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The influence of microstructure on hydrogen absorption properties of Ti–Cr–V alloys

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Abstract

The effect of the differences of melting method and heat treatment on their microstructures and the hydrogen absorption properties was examined. Arc-melting in a water-cooled Cu crucible causes a difference of microstructure between the crucible side and surface of the ingot. Even if it seems single-phase from the X-ray diffraction pattern, the surface side of the as-cast ingot shows dendritic crystal growth. Although dendrite disappears after heat treatment, the microstructure of the surface side is still different from the bottom of the ingot. Ti–Cr–V and Ti–Cr–V–Fe were selected to clarify the influence of microstructure on hydrogen absorption properties of alloys with BCC structure. As a result, the homogeneity of the specimen is important to increased hydrogen absorption capacity and durability. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ti–Cr–V alloy; Ti–Cr–V–Fe alloy; Microstructure; Arc-melting; Vacuum induction melting

1. Introduction

Body centred cubic (BCC) alloys like Ti–Cr–V system have a large hydrogen capacity, but they have been hardly used for any practical application so far. Although these alloys show large hydrogen absorbing capacity over 3 wt.% the first time, rechargeable hydrogen capacity around room temperature is limited to about 2.3 wt.%. This alloy has the possibility of absorbing much more hydrogen, but it also has the problems of large hysteresis, cyclic durability and so on [1]. It was reported that the hydrogen absorption properties of Ti–Cr–V alloy are sensitive to the thermal history of the specimen [2]. Suitable heat treatment is required for appearance of excellent hydrogen absorption properties. In this paper, it was aimed to clarify the effect of the differences of melting method and heat treatment on their microstructures and the hydrogen absorption properties.

2. Experimental details

Ti–Cr–V alloys were prepared by arc-melting in water-cooled Cu crucible into ~ϕ40 mm×22 mm (50 g). The target composition of arc-melted alloy was $Ti_{30}V_{20}Cr_{50}$. Ti–Cr–V–Fe alloy was made by vacuum induction melting (VIM) and followed by casting into 17 mm×220 mm×720 mm mold (40 kg). Fe was added as an element, which promotes homogenisation of the alloy. The target composition of VIM alloy was $Ti_{27.8}Cr_{42.2}V_{25}Fe_5$. From our previous experience, when a large amount of an alloy is made with a composition of little V or Fe free, smoothness in the plateau property has deteriorated. So, the composition was changed in each melting. Both ingots were heat-treated with various conditions under an argon atmosphere. After the heat treatment at 1473–1673 K for 1 min–6 h, Ti–Cr–V alloys made by arc-melting were water-quenched. Ti–Cr–V–Fe alloys made by VIM have a large volume, so that it was gas quenched in the furnace. As-cast ingots and heat-treated ones were respectively divided into some portions according to the position of the ingot. Every specimen underwent X-ray diffraction analysis, observation of the microstructure, and pressure–composition isotherm (P–C–T) measurements. Powder X-ray diffractions were measured with Cu Kα radiation. The measurements of hydrogen capacity and P–C–T characteristics were carried out in the range of temperature 285–293 K and of hydrogen pressure 0.001–5 MPa.

3. Results and discussion

Fig. 1 shows the P–C–T diagram of Ti–Cr–V alloys prepared by arc-melting and heat-treating with various

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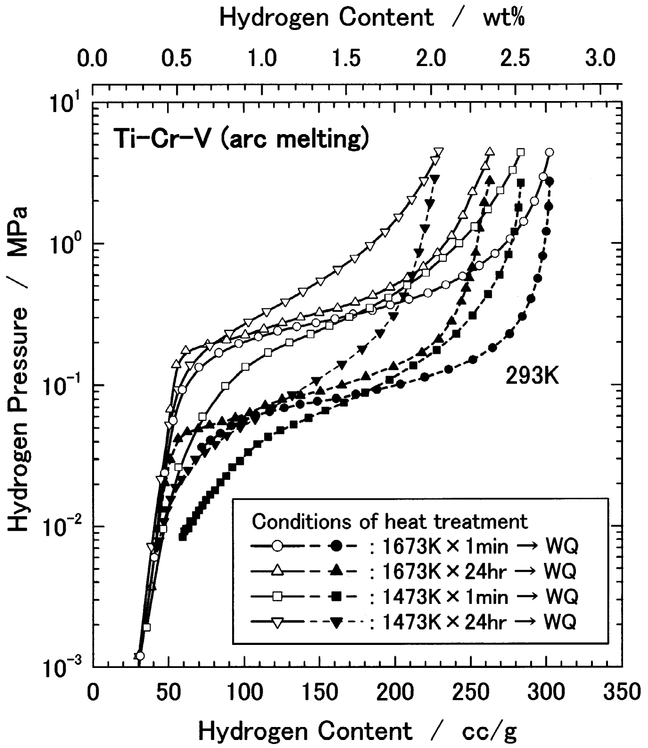

