EFFECT OF MILLING IN THE PLANETARY MILL ON Fe-Zr-Mn-TI ALLOY MICROSTRUCTURE

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INTRODUCTION

Energy crisis and the problem on protection of environment stimulated increasing interest in possibility for using hydrogen not only in the physical and chemical processes but as fuel or energy carrier in different devices directly or indirectly using energy evolving at hydrogen oxidation.

As compounds used for hydrogen storage in the chemically combined state the binary metal hydrides and hydride phases based on polymetallic compositions may be used.

It was found (1) that rendering amorphous hydride forming alloys used in power packs results in improving their charge-discharge characteristics. For example, the homogeneous amorphous Mg_2Ni alloy having nickel additive and showing high discharge capacity was produced by milling in the planetary ball mill for 36 hr. Electrochemical and microstructural characteristics of the alloy showed that the homogeneous amorphous structure of the alloy was an important factor for improving charge-discharge characteristics of this alloy.

RESULTS AND DISCUSSION

Such intermetallides as Fe_2Zr, $Fe_{1-x}Mn_xTi$, ZrNi etc. are promising for hydrogen storage.

The ball milling of $Zr_{0.82}Mn_{0.7}Fe_{1.3}Ti_{0.2}$ alloy has been conducted in the planetary mill for 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 hr in the inert atmosphere (argon) to produce homogeneous amorphous material of high discharge capacity.

X-ray phase composition of starting material has been studied before milling and after it. X-ray investigations of samples have been carried out on **ДРОН-3М** diffractometer in the filtered Cu radiation.

It has been determined that the starting material consists of the following phases: Fe_2Zr (majority phase, cubic lattice), Mn_2Zr (in little amounts, hexagonal lattice) and β-$FeMn_4$ (in little amounts, cubic structure).

After milling the phase composition did not change but intensive smearring the lines at low and high reflection angles occurred what indicates the substructure development in material.

To investigate the substructure development in material the Fe_2Zr phase has been chosen as it is the base of the material investigated. X-ray reflections from the cube plane (200) of the first and second orders have been recorded, recording speed was 1/4 dg/min.

The integral curve shape has been approximated by Gauss function $y(x)=e^{-\alpha x2}$. According to this distribution $\beta=(B_1^2 - b_1^2)^{1/2}$ where β - broadening the X-ray line because of the structure development in milling, i.e. comminution in ranges of coherent scattering and advent of microdeformations in the lattice; b_1 - X-ray line width for standard (the first order). Similarly B_2 and b_2 - the line widths of the second order are calculated. Then by formulae:

$$m_1=\beta_1\{B^2-(\beta_2/\beta_1)^2/B^2-A^2\}^{1/2};$$
$$n_2=\beta_2\{[A^{-2}-(\beta_1/\beta_2)^2]/[A^{-2}-B^{-2}]\}^{1/2}$$

where $A^2=(\cos\theta_1/\cos\theta_2)^2$; $B^2=(tg\theta_2/tg\theta_1)^2$ we calculate m_1 and n_2 - parts of broadening in the X-ray line. They are responsible for broadening caused by comminution of mosaic blocks and advent of microdeformations in the lattice, respectively.

Then by formulae $D=\lambda/m \cos \theta_1$ and $\Delta a/a=n/4\ tg\theta_2$ we calculate D (size of coherent scattering ranges) and $\Delta a/a$ (microdeformations in the lattice).

The values obtained give us possibility for calculating density of dislocation (ρ_D) occurring on the block surface due to milling and ρ_ξ - dislocation density in the lattice volume, and $\rho_{real}=(\rho_D \times \rho_\xi)^{1/2}$ (2).

We have also calculated a value of energy storaged in the lattice by Faulkner formula (3):

$$V=(15E\langle\varepsilon^2\rangle)/[2(3-4\nu+8\nu^2)]$$

We observe successive comminution of mosaic blocks and growth of deformations in the lattice, development of the dislocation structure leading to destabilization and destruction in the material crystalline structure in milling.

Obtained data are given in Table.

Characterization of substructure	Time of storage			
	10 hr	30 hr	50 hr	100 hr
Dx 10^6,cm	5,29	5,02	4,81	4,13
$\Delta a/a$ x10^3	2,11	2,31	2,60	3,10
ρ_D x 10^{-11},cm^{-2}	1,0	1,2	1.3	1,8
ρ_ξ x 10^{-11},cm^{-2}	0,69	0,83	1,04	1,49
$\rho_{ист}$ x 10^{-11},cm^{-2}	0,83	1,00	1,14	1,64
V, kilocalorie /kg	0,14	0,17	0,21	0,30

CONCLUSIONS

Thermal mechanical effects in milling result in the significant growth of the storaged energy that reaches 0.30 kkal/g in milling for 100 hr. In this case the bulk of material retaining a regular crystalline structure decreases. These effects are the base for transformation of the crystalline material supersaturated with defects into the amorphous state.

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