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Effects of processing on texture, internal stresses and mechanical properties during the pulsed electrodeposition of nanocrystalline and ultrafine-grained nickel

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Abstract

The mechanical properties of nanocrystalline and ultrafine-grained metals strongly depend on grain size, grain boundary segregation, texture and internal stresses. In this paper a thorough systematic analysis is given on the influence of different pulsed electrodeposition processing parameters and grain refiners on the grain size, texture and segregation of Ni and thus on internal stresses. The grain refiner content of the electrolyte, mainly the saccharin content, and the pulse parameters on- and off-time as well as the pulse current density were varied systematically. The combination of different methods of stress and texture analysis allows, among other things, a careful discussion of the influence of saccharin on stress and texture development. Massive tensile specimens were produced with different grain sizes and deformed in incremental load tests. These tests clearly demonstrate the strong effect of the production process on the deformation behavior under constant load.

Keywords: Nanocrystalline nickel; Pulse electrodeposition; Internal stresses; Tailored microstructure; Bulk material

1. Introduction

It is well known that process parameters for technical materials, such as steel, strongly influence material properties. Much money had to be invested before it was possible to control segregation, grain size distributions, eigenstresses and texture. These factors heavily influence the mechanical properties and thus limit the technical field of application. Consequently, in the comparatively new class of nanomaterials, these parameters have to be taken into account and mastered as well. This is of utmost importance if one wants to deduce the characteristics really related to the nano or ufg grain size of materials. However, it is still current practice to compare material behavior based solely on nano- and ultrafine-grained (ufg) samples of the base material, manufactured in different – often non-comparable – technical processes, as will be pointed out later on [1,2].

The sole selection criterion is often the producibility of the grain size or grain size range in question. This practice is not surprising, considering the complexity of producing bulk nanomaterials with broad grain size ranges for systematic mechanical studies (e.g. [3–5]).

Electrodeposition, and above all pulsed electrodeposition (PED), has lately established itself as an effective method for producing nanocrystalline materials. In particular, bulk samples of nanocrystalline nickel can be reliably produced using this method [3]. Despite the technical possibilities of producing bulk samples this way, it is still common practice

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to carry out studies using thin foils – with all known accompanying problems, like the variation in mechanical properties with varying foil thickness [6–8].

Grain sizes around 30 nm are already available on the market; Dalla Torre et al. [6] investigated two of those commercial samples of the same grain size and clearly demonstrated extreme differences in microstructure and thus mechanical properties like tensile strength, in spite of identical grain size.

In order to study the grain size dependence systematically, especially the transition from nano- to ultrafine grains and normal grain size behavior, it is necessary to process materials over the complete range of grain sizes keeping the other parameters, like texture, internal stresses or the content of impurities, as constant as possible.

The possibilities of producing nano- to ultrafine grains from a single nanograin-sized PED material by a heat treatment are limited, as this method causes abnormal grain growth, leading to bimodal grain size distributions [9,10]. Furthermore, during the heat treatment the grain boundaries embrittle, depending on the type and amount of additives in the solution, which leads to intercrystalline fracture under tension. Therefore, it is preferable to gain a variety of grain sizes using electrodeposition techniques, e.g. by varying the pulse function parameters or the electrolyte composition. Most commonly in the PED process, grain size variation is reached by the addition of so-called grain refiners (e.g. [3,11]). These grain refiners not only influence grain size: by the way they segregate at the grain boundaries, they can also alter the main crystallographic orientation, the grain size distribution, eigenstresses and many other factors [11].

As explained later, the grain boundary segregation and the eigenstresses have extreme implications for the mechanical behavior of the material. As the sample production and the mechanical investigation are (with few exceptions) not executed by the same groups, the exact circumstances of the production process and the ways that the grains are refined are not known by the tester. This leads to poorly defined sample material and scientifically invalid or at least questionably distorted test results, as well as contradictory conclusions about typical mechanical behavior of nanocrystalline materials. A misleading consequence of this separation of sample production and execution of material tests is the generalization of perceived material properties that are not at all typical to nanomaterials, but result solely from differences in the sample production process.

It is the goal of this paper to show how to reliably produce microstructures with well-defined grain sizes and grain boundary structures, mainly with respect to the state of segregation. The focus of these studies lies on the delivery of samples of different grain sizes with nearly identical states of segregation of the grain boundaries, in contrast to samples with identical grain sizes but very differently segregated grain boundaries. This will ultimately enable the systematic investigation and validation of the grain size effects of nanocrystalline nickel. In order to reach this goal, varying pulse parameters and variations of electrolyte compositions by the addition of different grain refiners have been systematically used during the electrodeposition of nickel in a sulfamate bath.

The effects on the resulting grain size are pointed out with particular respect to the different material properties, which, together with the grain size, are dependent on and changed by the specific production process parameters. These include eigenstresses and texture.

2. Experimental details of the pulse electrodeposition process

2.1. Basic electrolyte composition and experimental set-up

All the investigated Ni samples were produced by pulsed electrodeposition (PED) from a nickel sulfamate electrolyte. The concentration of Ni^{2+} in the aqueous sulfamate solution is 185 g/l. This high concentration facilitates the deposition of dense material in comparison to a Watts-type electrolyte with a concentration of 65 g/l. The exact electrolyte composition is listed in Table 1.

The electrodeposition was performed in a double-walled, water tempered (45 °C) reactor of glass, as proposed by Natter et al. [3]. Ni pellets of high purity were used as anode. A steel cathode was used for the preparation of samples for microstructural characterization and mechanical testing (see Sections 3.1, 3.2 and 3.4), whereas a copper substrate was used as the cathode for the measurements of the eigenstresses (see Section 3.3). The current is supplied by a galvanostat and modulated with an arbitrary waveform generator to provide a rectangular pulse function. The pH of the electrolyte was maintained between 3.5 and 3.7. To guarantee a homogeneous distribution of Ni^{2+}, the electrolyte was stirred mechanically.

2.2. Sample geometry

Ni plates with rectangular dimensions of 40 mm × 70 mm and thicknesses of 1.5–3 mm are required to cut tensile specimens with a gauge length of 17 mm and a width of 3 mm, used for the incremental load tests in Sections 3.4 and 4.4. Since the deposition time is determined by the thickness of the deposit, smaller sample geometries had to be used for the screening of the pulse parameters. Tensile tests were only done on specimens with defined texture, segregation and grain size as defined by this screening. Hence, Ni deposits of 200 μm thickness were plated on cylindrical substrates with a diameter of 12 mm only. These coatings were much thicker than the epitaxial first layers, which grow on the substrate within the first 400 mm and also thick enough for X-ray diffraction (XRD; the depth of penetration for Ni is 70 μm). The reproducibility of the deposition was ensured by, for example, keeping the distance between the anode and the cathode constant.

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