

Denitrification of Ti(C,N) based cermet during powder mixing process

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Changes in the nitrogen content of Ti(C,N)-based cermets during powder mixing and sintering processes were investigated and the denitrification mechanism was re-evaluated. The denitrification of N-containing cermets occurs mainly during the powder mixing process, and is relatively small during sintering periods. Denitrification during powder mixing is caused by oxidation of the Ti(C,N) powders in contrast to denitrification during sintering, which is caused by the decomposition of the nitrides due to the high nitrogen partial pressure. It was concluded that the main source of oxygen for the powder oxidation was the water present in the ethanol solvent. © 2002 Kluwer Academic Publishers

1. Introduction

TiC based cermets used in cutting tool materials show poor sinterability due to the high contact angle between the solid and liquid phase and suffer excessive grain growth during the sintering process. Though these problems can be solved by Mo addition [1–3], TiC-based cermets are used only for light cutting due to their poor toughness when compared to WC-Co cemented carbides. In the 1970's, Rudy *et al.* [4] improved the cutting performance of TiC-based cermets by the addition of TiN, which resulted in a refinement of the grain structure through the suppression of grain growth by the coalescence of TiC particles. Besides, nitrogen addition improves the oxidation-resistance, thermal shock-resistance and high temperature strength of TiN containing cermets. Recent trends in the development of Ti(C,N)-based cermet cutting tools is to have higher nitrogen contents, if possible. However, higher nitrogen containing cermets are more liable to carbo-nitride decomposition during the sintering process [5–7], which causes micro-pore formation in the sintered alloys and results in very poor alloy toughness. Therefore, it is necessary to both understand and control the denitrification mechanism during sintering for the development of high performance cermet cutting tools. Previous work [8] investigated denitrification during the sintering process due to equilibrium nitrogen pressure in carbonitride compound. In the present work, variations in the cermet nitrogen content were traced from powder mixing to the final sintering process and the denitrification during powder mixing is reported. The aim of this study was to clarify the mechanism of denitrification during powder mixing.

2. Experimental procedure

To investigate the denitrification of cermets during powder processing, cermets with varying C/N ratios ranging from 10/0 to 0/10 were prepared by conventional powder processing techniques. The raw material powders were Hermann C. Starck Ltd products. The average TiC particle sizes, TiC_{0.7}N_{0.3}, TiC_{0.5}N_{0.5}, TiC_{0.3}N_{0.7}, TiN were 1.2, 1.0, 1.7, 1.3, 0.6 μm and those of Mo₂C, Ni, Co were 3.3, 3.0, 1.5 μm , respectively. The chemical compositions of the experimental cermets are given in Table I. Powders were mixed in a stainless wall attritor mill including slurry circuit system. Each of alloy powders were mixed in an ethanol solvent with WC-Co carbide balls at 200 rpm and sampled after every 5 hours for analysis. The alloy powder samples were dried under vacuum (7×10^{-2} Torr, 80°C) and analysed for C, N, O contents and analyzed by x-ray diffraction method. The experiments were repeated testing for the effect of different purities of the ethanol solvent (50, 90, 95, 99.9%) on the denitrification of cermets during powder mixing process.

3. Result and discussion

3.1. Denitrification of Ti(C,N) powders during powder mixing process

Fig. 1 shows the variation in nitrogen content of TiC_{0.5}N_{0.5}-based cermet according to the mixing time during the powder mixing process and also according to the sintering temperature during the sintering process. The level of denitrification after 15 hours of mixing is quite noticeable while, in spite of its possible significance in surface composition and consequently the surface properties of the alloys, the contribution of

TABLE I The chemical compositions of experimental cermet (vol 1%)

C/N of Ti(C,N)					Mo ₂ C	Ni	Co
10/0	7/3	5/5	3/7	0/10			
75					10	6	9
	75				10	6	9
		75			10	6	9
			75		10	6	9
				75	10	6	9

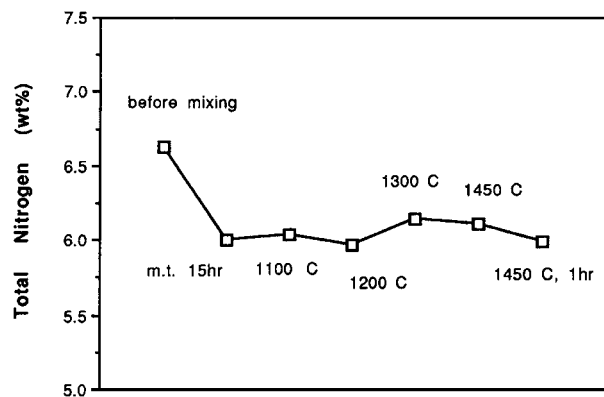


Figure 1 The variation of nitrogen contents of TiC_{0.5}N_{0.5}-based cermet powders during powder mixing and sintering process.