Fig. 1. Change of P–C–T diagrams with the conditions of heat treatment.

conditions. The alloy heat-treated in a short time at high temperature has the best plateau property. Heat treatment at high temperature makes the plateau slope flat (that means good homogeneity), and heat treatment in a short time enlarges hydrogen capacity. As the cause of these phenomena, it was reported that Ti-rich phases are formed more with increasing heat-treating temperature, and grow with increasing the heat-treating time [3]. Thus, the hydrogen plateau property of the Ti–Cr–V system alloy is greatly affected by the heat-treating conditions.

Fig. 2 shows the microstructures of the as-cast ingot prepared by arc-melting. The microstructure of this ingot is different between the crucible side and the other side. The boundary between both sides is very clear and its surface side shows dendritic crystal growth. Fig. 3 shows the microstructures of the heat-treated ingot at 1673 K for 1 min after arc-melting. The dendrite disappeared with heat treatment and large crystal growth was observed on the surface side. Although crystal growth was observed at the crucible side, the grain boundary is different on the surface side. At the surface side, it looks like the BCC phase separates into two phases. The X-ray diffraction pattern indicates only one BCC structure, so that both phases have BCC structure slightly different in lattice constant. Although it seems from the binary phase diagram that heat treatment at high temperature is effective for homogenizing and making a single phase of the BCC alloy, the Ti–Cr–V alloy has a slight instability and crystals grown to dendrite tends to cause phase separation even at high temperature. It is obvious that the characteristics of the alloy should be different between the surface side and the crucible side according to the extreme difference of microstructure. So, P–C–T characteristics were measured individually after dividing the heat-treating alloy into the surface side and the crucible side. Fig. 4 shows the difference of P–C–T characteristics of two portions of ingots. The equilibrium pressure of two positions is greatly different. From the results of X-ray diffraction measurement, both alloys have BCC structure but have different lattice constant. That of the crucible side is larger than that of the surface side. Also the composition of the alloy differs between the surface side and crucible side. The composition was determined by inductive coupled plasma analysis. The lattice constants and the compositions are summarized in Table 1. Comparing with the surface side, the alloy of the crucible side has Ti-rich composition, and the lattice constant of the crucible side is larger than that of the surface side. The relation of the equilibrium pressure between both alloys is corresponding to the relation of lattice constant between them. Thus, hydrogen-absorbing property is found to be greatly different even in the same ingot. Although the detailed ternary phase diagram is not clear, large temperature gradient and the difference between solidus and liquidus may cause formation of a Ti-rich phase. According to the microstructure of the alloy, this heterogeneity is a cause of the large slope of the plateau area.

It is well known that homogeneity of the alloy made by arc-melting is inferior to the VIM. It is important to be sure of the difference in hydrogen absorbing property between preparation methods. So, the VIM method was used for making BCC alloy. For casting, a thin mold (17 mm width) was used in order to increase the cooling rate. These alloys prepared by VIM are heat-treated in some conditions as follows; (1) heated for 6 h at 1473 K, (2) heated for 1 h at 1573 K, (3) heated for 1 min at 1673 K. Fig. 5 shows the microstructures of the Ti–Cr–V–Fe alloy in each position of the ingot and heat-treating condition. At the surface side, grain size is finer than the center side because the cooling rate during casting is faster in the surface side. Especially, the existence of spherical colonies consisting of ultra-fine crystals is specific to the surface side. The lattice constant of the surface side alloy is a little larger than that of the center side alloy. It means the difference of the cooling rate causes the difference of the lattice constant and size of the crystal grain. In the case of

Table 1
Lattice constants and compositions of Ti–Cr–V alloy

Position	Lattice constant (Å)	Actual compositions	Target compositions
Surface side	3.021	$Ti_{29}Cr_{51}V_{20}$	$Ti_{30}Cr_{50}V_{20}$
Crucible side	3.031	$Ti_{32}Cr_{48}V_{20}$	

