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Short Communication

Effect of high intensity ultrasound on Al_3Ni_2, Al_3Ni crystallite size in binary AlNi (50 wt% of Ni) alloy

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ABSTRACT

Crystallite size of the intermetallics is one of the most important parameters that can influence kinetics of catalytic reactions. Analysis of the crystallite sizes of Al_3Ni and Al_3Ni_2 intermetallic phases using Scherrer and Williamson–Hall methods reveals that the sonomechanical impact of ultrasound on suspensions of AlNi particles in ethanol results in crystallites growth and microstrain reduction.

1. Introduction

Aluminum–nickel alloys have gained significant amount of interest among researchers after Raney has introduced activated AlNi (50 wt% Ni) as a catalyst for hydrogenation [1] of vegetable oils. Shortly after, AlNi (50 wt% Ni) became very popular in industrial applications, particularly as a reagent or a catalyst in organic synthesis due to its high catalytic activity [2,3]. However, active Raney Ni is difficult to handle. It is pyrophoric and should be stored under distilled water in a special place. Recently, we proposed that AlNi alloys could be activated by treatment of aqueous suspensions of AlNi particles [4]. Ultrasonic modification of the metal particles in aqueous media leads to a partial oxidation of metal and formation of porous morphology of the catalyst. Furthermore, we observed that after sonication AlNi particles still have metallic skeleton [5]. Increased accessibility of active metal centers for substrate molecules was achieved by distribution of Al_3Ni and Al_3Ni_2 intermetallics [6] in the porous metal oxide matrix. Due to porous morphology, high surface area and high accessibility of active centers and metal/metal oxide composition ultrasonically activated AlNi catalyst has high catalytic activity and high stability in contrast to Raney nickel. However, the mechanism of the activation of alloys via ultrasonication has a number of open questions. One of them is how the crystal structure of metals is affected by ultrasonication.

Crystallographic parameters such as crystal system, orientation of crystallites and their size, as well as microstrain [7–9] are among the most important parameters that can influence kinetics and efficiency of catalytic reactions. Therefore, catalytic activity of ultrasonically activated AlNi alloy is to a high extent defined by presence of intermetallic compounds such as hexagonal (P-3m1) Al_3Ni_2 and orthorhombic (Pnma) Al_3Ni. We suggest that additionally to surface chemistry and morphology of AlNi particles high intensity ultrasound (HIUS) can also affect crystal structure of the intermetallics. Suslick et al. showed that due to effects of shock waves generated in ultrasonic field and intense interparticle collisions interfacial regions of metal particles can melt [10]. Thus, HIUS can provide enough energy to metals and stimulate rapid diffusion of metal atoms and cause changes of crystallite sizes as well as microstrain.

Here we report on investigation of HIUS effect on size and strain of the Al_3Ni_2 and Al_3Ni intermetallic compounds in AlNi (50 wt% of Ni) alloy. The structural determination of Al_3Ni_2 and Al_3Ni phases after ultrasonic treatment was performed by Rietveld refinement. Crystallite size with respect to the specific reflection planes was evaluated using Scherrer approach [11,12], while mean crystallite size and strain calculations were estimated by modified form of Williamson–Hall (WH) method [13–15] such as uniform deformation model (UDM).

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2. Experimental section

Aluminum–Nickel (50 wt% Ni) alloy powder with average particle size of 140 μm was purchased from Fluka as well as anhydrous ethanol. All chemicals were the highest purity grade available and were used as received without further purification.

Al/Ni alloy powder (4 g) was dispersed in (40 mL) of ethanol or ethylene glycol and sonicated for 60 min with a Hielscher UIP1000hd (Ultrasonics GmbH, Germany) operated at 20 kHz with a maximum output power of 1000 W. The apparatus was equipped with an ultrasonic horn BS2d22 (head area of 3.8 cm^2) and a booster B2–1.8. The maximum intensity was calculated to be 140 W cm^{-2} at mechanical amplitude of 106 μm. To avoid overheating during sonication the experiment was carried in a homemade thermostatic cell connected to a thermostat (Huber GmbH, Germany). The temperature was monitored during the treatment and kept at 298 K After HIUS treatment metal particles were separated from supernatant by centrifugation at a speed of 10,000 rpm for 1 h and washed with absolute ethanol followed by drying under vacuum at room temperature.

Powder X-ray diffraction (PXRD) analysis of the samples was performed using Stoe STADI P X-ray transmission diffractometer (CuKα radiation from the copper target using an in built nickel filter, λ = 1.54056 Å).

Crystallographic parameters such as crystallite size and microstrain were calculated using Scherrer and Williamson–Hall methods.

Scherrer method relies on utilizing the following equation:

$$D = \frac{k\lambda}{\beta_D \cos\theta} \tag{1}$$

where k is shape factor (a constant equals to 0.94), λ is the X-ray wavelength (1.54056 Å for CuK_α radiation), β_D is the instrumental corrected peak width at half-maximum intensity, θ is the peak position, and D is the effective crystallite size normalized to the reflecting planes. It is important to note that to avoid any misleading; only not overlapping peaks were chosen for data processing.

