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In spite of their interesting properties, nanostructured materials have found limited uses because of the cost of preparation and the limited range of materials that can be synthesized. It has been shown that most of these limitations can be overcome by subjecting a material to large-scale deformation, as occurs during common machining operations. The chips produced during lathe machining of a variety of pure metals, steels, and other alloys are shown to be nanostructured with grain (crystal) sizes between 100 and 800 nm. The hardness of the chips is found to be significantly greater than that of the bulk material.

Nanostructured materials, composed of submicron-sized grains (crystals), have novel attributes not typically found in conventional materials.[1,2] Furthermore, these attributes can be varied by changing the grain size. Nanostructured solids appear to have high hardness, strength, and ductility,[1,3] in addition to possessing interesting electrical and magnetic properties.[4] Superplasticity has been observed at relatively low temperatures in these materials.[5,6] While many new and exciting applications for nanostructured materials have been identified, a principal barrier to their widespread use has been cost, typically in the range of hundreds of dollars/pound.[7] This paper reports on a process for making nanostructured materials that will be approximately two orders less expensive.

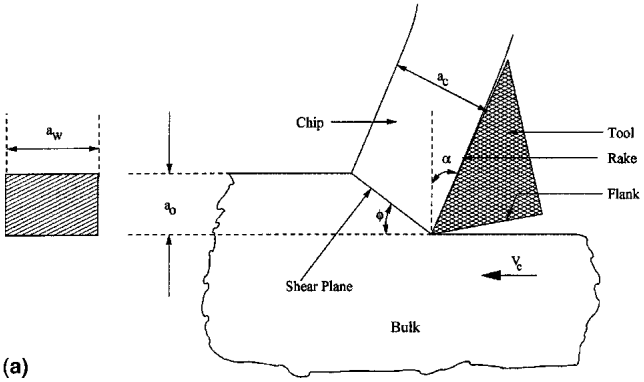
There have been two broad approaches for producing nanostructured materials, one for the production of fine powders and one for bulk materials. The most widely used techniques for synthesizing nanostructured metals in particulate form are condensation of metal atoms from the vapor phase[1,2] and high-energy ball milling.[8] The particulates can then be compacted and sintered to bulk form, often at a sintering temperature lower than that for microcrystalline powders and under conditions that suppress grain growth.[1] These processes for making particulate and small compacted samples provide excellent control over particle size, but costs are estimated as being in excess of 100 dollars/pound.[7]

Methods to make nanostructured metals and alloys directly in bulk form have relied on the use of very large strain deformation or severe plastic deformation (SPD) to achieve microstructure refinement.[9–12] The general experimental approach involves large-scale deformation using processes such as rolling, drawing, equal channel angular extrusion (ECAE), or high-pressure torsional straining. Very large plastic strains, typically in excess of four, are imposed in a sample by the cumulative application of plastic deformation in multiple stages, the effective plastic strain in each stage of deformation being approximately one.[10] Using this approach, nanostructured bulk materials have been produced from ductile metals and alloys of initial low to moderate strength.[11] However, high-strength metals and alloys are difficult to process by SPD methods. Furthermore, these methods require multistage deformation which make them cumbersome and expensive to scale up for large volume production.

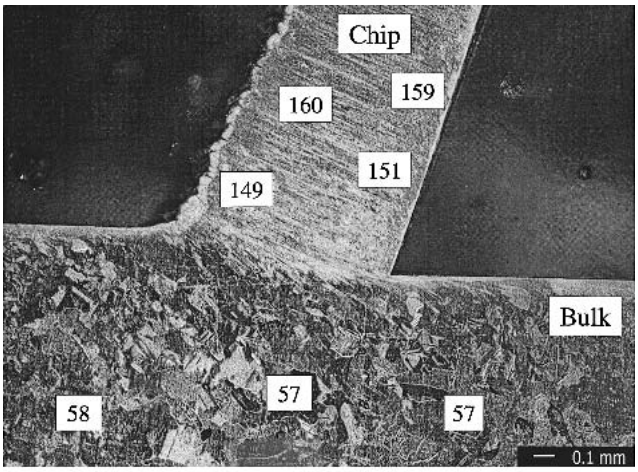
The stimulus for this work arose from the observation that chips produced in the machining of a material experience very large shear strains. This suggested that machining might be an attractive process for producing materials with nanocrystalline structures.

