. Because in technical cermets the binder phase is available in such an amount that during sintering the saturation of the melt in TiC and Mo<sub>2</sub>C is rapidly reached, the dissolution and reprecipitation mechanism can only be used as a model for the early stages of the liquid phase sintering of cermets. Because of the large grain size of the hot-pressed carbonitrides a better microchemical and metallographic characterization of these early stages is possible as compared to the use of powder compacts.

## References

- [1] B. Ozturk, *Metall. Trans. B*, 21 (1990) 879.
- [2] S. Binder, W. Lengauer and P. Ettmayer, *Proc. Titanium '92*, The Minerals, Metals and Materials Society, 1993, p. 689.
- [3] H. Holleck, *Binäre und ternäre Carbid- und Nitridsysteme der Übergangsmetalle*, Gebrüder Borntraeger, Berlin-Stuttgart, 1984.
- [4] S. Binder, W. Lengauer and P. Ettmayer, *J. Alloys Comp.*, 177 (1991) 119.
- [5] P. Ettmayer and H. Kolaska, *Konf. Forschungszent. Jülich*, 11 (1992) 86.
- [6] W. Lengauer, S. Binder, K. Aigner, P. Ettmayer, A. Guillou, J. Debuigne and G. Groboth, *J. Alloys Comp.*, 207 (1995) 137.