Structural peculiarities of cermets design based on titanium carbide

Part II *The increase of properties of high-temperature TiC-based cermets by intermetallic strengthening*

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The influence of nickel addition on microstructure and mechanical properties of titanium carbide frames with different chemical compositions and the cermets based on them, has been considered. It was shown that the increase of the nickel content in the initial charge leads to the refining of the frame microstructure and to a decrease of the porosity of titanium carbide frames which still remain open. Metallic or intermetallic layers appear in the intergranular areas. These factors have a significant influence on the mechanical properties of the cermets.

1. Introduction

As mentioned in Part I [1], the use of products of self-propagating high-temperature synthesis (SHS) in the form of porous frames and the control of their chemical composition allow higher strength properties to be achieved in cermets. However, a drawback of this process of frame production is the formation of residual metal layers along the grain boundaries of refractory phases, which has a negative effect on the mechanical properties of frames and cermets, particularly at high temperatures [2, 3].

The softening effect of the metal phase located along grain boundaries of refractory phases may be eliminated by the additional alloying of the initial charge with different elements. As a result, owing to the chemical reaction, new compounds with higher mechanical properties can be formed (for example, carbides, nitrides, intermetallic compounds).

This part of the work concerns the study of the influence of the addition of nickel on the microstructure and mechanical properties of titanium carbide frames having different chemical compositions, and cermets based on them.

2. Experimental procedure

Owing to a wide area of homogeneity of the titanium carbide, a different volume of residual metal phase in frames as a result of the SHS reaction can be obtained [4]. Nickel, in combination with the residual titanium phase, can produce several intermetallic compounds (NiTi, $NiTi_2$, Ni_3Ti) [5], with improved mechanical properties in different temperature intervals. The use of nickel as an alloying element is of special interest.

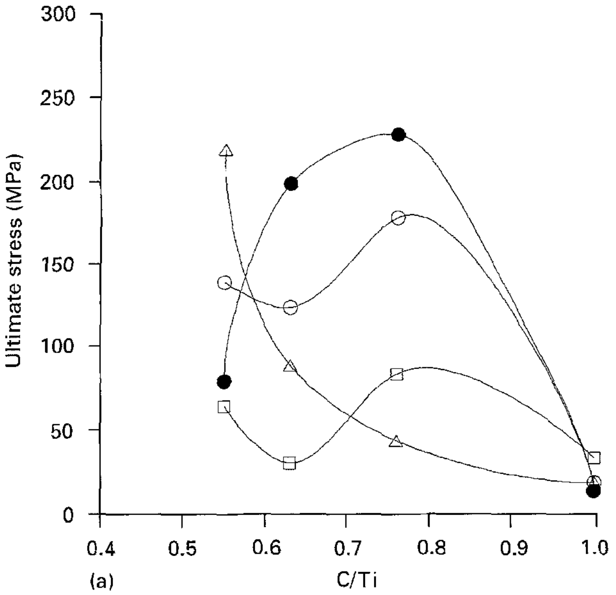
Different amounts of nickel powder (2.5, 5, 7.5, 10 and 15 wt %) were added to the initial charges of compositions of $TiC_{0.55}$, $TiC_{0.65}$, $TiC_{0.75}$ and $TiC_{1.0}$. The cold-pressed powder samples, with diameter 10 mm and height 20 mm, were annealed at 600 °C for 10 min in a vacuum at a residual pressure of 1.3 Pa. Thereafter, the combustion reaction was initiated without extracting the degased samples from the reactor.