According to WH method strain-induced broadening arising from crystal imperfections and distortion are related by:

$$\varepsilon \approx \frac{\beta_s}{\tan\theta} \tag{2}$$

Assuming that the size and strain contributions to the line broadening are independent of each other, the observed line breadth can be written as the sum of the two terms:

$$\beta_{hkl} = \beta_s + \beta_D \tag{3}$$

Substitution of Eqs. (1) and (2) into Eq. (3) results in the following:

$$\beta_{hkl} = \left(\frac{k\lambda}{D\cos\theta}\right) + (4\varepsilon\tan\theta) \tag{4}$$

After rearranging, Eq. (4) becomes:

$$\beta_{hkl}\cos\theta = \left(\frac{k\lambda}{D}\right) + (4\varepsilon\sin\theta) \tag{5}$$

The WH equation represents uniform deformation model (UDM) where the strain is assumed to be uniform in all crystallographic directions, thus considering the isotropic nature of the crystals, where all the material properties are independent of the direction along which they are measured. Plotting values of $\beta_{hkl}\cos\theta$ as a function of $4\varepsilon\sin\theta$ allows estimating microstrain ε (slope of the fitted line) and the average crystallite size D (y-intercept of the fitted line).

Transmission electron microscopy (TEM) was performed on LEO 922 EFTEM operating at 200 kV.

3. Results and discussion

In order to maximize the influence of HIUS on crystallites' sizes and exclude other possible effects of sonication e.g. particle fragmentation, change of surface roughness, formation of metal oxides/hydroxides 140 μm initial AlNi (50 wt% Ni) particles were sonicated in presence of ethanol. Especially, presence of metal oxides/hydroxides in the material can significantly complicate interpretation and evaluation of PXRD patterns. Indeed, the size and the morphology of the particles did not change after sonication in ethanol. Ethanol serves as a scavenger of OH radicals [16]. Its use as a sonication media can prevent partial oxidation of metals and, therefore, allow accurate monitoring of crystallite sizes' changes upon sonication. We used fixed sonication time of 60 min. Our previous works demonstrated that 60-min sonicated samples exhibited the best catalytic properties [4].

Effect of HIUS on the size of the crystallites can be seen in transmission electron spectroscopy (TEM) images in Fig. 1. The size of the crystallites in the ultrasonically treated samples has significantly increased. The crystallites are highlighted by the arrows in the images. Additional evaluation of the crystallites' sizes was done by applying Scherrer and Williamson–Hall approaches to powder X-ray diffraction (PXRD) patterns.

The PXRD patterns of initial and HIUS treated in presence of ethanol AlNi (50 wt% Ni) alloys are shown in Fig. 2. All detectable peaks could be indexed as either Al_3Ni_2 or Al_3Ni intermetallic phases found in the standard reference data (JCPDS: 00-014-0648) and (JCPDS: 00-002-0416). The patterns in Fig. 2 indicate that the materials before and after modification have absolutely identical XRD patterns. However, it is clearly seen that the reflection peaks became sharper after ultrasound treatment of AlNi alloy, indicating the crystallite size's change. The crystallite sizes of both Al_3Ni_2 and Al_3Ni intermetallic phases were determined by X-ray line broadening.

Scherrer analysis was used to evaluate crystallite size of Al_3Ni_2 and Al_3Ni intermetallics with respect to corresponding reflecting planes. The crystallographic parameters obtained from the Scherrer method are summarized in Tables 1 and 2. The values indicate that HIUS treatment of AlNi alloy results in gradual Al_3Ni_2 and Al_3Ni crystallite sizes' increase in all crystallographic directions including edge – (100), (020) and basal – (001), (002) planes. Thus, the average crystallite growth for Al_3Ni_2, as well as Al_3Ni intermetallics was calculated to be ~40% with respect to specific crystallographic plane. Although, Scherrer method does not provide any information in the case when in addition to size broadening strain-induced broadening occurs. For this reason we applied Williamson–Hall (WH) method for XRD reflection peak analysis.

The WH analysis of Al_3Ni_2 XRD reflection peaks is shown in Fig. 3(a–c). Great scatter of the points on Fig. 3(a) for the untreated sample is a direct indication of uneven microstrain distribution in grain boundaries throughout the sample. Nevertheless, the scattering of the points away from the linear fit is becoming less after HIUS treatment. Interestingly, along with scattering decrease for ultrasonically treated phases microstrain value (Table 1) is found to be closer to zero as oppose to untreated phases. These results indicate overall microstructuring and strain relaxation in grain boundaries. Further, the average crystallite size for all phases was estimated from the y-intercept Fig. 3(c). The values are in a good agreement with those obtained for the Al_3Ni_2 reflection planes using Scherrer method with the same tendency observed: crystallite size is increasing after ultrasound treatment. Similar analysis was carried out for Al_3Ni intermetallic compound present