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Activated Sintering and Interaction in the Titanium Nitride–Nickel System

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Abstract: Two ways to activate the process of sintering in the TiN–Ni system have been studied: by decreasing in the stoichiometry to $TiN_{0.83}$ and by reducing the TiN grain size to 50–70 nm. The formation of an annular structure has been revealed by sintering a disperse $TiN_{0.83}$ cermet in a vacuum and in the nitrogen atmosphere. The possibility is discussed that the annular structure formation is due to redistribution and diffusion of nitrogen. The cermet structure and phase composition have been studied as a function of sintering atmosphere and dispersion of the refractory compound. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

TiN-base cermets are promising corrosion-resistant and decorative gold-coloured materials.[1] Liquid-phase sintering of these cermets is complicated by poor wetting in the TiN-melted metal system, by denitrification of TiN during heating in vacuum and by prolonged sintering at high temperatures to achieve closed porosity.[2–5]

In this connection activation of sintering in this system is of interest. The use of non-stoichiometric TiN is one way to activate the process. Materials with closed porosity were obtained using $TiN_{0.83}$, which decreased the wetting angle to 30°[6] and suppressed the generation of nitrogen which inhibits proper shrinkage.[3,7] Further activation of sintering is possible by adding nitride-forming metals (e.g. Mo) into the bond[8] due to the improvement of wetting in the melted metal–refractory compound system.[2]

Another way to activate the sintering process is to decrease the refractory compound grain sizes to submicron levels. Using the nano-size particles (~60 nm) considerably activated the diffusion processes and 99% density was reached even for SiC, a covalent compound.[9]

2 EXPERIMENTAL PROCEDURE

Two powder species were studied. One was a dispersed powder of titanium nitride (79.6 wt% Ti, 19.8 wt% N, specific surface area $0.3\,m^2\,g^{-1}$) prepared by direct nitriding of titanium and supplied by Donetsk Plant of Chemical Reagents. TiN powder was crushed to produce a fine powder with $5\,m^2\,g^{-1}$, but its oxygen content increased from 0.3 to 1.4 wt%. It was Fe-ball-milled with carbonyl nickel and recovered molybdenum.

A nano-dispersed composition was prepared in Joint-stock company "Neomat" (Riga, Latvia) by combined nitriding powders of Ti and Ni in a stream of nitrogen plasma (mean grain size being 50–70 nm, specific surface area $10.2\,m^2\,g^{-1}$, 56.2 wt% Ti, 12.9 wt% N, 26.6 wt% Ni, 3.0 wt% O). The nano-dispersed powder consists of particles, Fig. 1, with cubic morphology the faces of which there are islands of settled Ni spherical segments. Also there are large spherical particles of nickel or, perhaps, of Ni-covered titanium particles. Nickel precipitation in the form of islands on TiN particles was also described in.[10]

A 2 wt% solution of synthetic rubber in benzene was used as a binder for pressing. Specimens were

Fig. 1. Scanning electron micrographs of TiN–Ni nanodispersed composition (×30 000).