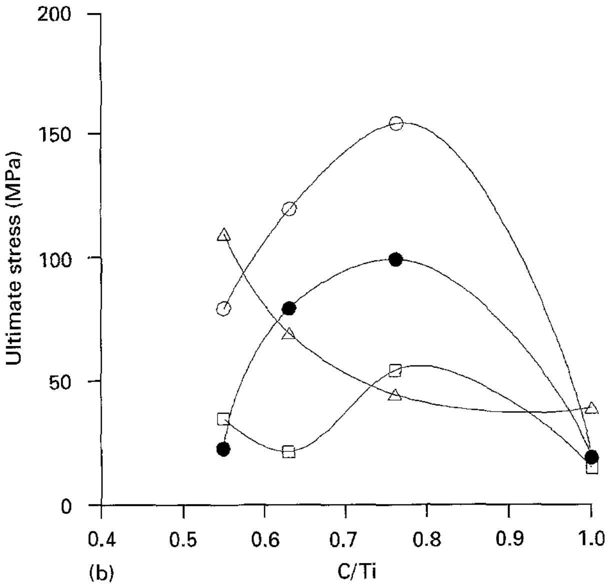
The methods of metallographic, X-ray analyses, porosity measurement, the compression tests and the production of cermets by vacuum infiltration were described in Part I [1].

3. Results and discussion

The results of high-temperature mechanical tests show that the chemical composition of frames and their alloying, significantly influence the ultimate stress at different temperatures (Fig. 1a–c). The ultimate stress of frames without the addition of nickel monotonically decreases with increasing C/Ti ratio at temperatures of 600–900 °C. The strength of the carbide frames at 1000 °C increases as their chemical composition approaches stoichiometry. The frames of stoichiometric composition have the highest strength properties at this temperature.

The addition of nickel to the initial charge changes the strength of the frames. The ultimate stress of the frames, having a C/Ti ratio from 0.65–0.75, strongly





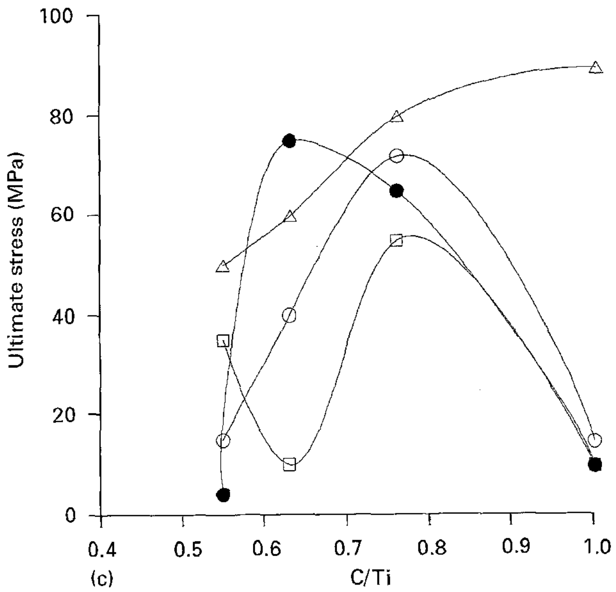


Figure 1 The dependence of ultimate stress on C/Ti ratio of titanium carbide frames with different amounts of nickel at (a) 800 °C, (b) 900 °C, and (c) 1000 °C, (△) without the addition of nickel, (○) 2.5% Ni, (●) 7.5% Ni, (□) 15% Ni.

depends on the amount of nickel, the greatest value of ultimate stress being observed when the nickel content is in the range 2.5–7.5 wt %.

The alloying of the stoichiometric frames with nickel results in an abrupt decrease of their strength only at a temperature of 1000 °C. However, the high mechanical properties of the frames with $TiC_{0.65}$ and $TiC_{0.75}$ compositions at this temperature (comparable with the properties of stoichiometric carbides) can be stabilized by adding 2.5%–7.5% Ni (Fig. 1c).

Thus, the addition of nickel to the initial charges of titanium carbide of non-stoichiometric compositions (C/Ti = 0.65–0.75), in amounts of 2.5%–7.5%, has a positive effect on the ultimate stress of porous frames in a wide interval of operating temperatures.