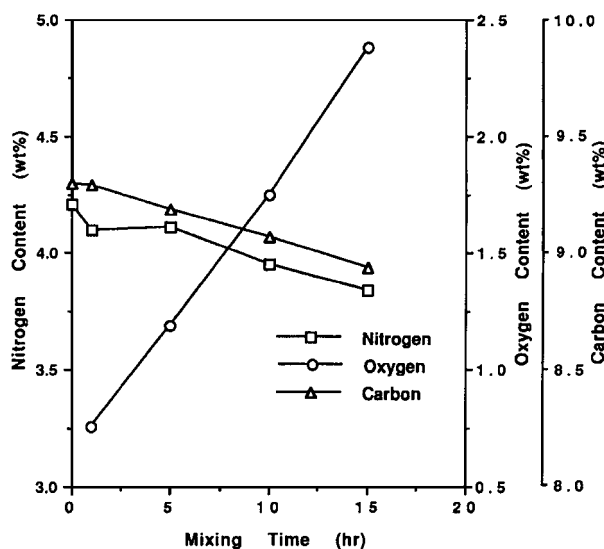


Figure 2 The changes of C, N, O contents in TiC_{0.7}N_{0.3}-based cermet powders mixed in 95% purity ethanol solvent.

denitrification during the sintering process to the total reduction of the alloy nitrogen content is not at all significant. Since carbon and oxygen occupies identical sites with nitrogen in the Ti(C,N) crystal lattice, it is quite probable that denitrification is associated with the variations in the carbon or oxygen content of the alloys. In an attempt to understand the nature of denitrification during powder mixing, the changes of C, N, and O content were analyzed according to mixing time. Fig. 2 shows variations in the C, N, and O content of TiC_{0.7}N_{0.3}-based cermet powders mixed in 95% purity ethanol solvent which is commercially adopted for the production of spray dried powders. The oxygen content

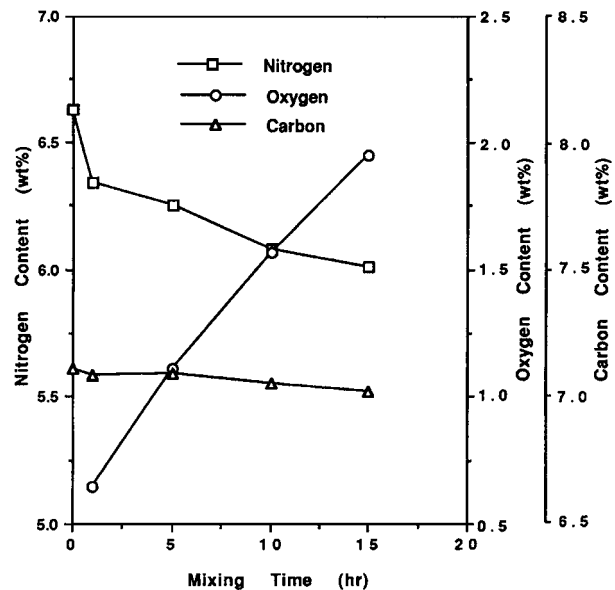


Figure 3 The changes of C, N, O contents in TiC_{0.5}N_{0.5}-based cermet powders mixed in 95% purity ethanol solvent.

