RESEARCH OF THE STRUCTURE AND PHASE COMPOSITION OF THE POWDER ALLOY BASED ON TITANIUM CARBIDE

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Abstract

The structure and phase composition of TiC-NiTi powder alloys, which were produced via controlled hot vacuum pressing, was ascertained. The alloys with 50% of TiC and Ni-Ti binder were under investigation. It was shown that the structure of TiC-NiTi alloys can be metastable. It was proved that alloy with 11,5% Ni content had stable structure, while alloy with 27%Ni was metastable and tended to phase transformation of NiTi. It was also shown that annealing at 1150°C caused stabilization of material.

Formulation of the problem

Development of carbide powder alloys based on the refractory metal carbides is one of the most preferred directions of material science research. Hard alloys based on tungsten carbide have found extensive use in industry. These materials, which usually are produced via powder metallurgy, show high wear resistance and agreeable impact strength, nevertheless, there are some disadvantages in its properties. Firstly, WC density is 15.8 g/cm^3, which means that specific density of any product is very high, as well as its cost. Secondly, WC-based alloys cannot provide sufficient thermal stability.

Such drawbacks predetermined searching of new alternative compounds of alloys. The powder alloy based on titanium carbide and Ti-Ni matrix is in the spotlight of the recent study.

Titanium carbide has low density 4.91 g/cm^3 and hardness (~29000 N/mm^2), melting temperature is equal to 3067°C [1]. These features make TiC to be promissory material for powder metallurgy instead of WC. While being very hard, TiC is more brittle than WC, therefore compensating lack of plastic properties the material for matrix should be selected from the ductile metals. In the recent research the matrix has been produced from nickel and titanium.

The powder alloys for study have been manufactured via controlled hot vacuum pressing technology (CHVP). Green compact was formed from TiC (stoichiometric composition), nickel and titanium powders. Chemical composition, density and porosity of alloys are shown in table 1.

For the purpose of obtaining alloys with structure of carbide and NiTi, compounds were chosen with regard to ternary Ni-Ti-C diagram [2]. However, achieving this structure one is faced with existence of several intermetallic phases such as Ni_4Ti_3, $Ni_{2,67}Ti_{1,33}$, Ti_2Ni, Ni_3Ti [2, 3].

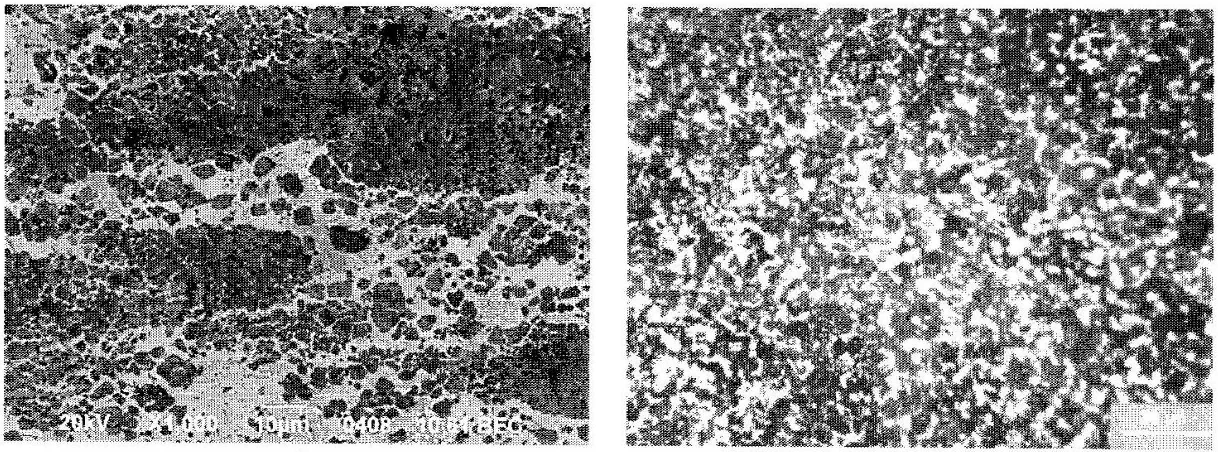
Tab. 1. Chemical composition, density and porosity of TiC-NiTi alloys

No.	**wt.%**			**Apparent density, g/cm^3**	**Density after sintering, g/cm^3**	**Porosity, %**
	Ti	**Ni**	**TiC**			
1	23.00	27.00	50.00	5.48	5.32	3.1
2	38.70	11.50	49.80	5.02	4.95	1.4

In spite of the fact that influence of intermetallic particles on bulk properties of TiC-NiTi powder alloys is a disputable question, most authors tend to claim it raises brittleness [4, 5].

