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Tungsten-Free Hard Alloys Based on Titanium Carbide

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Abstract—The properties of tungsten-free hard alloys based on titanium carbide prepared from chips of various titanium alloys were studied, and the conditions for the preparation of tungsten-free alloys were optimized. The properties of TiC-based alloys prepared from chips of the VT20, VT3-1, and VT25 titanium alloys, containing V, Mo, Zr, and Al, were shown to compare well with those of commercial analogs. Nickel vaporization during vacuum sintering of the hard alloys was studied, and the sintering conditions were optimized (residual pressure in the range 10–100 Pa, reduced sintering temperature).

Up to 80% of the cutting tools are manufactured from WC–(TiC,TaC)–Co alloys. At the same time, in view of the high cost of tungsten and cobalt, a great deal of attention is paid to the development and commercialization of tungsten-free hard alloys. Tools of TiC-based alloys feature a good wear resistance, high oxidation stability, and low friction coefficient. For this reason, these alloys, along with WC-based alloys, are the most-used [1].

However, TiC-based alloys are fairly brittle and have low thermal conductivity, which limits their use to finish and semifinish machining of steel. One way of improving the mechanical properties of TiC-based hard alloys and extend their application field is by enhancing the strength of the binding constituent and the plasticity of the carbide constituent, which can be achieved via alloying with aluminum, vanadium, zirconium, and other metals. In this context, the preparation of alloyed titanium carbide from chips of titanium alloys containing Al, V, Zr, Mo, and other elements appears attractive both economically—since it would ensure utilization of industrial waste—and technologically—since it might yield alloys with improved physical and mechanical properties.

The purpose of this work was to select titanium alloys suitable for the fabrication of high-performance tungsten-free alloys equivalent to the TN20 alloy and to optimize the conditions for the preparation of hard alloys from chips of the titanium alloys chosen.

Titanium carbide powders were prepared from chips of the titanium alloys VT1-0, VT25, VT5, VT3-1, VT20, and OT4-1 as described elsewhere [2]. The compositions of the chips and powders are given in Table 1.

The C_{total}, C_{free}, and O contents of the TiC powders prepared from VT3-1, VT20, OT4-1, VT25, and VT5 chips were essentially identical to those of the commercial carbothermic titanium carbide and the powder prepared from VT1-0 chips (unalloyed Ti).

The content of alloy additives (Mo, V, Zr, Mn) in the titanium carbide powders prepared from chips of titanium alloys differs insignificantly from that in the chips. As evidenced by earlier results [3], these metals are likely to be incorporated into a mixed, TiC-based car-

Table 1. Compositions of titanium-alloy chips and doped titanium carbide powders

Alloy	Chip composition, wt %						Powder composition, wt %							
	Al	V	Mo	Zr	O	Fe	C_{total}	C_{combined}	O	Al	V	Mo	Zr	Fe
VT1-0	0.2	–	–	–	0.6	0.3	18.77	0.42	0.14	0.1	–	–	–	0.2
VT3-1***	5.6	–	2.5	–	0.5	0.5	18.55	0.18	0.32	0.7	–	2.3	–	0.3
VT25*	6.9	–	2.5	1.7	0.5	0.3	18.39	0.22	0.37	0.8	–	2.4	1.6	0.3
VT5	5.3	–	–	–	0.6	0.4	18.63	0.31	0.29	0.7	–	–	–	0.2
VT20	6.5	1.3	1.8	1.8	0.5	0.4	18.46	0.12	0.43	0.8	1.0	1.6	1.6	0.3
OT4-1**	2.2	–	–	–	0.5	0.3	18.61	0.23	0.25	0.4	–	–	–	0.3

* 2.0% Sn in chips and 0.4% Sn in the TiC powder.
** 1.0% Mn in chips and 0.6% Mn in the TiC powder.
*** 1.8% Cr in chips and 0.9% Cr in the TiC powder.

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Table 2. Effect of sintering temperature on the porosity, microstructure, and properties of TiC–Ni–Mo alloys

