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Disintegration of Nb-Zr-Fe alloy in hydrogen atmosphere (0.1MPa , 300K)

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The disintegration due to hydrogenation of 35 different Nb-Zr-Fe alloys has been investigated. The hydrogenation was performed in a 0.1 MPa hydrogen atmosphere held at room temperature in an arc-melting chamber without exposure to air. Approximately 60% of the examined alloy compositions become powdered by reacting with the hydrogen. The disintegration phenomena of alloys in a hydrogen atmosphere were recorded by a digital video camera and the following stages were observed. During the violent disintegration stage, an intense ascending current of hydrogen gas occurred that surrounded a lump of alloy. Fine powder steps on this current carried a long distance. This phenomenon was considered to have originated during the outbreak of low pressure for a limited part of the alloy by absorbing a large amount of hydrogen gas in a short time. The hydrogen contents of the powders were measured by thermal and chemical analyses; For example, 1.5mass%H in $Nb_{0.40}Zr_{0.20}Fe_{0.40}$, 1.7mass%H in $Nb_{0.60}Zr_{0.25}Fe_{0.15}$ and 2.0mass%H in $Nb_{0.20}Zr_{0.65}Fe_{0.15}$.

Key words: Nb-Zr-Fe alloy, Powder, Disintegration, Hydrogen storage, Pulverization

1. INTRODUCTION

If various alloys of Nb, Zr, Ta used as high temperature materials, can be disintegrated by hydrogen gas at room temperature, the process should be evaluated as an extremely energy saving powder-making process, since no mechanical energy is needed for crush or grinding. During the refining process of niobium ore by arc melting in a hydrogen atmosphere, one of authors discovered the disintegration phenomenon of a lump of Nb rich ore 15 years ago. The composition range of the semi-refined Nb rich ore was near the composition of a Nb_3Al intermetallic compound.[1] The disintegration of Nb_3Al significantly depends on the degree of surface cleanness of the ingot alloy and hydrogen partial pressure in the atmosphere; the higher the hydrogen partial pressure produces a more violent disintegration.[2]. After this research, the disintegration mechanism of the Nb_3Al alloy by hydrogen was demonstrated by Semboshi et al. [3-4]. The disintegration phenomenon was reported to occur for two phases such as Nb_3Al and Nb_2Al in the Nb-Al alloys, and was caused by the large strain energy due to the difference in lattice expansions between the two phases solid solutions with hydrogenation.

In this study, we investigated the disintegration phenomena of three component alloys as Nb-Zr-Fe and characterized the pulverized powders.

2. EXPERIMENTAL

The raw materials were industrially-produced pure niobium (purity 99.9%), Zr (purity99.99%) and Fe (99.99%). The button ingots of the Nb-Zr-Fe alloy with 35 different compositions were prepared by arc-melting the raw materials five times in an argon atmosphere. The alloys were exposed to a hydrogen atmosphere for hydrogenation without exposing them to air. The amount of absorbed hydrogen was determined by chemical analysis and thermogravimetry (TG)

The stability of the Nb-Zr-Fe hydride was studied in pure flowing argon gas at a heating rate of 5 K/min using a differential scanning calorimeter(DSC), thermogravimetry (TG) and evolved gas analysis (EGA). The dehydrating process was performed at 1273 K for 3.6ks in an argon flow. The microstructure of each sample was observed by scanning electron microscopy (SEM), and the average particle size of the powder was estimated from the specific surface area measured by the BET method. The disintegration phenomenon of the alloys in the hydrogen atmosphere were recorded by a digital video camera (Sony DCR-TRV900)

3. RESULTS AND DISCUSSION

3.1 Disintegration phenomenon of Nb-Zr-Fe alloys by hydrogen

The phenomenon of disintegration of the alloys by hydrogen was continuously recorded by the video camera for all 35 Nb-Zr-Fe alloys. In this study, $Nb_{0.6}Zr_{0.25}Fe_{0.15}$ was chosen as a typical alloy, and the characteristics of its disintegration are described as follows.