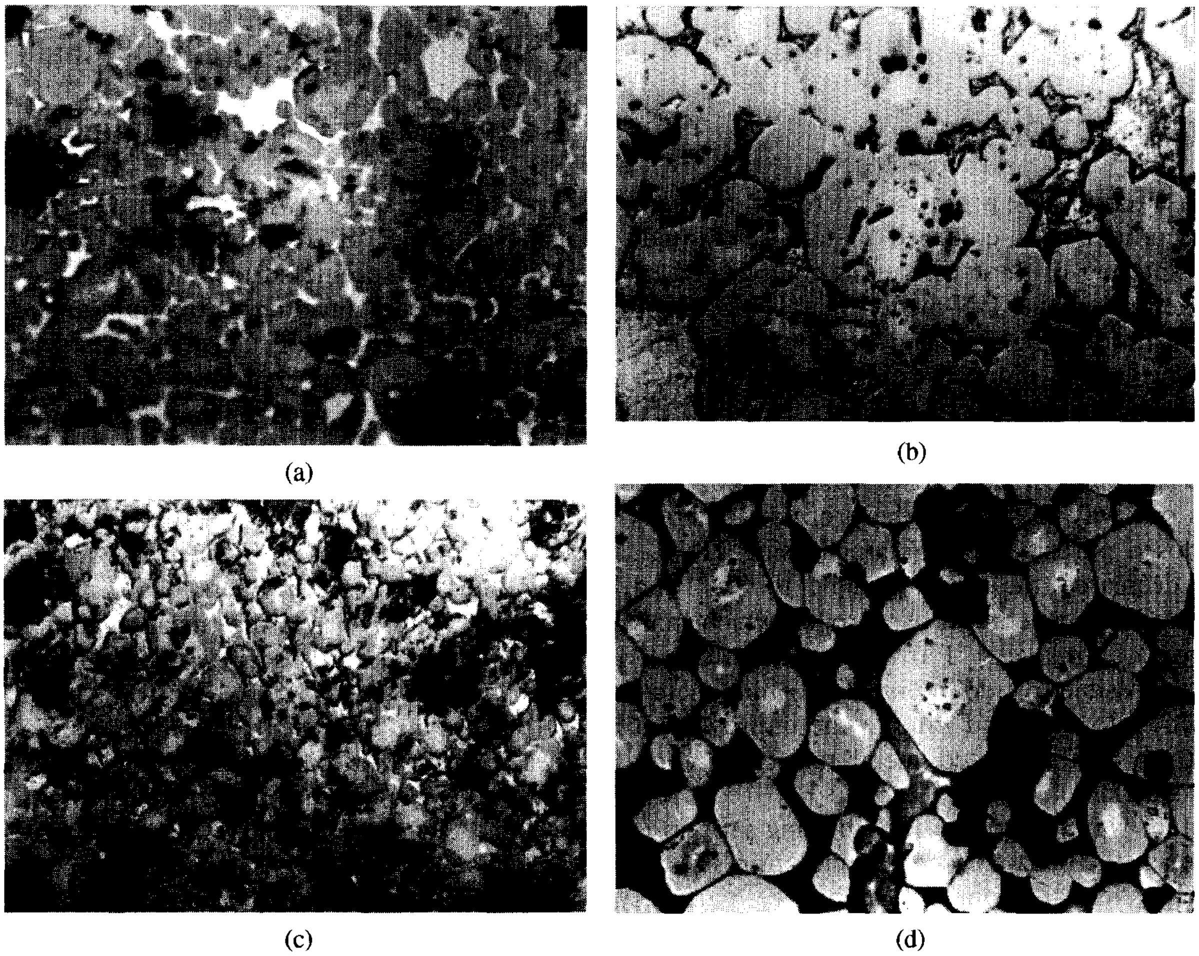
cold-pressed in a metallic die and sintered in a furnace with tungsten heater at temperature 1200–1800°C in a vacuum of 7×10^{-3} Pa or in pure nitrogen at 0.03 MPa for 1 h.

3 RESULTS AND DISCUSSION

Sintering either in a vacuum or in a nitrogen atmosphere leads to the formation of the annular (coaxial) structure (Fig. 2). A coaxial structure is known to exist on TiC grains in cermets based on WC and TiC.[11–13] Authors in Ref. 11 believe that TiC comprises the central part of a grain with external shells of a saturated solid solution (Ti,W)C or (Ti,Mo)C. With an increase in sintering temperature, the shell increases in thickness and then the annular structure disappears.

The shell on the surface of $TiN_{0.83}$ grains is TiN enriched with nitrogen. Its appearance can be easily explained if sintering was performed in a nitrogen atmosphere, but in case of vacuum sintering the formation of the shell at first glance seems to be unlikely, as it is known that heated TiN dissociates to liberate nitrogen gas.[7] Our findings show that titanium nitride becomes enriched with nitrogen up to the stoichiometric composition even during sintering in a vacuum (Table 1): simultaneous evaporation of the metallic binder takes place. The same process was observed in Ref. 3.

We believe that the mechanism of a coaxial structure formation is as follows. TiN on the surface of grains dissociates. Titanium, and in part nitrogen diffuse into the binder to form a solid solution in nickel. The amount of titanium reaches 25 wt%.



(a) (b) (c) (d)

Fig. 2. Microstructure of TiN–Ni (a,b) and TiN–Ni,Mo (c,d) cermets sintered in a vacuum (a,c) and in nitrogen (b,d) at 1450°C (a,c) and 1750°C (b,d) (×1000).

