

## YOUNG'S MODULUS AND HARDNESS AT GRAIN SIZES BELOW 30 nm IN NANOSTRUCTURED Ni-P

Y. Zhou<sup>a</sup>, U. Erb<sup>a</sup>, K.T. Aust<sup>a</sup> and G. Palumbo<sup>b</sup>

<sup>a</sup> *Department of Materials Science and Engineering, University of Toronto, 184 College Street, Toronto, Ontario, Canada M5S 3E4*

<sup>b</sup> *Integran Technologies Inc., 1 Meridian Road, Toronto, Ontario, Canada M9W 4Z6*

### Abstract

Nanocrystalline materials, usually defined as polycrystals with grain sizes below 100 nm, have attracted considerable interest due to their extensive application potential resulting from many of their unique and often beneficial properties. Many studies have suggested that properties such as increased strength, improved magnetic properties and enhanced localized corrosion resistance observed for many nanocrystalline metals, arise from the fact that a considerable fraction of atoms reside in the interface regions, i.e. grain boundaries (GB's) and triple junctions (TJ's).

The volume fraction of atoms located in the grain interiors, GB's and TJ's can be estimated when the grain shape is defined. Assuming a regular 14 sided tetrakaidecahedron as a grain shape and a GB thickness of 1 nm, it can be shown that the interface volume fraction is relatively low (<7%) at grain sizes above 50 nm. However, for grain sizes less than 30 nm, the volume fraction increases rapidly reaching about 30% at a grain size of 10 nm. This analysis strongly suggests that significant interface contributions to the properties of nanocrystalline materials most likely occur at grain sizes below 30 nm, because of the significant amount of atoms located in the grain boundaries as well as at the triple junctions.

In this study, a procedure of electrodeposition was developed to synthesize fully dense nanocrystalline Ni-P samples with essentially constant P content (2.5wt%) but varying grain sizes ranging from 4 to 29 nm. The Young's modulus and hardness of these samples were investigated by means of nanoindentation. Essentially the same Young's modulus was observed for grain sizes  $\geq 18$  nm. A noticeable decrease in Young's modulus was found at grain sizes  $\leq 17$  nm, followed by a relatively large drop at 4 nm and then a smooth transition towards the Young's modulus of amorphous Ni-P (Fig. 1).

Using the experimental results and a composite model with both upper and lower bound solutions, the Young's modulus value for the interfacial component was found to be 65-85% of the value for the grain interior or polycrystalline counterpart,  $E_0$ .

Positron annihilation lifetime spectroscopy measurements showed that the structures in grain boundaries and triple junctions share a common characteristic positron lifetime for the Ni-P samples (154-158 ps), significantly larger than that in the perfect crystalline Ni lattice (105-108 ps). An enhanced lifetime can be attributed to the excess free volume in GB's and TJ's with respect to the perfect lattice. This excess free volume leads to an enhanced average interatomic distance, likely accounting for the Young's modulus reduction in the interface region of nanocrystalline materials.

The hardness of the Ni-P samples was found to obey the Hall-Petch relationship at grain sizes larger than 7 nm with a positive slope of  $0.36 \text{ MPa}\cdot\text{m}^{0.5}$ . A peak hardness of 8.98 GPa was found at a grain size of 6.6 nm. For grain sizes less than 6.6 nm, the hardness decreased linearly all the way towards the hardness of the amorphous Ni-P sample with a negative slope of  $-0.17 \text{ MPa}\cdot\text{m}^{0.5}$  (Fig. 2). This finding is consistent with previous studies, which reported the inverse Hall-Petch relationship for several other nanocrystalline materials.

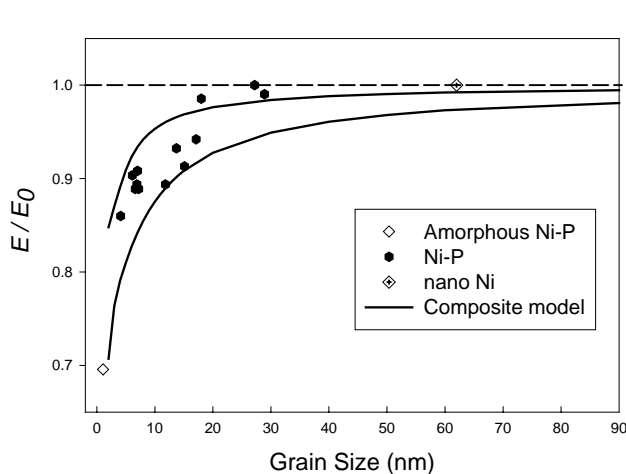


Fig. 1 Normalized Young's modulus,  $E/E_0$ , as a function of grain size for nanocrystalline Ni-P samples, together with amorphous Ni-P and Ni samples

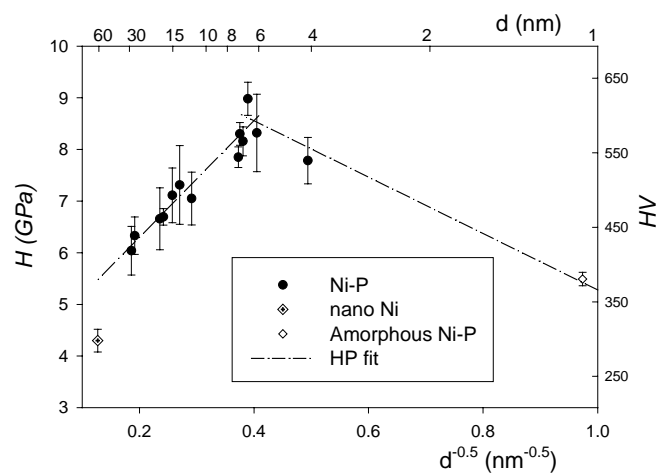


Fig. 2 Hardness as a function of grain size for nanocrystalline Ni-P samples, together with amorphous Ni-P and Ni samples