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Journal of Alloys and Compounds 408–412 (2006) 375–378

Journal of ALLOYS AND COMPOUNDS

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Hardness and oxidation resistance of the perovskite-type $RRh_3B_xC_{1-x}$ (R = Y, Sc)

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Abstract

Perovskite-type RRh_3B and RRh_3C (R = Y, Sc) form a continuous solid solution, $RRh_3B_xC_{1-x}$, in the range of $0 \leqq x \leqq 1$ with cubic structure (space group: $Pm3m$, $Z = 1$). The values of the microhardness of $YRh_3B_xC_{1-x}$ for $x = 0$, 0.25, 0.50, 0.75 and 1.00 are investigated as 4.4 ± 0.1, 4.9 ± 0.1, 5.5 ± 0.2, 6.4 ± 0.2 and 7.5 ± 0.15 GPa, respectively. On the other hand, the values of the microhardness of $ScRh_3B_xC_{1-x}$ for $x = 0$, 0.25, 0.50, 0.75 and 1.00 are 4.5 ± 0.2, 6.1 ± 0.2, 7.4 ± 0.2, 8.9 ± 0.2 and 9.6 ± 0.1 GPa, respectively. Thus, the microhardness of $RRh_3B_xC_{1-x}$ continuously becomes larger with increasing boron content. The oxidation onset temperatures of $YRh_3B_xC_{1-x}$ for $x = 0$, 0.25, 0.50, 0.75 and 1.00 are 604, 631, 655, 687 and 978 K, respectively. On the other hand, the oxidation onset temperatures of $ScRh_3B_xC_{1-x}$ for $x = 0$, 0.25, 0.50, 0.75 and 1.00 are 674, 675, 695, 725 and 753 K, respectively. Thermogravimetric analysis of the phase indicates that the oxidation onset temperature also increases with boron content. Thus, it appears that both mechanical strength and chemical stability of the $RRh_3B_xC_{1-x}$ phase essentially depend on its boron content. Ab initio calculations have been performed to obtain the equilibrium lattice constants and the bulk moduli. The calculated lattice constants are in excellent agreement with experimental results.

Keywords: $YRh_3B_xC_{1-x}$; $ScRh_3B_xC_{1-x}$; Perovskite-type phase; Microhardness; Oxidation resistance

1. Introduction

Perovskite related oxides have been studied because of their many interesting properties, including superconducting transitions, insulator–metal transitions, ion conductance, dielectric properties and ferroelasticity [1–4]. However, nonoxide perovskite-type compounds such as the ternary borides RRh_3B (R = rare earth) [5–7] have not yet been studied well. Investigation of the synthesis and fundamental characterization of nonoxide perovskite-type compounds is necessary.

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doi:10.1016/j.jallcom.2005.04.168

In this study, the authors synthesize the $RRh_3B_xC_{1-x}$ phase, namely, solid solution of the RRh_3B–RRh_3C system [8,9]. In this structure, R is at the eight corners of the cube, Rh is at the six face-centered sites and B and/or C at the body-centered site. Boron and carbon are selected because they have similar atomic radii, moreover, they are known to form covalent bonds with transition elements. Solid solubility in the system of RRh_3B [10–12]–RRh_3C is investigated. Then, microhardness and oxidation resistance of the samples are measured. The role of the atoms in the body-centered site in stabilizing this phase is analyzed from the obtained data of microhardness and oxidation resistance.

2. Experimental

The samples were prepared by the arc-melting method in a titanium-gettered argon atmosphere using 99.9% pure Y, Sc, Rh, B and 99.999% pure C as raw materials. Mixtures of the starting materials, about 2 g of each, were melted for 3 min in an argon arc plasma flame using a dc power source at 20 V and 100 A. The samples were turned over and were remelted three times under the same conditions. The synthesized samples were wrapped in tantalum foil and annealed at 1573 K for 20 h in vacuo to ensure homogeneity and accurate comparison of results.

