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The development of high-strength superductile hardmetals and tools based on these materials under ultrahigh isostatic pressure

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ABSTRACT

This work was designed to study compressibility behavior of nanopowders of various materials under ultrahigh cold isostatic pressing (CIP) in pure hydrostatic conditions. The results indicate that creation of hardmetals for large-size tools by high-pressure consolidation of nanoparticles is not a very promising approach. An alternative technique for producing hardmetals with the disperse substructure of carbide grains at ultrahigh pressure (CIP) in pure hydrostatic conditions has been developed. The new hardmetals thus obtained have dual properties of high strength and unique superductility under compression. The large-size tools based on these alloys have commercially demonstrated a record-breaking impact resistance an order of magnitude higher than that of the currently available standard hard-alloy tools.

1. Introduction

Tungsten carbide cobalt (WC–Co) based hardmetals thus far remain the most required materials for various technological applications [1]. The pressure treatment of metals during cold and hot upsetting operations, rod and steel wire drawing is typically performed with the use of headers, long-length puncheons, and dies made from coarse-grained or very large-grained hardmetals that account for more than 15% of the world hardmetal output. For operating at repeated impact loading, a hardmetal in such tools must be sufficiently strong and show maximum ductility under compression. Ductility of the existing industrial hardmetals can be enhanced only by creating coarse-grained structures containing from 8 to 20 mass% of cobalt. The highest ductility of hard WC–8%Co and WC–15%Co alloys under compression does not exceed 0.6% and 1.5% respectively.

In contrast, fine-grained hardmetals for cutting tools possess of high strength and wear resistance but virtually lack ductility. Nanoparticle powders are presently used to manufacture finely-dispersed hardmetals, and sophisticated technological procedures are developed for the production of such nanopowders as a base material for hard nanocrystalline alloys [2]. In accordance with a modern classification, hard nanocrystalline alloys are those having WC grains up to 100 nm in size as the main fraction [2,3]. The principal technological challenges for the production of the above alloys are removing impurities and preserving small grains at high temperatures because recrystallization during liquid-phase sintering inevitably results in an increase of the grain size (see [2] and references therein). Another serious problem arises from the difficulty of pressing nanopowders into large intricately-shaped billets. The pressing force, the drop in the compression speed, the probability of inhomogeneities and inner stresses in the compacts increase as the particle size decreases [2]. We have recently designed a new technique for the production of wear-resistant fine-grained hardmetals for cutting tools by preliminary mixing a plasma powder of WC nanoparticle agglomerates with a commercial hard-alloy mixture [4].

It was earlier maintained that many problems encountered in the work with nanoparticles can be solved by employing ultrahigh pressure to consolidate nanoparticles into a dense compact [2,5–7]. Much attention in the present article is given to fundamental studies on the behavior of nanoparticle powders of various materials at cold isostatic pressing (CIP) in pure hydrostatic conditions.

The ultimate purpose of the present work was to develop a commercially acceptable technique for producing large intricately-shaped workpieces from hardmetals that would simultaneously have the properties of both coarse-grained alloys showing ultraductility under compression and finely-dispersed hardmetals possess of high strength, durability and wear-resistance.

1.1. Results I

The main objective of preliminary experiments with nanoparticles at ultrahigh pressures was the production of high-density powders for further sintering. The first experiments on the consolidation of nanoparticles by CIP were carried out with Ni and Fe nanoparticles (20 nm and 60 nm) [8]. A “TOROID” high pressure device was used in these

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experiments [9]. Details of the experimental technique are described in earlier papers [8–13].

The results of Fe and Ni nanoparticle consolidation at ultrahigh pressures proved unexpected: the final porosity of the sample remained very high. It was known from the literature that uniaxial pressing of a hard-alloy nanopowder (7 nm fraction) at 1 GPa during 20 h in a press-form yields a workpiece having density less than 60% of the ideal one [5]. The data on significant resistance of the nanoparticles to compaction at ultrahigh pressure provided a basis for the detailed study of compressibility of nanoparticle powders of other materials.

Compressibility of powder compacts of various nanoscale materials was investigated under ultrahigh hydrostatic pressures up to 10 GPa. The unique strain gauge technique [10] and a "TOROID" high-pressure device [9] were used in the experiments. It was shown [11–13] that different powders of crystalline and amorphous nanoparticles (Fe 15, 30, 60 and 100 nm, Ni 20 nm, TiN 20 nm, Si_3N_4 15 nm, the glasses SiO_2 and GeO_2) exhibit under pressure abnormally weak and anomalously slow logarithmic relaxation at a fixed pressure (Fig. 1a, b). A similar behavior is inherent in systems having a hierarchy of energy barriers; specifically, logarithmic relaxation with time is attributable to the almost uniform distribution of activation energies [14]. In the case of powder systems, the slow (logarithmic) relaxation can be explained in terms of the model of a hierarchically organized mechanical system [12]. This inference is based on the fact that nanoparticles, unlike big particles, do not undergo plastic deformation under pressure and practically retain their shape and dimensions after the pressure is released [8] due to the absence of initial dislocations and the extremely high energy of the formation of new dislocations within individual nanoparticles. As a result, compaction of nanoparticles under ultrahigh pressure occurs only by virtue of their sliding and repacking [11,12]. Porosity of the compact remains very high after the pressure is released. Indeed, compact density for a Fe nanopowder (15 nm fraction) after the treatment under ultrahigh hydrostatic pressure (5 GPa) is only 65–67% of the ideal one (Fig. 1a).