Results and discussion

Experimental alloys have relatively high porosity 3.1% and 1.4% for alloy No. 1 and No. 2 respectively (table 1), but it means that increasing of Ti content leads to less porosity. Test pieces were both "green" (just after CHVP) and after annealing. The microstructure of alloys is depicted in figure 1.



a) b)

Fig. 1. Microstructure of alloys after controlled hot vacuum pressing, x1000 (unetched); a – alloy No. 1; b – alloy No. 2

It should be noted that titanium carbide is dark phase and the matrix is light one in these photos. As follows from fig.1a microstructure of alloy No. 1 is characterised by phase immiscibility. Using high magnification presence of large carbides aggregations, which were not divided by matrix, was detected. In contrast to alloy No. 1, the microstructure of alloy No. 2 (with increased Ti content) is more homogeneous as one can see in fig. 1b.

Annealing leaded to changing of ratio between part of the microslice square that is captured by the binder and carbide in case of alloy No.1 and caused no changes of this parameter in alloy No. 2. The results of calculation of average matrix content before and after annealing are shown in table 2.

Changing matrix amount is evidence of material metastable state right after manufacturing and annealing causes stabilization of the structure most probably due to phase transformation.

It should be noticed that one more annealing at 850±10°C was conducted, however, it caused spalling of carbides, and this treatment was not used later.

Tab. 2. The part of the microslice square that is captured by the matrix in TiC-TiNi alloys, %

Treatment	**Alloy No.1** (23%Ti+27%Ni+50%TiC)	**Alloy No.2** (38.7%Ti+11.5%Ni+ +49.8%TiC)
After CHVP	23.0±8.0	25.8±7.3
Annealing at 1150°C, 30 min.	32.0±4.7	23.7±2.4
Repeat annealing	34.5±4.9	was not conducted

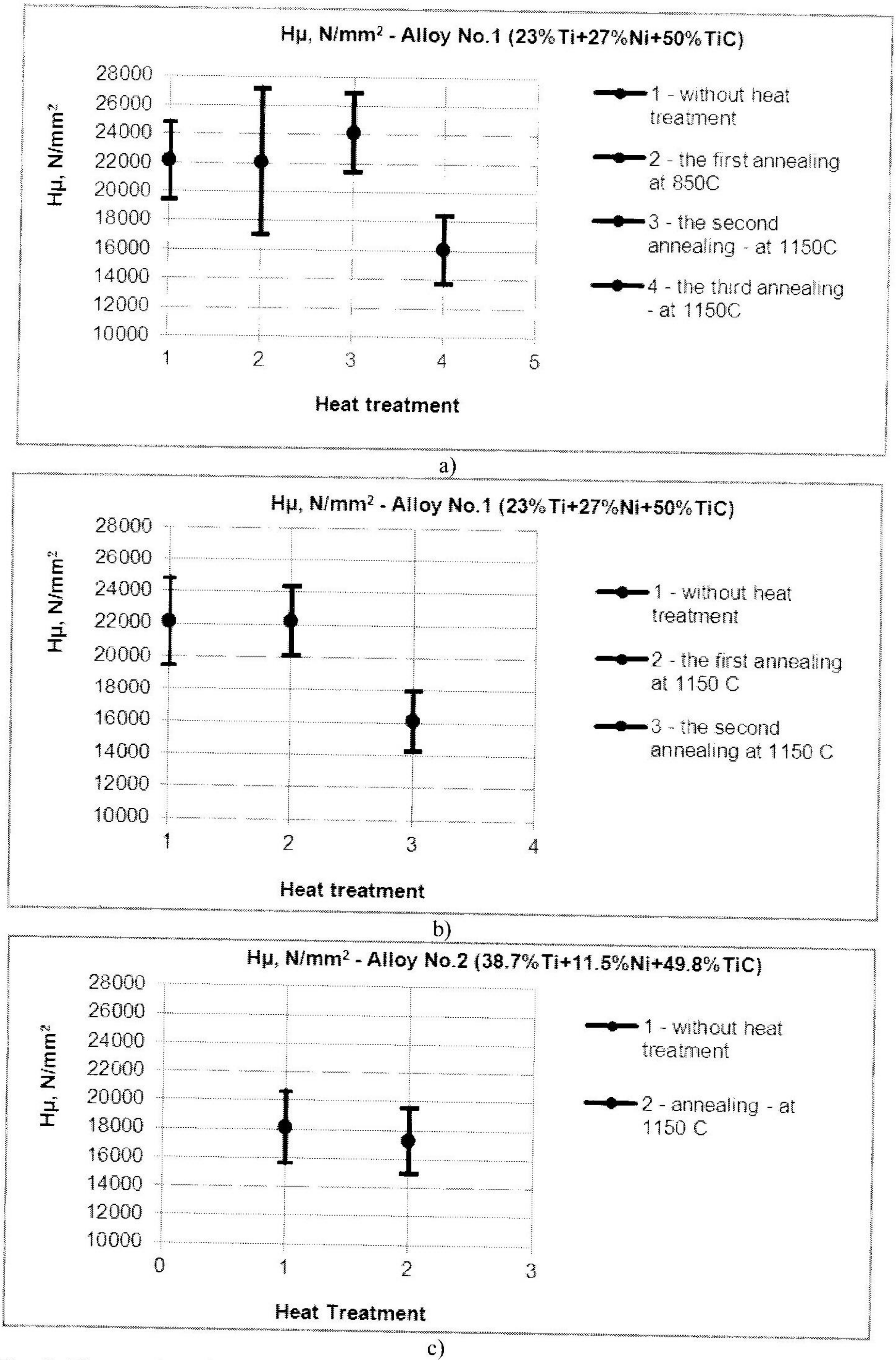
Estimating microhardness, it was determined decreasing of this feature of alloy No.1 after each annealing both with and without intermediate annealing at 850°C (fig. 1 a, b), while the microhardness of alloy No. 2 is virtually constant (fig. 2 c). The results of microhardness test also confirm the assumption about phase transformation after heat treatment. Therefore, each alloy underwent the X-ray structural analysis whose results are depicted in table 3.

