

# Mechanical, electrochemical and tribological properties of nanocrystalline surface of brass produced by sandblasting and annealing

Linchun Wang, D.Y. Li\*

*Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alta., Canada T6G 2G6*

## Abstract

Mechanical, electrochemical and tribological properties of nanocrystalline surfaces of a brass alloy (70–30) produced by sandblasting and annealing were investigated. The grain size of a nanocrystalline surface was determined by means of optical microscopy and transmission electron microscopy. The relationships between the grain size of a surface and its properties were investigated using nano-/micro-indentation, micro-scratch, electrochemical scratch and polarization techniques. It was demonstrated that the surface hardness and elastic behavior were improved as the grain size decreased, leading to markedly enhanced wear resistance. The efficiency of hardening by reduction of grain size became lower in the nanocrystalline region, compared to that in the microcrystalline region. The potentiodynamic polarization test indicated that the nanocrystalline surface had higher resistance to corrosion. Nano-indentation and micro-scratch test with in situ monitoring changes in contact electrical resistance demonstrated that the nanocrystallization was significantly beneficial to the mechanical behavior of the passive film. Mechanisms responsible for the beneficial effects of nanocrystallization on properties of brass and its passive films are briefly discussed.

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## 1. Introduction

Reducing grain size is an important approach to improve mechanical properties of a polycrystalline material. In recent years, the mechanical behavior of nanocrystalline materials has been a subject of many studies [1,2]. The research of this topic is motivated by potential application of nanocrystalline materials thanks to their novel mechanical and physical properties.

Many experimental studies have shown that nanocrystallization can increase hardness of a material, resulting from increased grain boundaries that retard the motion of dislocations. In general, the hardness of a polycrystalline material increases with a decrease in grain size, obeying the well-known Hall–Petch (H–P) relationship [3,4].

$$H = H_0 + kd^{-1/2} \quad (1)$$

where  $H$  is the hardness,  $d$  is the grain diameter, and  $H_0$  and  $k$  are material constants. For a regularly grained

material, the value of  $k$  is positive. Although the dependence of hardness on the grain size has been widely applied in practice, it is not very clear whether the H–P relationship can be extended to the nanocrystalline region. Conflicting phenomena were reported by different researchers [5–7]. For instance, it was observed that a nanocrystalline NiAl obeyed the H–P relationship [12]; while the H–P relationship became unsuitable when the grain size was smaller than  $\sim 1 \mu\text{m}$  for polycrystalline Armco iron [8] and nickel [9]. Jang and Koch [10] reported that nanocrystallization could strengthen iron but the strengthening rate with respect to the grain size was low. It is also reported that nanocrystalline Ni–P is softer than coarse-grained polycrystalline Ni–P [11]. As a matter of fact, the grain boundary may block dislocations, thus strengthening a material. However, possible grain boundary sliding may render the material softer. Therefore, whether or not the crystallization can strengthen a material largely depends on the grain boundary structure and properties; the situation changes from case to case.

In addition to the mechanical behavior, other properties are also affected by nanocrystallization, e.g. corrosion behavior. For passive alloys, local break down of a

\*Corresponding author. Tel.: +1-780-492-6750; fax: +1-780-492-2881.

E-mail address: [dongyang.li@ualberta.ca](mailto:dongyang.li@ualberta.ca) (D.Y. Li).

passive layer may lead to pitting corrosion [13–15]. The performance of a passive film formed on a nanocrystalline material could be very different from that of one on a conventional crystalline material. Recent studies on nanocrystalline 304 stainless steel have demonstrated that mechanical properties and the scratch resistance of the passive film on 304 stainless steel were markedly improved by nanocrystallization of the steel [16].

In many cases, failure of a work piece may initiate at surface, such as corrosion and wear. It is therefore effective and economical to modify the surface of a component for improved performance and prolonged service life. Surface nanocrystallization has attracted increasing interest. This paper reports our recent studies on surface nanocrystallization of brass (70–30) by sandblasting and annealing treatment. Such a nanocrystalline surface layer had a transition zone in which the grain size changed gradually from nano-scale to micro-scale, so that there was no problem with interface bonding. Effects of nanocrystallization on mechanical, electrochemical and tribological properties of the nanocrystalline surface were investigated. The influence of nanocrystallization on the passive film of brass was also studied.

