OBTAINING OF NANOCRYSTALLINE FUNCTIONAL MATERIALS IN HYDROGEN

Bulyk I.I.*, Basaraba Yu.B., Markovych V.I.
Karpenko Physico-Machanical Institute National Academy of Sciences of Ukraine,
5, Naukova St., L'viv 79601, Ukraine

Introduction

Functional materials take an important place among nanocrystalline materials, investigation of which is quickly recently developed.

Among several obtaining methods of these materials widely use mechanical method, which is carried out, as a rule, in inert atmosphere [1].

In this work investigation results of formation conditions of a nanocrystalline state some functional materials in hydrogen are presented.

Materials were obtained in two stages: disproportionation in mechanical mill in hydrogen; recrystallization-recombination using annealing.

Grain sizes were estimated by means of a determination of a widening of peaks of the X-ray diffraction (XRD) pattern. For the estimate of X-rays coherent scattering region sizes it was used approximation method [2]. It was investigated reflections of the first and second orders from (101) plane of $SmCo_5$ phase for KC-37 and (113) plane of $Sm_2(Co,Fe,Cu,Zr)_{17}$ phase for KC-25. The integral curve form was approximated by Gauss function $f(x)=\exp(-\alpha x^2)$. According to this distribution an integral width of a physical broadening curve is determined from equation $(\beta/B)^2=1-(b/B)^2$, where β – integral width of a physical broadening curve, which determines by a fine-grained structure and a microstrain; B – integral width of lines of a sample; b – integral width of lines of a reference. Then, by formula

$$m_1=\beta_1\{[\mu^2-(\beta_2/\beta_1)^2]/[\mu^2-\lambda^2]\}^{1/2},$$

where $\mu^2=(tg\Theta_2/tg\Theta_1)^2$; $\lambda^2=(\cos\Theta_1/\cos\Theta_2)^2$;
m_1 – a part of a width of the line that correspond to coherent scattering region sizes was calculated. Indices 1 and 2 correspond to lines of the first and second orders accordingly. After this by formula $D=\lambda/(m_1\cos\Theta_1)$ coherent scattering region sizes was calculated. It was admitted that $(b/B)^2 \ll 1$ and $\beta=B$.

Results and Discussion

1. A $Sm_2(Co,Fe,Cu,Zr)_{17}$ phase is the main phase of the initial alloy (Fig. 1). After milling in hydrogen the alloy was disproportionated into samarium hydride and solid solution of Fe(Co). Peaks both phases are very extended that indicates about their fine-grained structure. Recrystallization-recombination was carried out at 640, 750 and 820 °C. On first stage grains of the solid solution Fe(Co) appreciably increase and, as we suppose, Sm_2Co_7 phase was precipitated. After heating up to 750 °C the main phase of an $Sm_2(Co,Fe,Cu,Zr)_{17}$ alloy was restored. Furthermore, there are remains of the samarium hydride and Fe(Co). An increase of the temperature up to 820 °C leads to decreasing amount of the Fe(Co) and appearance of the Sm_2Co_7 phase. By the above-mentioned treatment the powder of the material with grain sizes of around 58-72 nm was obtained.

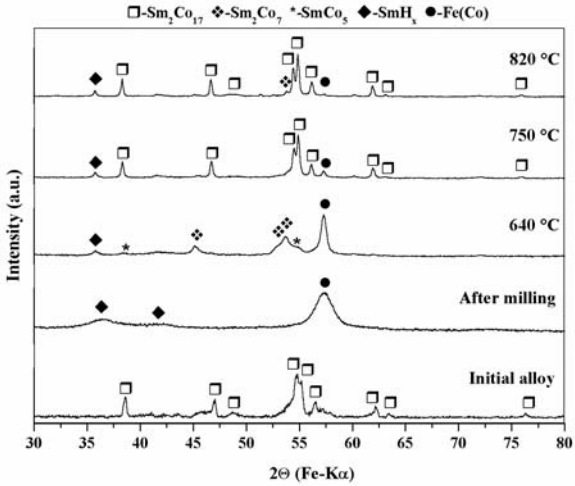

Fig. 1. XRD patterns of the KC25 alloy after different treatment stages and regimes.

2. After treatment of the initial KC37 alloy in planetary ball mill in hydrogen SmH_x and Co were registered (Fig. 2). The recombination annealing was carried out at 625 and 908 °C. The samarium hydride almost complete is decomposed at 625 °C. As a result of a recombination of the hydride and the cobalt, Sm_2Co_7 and Sm_2Co_{17} phases, as we suppose, are formed. An increase of the heating temperature up to 908 °C leads to a complete recombination of the $SmCo_5$ phase. Together with it the Sm_2Co_{17} phase was precipitated. Though, in the initial sample, as impurity, $SmCo_3$ was determined. The grain sizes of the main phase after treatment in a

* * Fax: +38 (0322) 64 94 27 e-mail: bulyk@ah.ipm.lviv.ua

hydrogen atmosphere using planetary ball milling are smaller 70 nm.