Table 1. The $TiN_{0.83}$–15% Ni cermet composition as a function of sintering temperature (vacuum, 30 min)

Sintering temperature (°C)	Element content (wt%)				Formula of the compound (calculation)
	of binder		of TiN grain		
	Ni	Ti	Ti	N	
Initial	15.0	—	68.2	16.8	$TiN_{0.83}$
1200	11.2	3.7	65.6	19.5	$TiN_{1.0}$
1400	7.8	2.6	69.3	20.3	$TiN_{0.99}$
1600	4.4	1.4	73.1	21.1	$TiN_{0.97}$

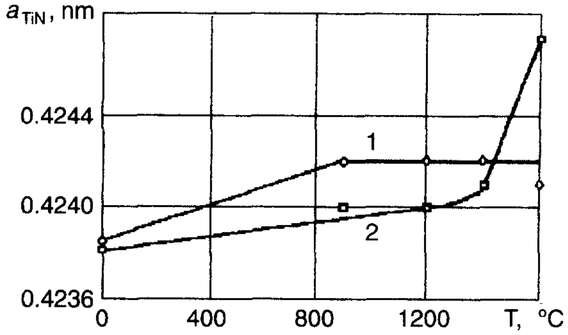


Fig. 3. Variations of the TiN lattice parameters in the process of sintering TiN–Ni cermets in a vacuum: 1 — dispersed powder, 2 — nano-dispersed powder.

The quantity of dissolved nitrogen is rather low and is determined by the phase diagram; at the eutectic temperature it equals about 0.06%. Most of the as-formed nitrogen enriches the surface of $TiN_{0.83}$ grains, thus decreasing its Ti/N ratio. It is known that the colour of TiN strongly depends on stoichiometry and changes from light-yellow for $TiN_{0.63}$ to bright-gold for $TiN_{1.0}$. A gold-coloured film of stoichiometric TiN forms on the surface of the refractory compound, in the case of a sufficient content of the metallic binder. The shell is separated from its substrate probably due to nitrogen trapping. The shell-forming process occurs during solid-phase sintering beginning at ~900°C and at the first stage of the liquid-phase sintering, i.e. during rearrangement of particles. The dissolution-precipitation (second stage) leads to further growth of the external shell of stoichiometric TiN. With increasing temperature and isothermal holding the whole grain becomes gold colour i e. titanium nitride is saturated with nitrogen up to its stoichiometric 1:1 composition.

