The structure and phase composition of hard alloys of the Cr$_3$C$_2$-Ti system produced by explosive compacting of powders

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Abstract. The work presents the findings of theoretical and experimental studies by scanning electron microscopy and energy-dispersive electron microprobe analysis of the phase composition of hard alloys produced by explosive compacting of the powders of chromium carbide Cr$_3$C$_2$ with titanium. It was found that when the powder mixture is heated in shock waves to 660 °C, the phase composition of hard alloys corresponds to that of the initial components of the powder mixture. With the increasing intensity of the explosive compacting, formation of secondary carbides is observed on the border of the initial components. A further increase in temperature results in a local melting and formation of new fine phases. With the subsequent temperature rise in the shock waves, a transition to the calculated equilibrium composition is observed.

1. Introduction

Explosive compacting is one of the promising types of impulse compaction, which significantly expands the capabilities of powder metallurgy technology in the creation of new materials [1]. The explosive processing enables achievement of the pressure sufficient for uniform compaction of powders to a practically pore-free state, and at the same time, the temperature required for consolidation (welding) of the structural components of powder material [2]. A short-term exposure to high pressure and temperature makes it possible to prevent the secondary interaction between the components of alloys that allows for using titanium, a metal reactive in high temperature, as a binder [3].

To analyse the processes occurring during both the shock-wave action on powder mixtures and the subsequent heating of hard alloys, it is very important to know the nature of the interfacial interactions between their components. We usually lack this knowledge when using new, little-known compositions of hard alloys. In these circumstances, we have to resort to computer thermodynamic simulation followed by direct experiments.

2. Materials and methods

We used hard alloy samples of the Cr$_3$C$_2$-Ti system, containing from 22 to 40 wt. % of titanium, produced by explosive compacting of the mixture of pure chromium carbide powders Cr$_3$C$_2$ KHN-1 (TU 14-22-28-90) with PT5 powders of titanium (TU 14-22-57-92) on the substrate of steel 09G2S according to the scheme of a normal-incidence detonation wave [4].
Chromium carbide (Cr$_3$C$_2$) was chosen as the alloy base because it is the most promising carbide for operation in oxidizing medium at temperatures of 300–400°C [5, 6], which correspond to the conditions typically achieved during the operation of friction assemblies of pumps for the transfer of overheated distillate. Titanium was used as the metallic binder due to its low acoustic stiffness, which ensures good compressibility of the powder mixture during explosive processing [7].

Compaction according to a similar scheme is accompanied by the propagation of the incident shock wave through the powder mixture and wave reflection from the surface of the monolithic substrate and the intermediate spacer. Simultaneously, the temperature increase in the powder material typically occurs in the incident wave travelling through the undisturbed powder, and the maximum pressure of its compression is achieved within the reflected shock waves, which is optimal for pressure welding.

The maximum pressure of the shock wave compression was calculated using the (P, u) diagram method based on the step-by-step determination of the characteristics of the incident and reflected waves by analysis of the intersection of shock adiabats of the spacer, powder, base, and detonation products in ‘pressure–mass velocity’ coordinates by applying the specially developed software. The powder heating temperature was calculated from the increase in its internal energy behind the front of the incident shock wave, which was determined by the mass velocity of the powder particles [8].

During the explosive compaction, the powder mixture in the shock waves was heated to 650–1300 °C, with the maximum compression pressure of 12 to 15 GPa, which ensured the obtaining of a monolithic hard alloy of the Cr$_3$C$_2$-Ti system at the compaction stage [9].

Thermodynamic calculations of the phase state were performed using the Thermo-Calc software package, based on the numerical simulation of phase equilibrium CALPHAD [10, 11].

Studies of the microstructure and the phase composition of the obtained materials were carried out using optical metallographic microscope Carl Zeiss Axiovert and a dual beam scanning electron microscope (SEM) ‘FEI Versa 3D’, equipped with gas-injection platinum deposition system GIS, transmitted electrons detector STEM that forms images in a dark-field (DF) and bright field (BF) transmission mode with high contrast to the crystallographic planes and the grain structure, accordingly. The integrated energy-dispersive electron microprobe analysis system ‘EDAX Apollo X’ allows a determination of the elemental composition with a high degree of localization on a specially prepared sample – foil of about 50–100 nm thick [12].

The foil preparation procedure involved the microsection preparation on a semi-automatic grinding-and-polishing machine with microprocessor control TegraPol-11. The sample was then placed in an electron microscope chamber, wherein a platinum layer, required to protect the surface from the ion beam effect, was deposited on the location of interest on the sample, using the gas-injection system. After that, cutting on the sides and etching with a focused ion beam of Ga$^+$ is carried out from above and below the platinum layer, thereby a special sample piece – a foil 20–25 μm long, 5–7 μm high, and 1–2 μm thick – is obtained for transmission microscopy. Then, a needle-manipulator is brought and soldered to the obtained plate by platinum deposition. At the next stage, the foil sample piece is transferred onto a special holder – a copper grid, and fixed to it. Next, the foil is thinned with an ion beam on both sides until it becomes electron-light (thickness of about 50–100 nm). Now, the copper grid with the fixed foil is placed in a special holder of the STEM detector.

