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Reduction of grain size in metals and metal mixtures processed by ball milling

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This study focuses on the microstructural refinement induced by ball milling in individual metals and Cu-based metal mixtures. A phenomenological model is developed to rationalize the kinetics of grain size reduction. A discontinuous change of the average grain size is predicted to occur in very small powder volumes during each collision. The final average grain size and the rate of grain size reduction are shown to vary with the composition depending on the difference in hardness between the metals.

Keywords: Powder processing; Metals and alloys; Nanocrystalline metal; Microstructure; Microstructural refinement

Ball milling (BM) is a relatively simple powder processing method capable of industrial exploitation on different scales [1–4]. In a typical BM experiment, the reactor is filled partially with powder and milling tools to the desired mass or volume ratio. Periodic movement of the reactor, or of one of its parts, allows the milling tools to collide with each other. During each collision, a fraction of the powder charge is trapped between the milling tools and submitted to a mechanical load, which generates non-hydrostatic stresses at the points of contact between powder particles. The intensity of these local stresses is high enough to induce severe mechanical deformation processes accompanied by cold-welding and fracturing [1–4].

Physical and chemical transformations can also take place, driven by the repeated mechanical deformation at relatively high strain rates. Individually processed metals typically develop a nanostructure with an average grain size in the range between 5 and 20 nm depending on metal and processing conditions [5–8]. For metal mixtures, the reduction in grain size can be accompanied by mechanical alloying, i.e., the formation of crystalline and amorphous alloys by gradual dissolution of the metals into each other [1–4].

The formation of a nanometer-sized structure must be related to the far-from-equilibrium processing conditions experienced by metals [9,10]. Characterizing these conditions in terms of fundamental quantities and throwing light on the mechanisms underlying transformations is a necessary step to foster definite progress in the field and meet the increasing demands for successful technological applications of BM. To this aim, various open issues need to be considered. For example, is it possible to relate the kinetics of grain size reduction to individual collisions? How do the properties of metals affect this process? In the case of binary mixtures, what is the effect of a given metal on the grain size refinement of the other constituent?

In this work, a first response to these questions is given by a systematic study of the grain refinement of different metals and Cu-based metal mixtures. A phenomenological model has been used to describe the kinetics of grain size reduction and to analyze the experimental data. It is shown that the reduction of grain size is governed by the volume of powder effectively processed during each collision and the hardness of the processed metals.

Experiments were performed using the metals listed in Table 1. These metals have been chosen because of their different Vickers hardness, the values of which are shown in Table 1 [11], and of their immiscibility with Cu [12]. For metal mixtures, this allows the steady state of microstructural refinement to be reached well before a

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Table 1. The metals used in experiments, the Vickers hardness H_v (GPa), the final average grain size, L_f (nm), and the apparent rate constant of microstructural refinement, k (10^{-6}).

Metal	Ag	Cu	Fe	Ta	Nb	W
H_v	251	369	608	873	1620	3430
L_f	17.3	15.5	11.9	6.8	7.9	6.0
k	2.1	2.9	3.6	4.3	8.6	9.2

significant fraction of alloy is formed [13]. Therefore, to a first approximation, the influence of mechanical alloying on the reduction of grain size can be neglected. The commercial powders, 99.99% pure, were sieved to homogenize the particle size in the range between 5 and 15 μm. The powders were handled inside a glovebox in an argon atmosphere with impurities below 10 ppm. BM experiments were performed on individual metals, or on binary mixtures of Cu with Ag, Fe, Nb, Ta and W. The volume fraction of Cu in the mixtures was varied between 0 and 1. Each milling run was performed with a total powder volume of 2 cm^3. This value refers to the volume occupied by ideal bulk solids, not by loose powders. It guarantees totally inelastic collisions, and consequently regular periodic BM dynamics [14,15]. The powder was sealed in a hardened steel reactor with a single stainless steel ball weighing 12 g. The reactor was installed on the arm of a Spex Mixer/Mill 8000, and moved at a frequency of ~20 Hz. The experimental conditions result in an inelastic collision regime characterized by an average collision frequency, N, of ~40 Hz, and an average collision velocity of ~5.6 m s^{-1} [14,15]. Under these circumstances, time t can be replaced by the total number of collisions $n = N\Delta t$ [14,15].

