Easily Sinterable Low-Alloy Steel Powders for P/M Diamond Tools

Janusz Konstanty * and Dorota Tyrala

Faculty of Metals Engineering and Industrial Computer Science, AGH University of Science and Technology, 30 Mickiewicz Avenue, 30-059 Krakow, Poland; dtyrala@agh.edu.pl
* Correspondence: konstant@agh.edu.pl; Tel.: +48-617-2627

Abstract: The work presents the design and fabrication procedures used to manufacture inexpensive iron-base powders employed as a matrix in diamond-impregnated tool components. Three newly developed low alloy steel powders, containing from 94.4 to 99.4 wt.% Fe, have been formulated with the assistance of ThermoCalc software and produced by means of a proprietary process patented by AGH-UST. It has been shown that the powders are readily pressureless sintered to a closed porosity condition (>95% theoretical density) at a temperature range between 840 and 950 °C. All as-consolidated materials achieve the desired tool matrix hardness of more than 200 HV. One of the experimental powders has been designed to partly melt within the sintering window. This is particularly important in fabrication of wire saw beads by the conventional press and sinter route because sintering of a diamond-impregnated ring and its further brazing to a tubular steel holder can be combined into one operation.

Keywords: sintered diamond tools; pressureless sintering; sinterability; low-alloy steel powders

1. Introduction

In the past millennium, the cost of sintered diamond tool components was markedly affected by the prevailing price of synthetic diamond [1]. Despite high cost and limited productivity, hot press technology was commonly used for the high-density consolidation of these tools. The sharp drop in the price of synthetic diamonds, which has been observed over the past three decades or so, increased interest and demand for inexpensive powders that could be readily pressureless sintered to virtually pore-free condition. To address this issue, laboratory work was initiated at Eurotungstene and Umicore in the late 1990s. This work resulted in the development of two iron-base powders which were soon offered commercially under the brand names Next400 (Eurotungstene [2]) and CobaliteCNF (Umicore [3]). Both these powders can be pressureless sintered to over 95% theoretical density (TD) at merely 900 °C [3–6].

A moderate sintering temperature is an important characteristic of a matrix powder because exposure to 1120 °C, typical in ferrous operations [7,8], may degrade strength and impact toughness of diamond crystals [9]. The matrix material should also meet some other application criteria, such as high hardness and yield strength, to improve the matrix capacity for diamond retention [9,10], as well as toughness and resistance to abrasion [2,9]. To facilitate the achievement of these demanding requirements, fine Fe-P powders are commonly admixed to the base matrix powder [6,11,12].

Nowadays, the conventional press and sinter route is rapidly gaining in popularity in the fabrication of diamond wire saw beads [3,12–18]. In addition to Next400 and CobaliteCNF, a wide range of grades is available for this application from mixing the two base powders with Fe-P and low melting additives so that a liquid is present during sintering [12]. Thereby, the sintering of a diamond-impregnated section and its further brazing to a tubular steel support can be combined into one operation, saving labour cost and process time.
The recent figures revealed for the Italian diamond tool industry confirm the growing importance of fine pre-alloyed powders (Next and Cobalite grades), which constitute the largest share of 40% of all matrix materials [19]. However, despite advantages over coarser pre-mixed powders, they are expensive to produce. The major reason for this is the hydrometallurgical extraction of water insoluble metal compounds (mainly hydroxides) from aqueous solutions of salts [20–22]. Large quantities of water are used, and environmentally harmful wastes are generated at this stage.

The method developed at AGH-UST replaces the expensive hydrometallurgical processing of metal salts with inexpensive high-energy milling of hydrogen-reducible compounds [23]. Another advantage is an extra degree of freedom in the selection of powder chemical composition. The resulting powders are fine, have the potential to be sintered to near-full density at temperatures far below 1120 °C, preferably below 950 °C, and thereby yield materials which meet acceptance criteria for the fabrication of premium quality tool components, such as diamond saw beads [18].

The main objective of the present work was to design and manufacture three low-alloy steel powders, which would combine good sinterability with high sintered hardness and strength. It is well established that a fine-grained structure, the presence of ferrite and liquid formation at the sintering temperature promote rapid densification that occurs due to the high diffusion rates of base metal atoms along grain boundaries, in the body-centred cubic (bcc) lattice and in the liquid, respectively [24,25]. Therefore, these three rapid diffusion paths became the most important powder design considerations. In all cases, phosphorus was used due to its potent hardening of iron and stabilisation of the bcc crystal structure [8]. Nickel, copper and tin were selected as additional alloying elements in order to stabilise austenite (Ni, Cu) and form a liquid phase (Sn).

