Preparation and hydrogenation of body-centered-cubic TiCr$_2$ alloy

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Abstract TiCr$_2$ with a body-centered-cubic (BCC) structure was synthesized successfully by mechanical alloying of elemental powders and mechanical grinding of as-cast ingots. The formation mechanisms of the TiCr$_2$ were investigated using X-ray diffraction (XRD) analysis. The thermal stability and hydrogen absorption kinetics were studied using a differential scanning calorimetry (DSC) and a volumetric method. The results showed that the formation mechanisms of TiCr$_2$ in the mechanical alloying and mechanical grinding were different. The mechanical alloy is superior to the mechanical grinding in processing TiCr$_2$ alloy for hydrogen storage.

Keywords: mechanical alloying, mechanical grinding, hydrogen storage alloy, body-centered-cubic structure.

1. Introduction

Recently, some alloys with body-centered-cubic (BCC) structures have been widely investigated due to their excellent hydrogen storage capacity [1-4]. It was reported that some Ti-V-Cr and Ti-V-Mn alloys exhibited large hydrogen capacities up to 2
mass% [5-8]. Especially, the Ti-5V-57.5Cr alloy with a BCC structure could absorb and desorb about 2.8 mass% hydrogen at 313K reversibly [9]. For a Ti-Cr binary system, the BCC structure is a metastable phase at room temperature, which can be obtained by adding vanadium. Normally, the stable phases in TiCr₂ alloy at room temperature are the mixture of C14 and C15 structures [2]. With increasing the vanadium to 15 mass%, a stable BCC structure can be achieved at room temperature. Though the vanadium rich Ti-V-Cr alloys have high hydrogen absorption capacities, they are difficult to be activated and have poor absorption/desorption kinetics. To solve these problems and reduce the cost, it is desirable to develop some alloys with lower vanadium content or without vanadium but still having a BCC structure. Both mechanical alloying (MA) and mechanical grinding (MG) have been extensively used to prepare metallic materials with metastable phases. It was reported that the Laves structure in TiCrₓ (x=1.5, 1.8, 2) alloys could be transformed into a BCC structure by mechanical grinding [10].

In this work, the metastable TiCr₂ alloy with a BCC structure was produced through mechanical alloying of elemental powders and mechanical grinding of as-cast ingots, respectively. The thermal stability and hydrogenation property of the MA and MG samples were also studied.

2. Experimental procedure

A mixture (atom ratio 1:2) of Ti (99.9mass%, 200 mesh) and Cr (99.98mass%, 100–200 mesh) powder was milled under an argon atmosphere in a high energy ball
mill (Spex 8000) with ball to powder ratio of 20:1. For MG method, the TiCr$_2$ alloy was firstly prepared by arc melting with electromagnetic stirring (EMS) in an argon atmosphere. The alloy ingot was turned upside down and melted for four times to make homogenization. The as-cast ingots were crushed into fine powder passing through a 0.5mm screen. Then, the powder of the as-cast alloy was mechanically ground under an argon atmosphere with a ball-to-powder weight ratio of 20:1, as same as MA process. The phases generated at various milling duration were detected by X-ray diffraction (XRD) analysis with a Rigaku X-ray diffractometer equipped with a graphite monochromator. The thermal stabilization of the MA and MG samples was tested using a Perkin-Elmer DSC in a flowing argon atmosphere at a heating rate of 20K/min. The absorption-desorption properties of the samples were measured using a volumetric method.

3. Results and discussion

Fig. 1 shows the formation course of the metastable phase TiCr$_2$ with a BCC structure milled from Ti and Cr powder under an argon atmosphere. After 3 h milling, the relative intensity of Ti decreases and the XRD peaks are broadened remarkably. On the other hand, the peaks of Cr shift to the lower angle region. After 8 h milling, the peaks of Ti almost disappear and the metastable TiCr$_2$ with a BCC structure becomes the principal phase in the mixture. Also, the peaks of TiCr$_2$ become broadened, which is due to the reduction of the granularity. Another possible reason is the concentrated micro-strain caused by the high-energy ball milling.
The XRD spectra as a function of milling time for the as-cast TiCr$_2$ under argon atmosphere are shown in Fig. 2. The curve $a$ shows the XRD profile of the as-cast TiCr$_2$ alloys. It indicates the existence of the phases with a hexagonal C14-type structure and a cubic C15-type structure. These patterns are consistent with the results of Takeichi et al [10]. After 1 h milling, the phase with C15 Laves structure comes to disappear and the phase with a BCC structure begins to form. After 5 h milling, the diffraction peaks of the C14 and C15 disappear and only the peaks of the metastable TiCr$_2$ with a BCC structure exist.

