Pressure-volume-temperature characteristics of cemented carbide feedstocks

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Abstract: Pressure-volume-temperature (PVT) characteristics of highly filled cemented carbide powder compounds were investigated on a high-pressure mercury dilatometer. The compounds containing cemented carbide powder and three components polymeric binder varied in the volume content of powder and the powder characteristics (particle size distribution and mean particle size). PVT data was found to be dependent on volume content (0–50 vol.%) of carbide powder in compounds; with increasing powder content, the discrepancies in a specific volume at applied pressure decreased, whereas melting temperatures remained unaffected as a polymeric binder was powder-filled (confirmed also with differential scanning calorimetry). Volumetric thermal expansion coefficient and compressibility were linearly and exponentially, respectively, dependent on pressure. Further, studied carbide compounds showed weakly pronounced shifts in volumetric thermal expansion coefficients and compressibility obtained for powders differing in their characteristics.

Key-Words: pressure-volume-temperature characteristics, high-pressure mercury dilatometer, powder injection molding, binder, cemented carbides

1   Introduction

Powder injection molding (PIM) has been used in metal and ceramic processing industries since 1970's [1]. The technology represents an effective alternative to the traditional processes (machining, investment casting) for production of small, complex-shaped metal and ceramic parts.

Although PIM applications can be found in medical, automotive, IT, telecommunications, and consumer sectors, the mass implementation of the technique on the global market is still limited by a number of quality issues.

2   Problem formulation

A process phase that requires further clarification and optimization is the flow of highly filled PIM feedstocks into mould cavities during injection moulding. The solution consists in a successful simulation of this step of the process.

The efficiency of currently available simulation approaches depends in the first place on reliable experimental data. Since PIM is a high-pressure moulding process, flow behavior and compressibility of powder and polymer-based binder in a pressurized melt-stage are key indicators for the assessment of processing conditions necessary for the production of defect-free, injection molded parts.

The pressure-volume-temperature (PVT) data provides information about the specific volume changes (shrinkage) of feedstock at the moulding temperature and pressure.

Although, PVT characteristics serves to set important parameters as temperature and hold pressure, the number of papers devoted to their evaluation is rather low.

Persson et al. [2] studied the thermal properties of 420 stainless steel based compounds on a PVT-100 (SWO, Germany) device at testing pressures in the range 150–350 MPa. Transition zones corresponding to the particular organic components of a binder could be easily derived from the PVT plots. Wei et al. [3]

investigated the pressure effects during injection molding process using the same tool (PVT-100) for 85 wt.% alumina in a paraffin wax based binder at pressures from 0.1 to 120 MPa. The system showed the transition zones indicating clearly the binder components.

Greene and Heaney [4] determined the thermal behavior of 61.1 vol.% carbonyl iron filled in a wax-polymer binder. In their study, the average volumetric shrinkage, derived from PVT measurements, was compared with the prediction obtained from a modified two-domain Tait PVT model, which represents a mathematical fitting of specific volume as a function of pressure and temperature. The PVT results proved that the hold pressure could be used to effectively control dimensions of the final sintered components.

In [5] coefficient of thermal expansion and curing shrinkage were investigated for two (vitreous silica and carbon black) highly-filled (82–94 wt.%) compounds with binders based on different resins. Crosslinking kinetic was evaluated using DSC and PVT. The experimental data of curing shrinkage during crosslinking, quantified via decrease of specific volume, were precisely fitted with a Tait model.

Binet et al. [6] studied PVT behavior of highly filled feedstock consisted of 65 vol.% 316L stainless steel and a three component binder (polyethylene, wax and lubricant). The experimental data were compared with mathematical models and simulated with Moldflow software for a case study item. The two-domain Tait PVT model was used for determination of the compressibility of feedstock, and the genetic algorithm was employed to fit the viscosity and specific volume characteristics at selected pressures.

Chandra et al. [7] considered the effect of filler concentration on the glass transition temperature obtained from PVT data measured on a Gnomix dilatometer operated at 0–200 MPa and 25–200 °C. Transition temperature was shifted to higher temperatures with increasing pressure and decreasing filler content. Thermal expansion coefficient decreased with increasing pressure and changed also upon addition of filler.