Fig.1 (a) shows the semispherical lump of the $Nb_{0.6}Zr_{0.25}Fe_{0.15}$ alloy on a water-cooled hearth after arc-melting in a argon atmosphere when the pure hydrogen was introduced into the arc-melting chamber, and the alloy began to immediately disintegrate. Fig.1 (b) shows the sample after 215 s . In this period, the disintegration violently occurred and a fine powder arose from the alloy lump in all directions. A current of hydrogen gas mainly intensified on the lump of metal. The fine powder was carried with this current of hydrogen gas, and it progressed very far from the lump. The cause of the intensified hydrogen gas current was estimated as follows. If much hydrogen were absorbed into the alloy for a short time, the hydrogen pressure would locally drop around the alloy. This pressure drop resulted in the hydrogen gas flow. Fig.1 (c) shows the sample after 365 s. The lump of alloy disappeared and the disintegration was then difficult to observe with the naked eye.

Fig.2 is a sketch of the disintegration of $Nb_{0.6}Zr_{0.25}Fe_{0.15}$ alloy introduced from the photograph recorded by the video camera. Although the locus on which particles disperse is visible in the photograph, the sketch was used as a supplementary means to explain the disintegration. When the disintegration of the alloy was the most intense, as shown in Fig. 2 (b), the hydrogen current ascended with the fine particles around the alloy.

3.2 SEM and thermal analysis of disintegrated powders

In this section, the $Nb_{0.6}Zr_{0.25}Fe_{0.15}$ results are shown

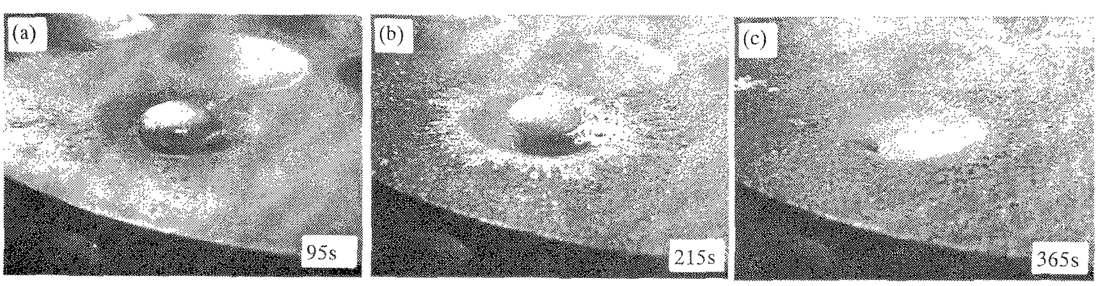

Fig.1 Disintegration phenomenon of $Nb_{0.60}Zr_{0.25}Fe_{0.15}$ alloy in 0.1Mpa hydrogen pressure. (a) initial stage of disintegration (after 95 second in hydrogen), (b) intermediate stage of disintegration (after 215 s) and final stage (after 365 s).

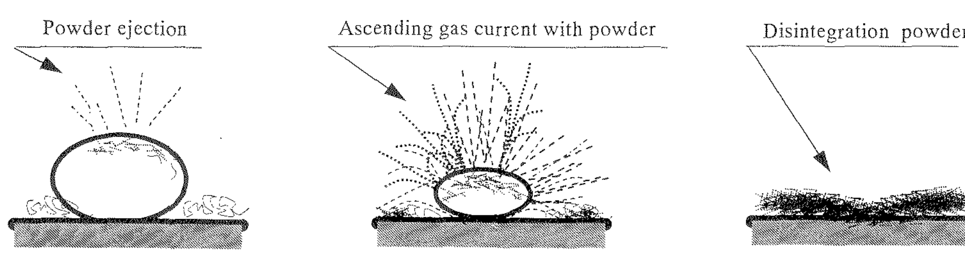

Fig.2 Sketch figure of disintegration of $Nb_{0.60}Zr_{0.25}Fe_{0.15}$ alloy from photograph of video camera. Each part of sketch correspond to the photos of Fig.1

as a typical alloy. Fig.3 is an SEM photograph of the powder prepared by the disintegration of the $Nb_{0.6}Zr_{0.25}Fe_{0.15}$.