For the chemical analysis, the samples were fused using $NaHSO_4$ powder as a flux reagent and then the resulting material was dissolved in HCl. The chemical composition of each solution was analyzed by induction-coupled plasma atomic emission spectrometry (ICP-AES) using Zn as the internal standard. The crystal structures and lattice parameters of the phases were characterized by the powder X-ray diffraction (XRD) method using Cu Kα as an X-ray source. The microhardness of the samples was measured at room temperature using a square-base diamond pyramid as an indenter. A load of 300 g was applied for 15 s and 10 impressions were recorded for each sample. The obtained values were averaged and the experimental error was estimated. Thermogravimetric (TG) analysis was performed between room temperature and 1473 K to study the oxidation resistance of the samples in air. Pulverized samples of about 25 mg were heated in air at a rate of $10\,K\,min^{-1}$.

3. Results and discussion

The prepared samples have a silvery metallic luster. During arc-melting, almost no weight loss due to evaporation of the constituent elements was observed. Chemical analysis revealed that the compositions of the synthesized samples were almost the same as the atomic ratios of the starting materials. In addition, contamination from the tungsten electrode and the copper hearth used in the arc-melting method was negligible.

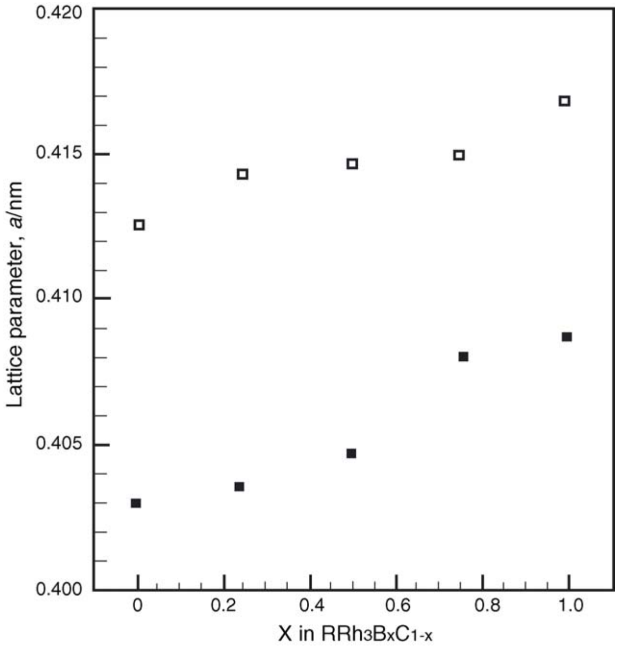

Fig. 1. Lattice parameter a as a function of x in the $RRh_3B_xC_{1-x}$ phase. (□): R = Y; (■): R = Sc.

By varying the values of x, the solid solubility and the resulting change of the crystal structure were studied. Crystal structure analysis reveals that RRh_3B and RRh_3C form a continuous solid solution as $RRh_3B_xC_{1-x}$ $(0 \leqq x \leqq 1)$ and the phase has a perovskite-type cubic structure (space group: $Pm3m$; $Z = 1$). Fig. 1 shows the relationship between x and the lattice parameter a of $RRh_3B_xC_{1-x}$. The lattice parameter a of $YRh_3B_xC_{1-x}$ for $x = 0$, 0.25, 0.50, 0.75 and 1.00 are 0.41262(4), 0.41428(6), 0.41462(5), 0.41506(5) and 0.41675(5) nm, respectively. On the other hand, the lattice parameter a of $ScRh_3B_xC_{1-x}$ for $x = 0$, 0.25, 0.50, 0.75 and 1.00 are 0.40296(6), 0.40347(3), 0.40477(3), 0.40686(9) and 0.40799(3) nm, respectively. As shown in Fig. 1, the lattice parameter a does not change linearly with x, which suggests that the interaction of boron and carbon in the compound changes with x in a complex manner.

The microhardness of the borides and carbides, one of the mechanical property [13–16], was examined for each sample. Fig. 2 shows the microhardness as a function of x in $RRh_3B_xC_{1-x}$. The values of the microhardness of $YRh_3B_xC_{1-x}$ for $x = 0$, 0.25, 0.50, 0.75 and 1.00 are 4.4 ± 1, 4.9 ± 0.1, 5.5 ± 0.2, 6.4 ± 0.2 and 7.5 ± 0.15 GPa, respectively. On the other hand, the values of the microhardness of $ScRh_3B_xC_{1-x}$ for $x = 0$, 0.25, 0.50, 0.75 and 1.00 are 4.5 ± 0.2, 6.1 ± 0.2, 7.4 ± 0.2, 8.9 ± 0.2 and 9.6 ± 1 GPa, respectively. Thus, the microhardness of $RRh_3B_xC_{1-x}$ continuously becomes larger with increasing boron content.