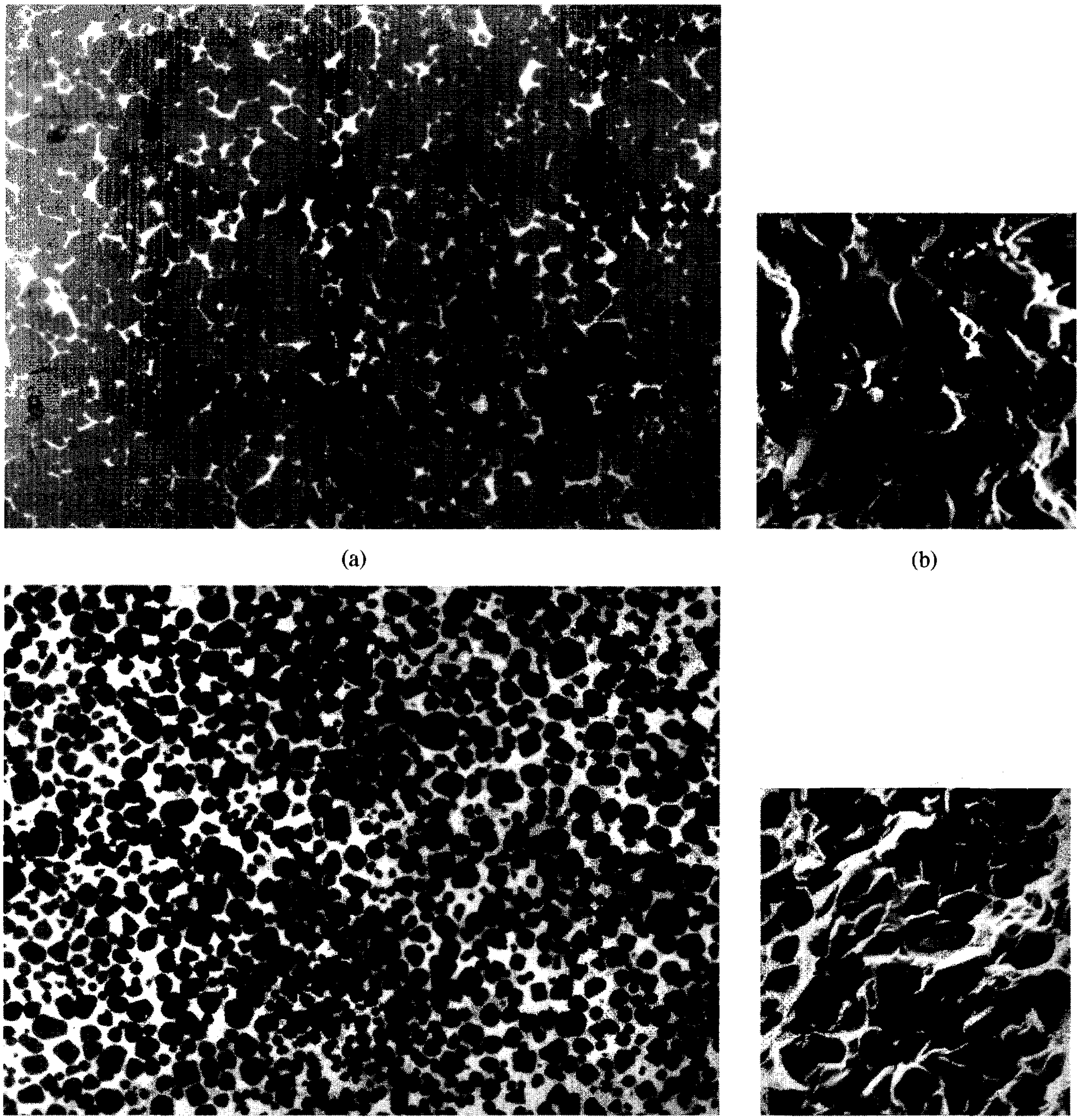
It should be noted that similar theory for the formation of annular structure in TiC-WC-Co materials has been advanced.[14] The boundary between the central and external parts of a grain arises from differences in carbon contents. If the initial solid solution is depleted in carbon, then, due to recrystallisation, its composition changes in the direction of carbon enrichment. According to Bernar,[14] when the carbon content of the initial solid solution approaches stoichiometry, the coaxial structure is not noticeable.

The lattice parameter of titanium nitride in its field of homogenity increases smoothly, from 0.4220 nm for $TiN_{0.6}$ to 0.4242 nm for the stoichiometric composition. Therefore the lattice parameter of the initial dispersed powder of $TiN_{0.83}$ is below the ideal value for TiN. With increasing sintering temperature due to changes in stoichiometry the titanium nitride lattice parameter rises [Fig. 3(1)]. The lattice parameters were obtained at 20°C after cooling the specimens. It is also known that the crystal structure of the nano-dispersed powder is in a stressed state which causes the TiN powder lattice parameter to decrease to 0.4238 nm. With increasing sintering temperature up to 1700°C, the lattice parameter grows and approaches that of a dispersed powder [Fig. 3(2)]. The use of nano-dispersed powders activates the sintering process and yields nonporous cermets (Fig. 4). Decreasing grain size causes the fracture to change from transcrystalline to intercrystalline.

An increase in temperature causes considerable changes in the cermet binder (Table 2). Initially titanium diffuses in binder forming a nickel-base solid solution. Above 1200°C during vacuum sintering, $TiNi_3$ intermetallic appears. In the system TiN_x–Ni the intermetallics were established; see Refs 15 and 16. The reason for the diffusion of a considerable quantity of titanium in a cementing binder is thermal decomposition of TiN. It should be noted that titanium diffuses in the binder before a liquid phase forms, i.e. as early as in solid phase interaction.

The composition of the binder can be regulated by changing from a vacuum sintering to sintering in nitrogen. When using a nitrogen atmosphere, the binder is metallic and, as shown in Table 3, consist of Ti–Ni a solid. In combined sintering the strength of cermets increases by 15%. This sintering is performed in several stages: the first stage is a vacuum heating up to the temperature of a liquid phase formation (to improve the spreading of the metal binder over TiN grains) and the second stage is an post-sintering in nitrogen, to depress the TiN dissociation and metal binder evaporation.