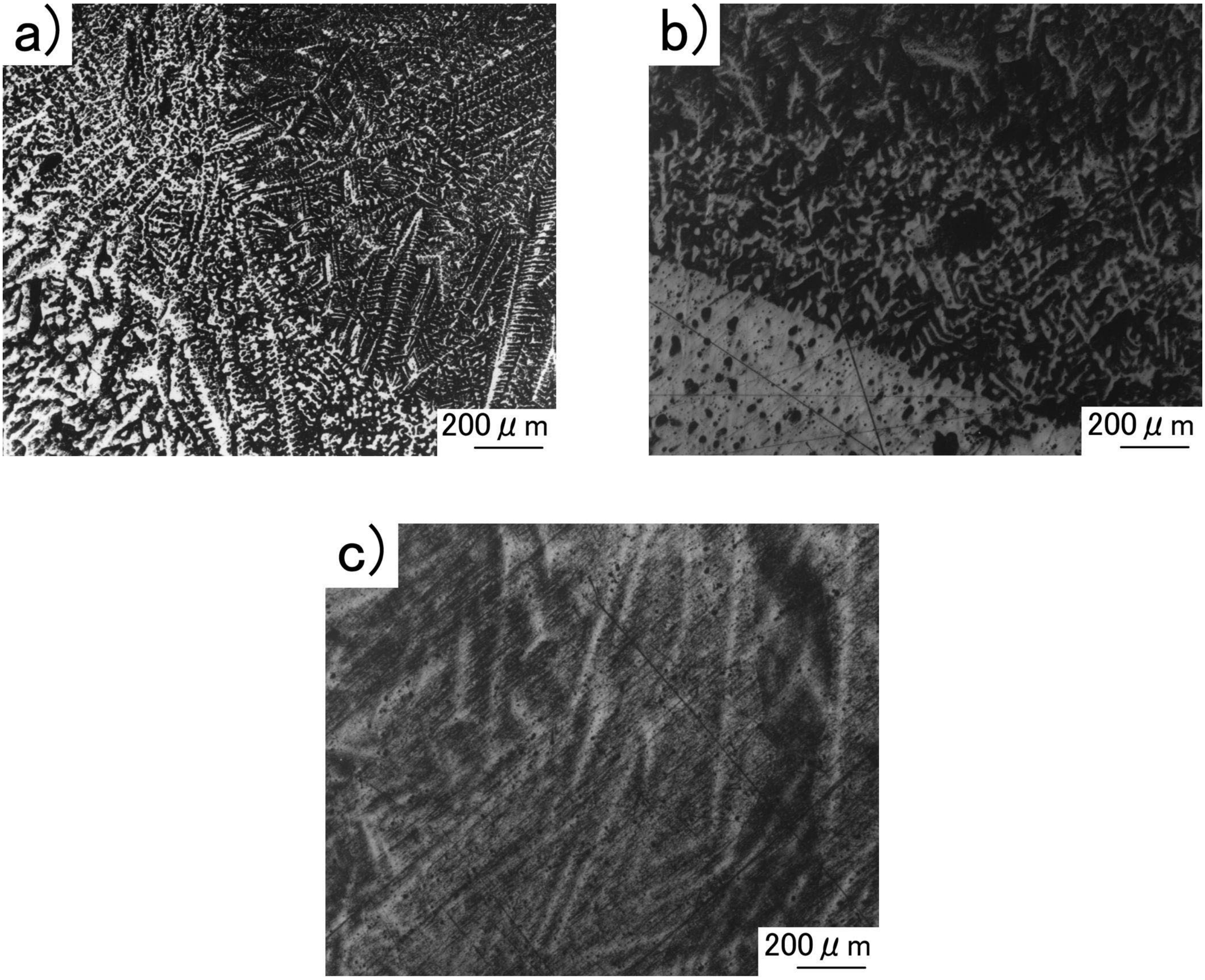

Fig. 2. Microstructures of Ti–Cr–V alloy prepared by arc-melting. (a) Surface side, (b) center side and (c) crucible side.

