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Effect of binder content on relative density, microstructure and properties of complex cemented carbides obtained by thermal explosion-pressing

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ABSTRACT

Combustion in thermal explosion mode of the mixtures (Ti–Cr–Mo–W-graphite) under low uniaxial pressure of 19 MPa was used to produce cemented carbides (complex carbides/iron–nickel alloy). The results of the investigations showed that ignition (T_{ign}) and combustion (T_{max}) temperatures, as well as material density, structure and properties, were sensitive to the iron–nickel additions. When the iron–nickel content increases, combustion is characterized by a lowering from T_{ign} and a reduction in reactions heating effect. The carbide formation was carried out by selective mechanism. Carbides of titanium (TiC) and chromium ($Cr_{23}C_6$) were formed instantaneously during the exothermic peak. However, the molybdenum carbide (Mo_2C) and mainly the tungsten carbide (W_2C) resulted from incomplete carbon diffusion in solid state. An isothermal maintenance under pressure at 1373 K, has allowed to accelerate the material densification mechanisms by viscous flow. At the same time, it completed the carbides formation thanks to the carbon diffusion mechanism as shown by the presence of new phases such as WC and Cr_7C_3. The maximum effect of densification was observed for a binder content of 50 wt.%, where the relative density of product attained 95%. The Vickers hardness ($HV_{0.15}$) depends also on the binder content and varies from 6300 MPa to 19,000 MPa. The best tribological behaviour was achieved on cermets with 30% (Fe–Ni).

1. Introduction

The hard cemented carbides such as wear-resistant materials are commonly produced following a powder metallurgy method which involves the synthesis of product powder, mixing with metal, granulation, cold pressing and liquid phase sintering.

Some of these operations require high temperature and long time. Long exposures at high temperatures affect the cost-effectiveness of the materials produced and generate an intense coarsening of microstructure.

These disadvantages were overcome thanks to other methods. As an example, the conventional combustion process based on exothermic reactions has been used to develop many materials such as cermets or cemented carbides [1]. However, the combustion in thermal explosion mode is more adapted because it offers the possibility of formation and densification of material at the same time. Unfortunately, it should be noted that there are few works related to the combustion of complex mixtures, with the objective of designing several carbides simultaneously, like titanium (TiC), chromium ($Cr_{23}C_6$ or Cr_7C_3), molybdenum (Mo_2C) and tungsten (WC) carbides.

Dynamic compression during combustion has been already applied to produce dense materials [2–5]. However, it remains limited to systems generating strong exothermic reactions. Other systems with thermodynamics limitation, i.e. low reaction enthalpies or relatively low adiabatic temperatures, such as SiC, WC, and TiB_2 cannot be manufactured by this method. An activation of the process is thus necessary, that is why processes such as FAPACS (field-activated, pressure-assisted combustion synthesis) [6] or MAFAPAS (mechanically activated field-activated pressure-assisted synthesis) [7] have been often applied to produce these materials.

In some cases, the appearance of a liquid phase during the heating period can also be determined in the synthesis ignition process and greatly enhances the densification rate of the thermal explosion product.

It has been already suggested by several studies concerning the liquid phase contribution in the combustion ignition of TiC [8–11], that the first molecules of carbide were formed in the drops of a liquid eutectic. Consequently, the ignition temperature was dictated by the eutectic temperature of Fe–Ti or Ni–Ti systems [12].

The objective of this work is to investigate the effect of the binder (Fe–Ni) content on the combustion characteristics of complex mixtures (Ti–Cr–Mo–W-graphite), when the thermal explosion mode is carried out under low pressure.

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Table 1
Characteristics of powders used in the present work.

Powder	Particle size (μm)	Purity (%)
Ti	<40	99.0
Cr	<45	99.5
Mo	~2	99.5
W	~100	99.5
Fe	~80	99.0
Ni	~10	99.5
Graphite	~1	99.0

The purpose is to examine the influence of the dilution rate on the densification, structure formation and properties of complex cemented carbides.

2. Experimental procedures

The characteristics of the starting materials are shown in Table 1.

The composition in weight of the samples is

$$B\%\ (80\%\ \mathrm{Fe} + 20\%\ \mathrm{Ni}) + C\%\ [88.8\%\ (25\%\ \mathrm{Ti} + 25\%\ \mathrm{Cr} + 25\%\ \mathrm{W} + 25\%\ \mathrm{Mo}) + 11.2\%\ \text{graphite}]$$

where $B = 0, 10, 20, 30, 40, 50$; $C = 100, 90, 80, 70, 60, 50$.

The samples were prepared by the following method: the initial components were mixed by ball-milling for 6 h using stainless steel balls and then dried in a furnace during 4 h at about 383 K to remove adsorbed water. Pellets, 13 mm diameter with a weight of 3.0 g were compacted in a tungsten carbide die with a green density of about 50%.