Machining is a process in which a hard, wedge-shaped indenter (tool) removes material (chip) from the surface of a solid (bulk) by very large strain deformation. Figure 1(a) shows a schematic of a machining process and associated geometric parameters. Chip formation occurs by concentrated shear deformation along a narrow zone called the shear plane [Figs. 1(a) and 1(b)]. The geometry of the deformation field is completely determined by the shear plane angle (ϕ).[13] Shear strains in the range of 2–10, strain rates of up to 10^6/s, and shear plane temperatures of up to 0.7 T_m are common features of machining.[13,14] Furthermore, significantly larger strains are imposed in a chip at the shear plane than can be realized uniformly in single or even multiple stages of SPD processes.

[a]Contributed equally to the work.



(a)



(b)

FIG. 1. (a) Schematic of 2-D plane strain machining. The amount of interference, a_o, between the tool and the chip is the undeformed chip thickness, and the relative velocity between the tool and the bulk sample is the cutting velocity (V_c). The width of the undeformed chip into the plane is a_w. The chip forms by a process of large strain plastic deformation occurring over a narrow zone that is idealized as the shear plane. The shear plane angle (ϕ) together with the rake angle (α) determine the average shear strain in the chip. The shear plane angle may be estimated from a measurement of the deformed (a_c) and undeformed chip thickness (a_o). Typical shear strains generated at the shear plane in machining are in the range 2–10. The cutting velocity (V_c) has a major influence on the strain rate and the temperature at the shear plane. This figure can be extended to 3-D lathe machining without loss of generality. (b) Microstructure of partially formed chips as yet not separated from the bulk that was produced in a specially devised "quick stop" experiment. Also shown, superimposed onto the microstructure, are Vickers hardness values (kg/mm^2) measured at different locations in the chip and the bulk. While large grains are visible in the bulk, the chip reveals only flow lines and a lack of visible grain structure suggesting that its grain size is submicron. A sudden change in the microstructure occurs over a narrow zone between the chip and the bulk; this zone is the shear plane. Note also a significant increase in hardness across the shear plane in going from the bulk into the chip.

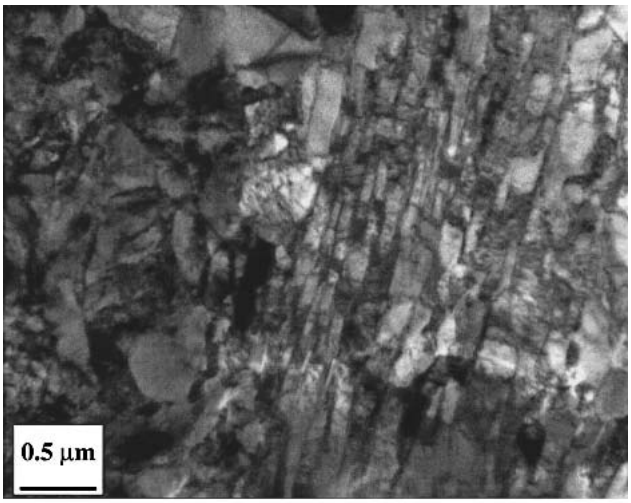
Chips of a variety of metals and alloys were produced by lathe machining. The materials ranged from soft metals, such as oxygen-free high conductivity (OFHC) copper and commercially pure iron, to high strength alloys such as AISI 52100 steel. The nominal composition of these materials, their initial state, and the machining conditions are given in Table I. Typical dimensions of chip samples examined were 100–3000 μm in width, 100–1000 μm in thickness, and at least 5 mm in length, with the smaller chips coming from the higher strength 52100 steel. The hardness and microstructure of the chip and host material prior to machining (bulk) were characterized. The machining conditions, as given in Table I, were selected so that the temperature increase in the shear plane was minimal for all materials.

