

Cr₃C₂ and VC influence on the structure and properties of WC-Co solid alloys

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Abstract. In this paper, the effect of inhibiting additives of highly dispersed vanadium and chromium carbides on the structure and properties of the VC6 hard alloy was studied. It has been established that a correctly selected amount of additives (up to 1.5% by weight) can significantly reduce the grain size (from 2.5 to 1.5 μm) of the strengthening phase.

1. Introduction

Carbides are known to be the alloys of metals with carbon and represent the most important and the broadest class of inorganic compounds with high mechanical and physical-chemical characteristics. Now we should focus the attention on tungsten carbide (WC) and the alloys with cobalt on its base, for instance, WC-Co. Hardness parameters for tungsten carbide are relatively stable and in comparison with other carbides, they change slightly at the temperature increase up to $\sim 1000^\circ\text{C}$. Moreover, in contrast with carbides of other transition metals tungsten carbide has higher Young's modulus ($\sim 700\text{GPa}$) and a lower coefficient of thermal expansion ($5.5 \cdot 10^{-6}\text{K}^{-1}$). It is the set of mentioned above characteristics and thermal stability that influence the use of WC as a base material in production of solid alloys suitable for metal working and drilling operations. Sintering is considered to be the most important stage of a conventional technique of solid alloys fabrication. The product is sintered from a pressed powder mixture with a plasticizer additive. After sintering, an average grain size of a carbide phase noticeably increases when compared with the grain size of the initial WC powder. Since fine-grained alloys display higher serviceability, the use of a fine-grained mixture for sintering will yield higher quality alloys. Alloying additives of other carbides are used to retard the grain growth in carbide phase of WC-C alloys. Growth inhibitors mainly find industrial application for sintering of WC-Co fine-grained solid alloys. The inhibitors could be arranged in the following order with regard to their relative efficiency: $\text{VC} > \text{Cr}_3\text{C}_2 > \text{NbC} > \text{TaC}$ [1].

Consequently, vanadium carbide (VC) and chromium carbide (Cr_3C_2) have the best effect on the grain growth. It is important to note that combination of VC with other additives ensures the most efficient growth control [2]. In spite of its best ability to inhibit grain growth and to increase the hardness of solid alloys significantly, some decrease in product strength and crack resistance could be observed. A negligible quantity of alloying additives (0.5-1.0 wt%) is added into the initial charge, but it's quite sufficient to improve the properties of solid alloys belonging to WC-Co system. The decrease in growth of tungsten carbide grains is explained by the fact that VC or other solid alloying additives segregate on WC crystal surfaces, that leads to reduction in WC solubility in Co by 2 – 4 times [3]. In turn, it impedes coalescence and formation of agglomerates during sintering [4]. Such an approach to inhibition of WC-Co grain growth appears to be the most perspective. It should be recognized that the



studied solid alloying additives were used in nanodisperse state. The information about the use of growth inhibiting additives with micron size particles is practically not available. The objective of this research is to study how the inhibitors of tungsten carbide (vanadium and chromium carbides) grain growth can affect the structure and properties of sintered solid alloys.

2. Materials and experimental procedure

Vanadium ($\text{VC}_{0.88}$) and chromium (Cr_3C_2) carbides were synthesized by the carbothermal method via reactions:



The synthesis technique is characterized by the use of nanofibrous carbon (NFC), which is a new kind of a carbon material. NFC consists of 4-8 mm granules formed by closely interwoven carbon nanofibers with the diameters of 30-100 nm. NFC is quite pure: its impurities are the residues of the starting catalyst (90 wt % Ni/10 wt % Al_2O_3) and their content does not exceed 1.0 wt % [5]. To carry out synthesis, the NFC granules were ground in an agate mortar and sifted through a sieve with a mesh size of 100 μm . The specific surface area of the powdered NFC is approximately equal to 150 000 m^2/kg , which is much higher compared with the specific surface area of lampblack ($\sim 50\,000\, \text{m}^2/\text{kg}$) [5, 6]. The other reagent was vanadium oxide (V_2O_3) (6-09-02-390-85 Specification, purity 99 wt. %, the average particle size is 0.92 μm). All of the starting reagents were dried in the oven at 100 $^\circ\text{C}$, to remove moisture before the experiment.

The synthesis of the above mentioned carbides was conducted in a crucible-type induction furnace under the inert gas (argon) atmosphere, thus eliminating the probability of undesirable nitriding of the reaction products. The starting reagents were measured out in doses in accordance with the stoichiometry of the reactions (1) and (2). The starting powders were mixed by passing them through a sieve with a mesh size of 100 μm . One-phase solid alloys were obtained at the holding time of 20 minutes and at 1500 $^\circ\text{C}$ for vanadium carbide and 1300 $^\circ\text{C}$ for chromium carbide. The impurity content did not exceed 2 wt % [7, 8].

