Microstructure engineering from metallic powder blends for enhanced mechanical properties

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Abstract. The present work focuses on the transformation of high-purity Ni powder blends of controlled volume fractions (40 and 60 %) of nanometre-sized (100 nm) and micrometre-sized (544 nm) particles into bulk samples as part of a strategy for producing ultrafine-grained materials usefully exhibiting both strength and ductility. The process involved cold isostatic pressing at 1.5 GPa and sintering. The resulting bulk samples had relative densities near 95 %, were texture-free, and exhibited two different grain size distributions with an average value of 600 ± 30 nm. The mechanical properties were investigated by compression and microhardness tests, both at room temperature, and compared to the behaviour of a sample processed from micrometre-sized powder only. Samples prepared from the blends exhibited high yield stresses of 440 and 550 MPa after compression, and they did sustain work hardening. Tests conducted before and after compression up to 50 % deformation showed the same relative amount of hardness increase around 20 %, which was three times lower than that of the monolithic sample for which a decrease of the average grain size close to 26 % was measured.

1. Introduction
Powder-metallurgy-based methods are versatile routes for producing in-demand microstructures of various types; centimetre-sized and fully dense, ultrafine-grained as well as nanostructured materials can indeed be processed in respect to the bottom-up approach through techniques such as hot isostatic pressing (HIP) [1] or differential hydrostatic extrusion combined to cold isostatic pressing (CIP) and sintering [2]. Those methods are therefore of prime interest for addressing the dual problem of improving both the strength and the ductility of these materials. Different strategies have yet been proposed to offset the low tensile ductility accompanying their high flow stress [3]; one of them deals with the incorporation of coarser grains, which are prone to store dislocations, in a fine-grained matrix. The bimodal grain structure can be achieved by heterogeneous grain growth in severely deformed materials; that way is already investigated for Ni [4]. Another way to produce such structures, which has been scarcely studied yet [5], relates to the sintering of blends of nanocrystalline and microcrystalline powders; the present work enters that scope and focuses on the transformation of high-purity Ni powder blends of controlled volume fractions of nanometre-sized and micrometre-sized particles into bulk samples.

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2. Experimental procedure
The experimental procedure has consisted in previously identifying the characteristics of each subsequent-blend component under the whole range of CIP and in processing the samples through the mixture of two starting powders, their compaction by CIP, their sintering, and their characterization along with the one of a reference sample submitted to the common process; characterizations have consisted in testing the sintered samples under compression and in proceeding, both before and after compression, with the last two items of the following detailed account of the experimental procedure:

- The starting nickel powders were commercial high-purity powders: the micrometre-sized powder was an Alfa Aera spherical Ni powder APS 3-7 µm of 99.9% purity and the nanometre-sized powder was an Argonide Corporation spherical Ni powder with an average grain size of 100 nm and a 99.9% purity, synthesized by electro-explosion of wires. The latter powder had previously been internally characterized in a separate earlier work, including the determination of its chemical composition by inductively coupled plasma spectroscopy [6].
- Micrometre-sized and nanometre-sized powders have been mixed in a three-dimensional shaker mixer (Turbula® type T2F) for 6 h at room temperature (RT) with two different controlled volume fractions (40 and 60%).
- CIP has been performed on laboratory equipment specifically designed and built (multi-ring HP cylinder reinforced by shrinkage) for containing fluid pressures up to 2 GPa at RT.
- Sintering has reproducibly been performed under 500 °C during 1 h.
- Compression tests have been carried out on cylindrical specimens having a diameter of 5 mm and a length of 6.5 mm with an Instron universal testing machine (model 1195) at a strain rate of \( \sim 10^{-4} \text{s}^{-1} \). Deformation has been exerted up to 50% for all the tested specimens.
- Vickers hardness measurements have been performed with a Struers microhardness tester (Duramin 20 model).
- The as-processed microstructures have been investigated by electron backscattering diffraction (EBSD) conducted on a conventional LEO S360 scanning electron microscope. Post-data treatment was carried out by using the OIM version 4 software from TexSEM Laboratories.