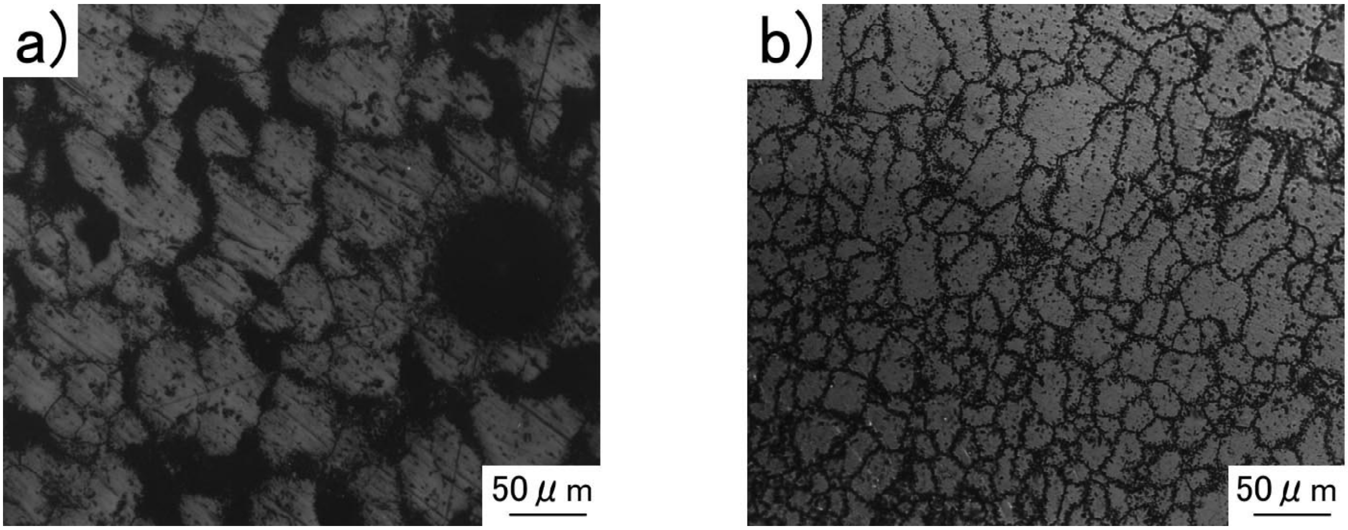

Fig. 3. Microstructures of Ti–Cr–V alloy after heat treatment at 1673 K for 1 min. (a) Surface side and (b) crucible side.

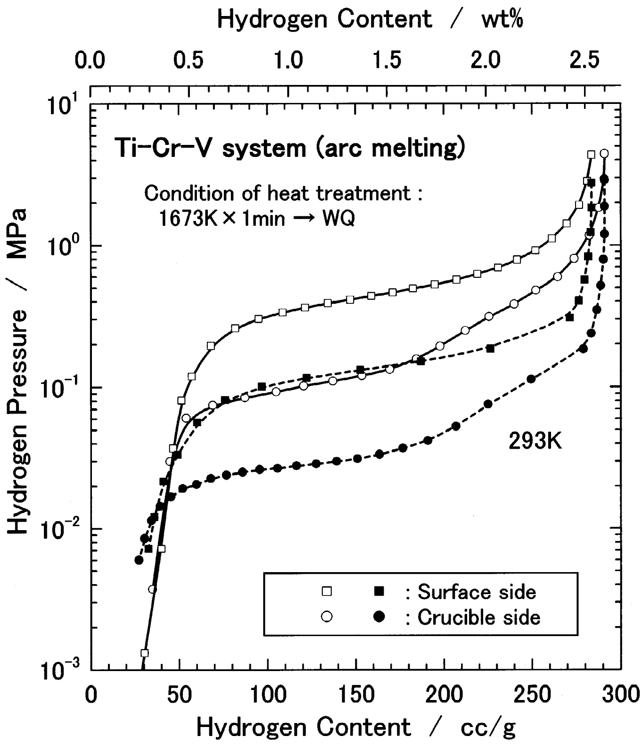

Fig. 4. Difference of P–C–T with the position in the ingot of the Ti–Cr–V alloy.