TG analysis was performed on the samples. Fig. 3 shows changes in the oxidation onset temperature with variations in x. The oxidation onset temperatures of $YRh_3B_xC_{1-x}$ for $x = 0$, 0.25, 0.50, 0.75 and 1.00 are 604, 631, 655, 687 and 978 K, respectively. On the other hand, the oxidation onset

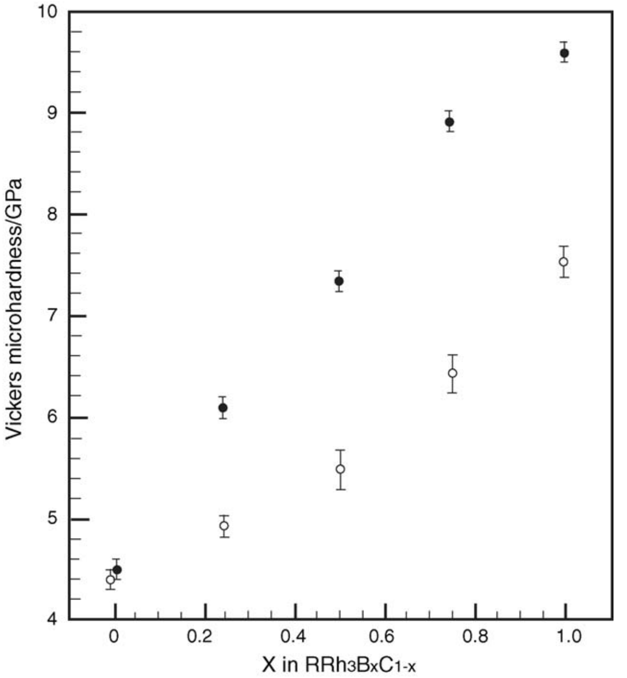

Fig. 2. Vickers microhardness as a function of x in the $RRh_3B_xC_{1-x}$ phase. (□): R = Y; (■): R = Sc.

temperatures of $ScRh_3B_xC_{1-x}$ for $x = 0$, 0.25, 0.50, 0.75 and 1.00 are 674, 675, 695, 725 and 753 K, respectively. The values also increase with increasing boron content.

In the present study, the authors have investigated the role of the body-centered atoms in stabilizing the perovskite-type structure. Both microhardness and oxidation onset temperature increase with increasing boron content x in $RRh_3B_xC_{1-x}$. The electronegativities of Y, Sc, Rh and the body-centered atoms B and C are 1.2, 1.3, 2.2, 2.0 and 2.5 [17], respectively. This suggests that covalency in this phase increases with increasing boron content. Hence, both microhardness and oxidation onset temperature are essentially proportional to the stability of the compound. The results of this study indicate that the mechanical strength and chemical stability of the $RRh_3B_xC_{1-x}$ phase increase with the boron content.

Hardness is known as a material parameter which indicates resistance to elastic/plastic deformation. To describe the origin at atomistic scale theoretically, first principles calculations were performed to estimate the bulk moduli, B, from the volume dependence of the total energy. We use the ab initio projected augmented wave (PAW) method [18,19] with the Vienna Ab initio Simulation Program (VASP) [20–22]. Minimization of the free energy over the degrees of freedom of the electron densities and atomic positions was performed using the conjugated-gradient iterative minimization technique [23]. The cutoff energy for the plane wave expansion was taken to be 257.2 eV for RRh_3B and 286.7 eV for RRh_3C, respectively, which was large enough to obtain good convergence. In the Brillouin zone (BZ) integrations, $8 \times 8 \times 8$ **k**-points were used. The exchange–correlation energy has been calculated within the generalized gradient approximation [24]. The total energy, u, is calculated as a function of the lattice parameter. The variation in the total energy as a function of the lattice parameter is shown in Fig. 4 for $ScRh_3C$. From the curve shown in Fig. 4, one can estimate the equilibrium lattice parameter a_0 and the bulk modulus, B, which

