Microstructures and mechanical properties of NbCr₂ and ZrCr₂ Laves phase alloys prepared by powder metallurgy

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Microstructures, mechanical properties and oxidation behavior were investigated on NbCr₂ and ZrCr₂ Laves phase alloys prepared by powder metallurgy (P/M), and also by arc-melting, i.e. ingot metallurgy (I/M). These properties were also evaluated, in terms of alloying, heat treatment and alloy stoichiometry. High-temperature yield strength and brittle ductile transition temperature (BDTT) were generally lower in alloys prepared by P/M process than in those prepared by I/M process while micro hardness and fracture toughness were higher in alloys prepared by P/M process than in those prepared by I/M process, irrespective of NbCr₂ or ZrCr₂ alloys. Also, high-temperature strength and micro hardness were higher in NbCr₂ alloys than in ZrCr₂ alloys while fracture toughness was lower in NbCr₂ alloys than in ZrCr₂ alloys, irrespective of P/M or I/M process. For oxidation behavior at 1223 K, NbCr₂ alloys showed linear increase with increasing time accompanied with irregular fluctuation, while ZrCr₂ alloys showed parabolic increase with increasing time. It was also found that alloy stoichiometry greatly affected micro hardness, fracture toughness and oxidation behavior in ZrCr2 alloys. © 2003 Kluwer Academic Publishers

1. Introduction

Intermetallic compounds generally have high melting point and low density, and show superior corrosin and oxidation resistance, and therefore are considered to be attractive candidates as high-temperature structural materials. Among many groups of intermetallic compounds, AB₂ Laves phase intermetallic compounds to which the largest number of alloys belong are known to be topologically close packed (TCP) compound [1–4] and to generally exist as a line compound with the atomic size ratio, R_A/R_B of ideally 1.225 (where R_A and $R_{\rm B}$ are diameters of A and B atoms, respectively). There are three types of Laves phases, i.e. cubic C15, hexagonal C14 and dihexagonal C36 [1–4]. Among many AB₂ Laves phase intermetallic compounds, XCr₂ Laves intermetallic compounds are particularly attractive for high-temperature structural materials because they contain Cr element. Cr combines with X elements such as refractory metals, Ti, Zr, Hf, Nb and Ta, and TiCr₂, ZrCr₂, HfCr₂ and TaCr₂ Laves phase intermetallic compounds are formed.

XCr₂ Laves phase intermetallic compounds as well as many other intermetallic compounds are however very brittle at low temperatures because they consist of

cancy concentration in off-stoichiometric compositions [7, 8, 19] and microstructural modification [9–16]. Consequently, the addition of Mo to NbCr₂ Laves phase intermetallic compound was shown to be effective in improving the compressive deformability at high temperature [6]. Also, it was shown that duplex microstructures with Cr solid solution and X solid solution are effective in decreasing ductile-brittle transition temperature (DBTT) [9, 10, 12, 13, 16]. However, the improvement of the deformability or fracture toughness at low temperatures has not been successful. A number of studies mentioned above have been

conducted using arc-melted buttons, i.e. the materials prepared by ingot metallurgy (I/M). It is well known that mechanical properties of alloys are affected by

complex crystal structures. Therefore, some attempts to improve the mechanical properties of XCr₂ Laves

intermetallic compounds have been performed so far

(see a recent review paper [5]). For examples, to improve the deformability of NbCr₂ [6-16] and ZrCr₂

[17–19] Laves phase intermetallic compounds that will

be investigated in this study, some attempts have been performed, based on various concepts (e.g. alloying

[6, 17, 18], selection of the anti-site atoms, control of va-

adopted fabrication and resultant microstructure. It is expected that materials prepared by powder process involving hand (or ball) milling, hot-pressing and the subsequent Hiping do not contain large porosities and have fine grain microstructure, resulting in the improvement of the mechanical properties. In this study, NbCr₂ and ZrCr₂ Laves phase intermetallic compounds, which contain ternary elements or have different alloy stoichiometry, are prepared by powder metallurgy (P/M), and their microstructures are firstly characterized. Next, the mechanical properties of these alloys are investigated at high and low temperatures, by compression test and indentation test, respectively. Oxidation behavior of these Laves phase intermetallic compounds is also evaluated. The obtained mechanical properties are compared with those observed in I/M materials. and discussed in association with the effect of alloying, grain microstructure and lattice defect structures.