As we have showed recently [8], particle size distribution and particle size dimensions of used filler play an important role in a bulk compressibility of PIM compounds. Therefore, the presented paper focuses on the influence of such powder parameters on pressure-volume-temperature behavior of cemented carbide compounds differing in their powder characteristics.

2.1 Materials

The experiments were carried out on PIM compounds based on tungsten carbide powder (provided by Sylvania

Tungsten, Czech Republic). Four grades, differing in their particle size distribution and mean particle dimension, were investigated. Shape of the particles was irregular with relatively broad particle size distributions and mean diameters: 1.24 μm (BC10U), 1.24 μm (BC17S), 3.32 μm (BC37S) and 7.38 μm (BC75H). A powder grade BC10U had bimodal size distribution, although overall its characteristic remains that of BC17S grade.

Polymeric binder used for compounds preparation consisted 53 vol.% low-density polyethylene Lacqtene 1,200 MN (Atochem), 26 vol.% paraffin wax and 21 vol.% ethylene-acrylic acid block copolymer Ex 225 (ExxonMobil Chemicals) with densities 0.918, 0.900 and 0.929 g/cm^3, respectively.

2.1.1 Blending procedure

Highly filled cemented carbide compounds were prepared on a laboratory kneader (Brabender Plasticorder, PL-2000-6, mixer type W 50E) at 150 °C and 40 rpm. The mixing chamber was filled in 70–80% of its volume. Firstly, small amount of polymeric binder was preheated in a mixing chamber for about 1 minute. Then, after interchangeable addition remaining binder and powder, the mixing was carried out for additional 4 minutes. The detailed composition of the prepared materials is summarized in Table 1. Density of investigated feedstocks was measured on injection molded samples (MINIMAX MOLDER CS-183 MMX, Costum Scientific Instruments, Inc., USA). Prepared samples in volumes about 2.55 cm^3 were used for density determination via Archimedes method in three different liquids: distilled water (1.000 g/cm^3), methyl alcohol (0.792 g/cm^3) and hexane (0.659 g/cm^3).

Table 1 Composition of carbide compounds.

Sample code	Powder type	Powder (vol.%)	Density (g/cm^3)
10U-30	BC10U	30	5.107 ± 0.064
10U-50		50	8.073 ± 0.003
17S-50	BC17S	50	8.117 ± 0.005
37S-50	BC37S	50	8.123 ± 0.012
75H-30	BC75H	30	4.929 ± 0.014
75H-50		50	8.372 ± 0.020

2.2 Methods

The pressure-volume-temperature (PVT) behavior was investigated on a fully automated high-pressure mercury dilatometer GNOMIX (Gnomix, Inc., USA). Gnomix PVT apparatus was used to determine specific volumes in pressure range 10–175 MPa at temperatures 25–210 °C under isobaric conditions. The heating and

cooling rates of 1 °C/min were selected for experimental runs.