These carbides were used as alloying additives to fabricate products from WC-Co (6 wt. % of Co) solid alloy. Sedimentation analysis was carried out with the use of the MicroSizer 201 facility to determine the average sizes of the powder particles, the degree of dispersion, values of standard deviations and to obtain asymmetry indicator (skewness) histograms. The above mentioned parameters are determined by means of the «geometric» method described in [9]. The obtained data are presented in table 1.

Table 1. The results of sedimentation analysis.

Sample	The average size of particles, μm	Standard deviation	Skewness
WC-Co	1.68	1.71	0.03
vanadium carbide	4.07	2.5	-0.01
chromium carbide	7.10	2.1	-0.18

The values of the standard deviations for the powder of WC-Co solid alloy are indicative of the fact that the particles are «moderately sorted», i.e. they are distinguished by a relatively wide range of particle size distribution. The values of the standard deviations for the powders of carbides give

evidence of a wide range of particle size distribution (they are «poorly sorted» or polydisperse). Comparatively low values of the asymmetry indicators must be a proof of the histograms symmetry.

The first stage of the powder mixture study presupposes preparation of suspension on the ethanol base. The powder content in the mixture equaled 60 wt %. Then, grain growth inhibitors were added into the WC-Co powder suspension. Vanadium and chromium carbides were chosen as the inhibitors in weight ratio of 1:1. Their content against WC-Co powder content was measured in wt %: 0.30 (0.15 + 0.15); 0.60 (0.30 + 0.30); 0.90 (0.45 + 0.45); 1.20 (0.60 + 0.60) и 1.50 (0.75 + 0.75). To achieve deagglomeration of WC-Co solid-alloyed mixtures and homogeneous distribution of inhibitors in WC-Co suspensions, they were exposed to ultrasound for 30 minutes with the use of 2kW generator.

The next stage presupposes granulation process to improve quality of the compacted samples (density increase). To increase strength of the pressed material, we added the PVAC100 bonding additive in proportion of 2wt % from the mass content of the powder. The suspension was dried at 110° C for 24 hours. Fritsch Analysette 3 vibrosieves were applied at the final stage of pressed-powder preparation. The size of the granules for molding was 100-250 µm. Mold pressing of the powder was done by uniaxial pressing with the «Instron 3369» universal electromechanical test machine, Great Britain. A metal press-mold was used for compacting the powder. The prepared compacts had the dimensions of 5x5x40mm. The compacts were sintered in the electric vacuum furnace with resistance of CTB- Liquid-phase sintering was carried out in vacuum of $2 \cdot 10^{-4}$ mm Mercury, at 1380°C, for 40-minute holding time. The heating rate was equal to 5°C/min. The sintered samples were cooled inside the furnace.

The density of the sintered samples was determined by hydrostatic weighing method (Archimedean method). Bending strength is considered to be one the main mechanical characteristics of metal ceramics. Three-point bending tests were conducted with the «Instron 3369» universal electromechanical testing machine. Vickers hardness was measured with the use of the 402 MVD hardness meter under 200g load. Fabrication of polished sections from solid-alloys includes the following stages: 1. The samples were cut with «Discotom-65» (StruersA/S) machine. 2. Filling of the material was completed on the SimpliMet press. 3. The sample sections were ground for surfacing on each abrasive disk of the «Buehler, Ltd» grinding/polishing machine. 4. The sections were polished on the hand machine with each of the polishing pastes (60/40, 28/20, 14/10 and 1/0 dispersiveness) for ten minutes. The polished sections were etched for 5 minutes in the fresh mixture of potassium ferrocyanide ($K_3[Fe(CN)_6]$), potassium hydroxide (KOH) or NaOH 20% solutions used in equal proportions. Microstructure studies of the prepared samples were conducted with the CarlZeiss EVO 50 scanning electron microscope (SEM). The sintered sample from WC-Co solid alloy without additives was studied to make correlation between the results of the analogous investigations.