3. Results and Discussion

Thermodynamic calculations (Figure 1) demonstrated that equilibrium phases in the alloys of chromium carbide and titanium in the investigated range of concentrations (up to 40 wt. % Ti) may be: starting chromium carbide Cr$_3$C$_2$, titanium carbide TiC, chromium carbides bound with carbon Cr$_7$C$_3$ and Cr$_{23}$C$_6$, and solid solution Ti in Cr.

Therefore, the exposure of a chromium carbide and titanium mixture to a rather high temperature should theoretically cause a change in the phase composition of the material. It can be expected that the interaction of the starting components in this case will result in the formation on the interface surface between Cr$_3$C$_2$ and Ti, of the alternating layers of stable phases TiC and Cr$_7$C$_3$, Cr$_{23}$C$_6$ or Cr,
the boundaries of which will move towards the initial phases up to the disappearance (full or partial) of the latter ones.

However, the study of the microstructure and line profile of the elements distribution between the phases of the hard alloy produced by explosion at a maximum compression pressure of 12 GPa, with simultaneous heating of powder chromium carbide mixture Cr$_3$C$_2$ with the titanium binder in the amount of 22 wt.% in the shock waves up to 660°C (Figure 2 a) showed no traces of chemical interaction between the components of the base powder mixture: all the titanium remained a part of the metal phase of the alloy, and chromium, and carbon – of the carbide phase.

The revealed fact can only be explained by an extremely short duration of the material exposure to pressure and temperature, within which the diffusion processes could not change the phase composition of the material in any noticeable degree.

With increasing explosive compacting pressure and a corresponding rise in the average heating temperature for the powder mixture in the shock waves, we nevertheless managed to find changes in the microstructure and nature of the elements distribution between the phases in the alloys containing 40 wt.% of titanium (Figure 2 b, c, d).

A double layer formed on the ‘carbide – binder’ border (Figure 2 b). On the outer side of the carbide particle, we detected a bright layer about 700 nm thick, and on the side of the material – a dark layer about 400 nm thick, which is indicative of a change in the average atomic number of the studied area [13].

The intensity distribution of the characteristic radiation of the carbon atoms along the scan line shows that as we approach the carbide particle boundary, we can see a slight decrease in the carbon
content in the near-surface layer of the chromium carbide particle, followed by an abrupt change at the electron probe exit on the boundary layer of the material binder, that can be explained by the diffusion of carbon in the boundary layers of the chromium carbide particles towards the titanium binder, with formation of the titanium carbide layer on its border.

With the increasing alloy heating temperature during explosive processing, we can see the signs of melting on the surface of the initial particles of chromium carbide and the material matrix [14], which causes the appearance of three fine phases in the metal binder which evolved during the melt crystallisation (Figure 2 c): of a presumably solid solution based on chromium, titanium carbide and Laves phase TiCr₂, which can thermodynamically emerge (Figure 1) because the content of titanium in the metal binder in the case of incomplete dissolution of the starting chromium carbide may greatly exceed 45 wt.%. These phase changes are manifested in the appearance of alternating peaks on the chromium and titanium percentage curves (Figure 2 c).

A further increase in the explosive loading rate results in a complete transition of a hard alloy in the equilibrium state: (Figure 2 d) chromium carbide particles Cr₃C₂ disappear from its structure, and particles of a new phase appear instead. They are round-shaped and sized from 500 nm to 1.2 µm, uniformly arranged in the matrix.

**Figure 2.** The microstructures of hard alloys of the Cr₃C₂-Ti system at various stages of interfacial interaction, SEM Versa 3D: a – the structure corresponding to the phase composition of the starting components; b – the stage of the double boundary layer; c – the melting stage with the appearance of fine phases; d – the equilibrium structure of hard alloy Cr₃C₂-Ti after explosive compaction.
The electron-probe test along the scan line indicates that particles of titanium and carbon have titanium and carbon in their composition in this case, whereas the alloy matrix consists essentially of chromium. This corresponds to the calculation of phase equilibria in the studied system (Figure 1), under which the hard metal carbide phase should be titanium carbide TiC, and a binder – a solid solution of titanium in chromium.

4. Conclusions
The phase composition of hard alloys of the Cr3C2-Ti system, produced by explosive compacting of powders on a steel base in the modes, providing heating of the powder mixture in the shock waves of up to 660°C, corresponds to the composition of the starting components of the powder mixture.

With the increasing intensity of the explosive loading, we observe interfacial interactions between the hard alloy components which mainly take place in the liquid phase, and result in the disappearance of the initial constituents and appearance of the new ones, thus the alloy becomes equilibrated: titanium carbide becomes the major carbide phase, and chromium - the metal binder.

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