2. Materials and Methods

Using the ThermoCalc software (version 2021, Thermo-Calc Software AB, Solna, Sweden), numerical simulations were carried out in order to formulate three pre-alloyed steel powders with desired phase compositions achieved within a relatively wide sintering window located below 950 °C. From 0.5 to 0.7%, phosphorus was assumed enough to guarantee the required hardness and strength, whereas the amount of the other alloying elements was kept to minimum.

The required proportions of commercial hematite, CuO, SnO₂, fine nickel and eutectic Fe-P powders were ball-milled in water using the Changsha Tianchuang Powder Technology Co., Ltd. (Changsha, Hunan Province, China) laboratory jar mill QM-5. The milling vial was filled to half of its volume with 12 mm diameter 100Cr6 steel balls. The ball-to-powder mass ratio was 10:1. The milling vial was set to run for 24 h at ~70% of the critical rotational speed.

The resulting slurry was subsequently dried and reduced at ~700 °C for 4 h in hydrogen. After deagglomeration, using in-house developed procedures, all powders were tested for hydrogen loss, apparent density and tap density, in compliance with relevant ISO standards [26–28]. Particle size distribution, particle shape and qualitative phase composition were also evaluated by means of a laser diffraction, scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The particle size distribution was estimated using the Winner2000B laser particle size analyser (Jinan Particle Instrument Co., Ltd., Jinan, China) fitted with a software package, including Mie light scattering theory [29]. The morphology of powders and other microstructural studies were performed using the FEI Inspect S520 scanning electron microscope (SEM, ThermoFisher Scientific, Hillsboro, OR, USA). The XRD data were collected on the Model D500 Siemens/Bruker diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) using CoKα radiation.

Knowing the apparent density, an appropriate amount of powder was volumetrically fed into a 12 mm × 40 mm cavity of a carbide die and cold compacted at 400 MPa, without lubrication, to obtain green specimens ~4 mm high. All green compacts were measured with a digital micrometre and weighted to determine their green densities.
Sintering was carried out in a laboratory tube furnace in hydrogen. Two green compacts were placed side by side on a ceramic substrate and a temperature-monitoring thermocouple was positioned adjacent to them. During heating, the green parts were held for 30 min. at 700 °C, for oxide reduction, before proceeding to the peak temperature that was maintained for 30 min.

After cooling to room temperature, the sintered parts were tested for density, hardness and bending strength, and subjected to metallographic observations on both fracture surfaces and metallographic cross sections. The sintered densities were measured, based on the Archimedes’ principle. The bending strength was tested by means of a proprietary nonstandard procedure described in detail in [30]. Hardness was determined on metallographic sections by means of the Innovatest Nexus 400 tester (Innovatest Europe BV, Maastricht, The Netherlands) using the Vickers hardness scale at a 1 kgf load.

3. Results
3.1. Powder Compositions and Characteristics

Using the computer simulation ThermoCalc software, a number of iterations were necessary to formulate three low-alloy steel powders, which satisfied the phase structure conditions described in the preceding sections.

Their chemical compositions are listed in Table 1.

Table 1. Chemical composition of the experimental powders.

| Powder Designation | Nominal Composition 1, wt.% |
|--------------------|---------------------------|
|                    | P  | Ni | Cu | Sn |
| F                  | 0.6 | -  | -  | -  |
| FA                 | 0.7 | 1.0| 2.3| -  |
| FAL                | 0.5 | 0.3| 4.0| 0.8|

1 Balance Fe

Theoretical (full) densities were subsequently calculated for each powder taking into account all equilibrium phases present at 25 °C. The TD values were estimated at 7.84, 7.86 and 7.86 g/cm³ for F, FA and FAL, respectively.

As demonstrated in Figure 1, powder F is ferritic up to the solidus temperature (1472 °C) although, for greater clarity of graphs, the range of temperatures higher than 1000 °C is not shown.

Powder FA has a duplex, ferritic-austenitic microstructure above 832 °C, with less than 0.55 vol.% (Cu) that completely dissolves in the iron matrix above 856 °C. In order to maximize the density of interphases and most effectively inhibit grain growth during sintering, the sintering window should hypothetically be centred around 910 °C, where the austenite-to-ferrite volume ratio reaches unity.