In case of a Ni–Mo binder, molybdenum in addition to nitrogen is responsible for the formation of an annular structure. The shell of a TiN grain is enriched with molybdenum up to 0.5–0.8 at%. As sintering temperatures increase owing to the process of diffusion distribution of Mo over the TiN grain it becomes more even and its content amounts to 0.3–0.4 at%. The structure of TiN–Ni,Mo



(a) (b)

(c) (d)

Fig. 4. Metallographic sections (a,c) (×800) and fracture surfaces (b,d) (×1200) of TiN–Ni dispersed (a,b) and nano-dispersed (c,d) powders sintered at 1600°C (a,b) and 1400°C (c,d).

cermets forms in the following way. Upon heating up to 800°C a portion of molybdenum forms Mo_2C which is seen as bright interlayers [Fig. 5(a)]. The molybdenum carbide formation is due to the fact that molybdenum, which has a high affinity for carbon, interacts with free carbon liberated as the organic binder is burnt out. With increasing temperature a solid-phase interaction occurs which results in dissolution of up to 15% Mo and up to 5% Ti in nickel. Titanium formed due to TiN dissociation diffuses into the binder. Molybdenum dissolution in nickel leads to the formation of a Ni-base solid solution, thus increasing a lattice parameter of the Ni phase from 0.3522 to 0.3600 nm.

After heating up to 1200°C, the cermet contains some quantity of $TiNi_3$ intermetallics. The binder phase, due to its inhomogeneity, melts in two stages. Endothermic effects are observed at 1330 and 1390°C. In reheating the sintered cermet, the binder melts in a narrow temperature range, shifted to the initial melting temperature of the cermet binder phase. This suggests a higher homogeneity of the binder formed during the first heating. With further increase in the sintering temperature, the

Table 2. Change of the binder phase composition in a vacuum sintering

Sintering temperature (°C)	Composition of the binder phase in TiN–25 wt% Ni cermet	
	Dispersed mixture	Nano-dispersed composition
Initial	Ni	Ni, Ti*
900	Ni	Ni, Ti*
1200	Ni(Ti), $TiNi_3$*	Ni(Ti), Ti*, $TiNi_3$*
1400	Ni(Ti), $TiNi_3$	Ni(Ti), $TiNi_3$
1600	$TiNi_3$, Ni(Ti)*	$TiNi_3$, Ni(Ti)*

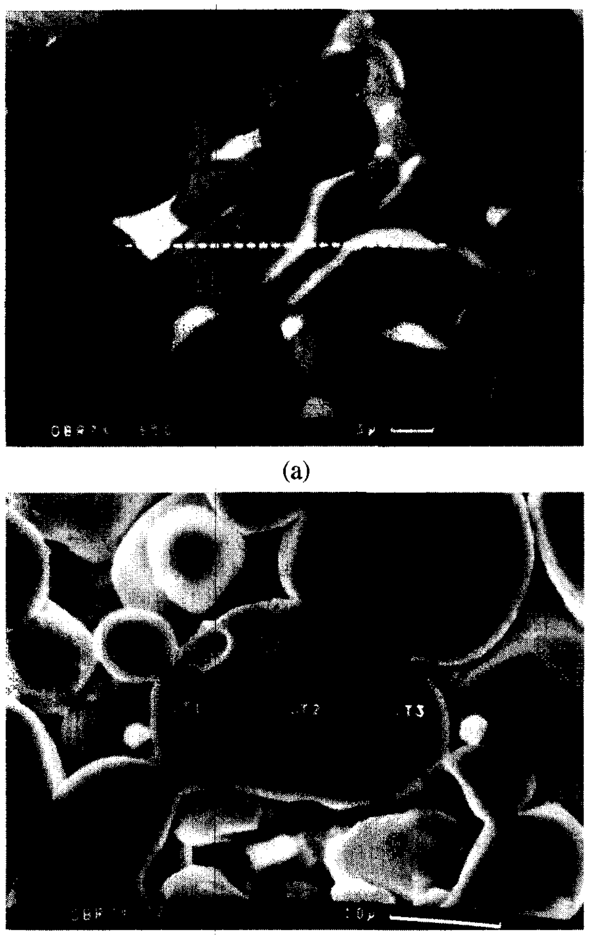
*Traces of phase.