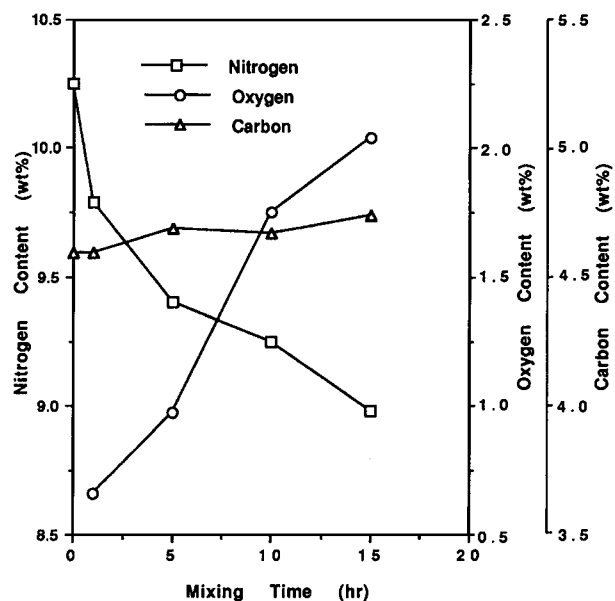
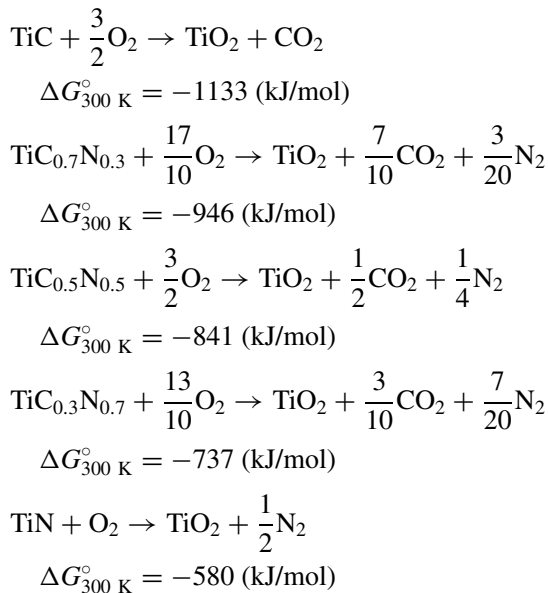


Figure 4 The changes of C, N, O contents in TiC_{0.3}N_{0.7}-based cermet powders mixed in 95% purity ethanol solvent.

in the mixed powders increases with increased mixing time, while the carbon and nitrogen content decreases. Oxidation of the TiC_{0.7}N_{0.3} powder is suggested in accordance with decarburization and denitrification. Similar trends were observed in TiC_{0.5}N_{0.5}-based (Fig. 3) and TiC_{0.3}N_{0.7}-based cermet (Fig. 4). With the increase in the N/C ratio, it can be seen that the tendency for denitrification increases, while that of oxidation slightly decreases. In case of TiC_{0.3}N_{0.7} powders, the carbon content in the powder tends to increase with mixing time. Carbon precipitation due to decomposition of the ethanol solvent during attritor mixing has been reported [9].

To support the assumption that denitrification occurs by oxidation of the powders during powder mixing in the ethanol solvent, the reactions and formation free energies of the titanium oxides from various powders

at room temperature were evaluated from thermodynamical data of the pure substances [10], given below. Because Ti has a higher oxygen affinity than Mo, Ni and Co it is assumed that Ti(C,N) powder reacts with oxygen to form TiO₂.



The above data suggest the strong possibility of decarburization and denitrification by oxidation of Ti(C,N)-based powders.

To confirm Ti(C,N) powder oxidation during attritor milling, XRD analysis was carried out on the milled powders. The specimens were prepared from TiC_{0.5}N_{0.5}-based cermets which showed a relatively high denitrification rate. Powders were attritor milled in a 50% ethanol + 50% water solvent and sampled after 1, 15, 40 hours of mixing. Fig. 5 shows the results obtained using a Mo target. After 1 hour mixing, Ti(C,N), Mo₂C, and Co peaks appeared along with WC peaks that result from WC-Co ball wear during the mixing process. After 15 hours milling, TiO₂ peaks ap-

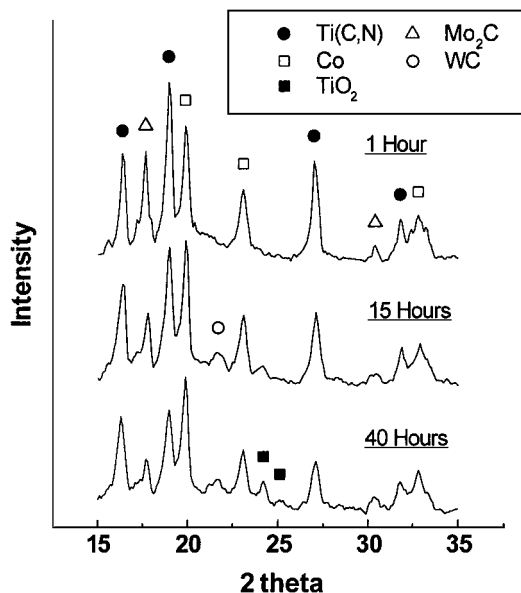


Figure 5 The results of X-ray analysis of in TiC_{0.5}N_{0.5}-based cermet powders mixed in 50% ethanol + 50% water solvent.

peared, and after 40 hours of mixing, the intensity of the TiO₂ peaks increased with accompanying decrease in Ti(C,N) peak intensities. This result strongly suggests that oxidation of the Ti(C,N) powders to form TiO₂ oxides probably occurred at the surface of the Ti(C,N) powders.