Powder FAL has a composition designed to provide a persistent liquid above 835 °C. The amount of liquid increases with temperature to reach the maximum level of around 2.4% at 867 °C. It enables processing the powder by supersolidus liquid-phase sintering (LPS) within a wide sintering window. Similar to FA, the FAL powder has a duplex, ferritic-austenitic microstructure between 860 and 935 °C. Around 1 vol.% (Cu), present at 860 °C, completely disappears at 867 °C due to dissolution into the solid or the formation of additional liquid, thus maximizing its relative volume.

The experimental powders were produced using the fabrication procedures described in the “Materials and Methods”. Their properties were determined according to the current ISO standards.

The results are summarised in Table 2, whereas the powder particle morphologies and XRD patterns are shown in Figures 2 and 3.
Figure 1. One axis equilibrium diagrams of the newly designed alloys: (a) F; (b) FA and (c) FAL.
Table 2. Main properties of the experimental steel powders.

| Powder Designation | Apparent Density, g/cm³ | Tap Density, g/cm³ | Laser Diffraction, µm | Hydrogen Loss, % |
|--------------------|-------------------------|--------------------|-----------------------|-----------------|
|                    | D10        | D50        | D90        | D99        | D [3,4] |                  |
| F                  | 0.82       | 1.82       | 1.90       | 5.18       | 10.16    | 12.47  | 5.61  | 0.69 |
| FA                 | 1.61       | 2.78       | 0.64       | 2.24       | 6.47     | 12.13  | 2.95  | 0.99 |
| FAL                | 0.98       | 2.06       | 1.22       | 3.97       | 8.77     | 12.97  | 4.54  | 0.74 |

Figure 2. SEM micrographs of the experimental powders: (a) F; (b) FA and (c) FAL.

3.2. Densities, Mechanical Properties and Microstructures of Sintered Specimens

The experimental powders were cold pressed at 400 MPa into 40 × 12 × ~4 mm green specimens and sintered to higher densities. Prior to sintering, the green parts were weighed and measured in order to calculate green densities. The rough estimates were 5.17, 5.14 and 5.13 g/cm³ for F, FA and FAL, respectively.

Two green compacts of the same powder were sintered together at a given temperature in a single furnace run. The sintered parts were subjected to density measurements, using the more accurate Archimedes’ method, and tested for yield strength ($\sigma_{0.2}$) and deformation ($\varepsilon_{pl}$) in three-point bending. After a microscopic examination of fracture surfaces, metallographic specimens were prepared by cutting out the central part of a bending bar using an alumina cut-off wheel and mounting it in Bakelite. The resulting sections were then wet ground on #220 SiC abrasive paper and successively polished on cloths impregnated with 9 and 3 µm diamond compound. The polished specimens were then used to measure Vickers hardness. After testing hardness, the metallographic sections were re-polished and mildly etched on the Struers OP-Chem cloth (Struers A/S, Ballerup, Denmark) with an active oxide suspension. The prepared specimens were then metallographically examined by SEM.
The sintered densities, hardness numbers and bending properties of the tested materials are compared in Figure 4.

![Figure 3. Diffraction patterns of the experimental powders.](image)

![Figure 4. Sintering curves (a); Vickers hardness (b); offset yield strength (c); plastic strain (d) in bending. The solid lines represent average values. The scatter bands in (b) have been calculated for 90% level of statistical confidence.](image)

The fracture surfaces and microstructures of selected specimens are demonstrated in Figures 5 and 6.
Figure 5. SEM fractographs of: (a) F sintered at 925 °C; (b) FA sintered at 900 °C; (c) FAL sintered at 840 °C; (d) FAL sintered at 940 °C.

Figure 6. SEM micrographs of: (a) F sintered at 925 °C; (b) FA sintered at 900 °C; (c) FAL sintered at 840 °C; (d) FAL sintered at 940 °C.
4. Discussion

The newly developed low-alloy steel powders, obtained by the patented AGH-UST process, meet the basic application criteria that are favourable for fabrication of diamond tool components. As shown in Table 2 and Figure 2, the powders are very fine and show narrow distributions of particle size. The XRD patterns given in Figure 3 indicate the complete dissolution of phosphorus in ferrite (F, FA, and FAL) and tin in copper (FAL). As opposed to thermodynamic stability calculations, monitoring intensities of the strongest (321) and (411) peaks did not detect Fe$_3$P in the experimental powders as a separate phase. Tin dissolved in copper increases its lattice parameter and shifts the (Cu) peaks toward lower 2θ angles (FAL).

