ESRF

Experiment title: Evolution of grain-growth kinetics in elemental nanocrystalline metals measured by rapid high-temperature wide-angle diffractometry	Experiment number: HS-477

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Report:

The goal of experiment HS-477 was to measure the evolution of the kinetics of grain growth in nanocrystalline Fe and Pd by means of high-temperature wide-angle powder diffractometry. It was expected that a plot of the average grain size iz against annealing time t would follow a power law of the form $\bar{R}^n(t) - \bar{R}^n(0) \propto t$, where $\bar{R}(0)$ is the initial grain size and n is the *grain-growth exponent*. Theory predicts a value of 2 for the exponent if grain growth occurs by the usual *curvature-driven* mechanism, whereas a value of 4 should be observed if growth is controlled by a so-called *stochastic* mechanism, in which atoms jump randomly across grain boundaries. Experiments often find a value for *n* lying between 2 and 4, so it has been suggested that both mechanisms may operate simultaneously. If this is the case, then one expects the stochastic mechanism to be most influential when $\bar{R}$ is small-i.e., the exponent should evolve from 4 to 2 with increasing grain size.

If the stochastic mechanism is truly active, then it should manifest itself most strongly in the growth behavior of nanocrystalline materials, in which $\bar{R}$ can be as small as 5 nm. The grain size of such a material can be determined by Bragg-peak profile analysis. We exploited this feature to follow the evolution of a in nanocrystalline samples held at elevated temperature in the high-resolution powder diffractometer on beamline BMl6. In this *preliminary* report, we discuss the grain-growth curves $\bar{R}(t)$ evaluated to date and their implications regarding the possible existence of a stochastic mechanism for grain growth. (The sheer task of processing the more than 2 gigabytes (!) of diffraction data that were recorded during experiment HS-477 has resulted in our not yet being able to file a final report on these measurements.)

A. Evolution of growth kinetics in nanocrystalline Fe

Nanocrystalline Fe powder was prepared by ball milling and sealed in quartz capillaries with ϕ = 0.7 mm. The capillaries were heated by a hot-air blower directed at the area struck by the x-ray beam (λ = 0.4898 A). The sample temperature could be determined to an accuracy of a few degrees by measuring the lattice parameter change upon heating and comparing it with tabulated values for the thermal expansion coefficient. Grain-size determination was performed by peak-width analysis of the (110) and (220) reflexes (more accurate results are expected from a Fourier analysis of the peak profiles, as was performed on Pd-see below).

Results of the lattice-parameter determination demonstrated that the samples reached a steady-state temperature within 5 to 8 minutes of being placed above the hot-air blower. The evolution of the average grain size $\bar{R}$ as a function of annealing time is shown in Fig. 1. The parabolic growth law $\bar{R}^2(t) - \bar{R}^2(0) \propto t$ shows good agreement with the curves recorded at the two lower temperatures but fits poorly to the two higher-temperature curves. After about 1 h at 570°C $\bar{R}$ approaches the apparent maximum measurable size of $\sim$ 600 nm, which is determined by the smallest amount of peak broadening that can be distinguished from the instrumental broadening of 0.007" (26). The scan at 515°C shows the most unusual behavior: at $\sim$ 1 h a "kink" in $\bar{R}(t)$ appears at which time the growth rate slows abruptly. While we do not yet understand the cause of the kink, we believe that it provides no evidence for an evolution from n = 4 to n = 2 growth kinetics, since a growth law with n = 4 fits the data points below the kink quite poorly (in fact, in this region, $\bar{R}(t)$ appears to-evolve linearly). We suspect that the seal of the capillary began to leak at around 1 h, since small iron oxide peaks became evident in the diffraction scans at long times. The presence of second-phase impurities could explain the observed slowing of the growth rate. The fact that a parabolic growth law (n = 2) provides a reasonable fit to the data recorded at 485°C and 495°C suggests that a stochastic mechanism has no measurable influence on the kinetics of grain growth in nanocrystalline Fe.

B. Abnormal grain growth observed in nanocrystalline Pd

Similar measurements were carried out on nanocrystalline Pd prepared by pulsed electrodeposition. The powder samples were sealed in quartz capillaries (ϕ = 0.5 mm), and diffraction scans were recorded in time steps of one minute with λ = 0.5498 A. Data analysis entailed fitting the (111) and (222) Bragg peaks with symmetric Pearson-VII functions and then performing a Warren-Averbach analysis of the fitted curves in order to determine $\bar{R}$. Here we report results of grain growth measured at 355°C; the evaluation of data recorded at five other annealing temperatures is not yet complete.

Single-peak fits to the 355°C data show excellent agreement between measured and fit intensities for annealing times t < 50 min and t > 120 min but poor fits at times in between. The inset in Fig. 2 reveals that the diffraction peaks at intermediate times appear to be a superposition of broad and narrow components. In such cases, the sum of two Pearson-VII functions of differing widths and identical centers provides an excellent description of the measured intensities. Performing peak-profile analysis of the component fit curves yielded two average grain sizes at each time step in the intermediate region. The resulting plot of microstructural evolution (Fig. 2) shows clear evidence for the development of a bimodal grain-size distribution. At early times, very little change in fi is observed, but at $t \gtrsim 50$ min some grains appear with $\bar{R} \gtrsim$ 150 nm. These large grains continue to grow to about 275 nm, at which point stagnation sets in. Further microstructural evolution consists of small grains being consumed by larger ones until only large grains remain. This is a classic example of *abnormal* grain growth, the kinetics of which has not yet, to our knowledge, been measured at the level of detail achieved in this experiment.

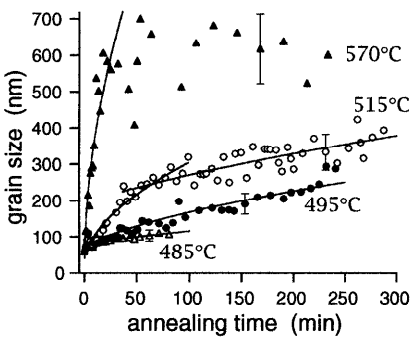

FIG. 1: Grain growth in nanocrystalline Fe measured by diffractometry. Solid lines are fits of a parabolic growth law *(n = 2)*.

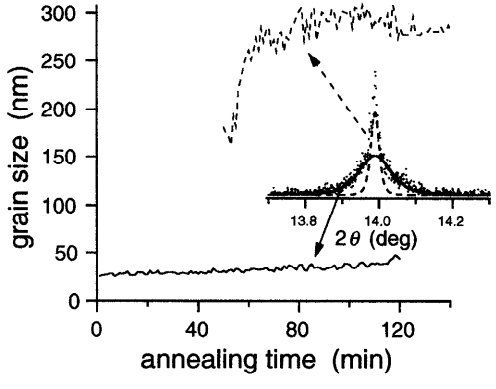

FIG. 2: Grain sizes in nanocrystalline Pd annealed at 355°C. Inset shows (111) peak along with narrow and broad component fitting functions.