2. Experimental procedures

NbCr₂ and ZrCr₂ alloys, intended to be in a single phase of C15 Laves structure, were prepared by P/M process, and also by arc melting, i.e. I/M process for comparison. For NbCr₂ alloys, binary NbCr₂ alloy with a just-stoichiometric composition and ternary NbCr₂ alloys with two compositions (i.e. Nb_{28.3}Cr_{66.7}Mo₅ and Nb_{33.3}Cr_{61.7}V₅) were prepared. According to substitution behavior and solubility limit of Mo and V elements in NbCr₂ [6, 12], Mo was substituted for Nb sites while V was substituted for Cr sites. For ZrCr₂ alloys, binary ZrCr₂ alloys with various off-stoichiometric compositions were prepared.

Starting row materials were purity of 99.99 wt%Cr, 99.5 wt%Nb, 99.9 wt%Zr, 99.7 wt%V and 99.9 wt%Mo. I/M materials with a diameter 30 mm were first prepared by non-consumable arc melting on water sealed Cu hearth in an argon environment. The button ingots were remelted several times to ensure chemical homogeneity. Some button ingots occasionally broke into some pieces during solidification. However, there was no difficulty for the subsequent fabrication because the cracked pieces were large enough. As-solidified ingots were then annealed in dynamic vacuum condition at 1623 K for 15 h in the case of NbCr₂ alloys and 1723 K for 24 h in the case of ZrCr₂ alloys, followed by cooling to room temperature at a rate of approximately 2 K/min. Chemical analysis of the prepared alloys were not carried out because mass losses during melting and annealing were very small, i.e. mostly less than 0.5%.

For P/M materials, arc-melted button ingots with prescheduled chemical compositions were used as starting materials. Powders were made by mechanically milling these arc-melted buttons, and then sieved under 100 μ m size. Powders were hot-pressed in carbon container with 60 mm diameter under argon atmosphere in conditions of 50 MPa at 1773 K for 2 h. Some of consolidated P/M materials (compacts) were then annealed in the same conditions as I/M materials.

Microstructures of NbCr₂ and ZrCr₂ alloys prepared by P/M process were observed using an optical microscope (OM) and a scanning electron microscope (SEM) in back scattering (BS) condition. To particularly observe the lattice defect structures such as stacking faults or micro twins, $ZrCr_2$ alloys were etched in a solution of 1 vol% HF + 10 vol% H₂O.

Compression specimens with a dimension of approximately $2.5 \times 2.5 \times 5 \text{ mm}^3$ were cut by a precision wheel cutter from a central region of compacts (or button ingots) with their axes parallel to the press direction (or to the solidification direction). The lateral faces of the specimens were abraded on sufficiently fine SiC paper. The high-temperature compression tests were carried out mostly at temperatures above 1273 K at an initial strain rate of 1.7×10^{-4} /s in a vacuum of approximately 3×10^{-3} Pa, using an Instron-type machine equipped with a vacuum vessel and a tungsten mesh heater.

Micro hardness and fracture toughness of NbCr₂ and ZrCr₂ alloys were evaluated at room temperature using Vickers micro indenter. A load of 200 g and duration time of 15 s were used for evaluation of micro hardness, while a load of 500 g and duration time of 15 s were used for evaluation of fracture toughness. Data on each alloy sample are averages of more than ten indentations. For fracture toughness evaluation, the impression diagonals and crack length (if initiating and propagating from corners of the impression diagonal) were measured using a scanning electron microscope (SEM). Fracture toughness values (K) were computed from the following equations [20]:

$$K = 0.016[E/H]^{1/2} P/(L)^{3/2}$$
(1)

where *P* is the load (kgf), *H* is the hardness value, and *L* is the average crack length. Young's modulus values (*E*) of 214 GPa in NbCr₂ alloys [21] and 165 GPa in ZrCr₂ alloys [22] were used to calculate the fracture toughness.

Oxidation property was evaluated using specimens with a dimension of approximately $1.5 \times 1.5 \times 2.0 \text{ mm}^3$. Their surfaces were abraded on sufficiently fine SiC paper. Oxidation tests were performed in air at 1223 K until 48 h using thermogravimetry (TG). Weight gains (or losses) were plotted as a function of holding time. Surfaces of the oxidized specimens were also observed by SEM.