3.2. Source of oxygen for the oxidation of Ti(C,N) powders

There are two possible sources of oxygen during powder processing, O₂ in the air and water in ethanol solvent. Firstly, in order to evaluate the effect that the water content in the ethanol solvent has on the oxidation of the powders, ethanol containing different water concentrations 0.1%, 5% and 10% were selected as mixing solvents. The results are shown in Figs 6–8. Fig. 6 shows the changes in the C, N, and O concentration in a TiC_{0.7}N_{0.3} alloy during the powder mixing process in 99.9% ethanol solvent. The oxygen content in the mixed powders decreased considerably compared to the result in the 95% ethanol solvent (Fig. 2) and the decrease in nitrogen concentration was minimized. The decrease in both oxidation (Fig. 7) and denitrification (Fig. 8) of the powders with decreasing water content in the ethanol was also confirmed in the case of TiC_{0.5}N_{0.5} alloys.

Secondly, the possibility of O₂ in air as an additional source of oxygen was investigated. The experiment was conducted in gas tight sealed jars purged with Ar to prevent contact with the oxygen in air. Fig. 9 compares the changes in C, N, and O concentration in the mixed powders milled in air (open symbol) and in the Ar atmosphere (solid symbol) using anhydrous ethanol solvent. The differences in denitrification and oxidation were not significant in comparison with the effects of the water content in the solvent. From this result, it can be concluded that the main source of oxygen in the oxidation of the powder during powder mixing processes is the water in the ethanol solvent.

In general, oxygen can exist in the powders as a form of (1) oxygen in a solid solution, (2) oxides at the

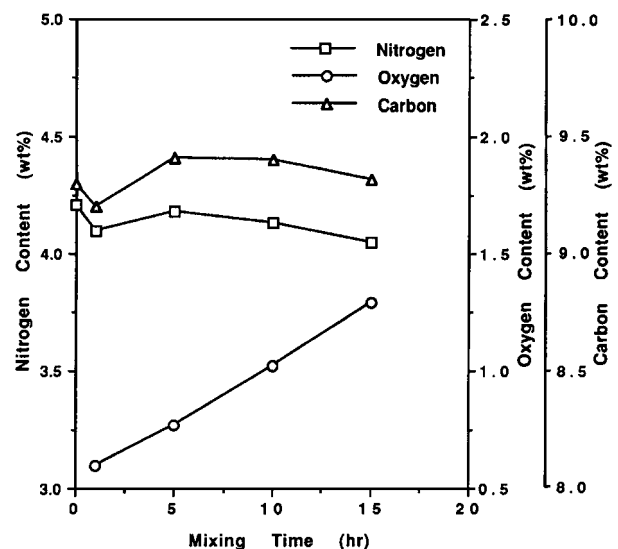


Figure 6 The changes of C, N, O contents in TiC_{0.7}N_{0.3}-based cermet powders mixed in 99.9% purity ethanol solvent.

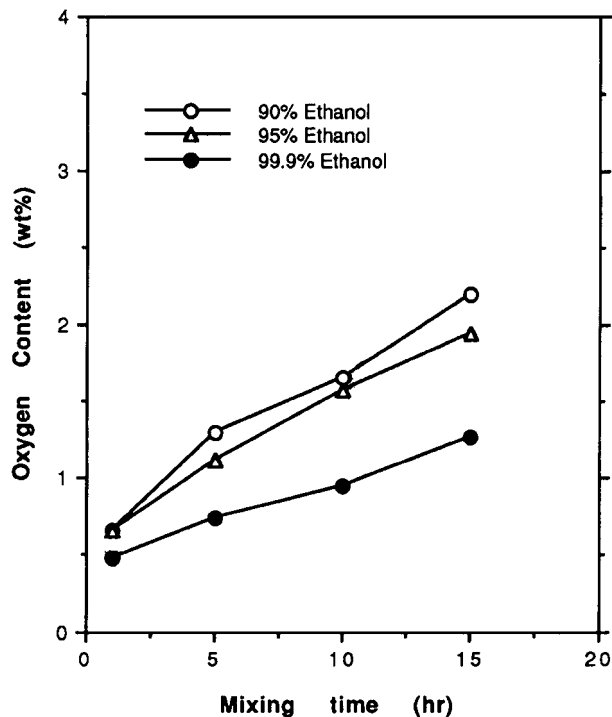


Figure 7 The changes of oxygen contents in $TiC_{0.5}N_{0.5}$ -based cermet powders mixed in different purity ethanol solvents.