The microstructure of processed powders was characterized by X-ray diffraction (XRD) on disk-shaped specimens prepared by cold compaction. XRD patterns were collected with a Miniflex II Rigaku diffractometer, using Cu K_α radiation, over a range of scattering angles from 20° to 120°, in steps of 0.01° with 20 s acquisition time per angle. The patterns were analyzed by best fitting the peak profiles with suitable sets of mathematical functions according to the Rietveld method [16]. The average size of the coherent diffraction domains and their average total strain content were estimated assuming isotropic size and strain content [16].

XRD analyses were carried out on powders milled for selected times. After the preparation of a sample, the reactor was emptied, suitably cleaned and refilled with a volume of unprocessed powder. The next mechanical treatment was started with a fresh powder charge and continued to the next sampling time.

The XRD patterns of metals processed individually or in mixtures share a common evolution. In agreement with the results discussed in the literature [1–4,7–15], the initially sharp profile of crystalline reflections becomes broader and their intensity lower as the number of collisions increases. Intensity fading and broadening are the characteristic signature of the microstructural refinement induced by BM, which consists of the decrease of the average grain size and the simultaneous increase of the average strain content due to the accumulation of lattice defects. In this work, attention is focused specifically on the reduction of the average grain size, L.

As shown in Figure 1a, the Rietveld method allows a satisfactory best fitting of the integral XRD profile of the metallic phases. Mathematical functions interpolate the experimental points almost perfectly, keeping the error very small. Under these circumstances, the L estimates are quite reliable. For both metals processed individually and in mixtures, L varies with the number of collisions, n, as can be seen in Figure 1b. It undergoes a smooth monotonic decrease from an initial value, L_0 to a final asymptotic one, L_f L_0 is not a meaningful quantity, being mostly determined by the process employed to produce commercial powders. Conversely, L_f depends on both metal properties and processing conditions [6–8].

The kinetics of microstructural refinement can be rationalized by taking into due account the fundamental features of BM. These can be summarized as follows: (i) only a small amount of powder is processed during each collision; (ii) an approximately stochastic dynamics governs the trapping of powder between the colliding milling tools; and (iii) the continual stirring of the granular body allows the processed powder to maintain a high degree of chemical uniformity throughout the mechanical treatment.

The mechanical stresses arising from each collision are expected to induce critical loading conditions (CLCs) in only a sub-volume V^* of the trapped powder related to the geometry of collisions, the size of milling tools and the total volume of powder, V, inside the reactor. Here, CLCs can be defined as the loading conditions that induce mechanical deformation severe enough to activate the process of grain size reduction. Then, V^* can be also regarded as the volume of effectively processed powder.

The powder charge can be divided into equal volume elements V^* having the same probability of being

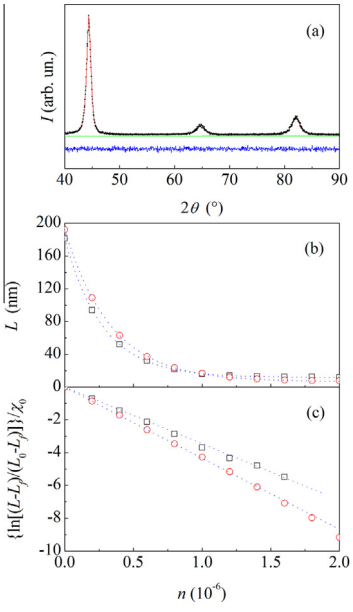

Fig. 1. (a) The XRD pattern of Fe after 2×10^6 collisions. The best-fitted Rietveld profile is shown together with the difference between experimental data and the best-fitted curve. (b) The average grain size, L, of individually processed Ag and Ta in a mixture with Cu volume fraction of 0.3 as a function of the number of collisions n. (c) The quantity $\{\ln[(L - L_f)/(L_0 - L_f)]\}/\chi_0$ as a function of n. Data refer to the systems considered in (b). Best-fitted curves and lines are also shown.