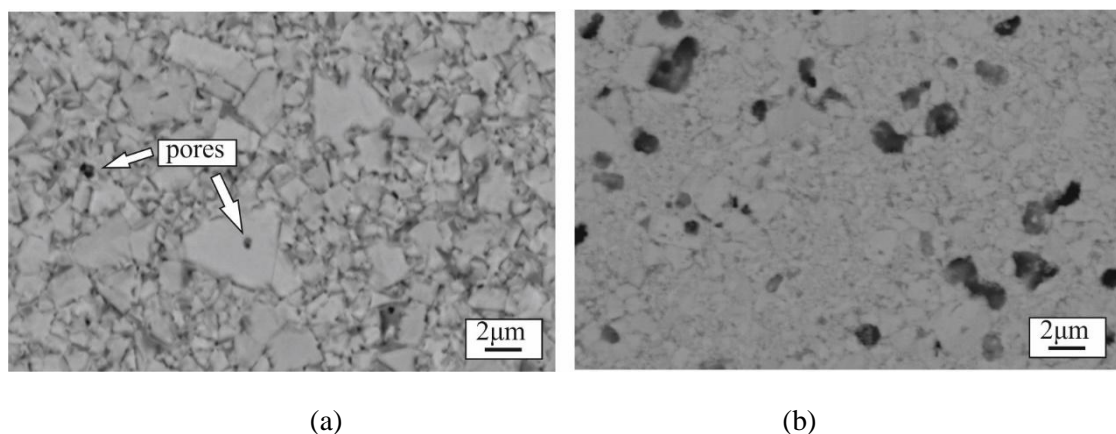
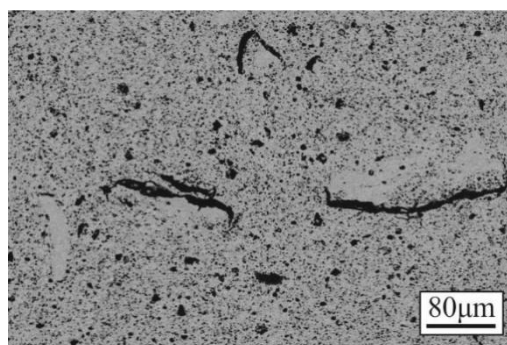
3. Results and discussion

Research results for all the series of experimental and reference samples made only from WC-Co solid alloy and from WC-Co solid alloy containing inhibiting additives are given in table 2. The experiments have proved that the materials containing vanadium and chromium carbides have lower strength and hardness values than WC-Co used as a reference material. At the same time, the addition of vanadium and chromium carbides results in significant microstructure refinement and, consequently, the additives act as grain growth inhibitors. Degradation of mechanical (strength and hardness) and physical characteristics (density) for the studied experimental samples series is related to the volume ratio of defects. Wedge-like discontinuities are thought to be the most common defects, which have greater impact on the material strength.

The analysis of changes in grain sizes revealed the efficiency of vanadium and chromium carbide mixtures used as grain growth inhibitors (figure 1). The size of the strengthening phase decreased from ≈ 2.5 µm up to 1.5 µm with the increase of the additives content. In these conditions, the maximum change in the grain size was registered for the material with 1.5 wt% of additives. At the same time, the greatest amount of macro-defects are observed (figure 2).

Table 2. Physical-mechanical properties and microstructure characteristics of WC-Co solid alloy with different content of alloying additives.

Sample	Relative density of a sintered sample, %	Hardness, HV	Flexure strength, MPa	Grain size, μm
WC	99.76	1810	760	2.5
WC + 0,15% VC + % 0,15 Cr_3C_2	83.65	1330	-	1.93
WC+0.3% VC + 0.3% Cr_3C_2	94.36	1510	-	1.91
WC+0.45% VC +0.45% Cr_3C_2	86.23	1510	562	1.76
WC +0.6 % VC + 0.6 % Cr_3C_2	84.79	1380	-	1.64
WC +0.75% VC + 0.75% Cr_3C_2	89.04	1070	400	1.5

**Figure 1.** WC-Co structure with out (a) and with 0.75% VC + 0.75% Cr_3C_2 (b).**Figure 2.** Typical defects of structures.

The morphology character of large defects is indicative of their formation just at the stage, when the experimental samples are being pressed. The dependence of samples micro-hardness on the content of a modifying additive is quite monotonous with the extremum for vanadium and chromium carbide content from 0.6 up to 0.9 % (1510 HV).

We managed to determine strength of materials only for the samples from series 4 and 6, and tensile strength at bending was equal to 562 and 400MPa, respectively. According to Hall-Petch relationship, the carbide phase refinement has to increase both strength and hardness of the material. However, the quality of the processing procedures has the greatest impact on mechanical and physical properties of brittle materials fabricated by powder metallurgy techniques. The defect structure formed in the material at the stage of pressing tends to affect the resulting properties of sintered materials.

The same results were obtained when vanadium carbide was used as an alloying additive.

4. Conclusion

The obtained characteristics of the sintered samples microstructure give evidence of the positive effect of highly dispersed vanadium and chromium carbides used as additives inhibiting tungsten carbide grain growth. Linear reduction of the grain size is detected due to the increase in alloying additives content. A minimum size of the major carbide phase is detected for the material with 1.5 wt% of vanadium and chromium carbide mixture.

Low rates of mechanical characteristics (strength, hardness) are indicative of high defect concentration in the sample material. It should be noted that high defect concentration of the samples depends on the material preparation procedures and prevents us from giving the correct estimation of the effect which the addition of chromium and vanadium carbides has on the mechanical-physical material properties. The objective of further investigations should be optimization of material preparation procedures aimed at the use of inhibiting additives from the transition metals carbides.

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