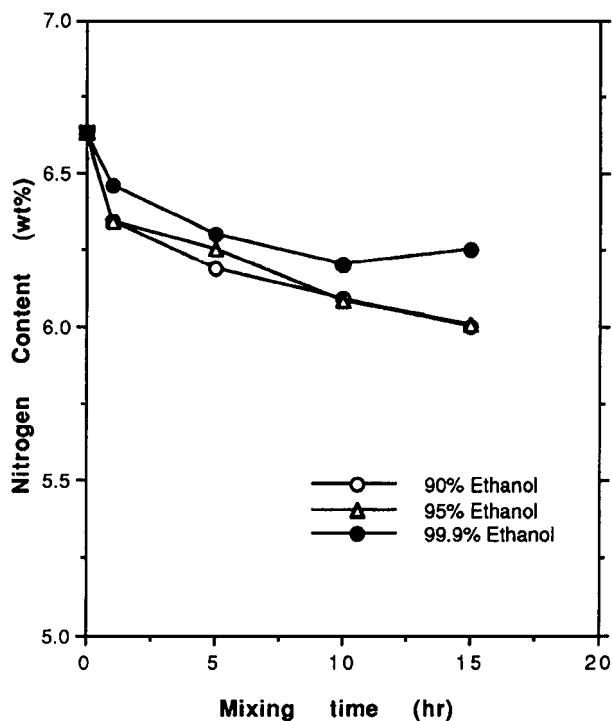


Figure 8 The changes of nitrogen contents in $TiC_{0.5}N_{0.5}$ -based cermet powders mixed in different purity ethanol solvents.

powder surface, and (3) adsorbed oxygen at the powder surface. However, oxidation during powder mixing resulted in the formation of oxide products at the powder surface. The denitrification of $Ti(C,N)$ powders during the powder mixing process could be suppressed by the prevention of $Ti(C,N)$ powder-oxidation at the powder surface. The present results show that as a method to prevent denitrification by surface oxidation, the use of dehydrated ethanol as a mixing solvent is quite effective. However, when anhydrous ethanol is used as a

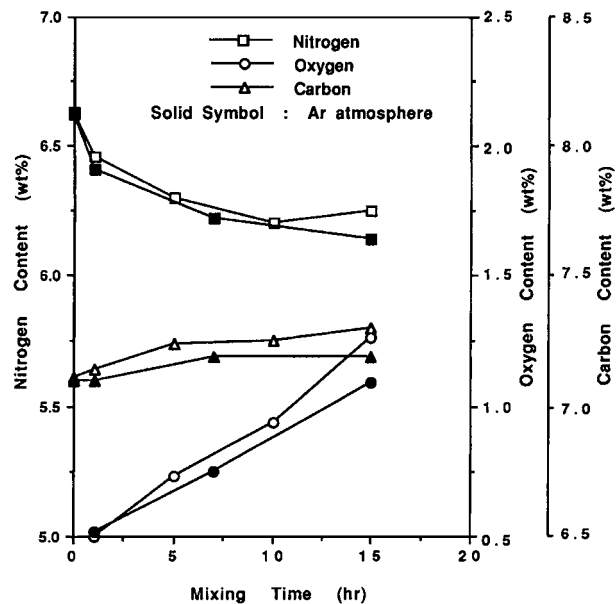


Figure 9 The changes of C, N, O contents in $TiC_{0.5}N_{0.5}$ -based cermet powders milled in air (open symbol) and in Ar atmosphere (solid symbol) using anhydrous ethanol solvent.

solvent, the powders do not dry properly during powder spray drying process due to the varying drying velocities of both inside and outside of the granules. It was considered that the addition of carbon to the mixed powders was another method to prevent oxidation. However carbon addition was not so effective in the prevention of surface oxidation and denitrification. Another approach to the reduction of nitrogen content in $Ti(C,N)$ powders during powder processing is the atmospheric sintering process. Denitrification during powder mixing could be compensated by nitrification during sintering in a nitrogen partial pressure.

4. Conclusion

The denitrification of nitrogen containing cermets mainly occurs during the powder mixing process. The decomposition of nitrides due to the high nitrogen partial pressure at the sintering temperature has little effect on the overall reduction in the total nitrogen content. Denitrification during powder mixing is associated with an increase in the oxygen content in the alloys. This was confirmed by XRD where the formation of TiO_2 oxides at the expense of $Ti(C,N)$ was observed.

The source of oxygen for the oxidation of the $Ti(C,N)$ powders during attritor milling was found to be the water in the ethanol solvent. A reduction in the water content in the ethanol solvent resulted in a reduction in both oxidation and denitrification. Atmospheric oxygen proved to have little effect on the oxidation of $Ti(C,N)$ powders.

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