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Controllable manipulation of crystallinity and morphology of aluminium surfaces using high intensity ultrasound

Anna Kollath, Pavel V. Cherepanov, Daria V. Andreeva *

Physical Chemistry II, University of Bayreuth, Universitätsstr. 30, 95440 Bayreuth, Germany

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ABSTRACT

High intensity ultrasound (HIUS) provides highly non-equilibrium condition for metal processing. Controllable manipulation of crystallinity and morphology of metal coatings is important for different applications including catalysis and corrosion protection. Investigation of effects of HIUS in different sonication media on microstructure and morphology of aluminium (Al) layers showed that HIUS can cause melting and recrystallization of Al. Due to high cooling rate the grain size of Al can be reduced. Ultrasonically induced structure refinement could potentially be used for enhancement of mechanical properties of coatings. If ultrasonically generated temperature is not high enough for metal melting, temperature induced atomic diffusion leads to grain growth, segregation and fragmentation of Al layers and, thus, the formation of attractive for catalytic application increased surface area.

1. Introduction

High intensity ultrasound (HIUS) is a unique technological approach for solid-state processing of metal particles and surfaces [1–3]. HIUS assisted metal treatment can provide metal surface with a number of beneficial features including the removal of surface passivating metal oxide layer with poor mechanical properties [4], increase of surface roughness [5], and effective surface area [6]. Thus, the ultrasonically modified surfaces possess enhanced adhesive properties [8], increased loading capacity [9,10] and can be used as efficient catalysts [11–13] or bioactive supports [14]. However, impact of cavitation on metal surface is still not very well understood.

HIUS provides highly non-equilibrium conditions [15] for chemical synthesis. It is known that extraordinary fast switching of heating/cooling cycles $\sim 10^9$ K s^{-1} [16] can occur in ultrasonically treated media. Collapsing cavitation bubbles create μm-sized areas of high temperature and pressure that are rapidly quenched by macroscopically "cold" sonication medium. HIUS induced local heating of metal surface can generate temperature gradient [17] that enhances atomic diffusion in metals and causes grains' growth [18].

In metallurgical industry the temperature forced grain growth is leading to undesirable metal materials softening [19]. In catalysis it is opposite; growth of crystallites might be beneficial if it is accompanied by increase of surface area and enhancement of accessibility of catalytically active sites [11–13]. However, if HIUS provides enough energy for metal melting fast cooling of ultrasonically heated metals could lead to structure refinement [20] as well as to enhanced mechanical properties of metal surfaces and coatings. In order to understand at which conditions HIUS is beneficial for a particular application we focused on the investigation of HIUS effects on morphology and crystallinity of the aluminium (Al) layers.

It has been reported that temperature inside the cavitation bubble and its collapse intensity significantly depend on physical and chemical properties of sonication media. Sonication media with low vapour pressure and high viscosity result in an increased cavitation collapse intensity (ethylene glycol) [4,21]. A higher vapour pressure (water, ethanol) leads to higher vapour content inside the cavitation bubble and lower interior temperature of the collapsing bubble [22,23]. Additionally, HIUS treatment of sonication medium leads to its sonolysis – generation of free radicals that trigger surface red–ox reactions [24,25]. By appropriate sonication medium choice during HIUS treatment, it is possible to control the amount of cavitation energy that can be supplied to metal surface [26] and interfacial red–ox processes [27]. Thus, use of particular sonication is essential for the achievement of desirable microstructural and morphological properties of metals.

Here we investigated the effect of HIUS on Al surface with respect to used sonication media. We used three industrially important and relatively harmless media: water, ethanol, and ethylene glycol. Influence of cavitation on crystallinity of Al was

* Corresponding author.
E-mail address: daria.andreeva@uni-bayreuth.de (D.V. Andreeva).

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studied using X-ray diffraction (XRD) analysis. The Scherrer method was applied for the grain size calculations. Cavitation impact on Al morphology was investigated by scanning electron microscopy (SEM) and light microscopy (LM).

2. Experimental

Silicon (Si) (100) with polished surface (CrystTec Kristalltechnologie) was used as substrate for Al layers. 3 nm Chromium (Cr) layer was deposited for better adhesion of Al layer to Si surface. 2 μm Al layer was deposited from vapour phase. Absolute ethanol AnalR NORMAPUR from VWR Chemicals and ethylene glycol (⩾99.5%) from Sigma Aldrich were used as received. Water was purified with Milli-Q Academic A10 Millipore to obtain milli-Q quality.

Al covered (100) Si were fixed in a home-made sample holder and sonicated for 1, 5 and 10 min in 350 ml of ethanol, ethylene glycol or water at 5 mm distance to sonotrode. Experiments were carried out using a UIP1000hd equipped with a B2-1.8 booster and a BS2d22 sonotrode (head area 3.8 cm^2) from Hielscher Ultrasound Technology. The operating frequency was 20 kHz with amplitude of 106 μm and a maximum intensity of 140 W/cm^2. The homemade sonication cell was thermostated at approx. 283 K. Keeping in mind that temperature of sonication media and distance to sonotrode can significantly influence the modification process; we fixed these parameters for all experiments. The samples modified in ethylene glycol or water were rinsed with ethanol after sonication.