Differential scanning calorimetry (DSC) tests were carried out on a DSC30 (Mettler, USA) apparatus under nitrogen atmosphere. The samples were heated from 25 °C to 210 °C at 1 °C/min, kept at 210 °C for 1 minute, and then cooled down to 25 °C at the same rate (1 °C/min).
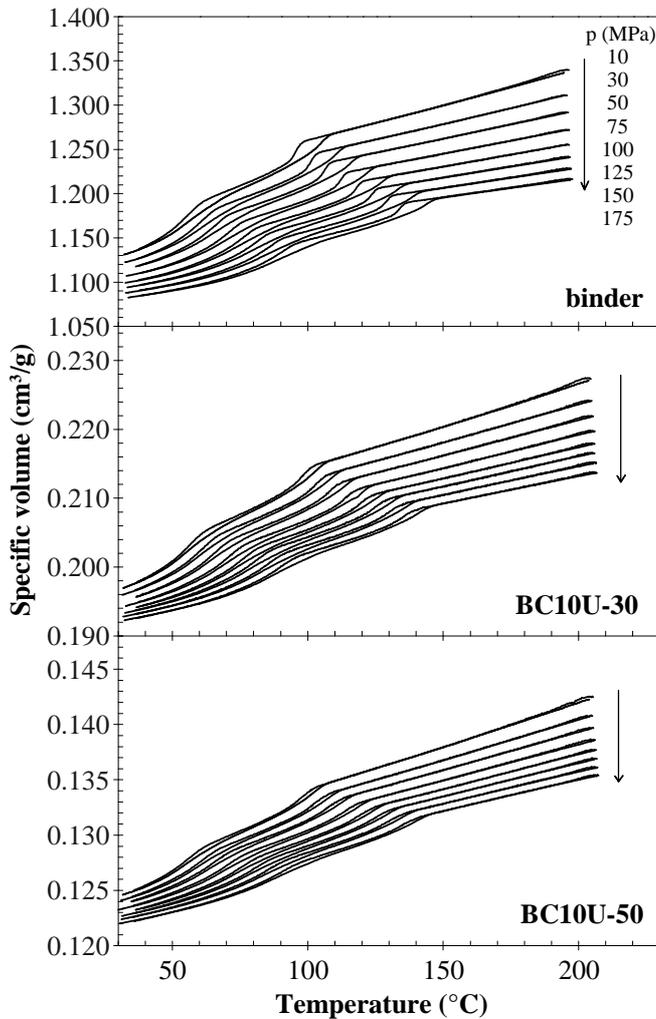
Fig.1 PVT characteristics of pure binder and feedstocks based on 30 and 50 vol.% BC10U powder.

3 Problem Solution

From a DSC analysis (not included) it is evident that the multicomponent binder shows only two phase transitions, because the melting temperatures of low-density polyethylene (107 °C) and ethylene-acrylic acid block copolymer (100 °C) are very close to each other, and therefore coincide into one phase transition. The second phase transition corresponds to the third component – paraffin wax (56 °C). Such cause is also detected on PVT curves of all materials tested as can be seen in Fig. 1 showing specific volume of binder,

BC10U-30 and BC10U-50 samples as a function of temperature and pressure in both, cooling and heating modes. Transition temperatures for feedstocks filled with 30 or 50 vol.% of tungsten carbide are in the same positions with respect to the pressure and temperature. The declined values of specific volume is evident with increasing amount of tungsten carbide powder in a feedstock (from 0 to 50 vol.%). The volume changes during injection molding process are caused by polymer fraction, and thus, with increasing powder content, they become less pronounced.

Two values of phase transitions can be discerned on the PVT plots within heating and cooling scans. The differences in specific volumes between heating and cooling curves as a function of temperature for polymeric binder are depicted in Fig.2. Each transition temperature corresponds to melting/crystallization rate peaks of the binder components, having different height and width. As the pressure increases, the peak at the first transition (corresponding to paraffin) shows a rigid translation to higher temperature, whereas the peak at higher transition (corresponding to polyethylene and copolymer) shows both translation to higher temperatures and lower peak value. It means that pressure influences both crystallization processes, but only for the crystallization of low density polyethylene and ethylene based copolymer the pressure causes a different effect on the melting and crystallization of the material.
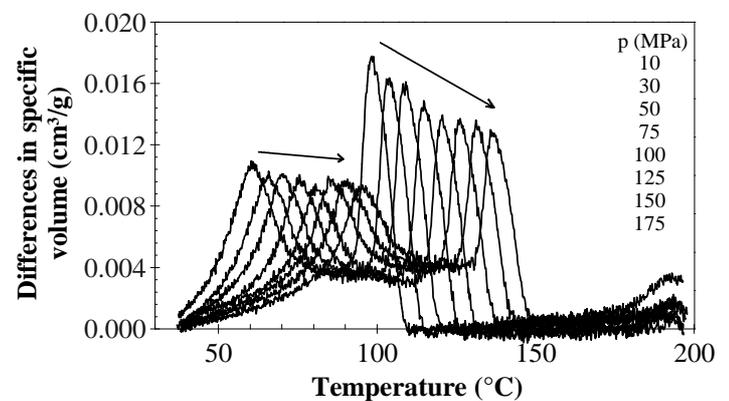
Fig.2 Specific volume differences between heating and cooling curves as a function of temperature for pure binder.