Alloy	Sintering temperature, °C	Porosity, %	Average grain size of the carbide phase, μm	Flexural strength, MPa*	HRA
VT1-0	1360	0.2	1.2	1037 ± 10	90.4
	1380	0.2	2.1	1070 ± 40	89.1
	1400	0.8	2.6	1016 ± 50	89.2
	1420	0.8	4.1	1060 ± 40	89.8
VT3-1	1360	0.2	1.2	1085 ± 30	91.6
	1380	0.2	1.8	992 ± 30	90.3
	1400	0.8	2.8	950 ± 50	89.1
	1420	0.8	4.2	720 ± 70	–
VT25	1360	0.8	1.2	720 ± 80	–
	1380	0.6	2.0	930 ± 30	89.6
	1400	0.4	3.1	978 ± 20	89.8
	1420	0.8	4.2	700 ± 80	–
VT5	1360	0.1	1.3	1015 ± 15	90.8
	1380	0.2	1.8	993 ± 70	89.6
	1400	0.8	2.9	1002 ± 20	88.8
	1420	0.8	4.3	1001 ± 40	88.8
VT20	1360	0.1	1.2	980 ± 20	91.1
	1380	0.1	2.3	1031 ± 55	91.0
	1400	0.4	2.8	955 ± 15	91.0
	1420	0.6	4.0	918 ± 35	91.0
OT4-1	1360	0.8	1.3	983 ± 15	87.3
	1380	0.8	2.4	852 ± 80	86.9
	1400	0.8	3.1	970 ± 40	87.0
	1420	0.8	4.2	1032 ± 50	88.0

* Tests on as-sintered samples.

bide. The Al content of the TiC powders (0.4–0.8 wt %) is lower than that of the respective chips (2.2–6.5 wt %). Clearly, the behavior of alloy additives during carburization depends on their partial vapor pressures.

The TiC powders obtained from chips were used to prepare TiC–Ni–Mo alloys (15 wt % Ni, 6 wt % Mo). Green compacts were obtained by pressing powder mixtures with a plasticizer (rubber dissolved in benzene) at 150 MPa. Initial sintering was performed in a hydrogen atmosphere at 700°C. Final sintering was performed in vacuum—first at 1200°C to remove oxide films and then at 1350–1420°C.

The physical and mechanical properties of tungsten-free alloys are determined by their composition, porosity, and grain size. The porosity and microstructure depend, in turn, on the particle size of the starting powders and sintering temperature and duration.

Increasing the sintering temperature leads, on the one hand, to a faster densification rate and, on the other, to growth of carbide grains and considerable vaporization of nickel from the liquid phase, accompanied by an increase in pore volume. Additives alter the sintering behavior of the alloy in comparison with TN20, which sinters well at 1380°C (Table 2).

The optimal sintering temperature varies from 1360 to 1420°C, depending on alloy composition. Alloys containing Al, V, Mo, and Zr can be sintered at 1360°C. The samples obtained at this temperature feature the lowest porosity and the smallest grain size of the carbide phase, which has a favorable effect on the mechanical properties and cutting capacity of the alloy. At higher sintering temperatures, the grain size of the carbide phase is larger (in the alloy prepared from VT20 chips, marked grain growth occurs starting at 1400°C, as illustrated in Fig. 1). Porosity also rises with sintering temperature as a result of nickel vaporization, which has an adverse effect on the cutting capacity of these alloys. This type of behavior is characteristic of the alloys prepared with the use of VT3-1, VT5, and VT20 chips.

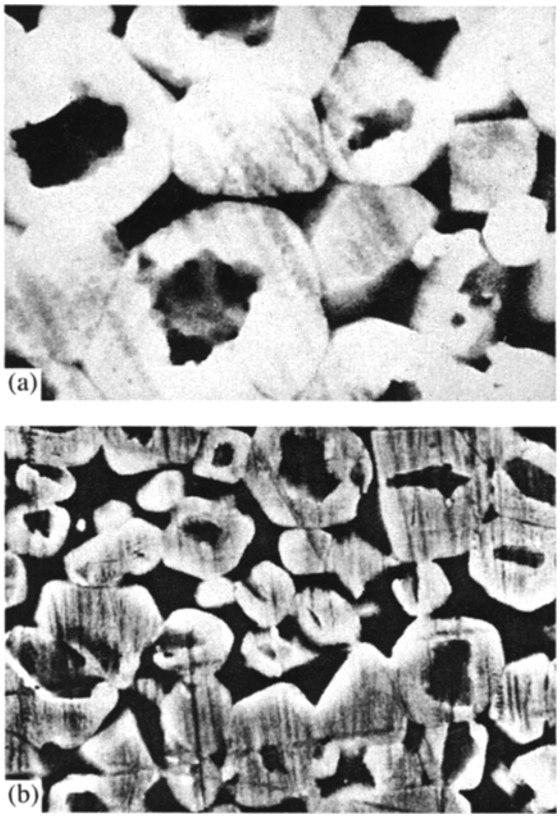

Fig. 1. Microstructure of a tungsten-free TiC-based alloy prepared from VT20 chips and sintered at 1400°C; (a) ×15000, (b) ×5000.