Both the grain size of the carbide phase and the porosity of the frames also depend considerably on the amount of nickel in the initial charge. On production of $TiC_{1.0}$ compound, the grain size decreases from 11.2 μm to 6.4 μm by increasing the nickel content from 2.5% to 15%. The porosity type remains predominantly open and changes from 65% at 2.5% Ni to 45% at 15% Ni. The volume of small closed pores is no more than 1%–2%.

For the non-stoichiometric composition frames, the decrease in the carbide grain size occurs more intensively with increasing nickel content in the initial charge. Thus by increasing the nickel content from 2.5% to 15% the average grain size decreases from 10 μm to 4 μm for the frames of $TiC_{0.75}$ composition and from 6 μm to 2 μm for the frames of $TiC_{0.55}$ composition. The porosity also decreases as the nickel content increases: for the $TiC_{0.75}$ frames, porosity decreases from 65% to 45% and for $TiC_{0.55}$ frames from 45% to 20%.

The fractographic investigations of the fracture surfaces of samples tested in a vacuum at different temperatures demonstrate that at temperatures lower than that of the ductile–brittle transition (DBT) the fracture of frames is of a brittle intergranular character, but when the temperature exceeds that of the DBT, a transcrystalline component appears on the fracture surface, the amount of this component increasing with increasing temperature.

The regularities of the changes in the properties of frames on alloying are also retained after infiltration by the superalloy (Table I). The ultimate stress of cermets based on stoichiometric titanium carbide decreases considerably in the case of alloying, particularly at high temperatures. Therefore, the ultimate stress decreases more than twice on the addition of 15% Ni into the frames.

The ultimate stress of cermets based on non-stoichiometric composition frames depends on the amount of the alloying element present. The strength of cermets does not change considerably with only a small amount of nickel (2.5%), although a slight decrease takes place. The ultimate stress of the samples on addition of 7.5% nickel distinctly increases within the whole range of test temperatures (Table I).

The differences in properties of different frames and cermets can be attributed to the features of their

TABLE I Mechanical properties of cermets of (TiC_x–Ni)–superalloy composition at different temperatures

Composition of cermets	Ultimate strength (MPa)					
	600 °C	700 °C	800 °C	900 °C	1000 °C	1100 °C
$TiC_{1.0}$ + superalloy	1550	1370	1200	940	700	370
($TiC_{1.0}$ + 2.5% Ni) + superalloy	1400	1270	1050	810	480	250
($TiC_{1.0}$ + 7.5% Ni) + superalloy	1300	1100	900	730	520	180
($TiC_{1.0}$ + 15% Ni) + superalloy	1350	1200	1000	750	350	140
$TiC0_{0.75}$ + superalloy	1600	1630	1250	900	580	220
($TiC_{0.75}$ + 2.5% Ni) + superalloy	1650	1600	1200	830	550	210
($TiC_{0.75}$ + 7.5% Ni) + superalloy	1850	1650	1300	1000	660	330

TABLE II Phase composition of carbide titanium frames at the addition of nickel

Chemical compounds	Amount of nickel (%)	Phase composition
$TiC_{0.55}$	–	$TiC_{0.55}$, α-Ti
	2.5	$TiC_{0.55}$, solid solution of Ni in α-Ti
	7.5	$TiC_{0.55}$, Ti_2Ni, solid solution of Ni in α-Ti
	15	$TiC_{0.55}$, Ti_2Ni
$TiC_{0.65}$	–	$TiC_{0.65}$, α-Ti
	2.5	$TiC_{0.65}$, Ti_2Ni, solid solution of Ni in α-Ti
	7.5	$TiC_{0.65}$, Ti_2Ni, solid solution of Ni in α-Ti
	15	$TiC_{0.65}$, Ti_2Ni, Ni
$TiC_{0.75}$	–	$TiC_{0.75}$, α-Ti
	2.5	$TiC_{0.75}$, Ti_2Ni, solid solution of Ni in α-Ti
	7.5	$TiC_{0.75}$, NiTi
	15	$TiC_{0.75}$, NiTi, Ni
$TiC1_{1.0}$	–	$TiC_{1.0}$
	2.5	$TiC_{1.0}$, Ni
	7.5	$TiC_{1.0}$, Ni
	15	$TiC_{1.0}$, Ni