For the hardness and microstructure analyses, the samples were mounted in epoxy and polished using successively finer silicon carbide abrasive papers of 120–1200 grit size followed by a sequence of 6-, 3-, 1-, and 0.25-μm diamond abrasive slurry. Final polishing was done with 0.05-μm aluminum oxide abrasive suspended in water until a surface finish of 5-nm Ra (arithmetic average roughness) was attained. Microhardness of the polished samples was measured by indentation with a Vickers indenter on a LECO M-400-H (LECO Corporation, St. Joseph, MI) hardness tester. In the making of hardness measurements, the indentation size, as measured by its diagonal length, was kept about the same in the bulk and chip samples by adjusting the indentation load to minimize any uncertainties in the hardness values arising from a possible indentation size effect. At least 30 indentations were made on the chip and bulk samples from each material. Because of its smaller size (approximately 100 μm in the minimum dimension), the hardness of the 52100 chip sample was measured using Berkovitch indentation on a Nanoindenter XP (MTS Systems Corp., Oak Ridge, TN) at a penetration depth of 200 nm, with the hardness value being obtained from a measurement of the load–penetration curve. Some of the polished samples were etched to develop their microstructure for observation. The etchants used were nitric acid and water in the ratio 1:1 by volume for the OFHC copper; nitric acid and ethanol in the ratio 2:98 by volume for the steels and the iron; and nitric acid and acetic acid in the ratio of 1:1 by volume for nickel. The etching time varied between 6 and 25 s. The etched samples were observed using an optical microscope (Nikon Epiphot 200) and an atomic force microscope (DI 3100 AFM, Digital Instruments, Santa Barbara, CA) to characterize microstructural aspects such as grain size, grain size distribution, and pearlite interlamellar spacing. Copper chip specimens were prepared for transmission electron microscopy (TEM) analysis by grinding to a thickness of 100–200 μm using an abrasive grinding wheel and punching out disks 3 mm in diameter. The disk specimens were thinned using electrolytic jet thinning (Struers Tenupol-2) to make electron transparent samples. Thinning was accomplished using a solution of 77% phosphoric acid and 23% water by volume at 20 °C, 2.2 V, and 24 mA for approximately 5 min. The electron

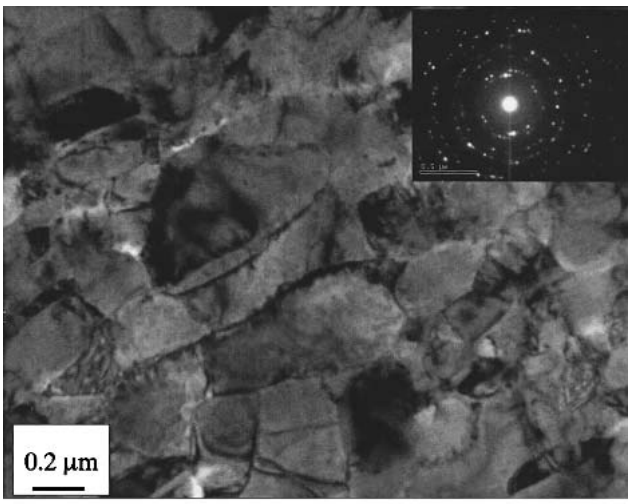
TABLE I. Bulk material state and machining parameters.[a]

Material and composition (by weight)	Bulk initial state	Machining params.
OFHC copper 99.99% Cu	Annealed at 400 °C for 4 h Grain size: 96 ± 24 μm	V_c = 0.47 m/s a_o = 0.21 mm a_w = 2.54 mm
Iron 99.80% Fe, 0.08% Mn, 0.02% C, 0.02% P, 0.01% S	Annealed at 600 °C for 4 h Grain size: 47 ± 4 μm	V_c = 0.11 m/s a_o = 0.21 mm a_w = 2.54 mm
1018 steel 99.0% Fe, 0.18% C, 0.75% Mn, 0.02% P, 0.03% S	Normalized at 1000 °C for 4 h Grain size (ferrite): 21 ± 8 μm	V_c = 0.11 m/s a_o = 0.21 mm a_w = 2.54 mm
AISI 52100 steel 1.45% Cr, 1% C, 0.31% Mn, 0.26% Si, 0.14% Ni, 0.04% Mo, 0.09% Cu, <0.019% S, <0.01% P	Tempered martensite	V_c = 1.25 m/s a_o = 0.1 mm a_w = 0.2 mm
316L Stainless steel 65.47% Fe, 0.03% C, 17% Cr, 12% Ni, 2.5% Mo, 1% Mn, 0.5% Si	Sintered Grain size: 22 ± 12 μm	V_c = 0.05 m/s a_o = 0.21 mm a_w = 1.52 mm
Nickel 99.0% Ni, 0.25% Cu, 0.40% Fe, 0.30% Mn	Annealed at 800 °C for 4 h Grain size: 72 ± 14 μm	V_c = 0.11 m/s a_o = 0.06 mm a_w = 2.54 mm

[a]All annealing was done in a controlled argon atmosphere. The copper, iron, 1018 steel, stainless steel, and nickel were produced by machining cylindrical rods on a lathe with a high-speed steel tool (rake angle +20°, clearance angle +10°). The tool cutting edge was sharpened by grinding with an aluminum oxide grinding wheel (grit size 46) prior to the machining. The 52100 steel chips were produced by machining a 52100 steel cylinder with a cubic boron nitride tool. The parameters V_c, a_o, and a_w are, respectively, cutting velocity, undeformed chip thickness, and depth of cut. These are defined in Fig. 1(a).