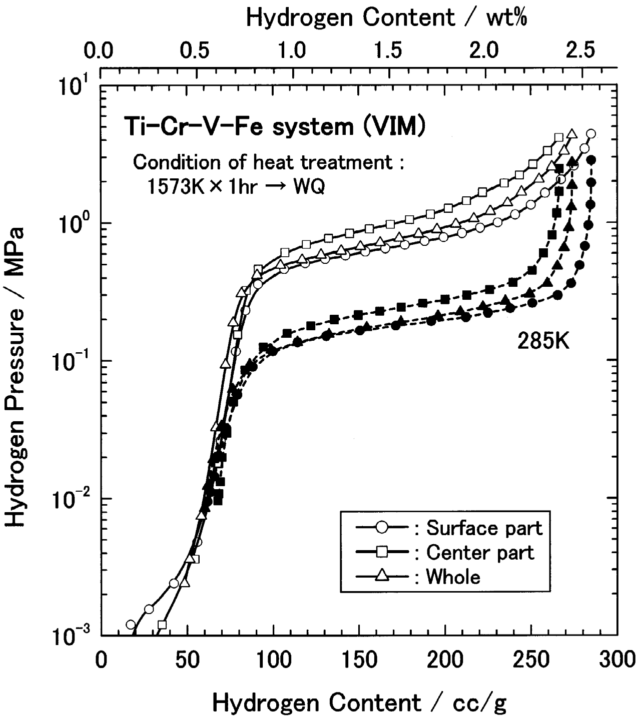

Fig. 6. P–C–T diagram of Ti–Cr–V–Fe alloy heat-treated at 1573 K for 1 h.

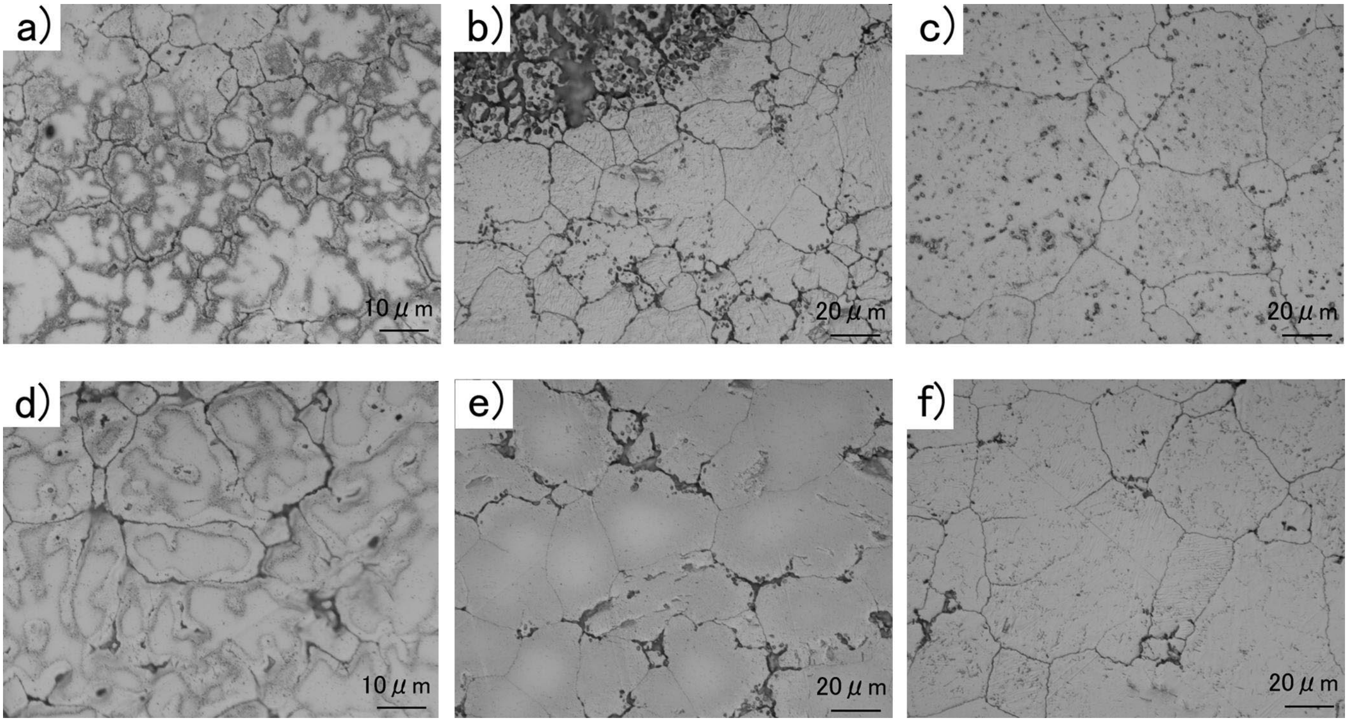

Fig. 5. Microstructures of Ti–Cr–V–Fe alloy prepared by VIM with changing its portion and heat-treatment. (a) As-cast surface side, (b) 1473 K, 6 h, surface side, (c) 1673 K, 1 min, surface side, (d) as-cast, center side, (e) 1473 K, 6 h, center side and (f) 1673 K, 1 min, center side.