Therefore, the formation mechanisms of the MA and MG samples are different. For the MA sample, after 3 h milling, the main peaks of Ti become broadened, showing a characteristic of amorphous phase. At the same time, the XRD spectra of Cr shift a little to lower angle region, indicating that some atoms of Ti are dissolved into Cr during the milling. Then, after 5 h milling, the relative intensity of all patterns decreases and the peaks become broadened; finally, the broad diffraction peaks representing the characteristic of the amorphous phase disappears, and the TiCr$_2$ with a BCC structure is formed. Therefore, MA process transformed titanium and chromium powders into the metastable BCC phase without the formation of a stable phase. In contrast, for the MG sample, C15 phase is dissolved into C14 phase continuously, and finally the TiCr$_2$ phase with a BCC structure is formed.

Fig. 3 and Fig. 4 show the DSC results measured in a flowing argon atmosphere and the XRD profiles after the DSC measurements, respectively. For the MA sample, the endothermic peak appears at 930K, while for the MG sample, the endothermic
peak starts at 1038K. It indicates that the MA sample has more chemically active than the MG sample. In Fig. 4, the phases in the MA and MG samples are mainly C14 and C15 after the DSC measurement. Some unknown phases in the MA samples are also identified. It is clear that both the MA and MG samples are thermally stable below 900K.

According to the DSC measurement, the temperature for annealing and activation treatment can be decided. Both the samples were annealed at 850K for 12 h in vacuum, and then were activated at 573K under the hydrogen pressure of 2.5 MPa. After the activation treatment, the ab/desorption capacities and kinetics at 323K were investigated, as shown in Fig. 5. It can be seen that both the MA and MG samples can absorb an amount of hydrogen. The maximum hydrogen absorption for the MA and MG samples under 2.5MPa hydrogen pressure is 1.0 and 0.7 mass%, respectively. The hydrogen desorption for the MA and MG samples is about 0.4 and 0.5 mass%, respectively. It proves that the MA sample has more reversible ab/desorption hydrogen capacities than that for the MG sample.

Fig. 6 shows the XRD profiles of the MA and MG samples before and after hydrogenation. The XRD patterns indicate the existence of a phase with a BCC structure. The diffraction peaks shift to lower angle region after hydrogenation. This indicates that hydrogen can stay in the MA and MG samples in a form of solid solution. As the MA sample has a higher hydrogen absorption capacity than the MG sample (Fig. 5), it is expected that there is a larger shift of the XRD peaks to the lower angle region in the MA sample as compared to the MG sample. However, in Fig. 6 the
peaks of the MG sample shift to the lower angle region a bit more than those of MA sample. This is because the MA sample is also superior to the MG sample in hydrogen desorption. If the XRD analysis is carried out in the air, the remaining hydrogen in the MA sample is actually less than that in the MG sample. Therefore, it gives another proof of the MA sample having a more reversible hydrogen absorption capacity than the MG sample.

4. Conclusion

The metastable TiCr$_2$ with a BCC structure was synthesized by mechanical alloying and mechanical grinding, respectively. The formation mechanisms of TiCr$_2$ in MA and MG methods are different. Both the MA and MG samples are thermally stable below 900K. The maximum hydrogen absorption and desorption capacities for the MA sample are about 1.0 and 0.4 mass% at 323K under 2.5MPa hydrogen pressure and those for the MG sample are about 0.7 and 0.5 mass%. Therefore, MA is superior to MG in processing TiCr2 alloy for hydrogen storage.

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References


Fig. 1 X-ray diffraction patterns for powder mixture of Ti and Cr after milling under argon atmosphere for various duration.

Fig. 2 X-ray diffraction patterns for as-cast TiCr$_2$ after milling under argon atmosphere for various duration.
Fig. 3 DSC analysis for milled samples

Fig. 4 X-ray diffraction patterns of the MA and MG samples after DSC measurement.
Fig. 5 Hydrogen ab/desorption capacities and kinetics for the MA and MG samples at 323K.
Fig. 6 XRD profiles of (a) MA, and (b) MG sample before and after hydrogenation at 323K