(a)



(b)

FIG. 2. TEM images of two OFHC copper chip samples showing nanocrystalline structures: (a) lower magnification image showing numerous elongated grains with aspect ratios of 3 to 6; (b) other magnification image with inset of a selected area diffraction pattern characteristic of a polycrystalline structure. The nanocrystalline nature of the grains is clearly seen in the images. Regions of high dislocation density can be seen in many of the grains suggesting that the grains are highly deformed.

transparent OFHC copper chip samples were observed in a JEOL-2000-FX TEM operating at 200 kV. Bright-field images were obtained, together with selected area and convergent beam electron diffraction (CBED) patterns from the imaged regions, to assess the grain size.

Figures 2(a) and 2(b) show bright-field TEM images from two typical OFHC copper chip samples. Also shown in the inset of Fig. 2(b) is the corresponding selected area diffraction (SAD) pattern which is clearly typical of a polycrystalline structure. Numerous grains, with elongated morphologies, can be seen in the images of Figs. 2(a) and 2(b). Examination of these images clearly shows that the grains, even in the elongated direction, have sizes under 1000 nm. Furthermore, the grains appear to be severely deformed with a high density of dislocations. A distinct change in grain aspect ratio is visible in Fig. 2(a), with higher aspect-ratio grains on the right of the image and lower aspect-ratio grains on the left. We surmise that these distinct regions were different grains, separated by a grain boundary in the material prior to machining, and that the grain aspect ratios are related to the cutting direction and the crystallographic orientation of the material. Observations of contrast changes in the TEM images occurring when a sample is tilted, together with CBED patterns from within and across grains, also confirmed that the chip samples are composed of nanocrystals with a mixture of small- and large-angle grain boundaries.

Thirty grains from TEM images obtained from four different copper chip samples were analyzed to obtain a mean value for the grain size, which was characterized in terms of the maximum width and maximum length of the grains. This analysis showed that the average size of a grain was 175 ± 100 nm in width by 685 ± 190 nm in length. Similar nanostructures have been observed in the iron chips. TEM of chip samples from a 52100 steel and an M2 high speed steel have shown them to be also nanocrystalline with grain sizes in the range of 100–300 nm. The grain sizes in the chips are influenced by the machining conditions.

Table II gives a summary of the hardness values measured on the chips and the bulk samples. As has been reported in many studies,[1–3,10,11] nanostructured metals have hardness significantly greater than that of their microcrystalline counterparts. Similarly, the chips are seen to be significantly harder than the corresponding bulk samples. The increase in hardness is about 200% in the case of the OFHC copper and iron chips, 225% for nickel chips, and 150% for the stainless steel chips. These increases in hardness are much higher than those typically resulting from strain hardening in a single stage of a deformation operation such as extrusion, forging, and rolling.[15] Indeed, in copper and iron, where hardness data from nanostructured samples produced by SPD are also available, the hardness of the chips is similar to that reported for SPD structures with grain/cell sizes in the range of 200–350 nm.[16–18] The initial state of cold work of the bulk sample was found to have a negligible influence on the chip hardness. Furthermore, the Vickers hardness measurements exhibited no evidence of hardness anisotropy in the chips. Table II shows the hardness of the 52100 steel chip to be 1310 kg/mm^2, which is comparable to that of patented steel wire, one of the hardest and strongest steel structures known.[19]

TABLE II. Hardness and grain size of the chip and bulk samples.