As seen in Figure 4a, green compacts of all tested powders, prepared by cold pressing to ~65% TD, can be sintered to a closed-pore condition below 950 °C, reaching densities in the range 94.4–98.4%. Densification of the FAL material via supersolidus LPS leads to 97% TD after a 0.5 hour hold at merely 840 °C, although this powder shows excellent sinterability even in the solid state (95.3% TD at 820 °C).

The obvious advantage of the experimental powders over fine pre-mixed powders is the ease of densification. As demonstrated in [31], Fe-0.8%P parts made from fine carbonyl iron and Fe$_3$P powder sinter to 7.44 and 7.56 g/cm$^3$ after 0.5 hour hold at 900 and 1000 °C, respectively. The similar F powder reaches 7.48 and 7.69 g/cm$^3$ at 900 and 950 °C, respectively.

It can be deduced from Figure 4 that the required combination of high density, hardness and yield strength with sufficient ductility is achieved for F, FA and FAL after sintering at ~925, ~900 °C and between 840 and 940 °C, respectively. Among the tested materials, FA shows the highest hardness and strength, but it is relatively brittle. The highest mechanical strength can be attributed to the highest degree of solid solution strengthening, provided mainly by 0.7% P and to a lower extent by 1.0% Ni. Despite their relatively high densities (~94.4% TD), both bending bars sintered from FA at 850 °C were fractured within the elastic region. From the diamond retention standpoint, it is desirable that the material has the ability to absorb some deflection, otherwise cracks may be initiated and propagated in the matrix as the result of large strains generated along the sharp diamond edges. It is, therefore, evident that densities higher than 96% TD (875 °C) are required to impart minimum ductility to the FA material.

The F powder can easily be sintered to ~98% TD between 925 and 950 °C offering the best ductility, but at the expense of marked losses in hardness and strength. It is noteworthy that one of the two F specimens sintered at 950 °C failed to break in the bending bar holding fixture and the test was stopped at $\varepsilon_{pl} = 9.7\%$ (see Figure 4d).

As seen in Figure 5, the fracture surfaces show a varying degree of ductile failure. Interestingly, the best ductility has the F material, shown in Figure 4a, although the FAL sample sintered at 940 °C shows much better developed ductile morphology with dimpled voids nucleated at relatively coarse inclusions. In other cases, mostly in F, inclusions are hardly visible, so voids most probably nucleated at grain boundaries.

Evidently, the ductility of the tested materials is influenced in a complex manner by their density, chemical/phase composition, grain size, pore size and shape, as well as contents of impurities.

The microstructures presented in Figure 6 clearly demonstrate that the tested specimens exhibit a homogeneous, fine-grained structure, with finely dispersed pores located predominantly at grain/interphase boundaries. The pores have a tendency for coagulation and rounding with increasing temperature (compare Figure 6c,d), and the grain grows in a similar manner. Interestingly, the grain growth has a marginal effect on hardness and yield strength of the FAL material. This offers greater flexibility in the selection of sintering conditions. Sintering within the higher range of the sintering window results in enhanced ductility (see Figure 4d), whereas sintering at 840 °C, or slightly above this temperature, generates lower operating cost.
5. Conclusions

The results of the current study show that the newly developed low-alloy steel powders are characterised by excellent sinterability. Additionally, they exhibit the required combination of hardness (>200 HV1) and yield strength ($\sigma_{0.2} > 1000$ MPa in bending) with minimum ductility. All these properties make them suitable for the fabrication of diamond tool components (e.g., diamond wire saw beads) by the conventional press and sinter route. Most commercial steel powders require sintering at a minimum of 1120 °C to reach the closed porosity level. The new powders can be sintered to near-full density at between 840 and 925 °C, reaching the best combination of hardness, strength and ductility. The FAL powder can be consolidated within a wide sintering window (840–940 °C) via supersolidus LPS. The persistent liquid, present at the peak temperature, imparts “self-brazing” characteristics to this powder and may potentially eliminate the brazing of diamond-containing parts to steel supports. Taking into account the aforementioned technical issues, it is reasonable to conclude that economic benefits may also be realised if this technique is brought to production scale.

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