



	<b>Experiment title:</b> Kinetics of grain growth in nanocrystalline Ni and Pd <sub>80</sub> Zr <sub>20</sub> measured by rapid high-temperature wide-angle diffractometry	<b>Experiment number:</b>  HS-859
<b>Beamline:</b>  BM16	<b>Date of Experiment:</b>  from: 1 June 1999                      to: 8 June 1999	<b>Date of Report:</b>  25 February 2000
<b>Shifts:</b>  20	<b>Local contact(s):</b>  Dr. Olivier Masson	<i>Received at ESRF:</i>
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### Report:

The goal of experiment HS-859 was to study the kinetics of grain growth in the nanocrystalline grain-size regime by means of high-temperature wide-angle powder diffractometry. From the time evolution of the average grain size  $\bar{R}$  and its dependence on temperature, we hoped to gain insight into the mechanism(s) controlling grain growth in nanocrystalline materials. In general,  $\bar{R}(t)$  is expected to follow a power law of the form  $\bar{R}^n(t) - \bar{R}^n(0) \propto t$ , with initial grain size  $\bar{R}(0)$ , annealing time  $t$  and grain-growth exponent  $n$ . Theory predicts  $n = 2$  if grain growth occurs by the *curvature-driven* mechanism and  $n = 4$  if growth is controlled by a *stochastic* mechanism, in which atoms jump randomly across grain boundaries. Experiments performed on coarse-grained polycrystalline materials ( $\bar{R} > 1 \mu\text{m}$ ) yield values for  $n$  ranging from 2 to 4 but tending toward 2 in the highest-purity specimens, suggesting that only the curvature-driven mechanism is important in such samples. According to theory, however, the stochastic mechanism should become increasingly dominant with decreasing initial average grain size.

In a previous experiment performed at BM16 (HS-477), we found no experimental evidence for the stochastic growth mechanism in nanocrystalline materials. This implies that under ordinary conditions the curvature-driven mechanism controls the kinetics of grain growth at all grain sizes in excess of  $\sim 10$  nm. (The stochastic mechanism might still be important at smaller grain sizes, but these are not accessible in highly pure nanocrystalline samples free of porosity.) Nevertheless, when curvature-driven boundary migration is suppressed by solute segregation, as we have recently demonstrated occurs in the alloy Pd<sub>80</sub>Zr<sub>20</sub> once  $\bar{R}$  reaches about 100 nm, further growth is possible only by the stochastic mechanism. In this case, theory predicts that the grain-size distribution will take on a characteristic shape that is much narrower than that which results from curvature-driven growth. We tested this hypothesis by measuring the evolution of the grain size and the width of the grain-size distribution in Pd<sub>80</sub>Zr<sub>20</sub> with increasing annealing temperature.

Secondly, the results of HS-477 showed that even in highly pure samples the kinetics of grain growth deviate from the expected power law in a manner characteristic of *solute drag*. This phenomenon results from the segregation of impurity atoms to the grain boundaries, which considerably slows the migration of the boundaries and can even bring them to a complete halt. Experiment HS-477 demonstrated that the kinetics of grain growth in nanocrystalline materials can be studied with unprecedented accuracy using high-temperature wide-angle x-ray diffraction; therefore, we elected to apply this method to a series of Ni samples containing known amounts of oxygen as impurity atoms. By studying the kinetics of growth as a function both of temperature and impurity concentration, we hoped to gain a better understanding of the role played by solute drag in

enhancing the thermal stability of nanocrystalline materials.

### A. Evolution of the grain-size distribution in Pd<sub>80</sub>Zr<sub>20</sub>

Nanocrystalline Pd<sub>80</sub>Zr<sub>20</sub> powder was prepared by mechanically alloying elemental Pd and Zr. Separate samples were annealed under vacuum at temperatures ranging from 800°C to 1125°C for 24 h and at 1500°C for 1 h. Wide-angle x-ray scans were recorded with  $\lambda = 0.74976 \text{ \AA}$  at room temperature from samples sealed in glass capillaries ( $\phi = 0.3 \text{ mm}$ ). Determination of the area and volume-weighted average grain sizes,  $\bar{R}_A$  and  $\bar{R}_V$ , was carried out by a Warren-Averbach analysis of split Pearson-VII functions fitted to the (111) and (222) peaks of the fcc diffraction scan. The ratio  $\xi = \bar{R}_V/\bar{R}_A$  is a measure for the width of the grain-size distribution in the samples. From the dependence of the grain sizes on the annealing temperature [Fig. 1(a)], it is apparent that growth continues until about 1125°C, but above this temperature we observe no increase beyond the uncertainty of the measurement technique. Apparently, the curvature-driven growth mechanism is completely suppressed at the highest temperatures. The ratio  $\xi$  increases with temperature, as well, until levelling off at 1125°C [Fig. 1(b)]. If the stochastic mechanism were the only growth mechanism active at 1500°C, we would expect  $\xi$  to approach 1.05; the fact that  $\xi$  remains above 1.3 suggests that stochastic grain growth—if it occurs at all—was too slow to exert a measurable influence on the grain-size distribution in this sample.