3. Results and discussion

3.1. Microstructures

Fig. 1 shows BS SEM microstructures of Nb-66.7at.%Cr (denoted Nb-66.7Cr in the following), Nb-66.7at.%Cr-5at.%Mo (Nb-Cr-5Mo) and Nb-61.7at.%Cr-5at.%V (Nb-Cr-5V) alloys in hot-pressed and heat-treated conditions, respectively which were made by P/M process. A number of micro voids were contained in these materials. The size and density of these micro voids were smaller in Nb-Cr-5Mo alloy than in Nb-66.7Cr and Nb-Cr-5V alloys. The volume fraction and size of these micro voids generally decreased by heat-treatment, but still remained, meaning that the time, load and temperature of isothermal pressing are insufficient. Also, NbCr₂ alloys made by P/M process more or less contained Nb solid solution



Figure 1 BS SEM microstructures of (a,d) Nb-66.7at.%Cr, (b,e) Nb-66.7at.%Cr-5at.%Mo and (c,f) Nb-61.7at.%Cr-5at.%V alloys in (a,b,c) hot-pressed and (d,e,f) heat-treated conditions, respectively.

phase (imaged by white color in SEM microstructures) in hot-pressed condition. Nb solid solution phase with volume fraction of $\sim 12\%$ and $\sim 2\%$ was contained in Nb-Cr-5Mo and Nb-Cr-5V alloys, respectively. However, Nb solid solution phase almost disappeared by heat-treatment.

Fig. 2 shows BS SEM microstructures of Zr-68.7at.%Cr (denoted Zr-68.7Cr in the following), Zr-66.7at.%Cr (Zr-66.7Cr) and Zr-65.7at.%Cr (Zr-65.7Cr) alloys in hot-pressed and heat-treated conditions, respectively which were made by P/M process. Again, a number of micro voids and Zr solid solution phase were contained in these materials, and seem to be primarily independent of alloys. However, these micro voids and second phase dispersions apparently decreased by heat-treatment. Besides, the heat-treated ZrCr₂ alloys contained a number of stacking faults (and/or micro twins) within their grains in addition to the micro voids, as shown in Fig. 3. These planer defects appear to be primarily independent of alloy stoichiometry and heat-treatment. This kind of planar faults have also been reported in the previous transmission electron microscopic (TEM) observation for as-solidified and well-annealed ZrCr₂ alloys [19]. It has been shown that as-cast ZrCr₂ alloys prepared by I/M process contained more or less residual high temperature phases such as the C14 phase and/or metastable C36 phase, and also stacking faults [19]. These residual high-temperature



Figure 2 BS SEM microstructures of (a,d) Zr-68.7at.%Cr, (b,e) Zr-66.7at.%Cr and (c,f) Zr-65.7at.%Cr alloys in (a,b,c) hot-pressed and (d,e,f) heat-treated conditions, respectively.



Figure 3 SEM microstructures of the heat-treated (a) Zr-68.7at.%Cr, (b) Zr-66.7at.%Cr and (c) Zr-65.7at.%Cr alloys.

phases disappeared by high temperature annealing but micro twins and stacking faults still remained in heattreated condition [19].

3.2. Mechanical properties *3.2.1. High temperature compression*

Fig. 4 shows 0.2% yield stress as a function of temperature for Nb-66.7Cr, Nb-Cr-5Mo and Nb-Cr-5V alloys. In this figure, the data of NbCr₂ alloys prepared by I/M process [6] are also included for comparison. Regarding the P/M materials, an apparent plastic deformation took place at temperatures above 1273 K. The brittleductile transition temperatures (BDTTs) of Nb-66.7Cr, Nb-Cr-5Mo and Nb-Cr-5V alloys were determined to be approximately 1373 K, 1323 K and 1273 K, respectively, thus indicating that the addition of Mo and V to NbCr₂ slightly decreases the BDTT. The previous TEM study showed that the plastic deformation of NbCr2 alloy at high temperatures is due to the activation of dislocations with the Burgers vector of 1/2(011), which are split into a pair of partials with the Burgers vectors of 1/6(112) (i.e. Shockley partials) bounded by widely extending stacking fault [23, 24].