Material	Sample	Vickers hardness[a] (kg/mm^2)	Grain size
OFHC copper	Bulk	56 ± 4	96 ± 24 μm
	Chip	152 ± 5	685 ± 190 nm (length) 175 ± 100 nm (width)
Iron	Bulk	85 ± 6	47 ± 4 μm
	Chip	292 ± 26	650–850 nm (length) 100–250 nm (width)
1018 steel	Bulk	142 ± 7	
	Chip	301 ± 11	
52100 steel[b]	Bulk	930 ± 75	
	Chip	1310 ± 65	100–300 nm
Stainless steel	Bulk	159 ± 10	
	Chip	367 ± 13	
Nickel	Bulk	112 ± 4	
	Chip	369 ± 8	

[a]In the Vickers indentation the maximum load was applied for a duration of 15 s and controlled by a timer. The diagonals of the indentation were measured, after unloading, using an optical microscope at a magnification of 400×. Typical indentation diagonal lengths were in the range of 35–50 μm. Care was taken to ensure that the extent of an indentation was at least five times smaller than the sample size, and the indentations were spaced sufficiently far apart from each other and the edges of the sample.
[b]Measured using nanoindentation with a Berkovitch indenter at 200-nm penetration depth.

Figure 1(b) shows an optical micrograph of the microstructure of a partially formed OFHC copper chip, as yet not separated from the bulk sample, that was produced in a specially devised experiment. Also shown superimposed on the microstructure are hardness values recorded at different locations in this sample. The hardness shows a steep increase over a very narrow zone separating the chip from the bulk. This zone can be identified with the shear plane where very large strain deformation, as seen in the flow lines of Fig. 1(b), results in a chip being formed. While grains are clearly visible in the bulk OFHC copper sample [Fig. 1(b)], no grains can be resolved in the chip or near the shear plane which is consistent with the TEM observation.

It is interesting to note that optical microscopy of some 52100 steel and M2 steel chips showed their microstructure to be a "white etching layer" similar to those observed on steel rail tracks and wheels[20,21] and on machined steel surfaces.[22] Fecht and co-workers[20] have recently analyzed white etching layers from steel rail tracks using the TEM and found them to be composed of nanostructures with grain sizes between 15 and 200 nm. These nanostructures are similar to those formed by sliding.[23,24] Furthermore, the hardness of 1310 ± 65 kg/mm^2 measured on the 52100 steel chips is in the nanohardness range of 1250–1400 kg/mm^2 reported for the nanocrystalline steel structures on the rail tracks.

Some of the OFHC copper, iron, and 1018 steel chips were annealed using various temperature–time cycles in a furnace under a controlled atmosphere (95% Ar and 5% H_2 by volume). The hardness and microstructure of the annealed samples were characterized. This showed that the hardness of the chip was retained even after 2 h at 100 °C for copper, 2 h at 520 °C for 1018 steel, and 2 h at 400 °C for iron.

An approximate estimate was made of the cost of making nanostructured materials by the process of lathe machining. On the basis of the economics typical of industrial machining operations, this cost was estimated to be no more than a few dollars/pound over the cost of the primary (bulk) material.

These preliminary experiments provide clear evidence that nanocrystalline metals and alloys are formed through the normal metal removal processes, such as lathe machining. Perhaps more important, this process provides an avenue for the production of nanocrystalline structures in a far wider group of materials and at far lower costs than has been foreseen using other processes.

A wide range of applications for these low-cost nanostructured solids is envisaged, both in monolithic and composite materials.[25] Comminution (e.g., ball, attrition, or jet milling) of the nanostructured chips is a straightforward route to producing nanostructured particulate, which can be consolidated and densified into bulk monolithic materials. In addition to the conversion of the particulates into solids using the usual powder metallurgy processes, the particulates can be considered as potentially important constituents in composites, both metal– and polymer–matrix. These are likely to be extremely attractive for applications in the ground transportation and aerospace industries where weight reduction is critical. Preliminary experiments with composites composed of M2 high-speed steel chips incorporated into both aluminum and bronze matrices by spontaneous (pressureless) melt infiltration have demonstrated that the high hardness of the particulates can be retained in the composite. Microscopic examination of the composites and nanoindentation examination of the chip–matrix interfaces indicated that these interfaces were continuous, suggesting good wetting of the chip with the matrix.

In summary, it has been demonstrated that chips formed when machining metals and alloys such as copper, iron, and steels are composed of nanocrystalline structures of high hardness. While much remains to be understood, especially about the mechanism of formation of these nanostructures by very large strain deformation and of the relative contributions of defect structures and grain size to the enhanced hardness of chips, the current experiments have demonstrated a very low cost process for making nanostructured metals and alloys in large volume. The process can be easily applied to a wide variety of metallic materials and alloy compositions and equally as well to materials of low or high strength. It is quite likely that the enormous quantities of chips generated in industrial machining operations, which are currently remelted or disposed of as scrap, are all composed of ultrafine-grained structures. The economic and environmental benefits associated with reutilization of these chips should also be significant.

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