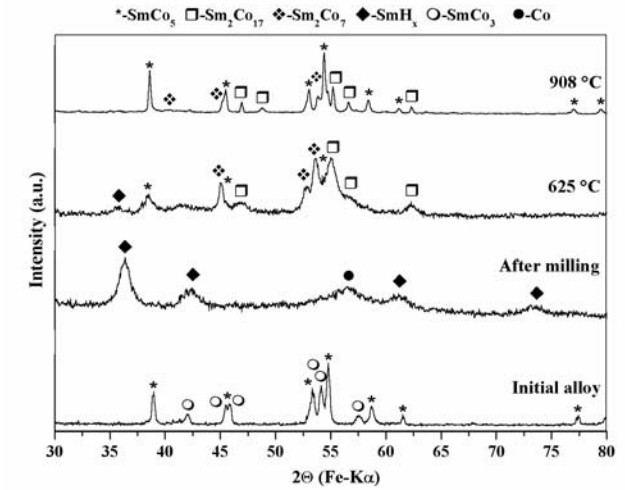

Fig. 2. XRD patterns of the KC37 alloy after different treatment stages and regimes.

3. A decrease of grain sizes of the $LaNi_{4.5}Al_{0.5}$ compound in dependence on the milling speed in hydrogen is seen from XRD patterns (Fig.3). Fig.3*d*,*e*,*f* demonstrates that increasing of the process duration at constant speed leads to the disproportionation of the $LaNi_{4.5}Al_{0.5}$ compound. According to the results of the X-rays phase

Fig. 3. XRD patterns of the $LaNi_{4.5}Al_{0.5}$ alloy: a – initial alloy; after milling during 30 min with the speed of 400 (*b*), 500 (*c*); 600 r.p.m. (*d*) and during 24 (*e*) and 72 hours (*f*) with the speed of 600 r.p.m..

analysis only Ni_3Al intermetallic compounds among the products of disproportionation was registered.

After hydrogen desorption the Ni_3Al phase is remained and the lanthanum is oxidized to La_2O_3 (Fig. 4).

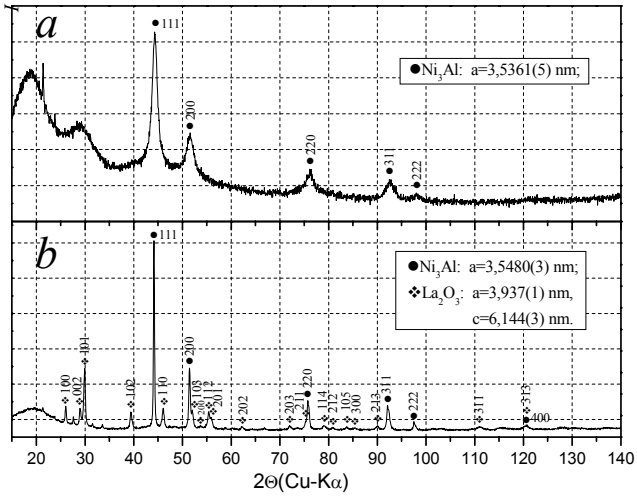

Fig. 4. XRD patterns of the $LaNi_{4.5}Al_{0.5}$ alloy after annealing at 520 (*a*) та 900 °C (*b*).

Grain sizes of the $LaNi_{4.5}Al_{0.5}$ after milling with the speed of 400-600 r.p.m., 30 min were estimated around 50-80 nm and for Ni_3Al 20-30 nm after milling and 100-150 nm after annealing.

Conclusions

It was demonstrated a principal possibility of the application of hydrogen as a medium and a reagent for obtaining of nanocrystalline functional materials. Hydrogen changes a mechanism of a obtaining process of nanocrystalline functional materials. Obtaining of a nanostructure in hydrogen occurs with phase transformations, and not by change of a short range ordering into long range ordering (the last occur during milling of materials in inert atmosphere).

References

1. Bernardi J, Schrefl T, Fidler J, Rijks T, de Kort K, Archambault V, Pere D, David S, Givord D, Sullivan JF, Smith P, Coey JMD, Czernik U and Gronefeld M. J.Magn. Magn. Mater. 219(2000)186.

2. Kovba LM and Trunov VK. X-ray phase analysis: Moscow State University Publishing House, 1976 (In Russian).