Comparing with the results of I/M materials [6], it is evident that not only BDTT but also 0.2% yield stress substantially decreased, irrespective of alloys. It is thus suggested that fine grain microstructure in NbCr₂ alloys made by P/M process promotes grain boundary slip, emits many dislocations from grain boundaries, and consequently reduces the flow strength as well as BDTT. However, the alloying effect (the addition of Mo and V) on the yield stress and BDTT was different between the P/M and I/M materials. In the I/M materials, the addition of Mo to NbCr2 resulted in decreased vield stress as well as BDTT, while the addition of V to NbCr₂ resulted in increased yield stress but did not affect BDTT [6]. In the P/M materials, the addition of both Mo and V to NbCr₂ resulted in decreased BTTT but did not so much affect the yield stress. This reason is not clear at the moment but the contained second phase dispersions (i.e. Nb solid solution) or fine gain microstructure seem to result in such unusual behavior.

Fig. 5 shows 0.2% yield stress as a function of temperature for $ZrCr_2$ alloys. In this figure, the data of



Figure 5 Variations of 0.2% yield stress with temperature for Zr-68.7at.%Cr, Zr-66.7at.%Cr and Zr-65.7at.%Cr alloys.

Zr-66.7Cr alloy made by I/M process and also Nb-66.7Cr alloy made by P/M process are included for comparison. The measured BDTTs were primarily independent of alloy composition (i.e. alloy stoichiometry), i.e. approximately 1323 K, but definitely lower than that of Zr-66.7Cr alloy made by I/M process. On the other hand, 0.2% yield stress was lower in ZrCr₂ alloys made by P/M process than in those made by I/M process. It is again suggested that fine grain microstructure in ZrCr₂ alloys made by P/M process enhances grain boundary slip, and emits many dislocations from grain boundaries, resulting in decreasd yield stress and BDTT. Comparing with NbCr₂ alloy made by P/M process, BDTTs as well as yield stresses were lower in ZrCr₂ alloys than in NbCr₂ alloy. This result may be attributed to difference in melting point between ZrCr₂ and NbCr₂ alloys. The plastic deformation in AB₂ Laves phase alloys normally occurs only at temperatures greater than about two-thirds of the melting temperature. Plastic deformation and related flow stress, which involve dislocation movement at high temperatures, are related to diffusion of constituent atoms. Therefore, it follows that ZrCr₂ alloys with low melting point plastically deform at lower temperatures than NbCr₂ alloys.

3.2.2. Micro hardness test

Fig. 6 shows the effects of process, alloying and heattreatment on the micro hardness of NbCr₂ alloys. It



Figure 4 Variations of 0.2% yield stress with temperature for Nb-66.7at.%Cr, Nb-66.7at.%Cr-5at.%Mo and Nb-61.7at.%Cr-5at.%V alloys.



Figure 6 Vickers hardness values of hot-pressed and heat-treated Nb-66.7at.%Cr, Nb-66.7at.%Cr-5at.%Mo and Nb-61.7at.%Cr-5at.%V alloys that were made by P/M and I/M processes, respectively.

appears that the micro hardness is primarily independent of alloying as well as heat-treatment but clearly dependent on process. Higher micro hardness was observed in NbCr₂ alloys made by P/M process than in those made by I/M process. At the moment, it is uncertain whether plastic deformation responding to indentation load at room temperature is due to glide deformation or mechanical twinning. However, it is suggested that fine grain microstructures in NbCr₂ alloys made by P/M process enhance the micro hardness at ambient temperatures because grain boundaries act as obstacles to plastic deformation (or twinning). As has been reported in the previous TEM observation, the microstructure of the NbCr₂ alloy is composed of stable C15 structure in both hot-pressed (~1773 K) and annealed (~1623 K) conditions [23, 24]. Accordingly, it is likely that both the hot-pressed and heat-treated NbCr₂ alloys have similar microstructure and show similar micro hardness.