microstructures. X-ray analysis of the frames shows that the addition of nickel powders into the initial mixture of the stoichiometric titanium carbide leads to the formation of nickel-phase layers along the grain boundaries (Table II). The distribution of the nickel phase is inhomogeneous in the carbide frames with a small amount of nickel, and as a result, some boundaries of a carbide–carbide type are retained (Fig. 2a). The distribution of the metal phase in frames is more homogeneous when the concentration of nickel is increased to 10%, and in this case, all grain boundaries are transformed to interphase ones of a carbide–nickel type (Fig. 2b). When there is 15% Ni, massive precipitations appear in triple junctions of carbide grains (Fig. 2c). The ultimate stress of the nickel phase depends more strongly on the temperature than that of the carbide phase. For this reason, the increase in the interphase boundaries of the carbide–nickel type results in an abrupt softening of frames and, consequently, of cermets based on them. On the other hand, the refining of the grains upon addition of nickel must lead to an abrupt rise in the strength [6]. The refining of structure is accompanied by some decrease of porosity, which in turn increases the true cross-section of the frames. However, as can be seen from the test results, the intergranular metal phase considerably influences the strength properties and the effect of softening essentially exceeds that of hardening.

The alloying with nickel results in the appearance of layers between carbide grains in non-stoichiometric composition frames as well (Fig. 2d). However, in this case, nickel is allowed to form intermetallic compounds from the surplus titanium phase. $NiTi_2$–intermetallic compound is formed with a small nickel content, and as this increases up to 7.5% the NiTi–intermetallic compound appears (Table II). If the titanium phase is in excess of that required for the formation of the intermetallics that it can retain, and if the titanium phase is in short supply for the formation of intermetallics, then surplus nickel phase can be formed. The phase composition does not change on further increase of the nickel amount up to 15% and the formation of the Ni_3Ti–intermetallic compound is not observed. Apparently, the reason for these phenomena is the insufficient amount of nickel for the formation Ni_3Ti compound.

The formation of intermetallic compounds between carbide grains increases the ultimate stress of the frames, because the mechanical properties of intermetallics are higher than that of nickel, particularly at high temperatures. The effect of strength increase is higher for the NiTi–intermetallic compound compared to the $NiTi_2$ compound owing to the higher melting temperature of NiTi [7]. Moreover, the refining of the carbide grains contributes to the strength increase in such materials as well. The structure of frames does not essentially change on subsequent