Table 3. Composition of the binder phase in liquid-phase sintering of TiN–25 wt% Ni cermet

Sintering atmosphere	Composition of the binder phase	Element concentration (wt%)		
		Ni	Ti	Fe impurity
Vacuum	$TiNi_3$, Ni(Ti)*	73.2±0.8	23.9±0.3	2.9±0.2
Nitroden	Ni(Ti)	89.7±0.9	8.9±0.4	2.4±0.2
Combined**	Ni(Ti), $TiNi_3$*	92.7±1.0	5.2±0.2	2.1±0.2

*Traces of phase.

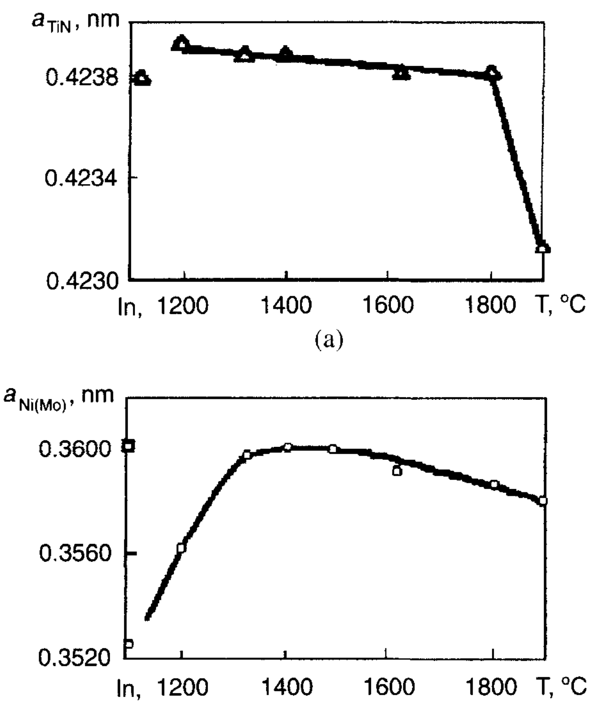
**Combined sintering includes preheating in a vacuum and sintering in nitrogen.



(a)

(b)

Fig. 5. Metallographic sections of TiN–Ni,Mo cermets sintered in nitrogen: (a) Ni–Mo binder (1650°C); (b) TiN grain (1800°C).



(a)

(b)

Fig. 6. Variations in the lattice parameters of (a) TiN and (b) Ni(Mo) binder in the process of TiN-Ni,Mo cermet sintering.

dissolution of Mo_2C in the binder results in a higher (up to 20%) Mo content of the Ni-base solid solution. Therefore, the intensity of molybdenum carbide reflections in X-ray patterns becomes less. During the second stage of a liquid-phase sintering, a portion of molybdenum and, obviously, carbon diffuses into TiN grains: Fig. 6 shows the resulting decrease of the lattice parameters both of (a) TiN and (b) the binder phase. A decrease in the lattice parameter of the molybdenum solid solution in nickel is obviously due to a decrease in its molybdenum content, while a decrease in the TiN lattice parameter could be explained by an increase of the molybdenum content of TiN grains as it was the case with TiC.[17] An increase in the metal binder content of cermets increases their strength and decreases the elastic moduli.

The kinetics of liquid-phase sintering of TiN–Ni,Mo cermets in nitrogen and in vacuum were studied. The first stage (a rearrangement of particles) lasts about 5 min. The reduction in the rearrangement stage from 80 min for $TiN_{0.97}$–Ni down to 5 min for $TiN_{0.83}$–Ni, Mo could be explained by a suppression of TiN denitrification as advanced in Ref. 15 and by a higher TiN dissolution in the binder when adding molybdenum.[2]

Activation energy of the second stage (solution-reprecipitation) is 310 kJ mol^{-1} in a vacuum and 409 kJ mol^{-1} in nitrogen. The sintering rate of the second stage is limited by the process of TiN grain dissolution in the liquid phase. The presence of nitrogen hinders the process and therefore the sintering activation energy is higher.

Our studies have permitted us to obtain TiN-base cermets of the lowest porosity and optimum strength.

4 CONCLUSIONS

1. The process of sintering in the TiN-Ni system may be activated by two ways: by decreasing the stoichiometry down to $TiN_{0.83}$ and reducing TiN grain size down to 50–70 nm.
2. The formation of an annular structure has been revealed in the dispersed $TiN_{0.83}$ cermet in the process of sintering both in a vacuum and in a nitrogen atmosphere. Discussed is the annular structure formation due to redistribution and diffusion of nitrogen.
3. The cermet structure and phase composition depend on sintering media and dispersity of the refractory compound.

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