Fig. 7 shows the effects of process, alloying and heattreatment on the micro hardness of ZrCr2 alloys. The data were plotted as a function of alloy composition within or near Laves single-phase region. In this alloy system, the micro hardness was generally independent of process but clearly dependent on alloy stoichiometry. However, it appears that heat-treatment results in decrease in the micro hardness. By heat-treatment, grain size increases, and retained high temperature phases or density of micro twins and stacking faults decrease, resulting in decreased micro hardness. Concerning the effect of alloy stoichiometry, it is apparent that the measured micro hardness is lowest in a just-stoichiometric composition and increases with departing from a just-stoichiometric composition, regardless of process or heat treatment. This variation should be correlated with lattice defect structures introduced in two off-stoichiometric compositions. It has been reported that the anti-site defect is introduced in Cr-rich alloy composition while the vacancy-type defect mixed with the anti-site defect is introduced in Zr-rich alloy composition [19]. Therefore, it is expected that the lattice defect structures in both the off-stoichiometric alloy compositions enhance the micro hardness, due to relatively large elastic interaction between atomic defects and glide (or twinning) dislocations.



Figure 7 Vickers hardness values of hot-pressed and heat-treated $ZrCr_2$ alloys that were made by P/M and I/M processes, respectively.

3.2.3. Fracture toughness

Fig. 8 shows the effects of process, alloying and heattreatment on the fracture toughness of NbCr₂ alloys. It is apparent that the fracture toughness is consistently higher in NbCr₂ alloys made by P/M process than in NbCr₂ alloys made by I/M process, regardless of alloying or heat treatment. Thus, fine grain microstructures result in increased fracture toughness in NbCr₂ alloys. If the fracture toughness is affected only by



Figure 8 Fracture toughness values of hot-pressed and heat-treated Nb-66.7at.%Cr, Nb-66.7at.%Cr-5at.%Mo and Nb-61.7at.%Cr-5at.%V alloys that were made by P/M and I/M processes, respectively.



Figure 9 Fracture toughness values of hot-pressed and heat-treated ZrCr₂ alloys that were made by P/M and I/M processes, respectively.



Figure 10 Weight changes in air by holding time at 1223 K for NbCr₂ alloys and ZrCr₂ alloys.



Figure 11 SEM observation for surfaces of (a) Nb-66.7at.%Cr alloy, (b) Nb-66.7at.%Cr-5at.%Mo and (c) Nb-61.7at.%Cr-5at.%V alloys which were oxidized in air at 1223 K until 48 h.

hardness value as expressed by Equation 1, materials with higher hardness, i.e. NbCr₂ alloys made by P/M process should show lower fracture toughness than materials with lower hardness, i.e. NbCr₂ alloys made by I/M process. The obtained result is inconsistent with this prediction, meaning that materials parameters such as grain size, microstructure and lattice defect structure directly affect the fracture toughness of NbCr₂ alloys. It is widely accepted that fine microstructures relax stress concentration at grain boundaries under loading, restrain the generation of crack, and delay the propagation to another crystal grain, resulting in increase in fracture toughness values. In addition, it was occasionally observed in these P/M materials that the tip of crack ran into the micro void and stopped there. This effect may hinder crack growth. On the other hand, Fig. 8 indicates that heat-treatment as well as ternary element does not so much affect the fracture toughness.

Fig. 9 shows the effects of process, alloying and heat treatment on the fracture toughness of ZrCr₂ alloys. The data were plotted as a function of alloy composition within or near Laves single-phase region. The fracture toughness was higher in ZrCr₂ alloys made by P/M process than in ZrCr₂ alloys made by I/M process. Referring to the results of the micro hardness (Fig. 7), it is again evident that the fracture toughness is affected not by micro hardness (as expressed by Equation 1) but by material parameters. Obviously, fine grain microstructures result in increased fracture toughness in ZrCr₂ alloys. This figure also shows that hot-pressed ZrCr₂ alloys showed higher fracture toughness than heat-treated ZrCr₂ alloys. High temperature residual C14 (or C36) structures have been observed in as-cast materials of ZrCr₂ alloys [19]. Such meta-stable microstructures may promote twinning or glide motion of dislocations, that is, a sort of transformation-induced deformation may take place. Consequently, the increased fracture toughness can be expected in hot-pressed ZrCr₂ alloys, as has been discussed in the previous studies [9, 25, 26].