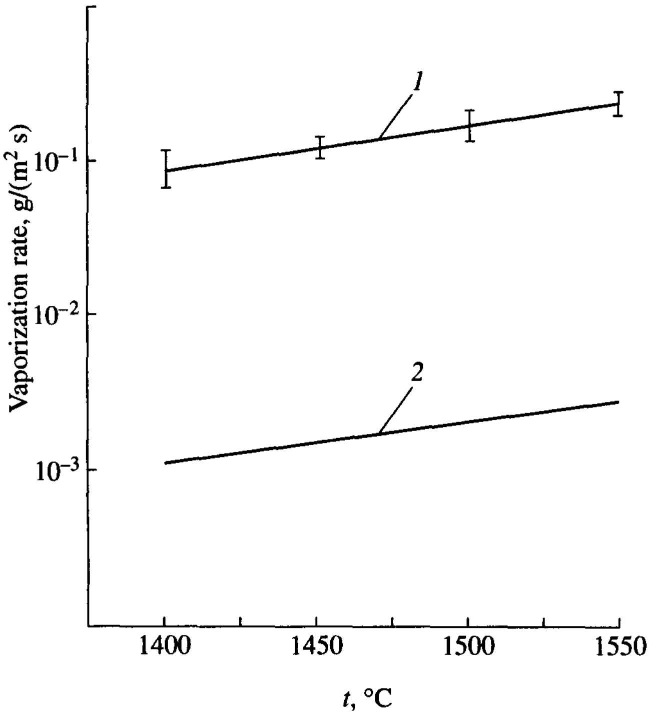

Fig. 2. Vaporization rate of nickel as a function of sintering temperature for (*1*) TN20 and (2) Ni metal [4].

The alloys prepared with the use of VT25 chips (2.0 wt % Sn) sinter at a higher temperature of 1400°C and rank below the other alloys in physical and mechanical properties. Similar results were obtained with OT4-1 chips, containing Mn. At none of the sintering temperatures tested was the porosity of the alloys prepared from these chips below 0.8%. Alloy additives have different effects on the wettability of titanium carbide by the melt. Mo, Al, V, and Zr are likely to improve wettability, which allows dense alloys to be obtained at relatively low temperatures.

The sintering behavior of the TiC–Ni–Mo alloys was also characterized by weight-loss measurements. The vaporization rate of metals can be evaluated using Langmuir's equation,

$$W = \alpha p[M/(2\pi RT)],$$

where W is the weight loss per unit time per unit surface area at temperature T, p is the partial vapor pressure, α is the condensation coefficient, M is the molecular weight of the material (atomic weight in the case metals), and R is the gas constant. Using weight-loss data and the known sample area and vaporization time, we evaluated the vaporization rates of nickel and TN20 and compared with calculated rates [4] (Fig. 2). The vaporization rate of nickel in TiC–Ni–Mo was found to be higher than that in Ni metal, because of the eutectic melting of the alloy at 1280°C. A similar effect was observed earlier in metal–carbon systems [5].

During sintering of TiC–Ni–Mo alloys at 1400°C and a residual pressure of 1 Pa, the weight loss due to nickel vaporization attains 8% (5.0-g sample), which leads to considerable porosity and impairs the physical and mechanical properties of the material. Therefore, these alloys should be sintered at higher residual pressures (10–100 Pa) and as low temperatures as possible.

Taking into account nickel vaporization and the sintering behavior of the hard alloys, we optimized the sintering conditions for the TiC-based alloys prepared from titanium alloy chips (Table 3).

The starting titanium alloys, used in the form of chips to prepare hard alloys, can be divided into two groups:

(1) alloys which impair the properties of hard alloys (OT4-1 and VT25, containing Mn and Sn);

(2) alloys which do not impair or improve the properties of hard alloys (VT3-1, VT20, and VT5, containing Al, V, Mo, and Zr).

We believe that the properties of the resulting tungsten-free alloys can be improved further by optimizing the content of alloy additives. To this end, it is of interest to prepare tungsten-free hard alloys through the introduction of alloy additives both in the form of titanium carbide prepared from titanium-alloy chips and in

Table 3. Optimized sintering conditions for TiC-based hard alloys

Starting chips	Sintering temperature, °C	Sintering time, h	Residual pressure, Pa
VT1-0	1380	1	40
VT3-1	1360	1	10
VT25	1400	1	40
VT5	1360	1	10
VT20	1360	1	10
OT4-1	1420	0.5	100

the form of powder Al, Zr, and V or their refractory compounds.

CONCLUSION

The sintering conditions for tungsten-free alloys based on titanium carbide prepared from VT20, VT3-1, VT5, VT25, and OT4-1 chips were optimized.

Chips of titanium alloys containing no tin or manganese are shown to be suitable for the preparation of hard alloys.

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