The particles were flakes showed like, and their sizes ranged from 5 to 200 micrometers as seen from Fig3 (a). By high magnification, it was evident that the particles were dotted with many cracks that ranged from 1 to 5 micrometers as seen in Fig.3 (b) or Fig.3 (c). Each particle seen at low magnification in Fig.3 (a) was an aggregated form.

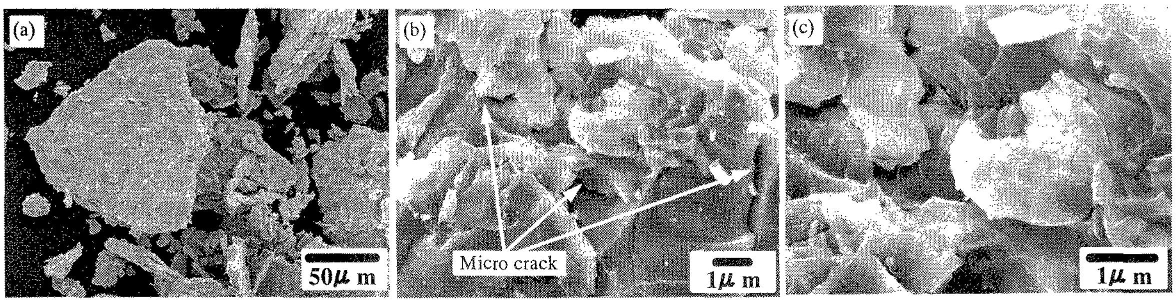

Fig.3 SEM photographs of hydrided $Nb_{0.60}Zr_{0.25}Fe_{0.15}$ alloy powders

Table 1 The average size of particles of hydrided $Nb_{0.60}Zr_{0.25}Fe_{0.15}$ alloys

Alloys	Surface Area ($10^3 m^2/kg$)	Diameter (calc.) from S.A (μ m)
$Nb_{60}Zr_{25}Fe_{15}$	1.27	1.2

The specific surface area measured by the BET method, and the calculated particle diameter are listed in Table 1. The particle diameter was calculated on the basis of the specific surface area, assuming that each particle was spherical. The average particle size of the hydrided $Nb_{0.6}Zr_{0.25}Fe_{0.15}$ alloy is approximately 1.2 microns. The mean size seems smaller than that observed by SEM photograph in Fig.3, but it is an appropriate value if the effect of many cracks in the particles is taken into consideration

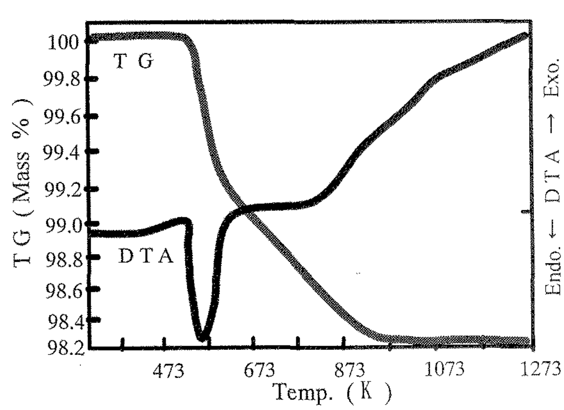

Fig.4 TG-DTA curve of hydrided $Nb_{0.6}0Zr_{0.25}Fe_{0.15}$ alloy powder

The thermal stability of the hydrogen sorbed in the powder is an important factor for hydrogen storage alloys. The stability of the hydrogen in the powder was deteremined by the TG –DTA measurement. Fig.4 shows TG-DTA curves of the hydrided powder of the $Nb_{0.6}Zr_{0.25}Fe_{0.15}$ alloy analyzed at the heating rate of 5 K/min. One large endothermic peak around 528 K and a weight decrease in the range of 528 K to 728 K are observed. From the weight loss, it is seen that the hydrogen storage capacity of this alloy reaches about 1.8 wt% and that this alloy absorbs hydrogen at room temperature, and stored the hydrogen up to 528K.