For the effect of alloy composition (i.e. alloy stoichiometry), the measured fracture toughness was lowest in a just-stoichiometric composition and increases with departing from a just-stoichiometric composition, regardless of processing or heat-treatment. Considering Fig. 7 and Equation 1, this variation (Fig. 9) again suggests that the fracture toughness is not affected simply by micro hardness but by materials parameters. The fracture toughness should be correlated with lattice defect structures introduced in two off-stoichiometric compositions [19]. It is possible that such lattice defects increase atomic free volumes on {111} glide planes on which Shockley partial dislocations move and promote mechanical twinning by their synchro-shear movement [25-27]. This situation may allow greater deformation and therefore fracture toughness in both the offstoichiometric alloy compositions of ZrCr₂ alloy.

3.3. Oxidation behavior

Fig. 10 shows weight changes in air as a function of holding time at 1223 K for some NbCr2 and ZrCr2 alloys made by P/M process. The weight of all alloys increased with increasing time, indicating that materials were not substantially evaporated but actually oxidized, forming oxidized surface films. For ZrCr₂ alloys, the measured weight increased parabolically with increasing time. This result suggests that the oxidation is basically controlled by the bulk diffusion. In this figure, ZrCr₂ alloy with high Cr content showed more rapid oxidation curve than that with low Cr content, meaning that the increase of Cr does not always results in higher oxidation resistance. Other materials parameters such as (micro)structure, chemistry and adhesion to matrix should be taken into consideration of oxidation behavior. On the other hand, weight gain for three NbCr₂ alloys (i.e. Nb-66.7Cr, Nb-Cr-5Mo and Nb-Cr-5V alloys) was lower than those for ZrCr2 alloys within measured time, but unusual, that is, linearly increased with increasing time, accompanied with certain fluctuation.



Figure 12 SEM observation for surface of Zr-65.7at.%Cr alloy that was oxidized in air at 1223 K until 48 h.

Among three NbCr₂ alloys, largest weight gain was observed in Nb-Cr-5V alloy while smallest weight gain was observed in Nb-Cr-5Mo alloy. However, it is very likely that at longer holding time (>50 h) the weight gain for NbCr₂ alloys will exceed that for ZrCr₂ alloys. Consequently, it is suggested that the oxidation resistance of NbCr₂ alloys is fundamentally inferior to that of ZrCr₂ alloys. For NbCr₂ alloys, it is suggested that oxidation kinetics is governed by short circuit path of atoms, e.g. grain boundary diffusion. Such a situation is likely to be operated in NbCr₂ alloys because they are P/M materials and contain high area fraction of grain boundaries.

Figs 11 and 12 show SEM images of surfaces of NbCr₂ alloys and ZrCr₂ alloy, respectively which were oxidized in air at 1223 K until 48 h. The difference in SEM images between NbCr₂ alloys and ZrCr₂ alloy is not so obvious. However, it may be pointed that many granular-shape particles and deep grooves are highly distributed in the surfaces of NbCr₂ alloys, and are associated with unusual (rapid) oxidation kinetics of these alloys. Certainly, much detailed works, e.g. chemical and microstructural observation on oxidizing surface films, are needed to more clarify the oxidation mechanisms of these Laves alloys.

4. Conclusions

Microstructures, high-temperature compressive deformation, micro hardness, fracture toughness and oxidation behavior were investigated on NbCr₂ and ZrCr₂ Laves phase alloys prepared by powder metallurgy (P/M), and also by ingot metallurgy (I/M).

1. In two alloy systems, high-temperature yield strength and BDTT were generally lower in the alloys prepared by P/M process than in those prepared by I/M process, while micro hardness and fracture toughness were higher in the alloys prepared by P/M process than in those prepared by I/M process.

2. In two P/M and I/M processes, high-temperature strength and micro hardness were higher in NbCr₂ alloys than in $ZrCr_2$ alloys, while fracture toughness was lower in NbCr₂-based alloys than in $ZrCr_2$ alloys.

3. For oxidation behavior, NbCr₂ alloys showed linear increase with increasing time, accompanied with irregular fluctuation, while $ZrCr_2$ alloys showed parabolic increase with increasing time.

4. It was also found that alloy stoichiometry greatly affected micro hardness, fracture toughness and oxidation behavior in $ZrCr_2$ alloy.

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