Linear relationship between volumetric thermal expansion coefficient and pressure was obtained for all materials investigated (Fig.3a). Generally, polymers have relatively high coefficients of thermal expansion and are highly compressible in the molten state. It should be noted that the system with the largest particle sizes (BC75H - diameter at 10 %: 2.19 μm, 50 %: 15.38 μm, 90 %: 28.06 μm) shows the highest thermal expansion. Accordingly, the system based on smallest

particle dimensions and bimodal distribution (BC10U having diameter at 10 %: 0.45 μm, 50 %: 1.11 μm, 90%: 3.75 μm) results in the lowest compressibility as illustrated in Fig.3b. As expected, compressibility of pure polymeric binder decreases with increasing powder content (Fig.3c). Such a decay is in accordance with the increase of volume content of binder component, which is the compressible part in the feedstock. However, Persson et al. [2] described that the decreasing trend could be attributed to enhanced physical interactions between metal particles at higher powder loading and higher applied pressure.
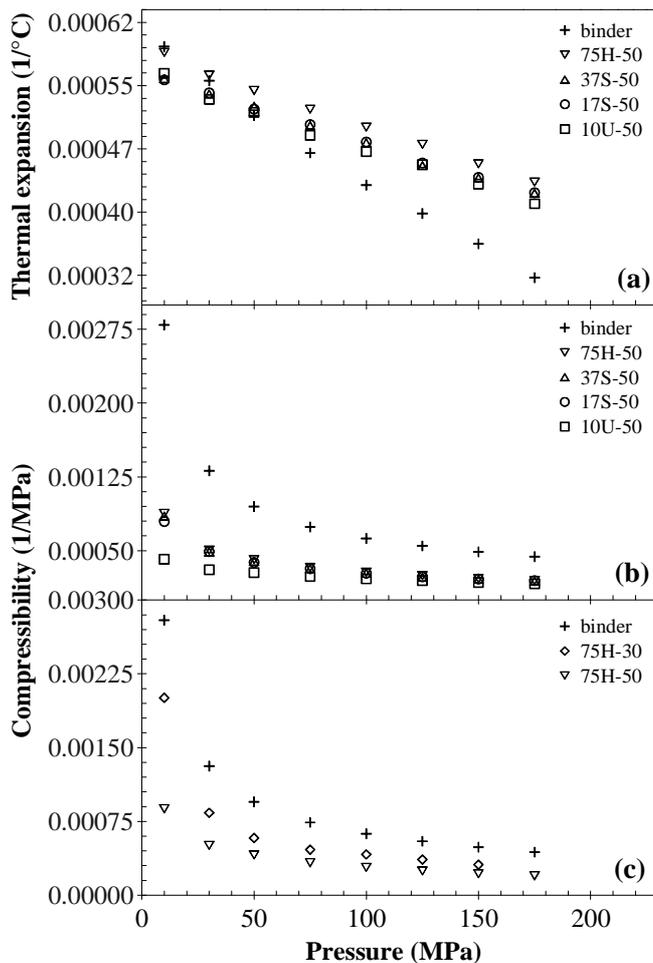
Fig.3 Volumetric thermal expansion coefficient and compressibility versus pressure for tungsten carbide based PIM compounds.

4 Conclusion

The pressure-volume-temperature (PVT) characteristics of tungsten carbide based PIM systems were investigated using high-pressure mercury dilatometer.

The volumetric thermal expansion coefficient and compressibility of investigated compounds become reduced as the powder amount increases up to 50 vol.%. Further, the volumetric thermal expansion coefficients

are linearly dependent on pressure, whereas the compressibility shows an exponential trend.

The results obtained for four types of feedstocks differing in powders used verified that particle size distribution has a weakly pronounced effect on PVT behavior of PIM compounds, which becomes more evident if very fine tungsten carbide feedstock (BC10U) is compared with the coarse one (BC75H).

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