APPLICATION PROPERTIES OF AB₂-TYPE HYDROGEN ABSORBING ALLOYS.

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1. Introduction

Use of hydrogen absorbing alloys in various practical applications is always connected with the problem of production of starting alloys. The transition from laboratory samples to small-scale production involves the change of furnace and its operation mode and this has an effect on the preparation method of mixture of starting metal. Also, for some applications such as thermosorption compressors the exact values of thermodynamical parameters of reaction are needed. In the present work we present the results of investigation of series Laves phase hydrogen-absorbing alloys which can be promising in for use in different devices.

2. Experimental Part

Alloys were prepared by conventional arc melting. Manganese was taken in an excess of 3 (Alloys 3, 6-12 according to Table 1) or 7 mass.% (Alloys 1, 2, 4, 5) to the calculated quantity to reduce the loss due to fugacity while melting. Obtained samples were analysed by X-ray, atomic absorption spectroscopy, and energy dispersion X-ray analysis (EDXA). Hydriding and isotherm measurements were carried out in a standard Sieverts type apparatus. Hydrogen was of 99.999% purity obtained from LaNi₅ hydrogen accumulator.

Chemical analysis was performed by atomic absorption method according to following schedule:

1. Investigation and choice of a way of dissolution for alloy with the purpose of creation of optimum conditions of atomic absorption determination of elements;

2. Choice of a way of graduation of used AA spectrometers;

3. Development of a course of the alloy analysis in view of peculiarities of its chemical probe preparation and atomic absorption analysis of multicomponent alloys;

The measurements were carried out on one-beam atomic AA spectrometer "Hitachi". The prospective unified way of dissolution for multicomponent alloys, namely in a mixture of saturated nitric and hydrochloric acids with the subsequent addition of hydrofluoric and nitric acids corrected depending on structure of analysed samples and on element to be determined by AA method.

For the analysis of titanium and iron the most expedient way of alloy dissolution for this type of alloys type for simultaneous definition of the specified elements in a solution of a sulphuric acid (1:3) or (1:4) was chosen, since it was necessary to avoid using HBF_4 acid.

Graduation solutions should contain the same quantity of chromium (for titanium) and titanium (for iron) and should be used through the whole course of the analysis. Check of correctness was carried out by a method "entered - found ".

3.Results and Discussion

The composition of starting alloys according to alloying mixture of metals in presented in Table 1. The results of chemical analysis of some alloys are presented in Table 2. Comparing the data it is clear that the actual composition of some of the obtained samples (1, 3 and 6) differs from that of the alloying mixture. The reason for this is at first the fugacity of manganese during melting which leads to some loss of these metals and conformably to the change of the composition. Since the excess of manganese was always the same the data shows that it is necessary to determine the exact amount of metal excess in every case.

| Alloy No. | Ti | Zr | Mn | Cr | Fe | V | Ni | Co | Al | Cu |
|--------------|------|------|------|------|------|------|------|------|-----|-----|
| 1 | 0.95 | 0.05 | 1.35 | 0.45 | 0.2 | | | | | |
| 2 | 0.95 | 0.05 | 1.2 | 0.3 | 0.5 | | | | | |
| 3 | 0.9 | 0.1 | 1.5 | 0.1 | 0.05 | 0.25 | 0.05 | 0.05 | | |
| 4 | 0.9 | 0.1 | 1.5 | 0.1 | 0.05 | 0.25 | 0.05 | 0.05 | | |
| 5 | 0.9 | 0.1 | 1.5 | 0.4 | 0.1 | | | | | |
| 6 | 0.9 | 0.1 | 1.2 | 0.6 | | 0.2 | | | | |
| 7 | 0.85 | 0.15 | 1.5 | 0.1 | 0.05 | 0.25 | 0.05 | 0.05 | | |
| 8 | 0.8 | 0.2 | 1.8 | | | 0.1 | | | 0.1 | |
| 9 | 0.8 | 0.2 | 1.7 | 0.1 | | 0.2 | | | | |
| 10 | 0.8 | 0.2 | 1.5 | 0.1 | 0.05 | 0.25 | 0.05 | 0.05 | | |
| 11 | 0.8 | 0.2 | 1 | 0.9 | | | | | | 0.1 |
| 12 | 0.7 | 0.3 | 1.5 | 0.1 | 0.05 | 0.3 | 0.05 | | | |

TABLE 1. Composition of starting alloys.

TABLE 2. Chemical analysis of alloy composition.

| Alloy No. | Ti | Zr | Mn | Cr | Fe | V | Ni | Со |
|--------------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1 | 1.36 | 0.06 | 0.70 | 0.51 | 0.37 | | | |
| 2 | 1.26 | 0.06 | 0.74 | 0.38 | 0.56 | | | |
| 5 | 1.07 | 0.11 | 1.39 | 0.42 | 0.01 | | | |
| 10 | 0.683 | 0.288 | 1.523 | 0.096 | 0.051 | 0.304 | 0.055 | |
| 12 | 0.781 | 0.201 | 1.535 | 0.088 | 0.069 | 0.227 | 0.046 | 0.052 |