## 2. Experimental procedure

Commercial brass (70–30) plates with dimensions of  $35 \times 20 \times 3$  mm<sup>3</sup> were used for the study. After ground using a 600 grit SiC paper, all samples were sand blasted under a blasting pressure 300 kPa for 10 min to produce nanocrystalline surface layers. The sand flow rate was 5 g/s. The mean roughness of the sandblasted surface was approximately 3  $\mu$ m. The samples were then annealed at 150, 250, 350, 500 and 600 °C, respectively, for 1 h and cooled in air to obtain different grain sizes in the sandblasted surface layer. Surfaces of the samples were lightly polished using 0.05- $\mu$ m alumina trioxide and etched with FeCl+HCl. Some of the samples experienced passivation treatment in a 3.5% NaCl solution for 24 h. Such treatment may create a complex passive layer consisting of ZnO, CuCl and Cu<sub>2</sub>O [15].

The crystalline size of a sample, after being etched in an alcoholic ferric chloride solution, was determined using optical microscopy. TEM (JEOL 2010) was employed to determine the size of grains in a nanocrystalline surface layer.

Microhardness of the samples was determined using a micro-indenter (from Fischer Technology, Inc.). Each hardness value is an average of 10 measurements. The ratio ( $\eta$ ) of the elastic deformation energy to the total deformation energy, which reflects the elastic behavior of a material, was determined based on its loading–unloading curve [17].

The wear resistance of a surface was evaluated using a universal micro-tribometer (UMT) made by the Center for Tribology (CA, USA). During the test, a diamond tip scratched a surface under a constant load of 10 g at a velocity of 0.02 mm/s. The volume loss was determined.

A Gamry PC4/750 system was used to investigate the polarization behavior of the samples. The scan rate was 0.33 mV/s. A saturated calomel electrode was used as the reference electrode, and a piece of platinum was used as an auxiliary electrode.

A nano-mechanical probe with a pyramidal diamond indenter (Hysitron), was used to determine the hardness and  $\eta$  values of passive films on the samples after the passivation treatment. The nano-indentation tests were performed in surface areas with their roughness ( $R_a$ ) approximately equal to 0.02  $\mu$ m. The force resolution of the instrument was 0.1  $\mu$ N and the displacement resolution was 0.2 nm.

The resistance of a passive film to scratch was evaluated using the UMT. During the test, a diamond tip scratched a surface at a velocity of 0.02 mm/s under a normal load that was increased from 0 to a designed level. Failure of the passive film during scratch was determined by monitoring variations in the contact electrical resistance (CER) between the tip and the sample surface.

Corrosive wear of a sample was evaluated using an electrochemical scratch technique. During the test, a diamond tip scratched a sample surface immersed in a 3.5% NaCl solution under an applied potential and a constant load. Variations in current reflected the resistance of the surface to corrosive scratch. The tip velocity was 5 mm/s and the duration of scratching was 0.05 s.

## 3. Results and discussion

### 3.1. Grain size of the nanocrystalline surface

Surface microstructures and grain sizes of the sandblasted and annealed samples were examined under an optical microscope. Figs. 1(a)–(d) illustrate cross-sectional optical images of some of the samples. The thickness of the modified layer was approximately 25  $\mu$ m. Since the grain size of the sample annealed at 150 °C could not be determined using the optical microscope, a transmission electron microscope (TEM) was employed to observe the nanocrystalline surface layer. Figs. 2(a) and (b) show bright- and dark-field images of a near-surface layer of the sample. One may see ultrafine grains that are equi-axed with their mean grain size approximately 20 nm. The corresponding diffraction pattern (Fig. 2a) indicates that the ultrafine grains were randomly oriented. After annealing at 250, 350, 500 and 600 °C, the grain size of the sandblasted surface layer increased as shown in Figs. 1(b) and (c). Average grain