3.3 Disintegration composition and its hydrogen content to be stored

The disintegration range of the Nb-Zr-Fe alloy is shown in Fig.5, where the mark of ○ shows a slow disintegration, ◎a rapid disintegration, △no disintegration. The numerical value noted on the figure in the disintegrating region is the hydrogen content (wt%) of each alloy. The composition of the disintegration in Fig. 5 is in the range by connecting point A to point G in the figure shown by the dashed line. From the composition of the alloys that are disintegrated by the hydrogen, it is seen that iron has an important role in the disintegration, that is, the alloy is disintegrated when the content of iron in the alloy is

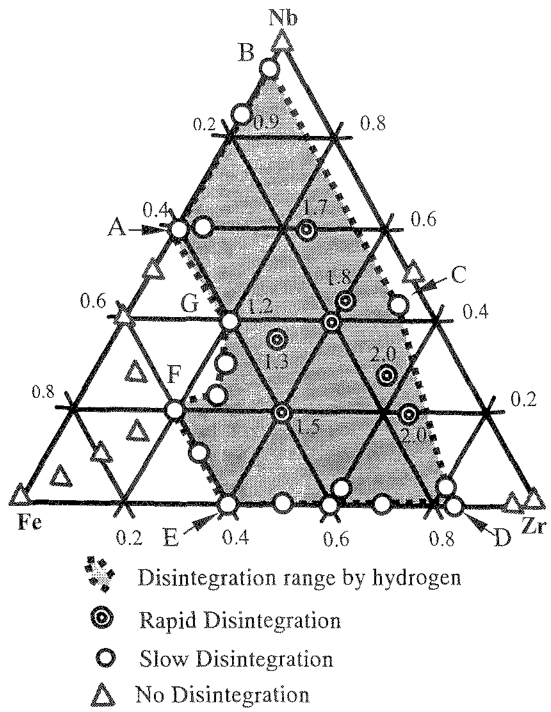

Fig. 5 Disintegration range and hydrogen content of hydrided Nb-Zr-Fe alloys

high enough. It is well known that Nb or Zr alloys have the ability to absorb hydrogen in large quantities, but there is no date about absorbing hydrogen under the conditions of 0.1 MPa hydrogen pressure at room temperature. By adding the proper quantity of iron to the Nb-Zr alloys, the alloys easily being to absorb hydrogen which results in its disintegration into a powder. The necessary conditions that an alloy disintegrates into a powder and the hydrogen content of the disintegrated alloys are shown in Fig.5.

For example, the hydrogen contents of the $Nb_{0.4}Zr_{0.2}Fe_{0.4}$ alloy, $Nb_{0.2}Zr_{0.2}Fe_{0.4}$ alloy, $Nb_{0.6}Zr_{0.2}Fe_{0.15}$ alloy, and $Nb_{0.2}Zr_{0.65}Fe_{0.15}$ alloy are 1.2 mass% H, 1.5 mass% H, 1.7 mass% H, and 2.0 mass% H, respectively. The following features are observed based on the experiment results. When the Fe concentration in the Nb-Zr-Fe alloy is fixed and the ratio of Nb to Zr is changed, the hydrogen contents of the Nb-Zr-Fe alloys increase with an increase in the Zr concentration. When the rate of Nb and Zr is fixed and the Fe concentration is changed, the hydrogen concentrations decrease with an increase in the Fe concentration. The hydrogen storage capability is as high as 1-2.mass% H in the Nb-Zr-Fe alloys for a wide range of composition.

4. CONCLUSION

The following conclusions can be drawn from the present study. The disintegration due to the hydrogenation of the Nb-Zr-Fe alloys of 35 different compositions has been investigated. About 60% of the alloy compositions become powdered by absorbing the hydrogen gas at 0.1MPa and room temperature. The phenomenon of disintegration by hydrogen was recorded by a video camera for all the 35 Nb-Zr-Fe alloys. When an alloy violently collapsed into a powder, it was observed by video that a hydrogen gas current occurs. This causes a fall in the pressure by hydrogen being absorbed into an alloy. The iron content has an important role in the disintegration, that is, the alloy is disintegrated when the content of iron in the alloys is high enough. The hydrogen storage capability is as high as 1-2.mass% H in the Nb-Zr-Fe alloys over a wide range of compositions.

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