3. Results and discussion
CIP constitutes a consolidation step during which most of the densification shall take place prior to any further ultimate-densification processing route such as HIP, and it therefore requires special attention. Its results are illustrated for each of the subsequent-blend components by figure 1 according to the Shapiro-Kolthoff’s plot primarily adopted for powder die compaction [7]. This plot is consistent with the integration of the differential equation that Heckel developed by assuming similarity to a first-order chemical reaction with porosity and pressure substituting for concentration and time respectively [8]:

\[
\frac{dD}{dp} = K(1-D)
\]  

where \( D \) is the relative green density, \( p \) the applied pressure and \( K \) a constant. Equation (1) stands for the underlying assumption that the rate of change in density with respect to pressure is directly proportional to the remaining porosity. By integration, it gives

\[
\ln \frac{1}{1-D} = Kp + A
\]  

where \( A \) is a constant. It is agreed that such a simple model as equation (2) can for the best fit the data in either the initial or the final stage of the densification process; Heckel claimed on his own that constant \( K \) should relate to plastic deformation for ductile materials whereas constant \( A \) would represent the close packing achieved at low pressures from a loose array as a result of rearrangement before appreciable amounts of inter-particle bonding occur. Although continuum and mechanistic modelling approaches have introduced many more equations that fit compaction data better under
particular circumstances [9], the Shapiro-Kolthoff’s plot remains phenomenologically convenient for fitting at once the consecutive CIP stages of consolidation through rearrangement and deformation that actually give rise to two distinct linear-relationship domains as yet observed for die-compacted Fe powders for instance [10]. Figure 1 also emphasizes the two distinct “compactibilities” of the starting powders depending on their average grain size; analyses had shown that the micrometre-sized powder corresponds to spherical clusters of particles whose actual average size is 544 nm. It is worth noting that, despite a lower “compactibility”, the nanometre-sized powder sample CIPed at 2 GPa attained a relative green density of 92%.

![Figure 1. Shapiro-Kolthoff’s plot of relative green density D versus isostatic pressure applied for compacting micrometre-sized (squares) and nanometre-sized (triangles) Ni powders.](image)

In order to limit the number of parameters used for this experiment, CIP has been performed at 1.5 GPa only for processing all the samples along with sintering. Table 1 summarizes the main characteristics of the resulting bulk samples that were texture-free as confirmed by the random EBSD-analysed grain orientations and structurally homogeneous as confirmed by the quite uniform hardness distributions, and that exhibited different grain size distributions as a consequence of the dislocations induced during CIP in the second linear-relationship domain and of their arrangement into large-angle boundaries during sintering. In regard to residual porosity, deformation was appropriately limited to compressive testing; the resulting main characteristics are summarized in table 2.

| Composition (%) | Relative density (%) | Vickers hardness | Grain size<sup>b</sup> (nm) |
|-----------------|---------------------|-----------------|-----------------------------|
| 0:100           | 94.62               | 125 ± 4         | 848                         |
| 40:60           | 93.10               | 186 ± 8         | 623                         |
| 60:40           | 94.12               | 204 ± 19        | 579                         |

<sup>a</sup> Initial nanometre-sized to micrometre-sized powder volume percentage ratio.

<sup>b</sup> Average value based on the EBSD analysis of the grain size distribution.

| Composition | Yield stress (MPa) | Vickers hardness | Grain size (nm) |
|-------------|-------------------|-----------------|-----------------|
| 0:100       | 250               | 212 ± 10        | 629             |
| 40:60       | 440               | 225 ± 9         | 589             |
| 60:40       | 550               | 240 ± 6         | 568             |

The mechanical properties are in direct line with the seminal Hall-Petch relationship which states that the flow stress, which can be related to hardness under certain circumstances, increases when the grain size of metallic polycrystals decreases [11]. The microstructure-dependent yield stress itself increases significantly and is accompanied by an impressive deformation whereas a reduced strain hardening contributes, for the samples prepared from the blends, to a strength level finally similar to the one of the reference sample. Figure 2 emphasizes the respective evolutions of hardness and grain
size in regard to initial blend composition. Analyses conducted before and after compression show relative amounts of hardness increase of 21.6% and 17.7% for the samples prepared from the blends but no significant grain size reduction, compared to a 69.6% increase and a 25.8% reduction for the monolithic sample respectively, which also denote an enhanced structural stability.

4. Concluding remarks
Samples prepared from the blends exhibited high yield stresses of 440 and 550 MPa after compression, depending on the grain size distribution, and did sustain work hardening. Analyses conducted before and after compression also denoted through hardness and grain size an enhanced structural stability. Yet, ductility should be evaluated through tensile testing that requires full densification. The optimization of the process is therefore underway, either by varying the presently fixed parameters or by combining HIP or differential hydrostatic extrusion to CIP, and remains aimed at getting a better trade-off between strength and ductility.

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