### B. Solute drag in nanocrystalline Ni

Nanocrystalline Ni samples doped with 900, 2000 and 6000 wt.ppm oxygen were prepared by pulsed electrodeposition. The samples were ground into powder form and sealed in quartz capillaries ( $\phi = 0.5 \text{ mm}$ ), which were mounted above a hot-air blower capable of heating the samples to temperatures in excess of 800°C. Diffraction scans were recorded at intervals of 1 minute with  $\lambda = 0.34912 \text{ \AA}$ . Data analysis entailed fitting the (111) and (222) Bragg peaks with split Pearson-VII functions and then performing a Warren-Averbach analysis of the fitted curves in order to determine  $\bar{R}_A$  and  $\bar{R}_V$ . The data points of Fig. 2 illustrate typical growth behavior for a sample manifesting solute drag: initially, the grain size increases rapidly, but at longer times it approaches a constant, maximum value  $\bar{R}_{\text{max}}$ . It is apparent that  $\bar{R}_{\text{max}}$  depends strongly on the impurity concentration [Fig. 2(a)] as well as on the temperature [Fig. 2(b)]. Even relatively low impurity concentrations suffice to stabilize the grain size of Ni in the nanocrystalline size regime up to high temperatures. This suggests that the unusually high stability with respect to grain growth that has frequently been reported in nanocrystalline materials arises—at least in part—from impurity-induced solute drag.

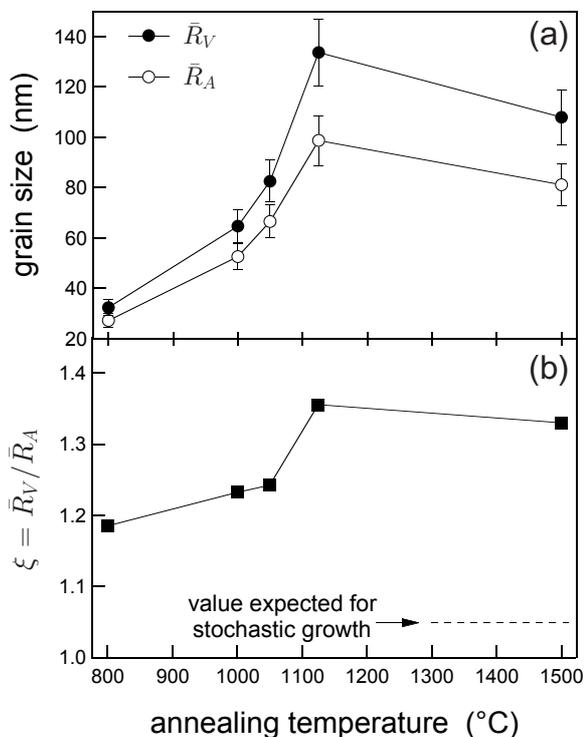


FIG. 1: (a) Grain sizes  $\bar{R}_A$  and  $\bar{R}_V$  and (b) the ratio  $\xi = \bar{R}_V/\bar{R}_A$  in nanocrystalline Pd<sub>80</sub>Zr<sub>20</sub>, plotted as a function of annealing temperature (24 h at temperatures up to 1125°C and 1 h at 1500°C).

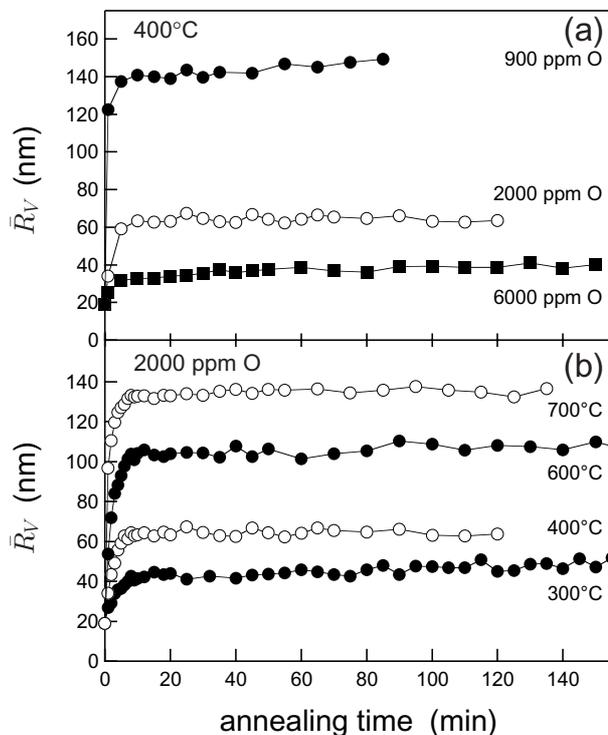


FIG. 2: (a) Grain growth at 400°C in nanocrystalline Ni containing various concentrations of oxygen; (b) Dependence of grain growth in nanocrystalline Ni(2000 wt.ppm O) on the annealing temperature.