To carry out the experiments, a special assembly was implemented. The combustion in thermal explosion mode was realized according to the following procedure: the cold pre-compacted was introduced in a graphite die under a low uniaxial pressure of 19 MPa. The synthesis was initiated by induction heating of the graphite die, under argon gas. The studied regime consisted of a heating under load using an induction furnace with heating rate about of 10 K/s.

The thermal explosion product was maintained under pressure at a temperature of 1373 K during 0, 150, 300 and 450 s. However, to detect the starting, the end of the exothermic reactions and to control the temperature of isothermal maintenance, a thermocouple Pt/Pt–10%Rh was introduced into the graphite die.

On the other hand, the real parameters of the thermal explosion (T_{ign}, T_{max}), were measured with a pyrometer (IS5 Linn High Therm) during the preliminary tests without pressure application. After the isothermal maintenance, the sample was cooled to room temperature at a rate of about 7 K/s.

The thermal explosion-pressing reactor used in this study is illustrated in Fig. 1.

In order to understand the role of the metal binder in the densification process, the synthesis of cermets was accomplished via three different processing routes:

Regime 1: thermal explosion (TE) + isothermal maintenance (IM);
Regime 2: TE under pressure + IM;
Regime 3: (TE + IM) under pressure.

Green densities of cold-pressed compacts and densities of samples obtained by thermal explosion-pressing, were determined using bulk-density calculations based on sample weight and volume (diameter and thickness) measurements.

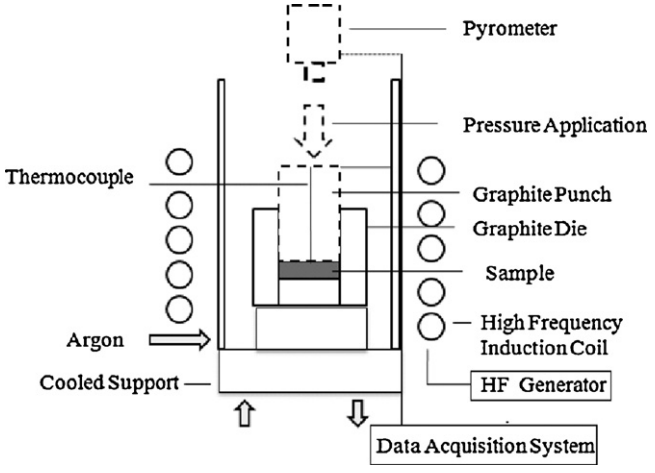

Fig. 1. Schematic representation of the thermal explosion-pressing reactor.

Fig. 2. Photograph of thermal explosion-pressing specimen.

The reaction processes of reactant mixtures were studied by differential thermal analysis (DTA) (model Netzsch DTA/DSC 404 PC) using a heating rate of 15 K/min under an argon protective atmosphere.

Compositional and microstructural analyses of the thermal explosion-pressing products were made through X-ray diffraction (XRD) with a Cu Kα radiation, optical microscopy and scanning electron microscopy (SEM).

The samples were also characterized by different methods such as measurements of Vickers pyramid hardness (under a load of 0.15 kg), appreciation of the wear resistance and determination of friction coefficient.

3. Experimental results and discussion

3.1. Thermal explosion under pressure and carbides formation

Fig. 2 shows a specimen of the cermets obtained by thermal explosion under pressure, after a summary surface correction.

The temperature–time profiles of samples S_1 (10 wt.%Fe–Ni) and S_5 (50 wt.%Fe–Ni), during the thermal explosion are shown in Fig. 3. The thermograms are characteristics of a continuous heating through the whole surface of the sample. The time scale in the temperature–time profiles corresponds to three stages: incubation period, thermal explosion peak, and cooling period. Considering that the sample has a low thickness, the heating was realized practically without temperature gradient between the surface and the core. At the critical temperature (T_{ign}), the exothermic reaction was started simultaneously in the whole volume of the sample.

It can be seen from Fig. 3, that the ignition temperature depends on the dilution rate. More precise measurements of temperature were taken in order to understand the influence of (Fe–Ni) content on the thermal explosion course. The results of these measurements are given in Table 2.

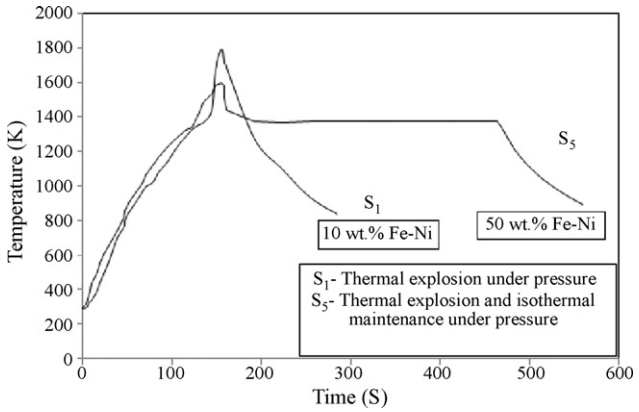

Fig. 3. Temperature–time profiles during the SHS in thermal explosion mode of samples S_1 and S_5.