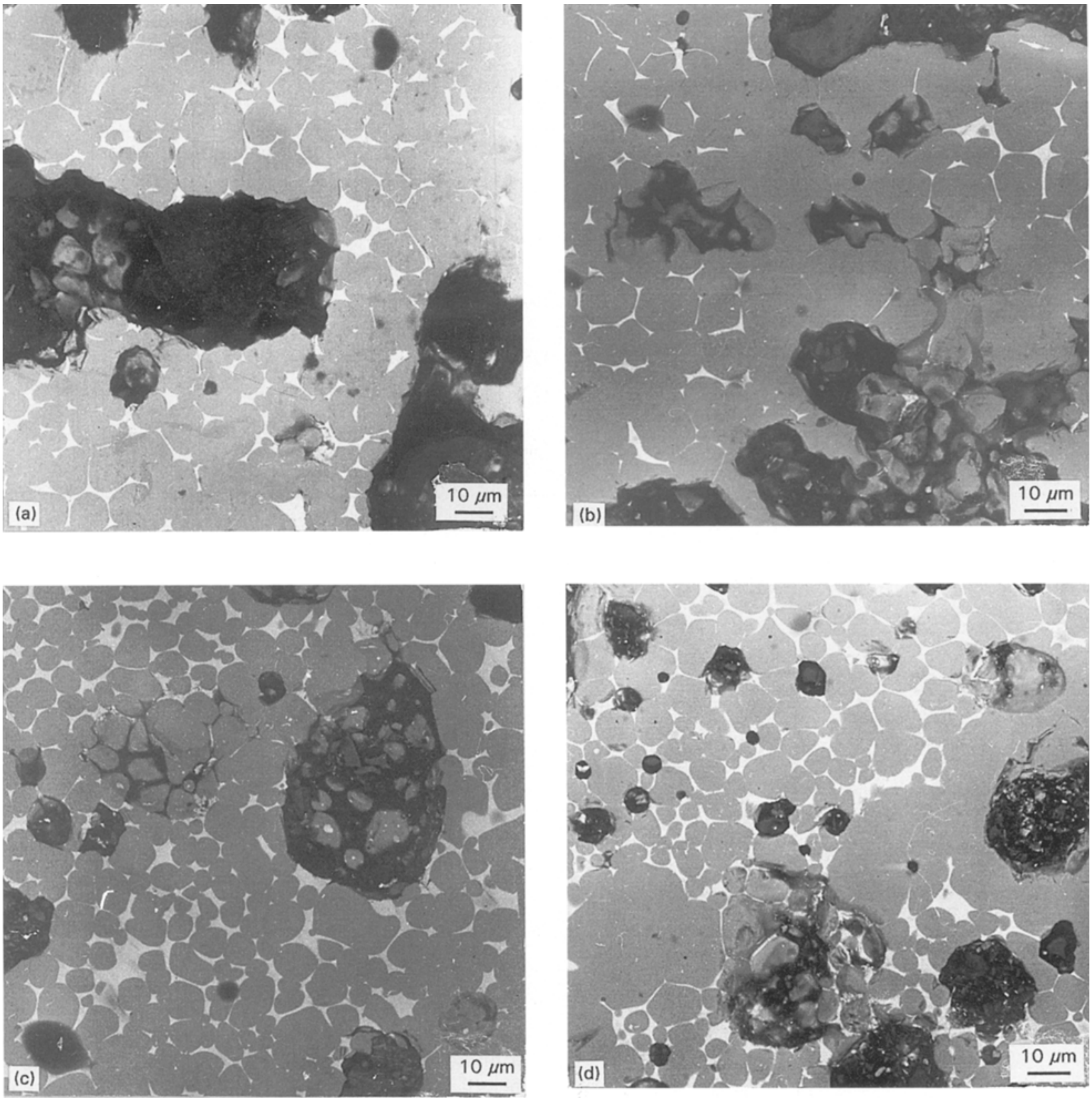


Figure 2 The microstructure of titanium carbide frames with different amounts of nickel. (a) $TiC_{1.0}$–2.5% Ni, (b) $TiC_{1.0}$–7.5% Ni, (c) $TiC_{1.0}$–15% Ni, (d) $TiC_{0.75}$–7.5% Ni. The structural elements seen are as follows: the grey phase is grains of the titanium carbide, the light phase is the phase on nickel base, and the dark phase is the pores.

infiltration and cermets based on such frames are characterized by higher strength properties (Table I).

The studies show that the fracture of the cement surfaces in this case is mainly of a transcrystalline type. This can be explained by additional hardening of the intergranular space by γ'-phase during infiltration.

4. Conclusions

1. During the production of the titanium carbide frames by means of SHS, the increase in the nickel content in the initial charge leads to refining of the frame microstructure and to a decrease of their porosity. Layers of metallic phase and/or intermetallic compounds appear in the intergranular space.

2. The composition of the intergranular phase of refractory frames exerts a dominating influence on the mechanical properties of cermets. A higher level of high-temperature properties can be obtained by the formation of intermetallic compounds in the intergranular space.

3. Higher strength properties of cermets are observed at the transcrystalline type of fracture, which can be obtained by hardening the intergranular boundaries in the carbide frame.

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