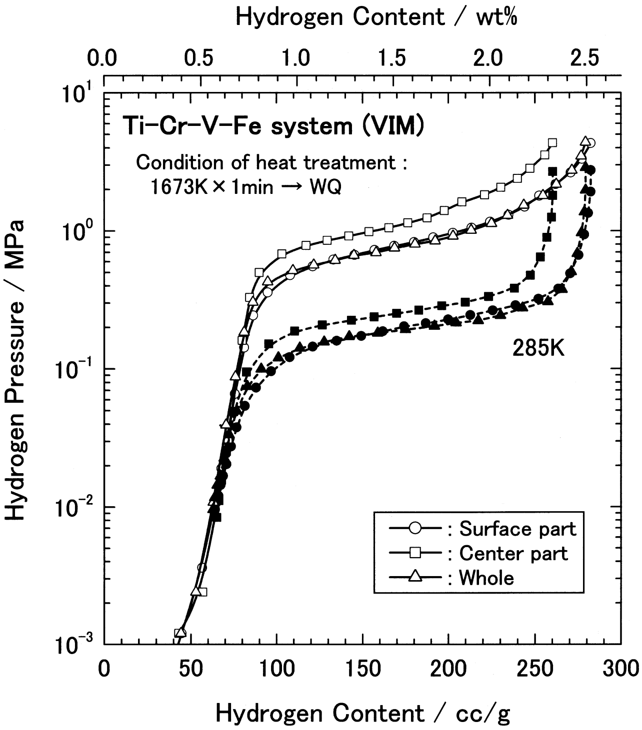

Fig. 7. P–C–T diagram of Ti–Cr–V–Fe alloy heat-treated at 1673 K for 1 min.

VIM, there are no dendritic structures as shown in the surface side of the arc-melted ingot. In compensation for disappearance of the dendrite, difference in contrast was observed near the grain boundary. It may indicate the slight compositional changes in the grain. It is considered that dendrite is specific to the arc-melting method, where the cooling rate on the surface side is relatively slow. Fig. 6 shows the P–C–T diagram of the alloy, prepared by VIM and heat-treated for 1 h at 1573 K. P–C–T measurement was carried out in three cases as follows, (1) the whole part in the direction of the thickness of the ingot, (2) the surface part of the ingot, (3) the center part of the ingot. The equilibrium pressure of the surface part was the lowest among the three cases. Oppositely, the equilibrium pressure increased in the center part. The whole part adjusted to the equilibrium pressure of the middle of the surface part and center part. The relation of the equilibrium pressure corresponds to the lattice constant. Regardless of melting method, the equilibrium pressure has been lowered in the part where the cooling rate is fast. Fig. 7 shows the P–C–T diagram of the alloy, also prepared by VIM and heated for 1 min at 1673 K. As shown in Fig. 7, the same behaviors as indicated in Fig. 6 were observed, regarding the difference of equilibrium pressure between the ingot parts. P–C–T characteristic of the whole part was almost the same as the surface part. It is considered that homogenizing is not sufficiently achieved when the heat-treating temperature is low, and the whole part is thought to be a simple mixture of the surface part and the center part, but when the heat-treating temperature is high, homogenizing proceeds even for a short time, and only one part near the center remains without homogenizing. So, it is suggested that the most suitable heat-treating time would make the whole of the alloy homogenized (in this case, heat-treating time should be lengthened).

4. Conclusion

It was found that melting methods and thermal history highly influence the hydrogen absorption properties of Ti–Cr–V system BCC alloy. As for the alloy prepared by arc-melting, the microstructure and lattice constant were extremely different between the surface side and the crucible side, as a result, P–C–T characteristic was greatly different. On the other hand, as for the alloy prepared by VIM, the microstructure and lattice constant were slightly different, so P–C–T characteristic was not different enough by its position as arc-melting alloy. Heat treatment at high temperature was found to improve homogeneity, and fast cooling rate during casting makes the structure fine grained and enlarges the lattice constant.

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