According to ternary Ni-Ti-C diagram [2], experimental materials must have structure (at RT): alloy No. 1 – ($Ti+TiC+Ti_2Ni$) and alloy No. 2 – ($TiC+Ti_2Ni+TiNi$). However, as it has been mentioned before, such precise compound can hardly be achieved in real working conditions due to non-equilibrium cooling, fluctuations, etc.

Thusly phase composition of alloys consists of different intermetallics of Ni-Ti and titanium carbide. Despite the fact that material was pressed in vacuum, the presence of titanium oxide was indicated, although, it could be formed while preparing the samples.

It is known that B2 and B19` are two modifications of NiTi which can exist at different temperatures, it is so-called "austenite" and "martensite" of titanium nickelide respectively [6, 7]. These names occurred because of transition B2→B19` on which basis "shape memory effect" is carried out. Main mechanism of strain-induced deformation accumulation and the following shape recovery is reversible thermoelastic martensitic transformation and reversible reorientation of martensite [6]. Initial high-temperature B2 phase transforms into B19` phase directly or through intermediate rhombohedral phase under load or after unloading.

According to the last research [6], the temperature of direct transformation B2→B19` is +78...-63°C during quenching from 700°C and this temperature is rising with decreasing of nickel content. While slow cooling B2→R→B19` transformation takes place. In addition, temperatures of transformation strongly depend on structure imperfection, dislocation density and previous heat treatment [7].



a)

b)

c)

Fig. 2. The results of microhardness test: a, b – alloy No. 1, c – alloy No. 2 (annealing procedures were done following each other)

Tab. 3. The results of X-ray structural analysis

Possible phases	Structure type [3]	Alloy No. 1		Alloy No. 2
		After CHVP	Annealing at 1150°C	After CHVP
TiC	Cubic (Fm3m)	✓	✓	✓
(Ni,Ti)	Hexagonal	✓	✓	✓
NiTi	Cubic (B2)	✓	Not ID	Not ID
NiTi	Monoclinic (B-19`)	✓	✓	✓
Ni_4Ti_3	Rhombohedral	✓	Not ID	Not ID
Ni_3Ti	Hexagonal (P63/mmc)	✓	✓	✓
Ti_2Ni	Cubic (Fd3m)	✓	✓	✓
TiO	Monoclinic (F2/m)	✓*	✓*	✓*

✓* - doubtful estimate

Analysing results of X-ray tests (table 3) one can admit that there is no B2-phase and Ni_4Ti_3 in alloy No. 2 as opposed to alloy No.1. After CHVP material was cooling slowly to RT, that is why most probably the B2→R→B19` transformation occurred. This result is shown by alloy No. 1.

There is neither rhombohedral, nor B2-phase in alloy No. 2. A Similar situation is observed in alloy No. 1 after annealing at high temperature. It means that phase transformation occurred after heat treatment.

Alloy No. 2 has lower content of nickel and it can be the reason for a different structure of alloy. It is most likely that changing of chemical composition caused rising of transition temperature, so that alloy No. 2 after pressing has B19`-NiTi without retained B2-phase.

Conclusion

To sum up, it was shown that structure of TiC-NiTi alloys right after controlled hot vacuum pressing is metastable and tends to transformations. Investigated samples have the following phase composition:

1) Alloy No.1 (23%Ti+27%Ni+50%TiC) – carbides TiC, intermetallic phases Ni_4Ti_3, Ti_2Ni, Ni_3Ti and both B2 and B19`-NiTi;

2) Alloy No.2 with lower Ni content (38.7%Ti+11.5%Ni+49.8%TiC) – carbides TiC, intermetallic phases Ti_2Ni, Ni_3Ti and only B19`-NiTi.

After annealing B2-NiTi and Ni_4Ti_3 was not identified in alloy No. 2 as a result of B2→B19` transformation, in consequence of which the change in volume content of matrix and level of hardness was changed. The part of the microslice square that is captured by the binder is increasing after each following treatment at 1150°C in alloy No. 1, while the microhardness is declining. As a consequence there is a growing share of B19`-NiTi in the structure. In alloy No. 2 both parameters are staying at a constant level, which can be considered as evidence of phase transformation absence that can be suppressed by lower Ni content.

Thus, the structure and phase composition of TiC-NiTi powder alloys was ascertained and the following step for studying is to estimate mechanical properties and the influence of intermetallic particles on it.

References

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