According to X-ray analysis all alloys are multiphase samples with phase of hexagonal structure typical of Laves phases being the main one. In fact the same result for other AB₂ alloys was obtained in [1]. Comparison of X-ray patterns of our samples with those presented in [1] shows that they are very much alike. This proves our assumption that the minor phases in our case are also $(Ti,Zr)(Mn,Cr,Fe)O_3$ oxide phase and unidentified cubic phase with cell parameter a = 2.43 Å. This results is confirmed by the data obtained by EDXA which shows that all samples contain at least two different phases (Table 3). The main phase is represented on the images like a bright field having inclusions of dark and black colour. Its composition differs considerably from that according to chemical analysis. On the other hand the overall composition as measured by EDXA well enough coincides with the latter. And all of them differ from the initial metal ratio of the melting schist. This is mainly due to the fact that the fugacity of chromium and especially manganese plays the leading role in the process of preparation of alloys and should be thoroughly controlled.

| Alloy | Composition | Overall | Main | Dark | Black | Chemical |
|-------|-------------|---------|-------|-------|-------|----------|
| No. | | | phase | phase | phase | analysis |
| | Ti | 1.10 | 1.57 | 1.01 | | 1.26 |
| | Zr | 0.07 | 0.07 | 0.07 | | 0.06 |
| 2 | Mn | 0.98 | 0.73 | 0.98 | | 0.74 |
| | Cr | 0.34 | 0.21 | 0.40 | | 0.38 |
| | Fe | 0.51 | 0.44 | 0.54 | | 0.56 |
| | Ti | 1.05 | 1.46 | 0.93 | 1.94 | 1.07 |
| 5 | Zr | 0.12 | 0.13 | 0.14 | 0.08 | 0.11 |
| | Mn | 1.39 | 1.16 | 1.40 | 0.85 | 1.39 |
| | Cr | 0.44 | 0.25 | 0.53 | 0.13 | 0.42 |
| | Fe | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |

TABLE 3. Composition of phases in alloys according to EDXA and chemical analysis.

The desorption isotherms for investigated systems are shown in Fig.1-5. Hydrogen sorption properties are presented in Table 4. All alloys begin hydriding rather easily without preliminary activation at pressure about 50 atm. However, for those systems when the dissociation pressure is higher complete hydriding requires pressures about 100 atm. Still for the Alloy 2 this maximum experimental pressure is not enough to form hydride phase at ambient temperature even after cooling the sample to the liquid nitrogen temperature (curve 2, Fig.5) to eliminate the influence of the hysteresis effect. In fact the hysteresis factor $ln(P_{abs}/P_{des})$ is about 1.3 in this case.

The value of the dissociation pressure at ambient temperature varies in a wide range from 0.3 to 60 atm. Hydrogen content is rather high for this type of alloys and reaches a value of 2 mass.% in some cases.

| Alloy No. | T _e (K) | P _{diss} (atm) | Absorption capacity | | ∆H, kJ/mole | ΔS, .I/K-mole |
|--------------|-----------------------|----------------------------|------------------------|--------|----------------|------------------|
| | | | H/AB ₂ | Mass.% | | of ix more |
| | 253 | 5.6 | 3.08 | 1.90 | | |
| 1 | 273 | 10.9 | 2.72 | 1.68 | 19.2 | 90.2 |
| | 293 | 20.2 | 2.42 | 1.50 | | |
| | 253 | 19.7 | 3.8 | 3.06 | | |
| 2 | 273 | 34.9 | 3.19 | 2.56 | 16.4 | 89.6 |
| | 293 | 57.2 | 3.10 | 1.88 | | |
| 3 | 293 | 5.2 | 3.01 | 1.83 | | |
| 4 | 293 | 5.6 | 2.57 | 1.55 | | |
| | 253 | 1.8 | 3.72 | 2.25 | | |
| 5 | 273 | 3.4 | 3.29 | 2.00 | 18.3 | 77.1 |
| | 293 | 5.8 | 2.93 | 1.79 | | |
| 6 | 293 | 6.5 | 3.02 | 1.86 | | |
| 7 | 293 | 2.6 | 2.98 | 1.78 | | |
| 8 | 293 | 7.0 | 2.76 | 1.66 | | |
| 9 | 293 | 3.0 | 2.74 | 1.63 | | |
| 10 | 293 | 1.4 | 2.95 | 1.75 | | |
| 11 | 293 | 6.0 | 3.07 | 1.83 | | |
| 12 | 293 | 0.3 | 3.29 | 1.94 | | |

TABLE 4. Absorption properties of investigated alloys

4. Conclusions

The results of the present work show that one of the main problems for the application of AB_2 -type hydrides in metal-hydride technology is the preparation of alloys and unlike the LaNi₅-type alloys the expenditure of some components particularly manganese and chromium should be thoroughly controlled. The investigated alloys are characterised by good sorption properties and can be proposed for use in such systems as thermosorption compressors and refrigerators.

5. Acknowledgement

This work was supported in part by the Russian Foundation for Basic Research Grant No.95-03-08787.

6. Reference

1. Huot, J., Akiba, E., and Ishido, Y. Crystal Structure of Multiphase Alloys (Ti,Zr)(Mn,V)₂, J. of Alloys and Compounds, 231, (1995), 85-89.



Figure 1. Desorption isotherms for alloys 3, 4, 6 and 7 at 293 K.



Figure 2. Desorption isotherm for alloys 8-12 at 293 K.



Figure 3. Desorption isotherms for the system Alloy $1 - H_2$.



Figure 4. Desorption isotherms for the system Alloy $2 - H_2$.



Figure 5. Desorption isotherms for the system Alloy $5 - H_2$.