Scanning electron microscopy (SEM) was performed with a Zeiss Leo 1530 (operating voltage 3 kV). Analysis of SEM images was carried out using the program ImageJ. Grain size was determined from SEM by taking an average grain size of grains of three different surface areas. Microprobe analysis was performed using energy dispersive spectrometry (EDS) Model 6587, Pentafet Link, Oxford microanalysis group, UK. Light microscopy (LM) was carried out using a Zeiss Axioskop 2 MAT.

For sample characterization, X-ray diffraction (XRD) analysis was performed using a Panalytical X'Pert Pro MPD with monochromatic Cu Kα radiation. The program X'Pert HighScore Plus was used for data evaluation. The detailed method of grain size calculation by Scherrer is described elsewhere [18].

3. Results and discussion

3.1. Effect of HIUS on morphology and crystallinity of Al surface

The Al surfaces were investigated by SEM in order to determine the effects of HIUS on morphology and crystallinity of metal interfaces. Fig. 1a shows representative SEM images of the samples that were sonicated for 1, 5, and 10 min in the presence of water, ethanol, and ethylene glycol respectively. All samples exhibit polycrystalline structures with well-defined grains that are highlighted on the images.

The average grain size of the Al surface was estimated using SEM images. The grain size of the Al surface is plotted vs. sonication time for the used sonication media and shown in Fig. 1b. The initial grain size of the untreated samples was found to be 170 ± 10 nm. After 10 min of sonication the grain size reached its maximum value of 200 ± 20 nm for all samples. This probably corresponds to grain's size with minimum interfacial energy for the used material. Thus, the 10-min sonicated Al surface showed similar crystallinity for the all used sonication media.

However, the grain sizes of the 1-min-sonicated Al surfaces in the presence of ethanol and ethylene glycol were significantly smaller, then those of the initial Al surface and the 10-min-sonicated Al surfaces. In the presence of ethanol the average grain size was 140 ± 20 nm and in the presence of ethylene glycol – 120 ± 30 nm.

Partial melting and fast solidification of the ultrasonically treated metal surfaces might explain reduction of the grain size of the Al surface. Macroscopically "cold" sonication medium rapidly cools the ultrasonically heated metal surface and leads to the grain size reduction. Thus, in ethanol and ethylene glycol HIUS transfers enough energy to the surface to heat it above the melting point of Al (>933 K).

Overall in aqueous medium HIUS treatment of metal surface did not lead to significant changes of the grain sizes. The size of the grains slightly increased from 170 ± 10 nm to 200 ± 20 nm. A reduction of the grain sizes of the sonicated surface was not observed. However, EDS analysis of the samples showed an increased concentration of oxygen (up to 5 at.%) on the ultrasonically treated in water Al surface. EDS of the samples prepared in ethylene glycol and ethanol did not reveal an increase of oxygen concentration after the HIUS treatment.

It is known that aqueous media are strong oxidants [24]. In the presence of water the ultrasonically generated OH radicals rapidly oxidize Al surface [7,11–13,20]. The generation of a thin metal oxide layer (2–3 nm) [7] might influence the HIUS assisted modification of Al. First of all, a thin metal oxide layer might prevent metal melting. Furthermore, in oxidative medium a part of mechanical energy of ultrasound is continuously used for sonochemical surface oxidation that followed by decomposition of metal oxides.

Recently the continuous oxidation of Al by HIUS in water was investigated by XRD and solid state ^{27}Al NMR [7]. The formation of metastable Al hydroxides (bayerite and boehmite) was observed. These Al hydroxides are decomposed at approx. 573 K and converted to Al oxides with very high melting temperature. Thus, we suggest that in aqueous media the energy provided by HIUS is rather used for the continuous formation and decomposition of Al oxides/hydroxides than for observed in organic media melting/recrystallization processes.

3.2. Effect of HIUS on the bulk crystallinity of Al layer

In order to study the effect of HIUS on bulk crystallinity of Al layers we analysed microstructure of the samples using XRD. The XRD patterns of initial sample and the samples sonicated for 1 (Fig. 2a), 5 (Fig. 2b), and 10 (Fig. 2c) min in the presence of water, ethanol, and ethylene glycol are shown in Fig. 2. The observed peaks around 38° (111), 42° (200), 62° (220), and 79° (311) are assigned to Al (JCPDS: 00-001-1176). All Al layers showed (111) preferential orientations at all experimental conditions. Thus, we used the (111) peak for the analysis of microstructure of the samples.

The peak broadening together with peak shifting that can be seen in Fig. 2 serves as an evidence of the possible changes of crystal size and non-uniform strain in the samples [28]. The XRD spectra demonstrate that the full width at half maximum (FWHM) and the position of the peak (111) changes depending on the sonication time and sonication media.

We observed noticeable (111) peak broadening in XRD patterns of the samples sonicated for 10 min in the presence of ethanol and ethylene glycol. XRD peak broadening occurs due to reduction of grain size of a sample. In contrast, XRD patterns of the 1-min sonicated samples in ethanol and 5-min sonicated samples in ethylene glycol showed the narrowing of (111) peak that indicates the grain growth.