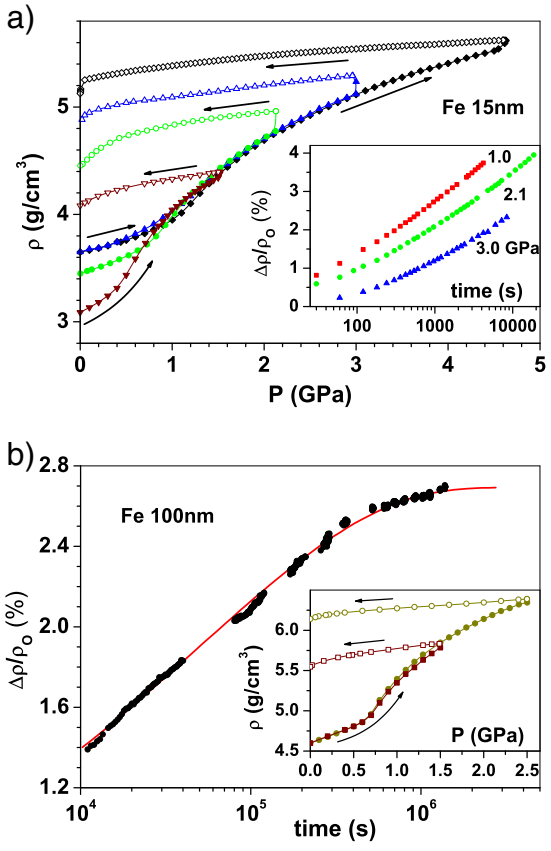

Fig. 1. Compressibility of 15 nm Fe powder compacts previously compressed to 0.2, 0.5 and 0.7 GPa. The results of several experiments at different maximum pressures and exposure times are presented. The insert shows plots of relative density vs holding time at a fixed pressure (a). Density relaxation in 100 nm Fe powder compacts at a fixed 1.5 GPa pressure. A long-term (2 weeks!) experiment showed that density saturation can be reached within a reasonable time given that the range of the system's hierarchical structural scales is not too wide (here, the sample size to particle size ratio is five orders of magnitude). The insert presents compressibility curves for 100 nm Fe powder compacts previously pressurized to 0.7 GPa. The results of two experiments up to 1.5 and 2.5 GPa respectively are displayed (b).

Note that nanoparticles as a rule tend to aggregate into spheres or ellipsoids (Fig. 2) regardless of technology chosen to produce the starting powders (plasma technique, mechanical synthesis, thermal and electrochemical methods). The size of these spongy structures varies from several to hundreds of microns. In other words, a powder is initially a hierarchical system in terms of both the size and the shape of nanoparticle agglomerates. When a powder composite of nanoparticle agglomerates undergoes volume compression, the external pressure is applied in the first place to the frame of agglomerates of various size and shape. The agglomerates begin to collapse as they undergo repacking. This is why the powder densification procedure involves nanoparticles localized within the agglomerates, disintregrated agglomerates, and free nanoparticles. At high pressure, a sample consists of very small agglomerates and free nanoparticles which retain the ability for further small shifts with time. The time dependence of nanoparticle powder composite density at a fixed pressure obeys the logarithmic law over a very broad time range. It stops to grow only at extremely large times and tends to the density of chaotically dense particle packing (Fig. 1b).

It can be concluded from the above results of research on CIP of nanoparticle compacts that it is impossible to obtain a large durable high-density workpiece suitable for subsequent sintering into the real tool. Certainly, it is possible to obtain positive results in manufacturing small cutting tools with the help of expensive technologies for deep purification of nanopowders and rapid hot isostatic pressing (HIP) [2,5–7]. However, the approach based on consolidation of nanoparticles under ultrahigh pressure for the production of hardmetals to manufacture large intricately-shaped tools designed to operate under repeated impact loading is of little promise.

1.2. Results II

To settle the problem of the formation of a finely-dispersed superductile hardmetal for the tools operating under impact loading, we proposed an alternative way of using ultrahigh pressure. The idea behind this method is a hardmetal containing highly-dispersed WC grains which can be obtained by means of strong dispersion of large WC grains in a powder under (CIP) in pure hydrostatic conditions.

A powder green body exposed to pressure is a low-density compact having randomly positioned particles. The contacts between the particles can be of different shape but most contact areas are small. As a result, due to repeated multiplication of the pressure applied to the entire particle, very high shear stresses emerge on the contacts and dislocations can form inside the particles. Under real conditions, a particle experiences compression from several (mean 4–8) surrounding particles existing in the same conditions. This leads to the formation of a dislocation network at each particle contact site and to particle destruction. In modern commercial cold isostatic press for powdered workpiece compaction, the pressure is 0.1–0.2 GPa; in this case no noticeable dispersion of the particles occurs. Therefore, a higher pressure is needed for the formation of dislocation networks and particle destruction.

A uniaxial non-isostatic compression of a large powder green body in a mechanical press-form leads to an extremely non-uniform pressure distribution and highly variable porosity in different parts of the specimen. One should use CIP to ensure uniform properties of a pressurized billet.