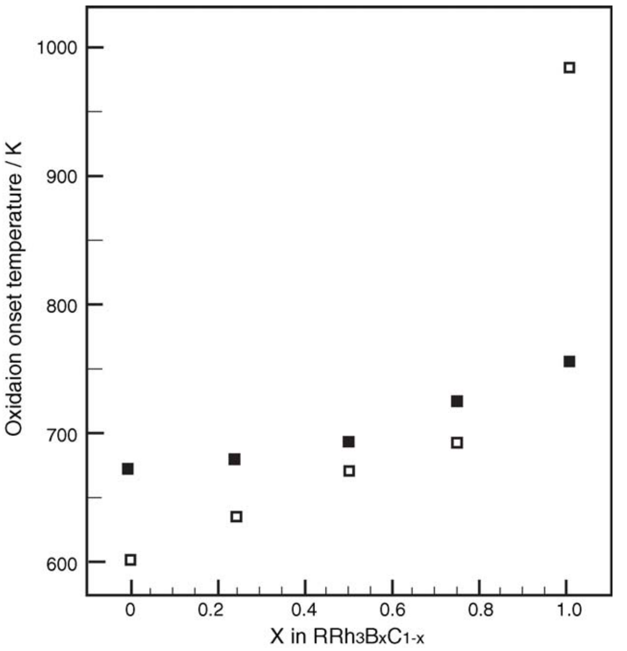

Fig. 3. Oxidation onset temperature as a function of x in the $RRh_3B_xC_{1-x}$ phase. (□): R = Y; (■): R = Sc.

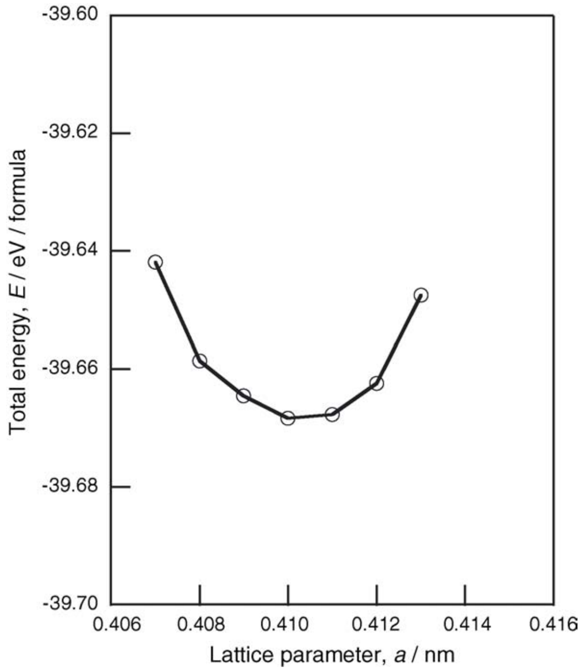

Fig. 4. The calculated total energy per formula unit as a function of the lattice parameter for $ScRh_3C$.

Table 1
Calculated lattice parameter (a_0) and the bulk modulus (B)

	a_0 (nm)	B (GPa)
YRh_3B	0.422	177.4
YRh_3C	0.419	199.9
$ScRh_3B$	0.413	200.1
$ScRh_3C$	0.410	222.3

is defined as:

$$B = -\frac{V\,\mathrm{d}p}{\mathrm{d}V} = \frac{V\,\mathrm{d}^2u}{\mathrm{d}V^2}$$

where V is the volume of the unit cell and p is the pressure. Table 1 shows the obtained equilibrium lattice parameter, a_0, and B for RRh_3B and RRh_3C (R = Y, Sc). The lattice parameter are in excellent agreement with the experimental results.

The difference of the equilibrium lattice parameter between the calculated result and the experimental value is only around 1%. From Table 1, it is observed that a decrease in the lattice parameter leads to an enhancement in the bulk modulus for both the RRh_3B and RRh_3C system. As it is discussed in Ref. [25], the electronic structures of the compounds obtained by full potential linearized augmented plane wave (FLAPW) method show that the covalency between boron and rhodium atoms decreases with the atomic number of R. It may be concluded that more the covalent character in the bond between boron and rhodium atoms is, harder the mechanical property the compounds have.

4. Conclusion

Perovskite-type RRh_3B and RRh_3C (R = Y, Sc) form a solid solution $RRh_3B_xC_{1-x}$ in the full range of $0 \leqq x \leqq 1$. This phase crystallizes into a cubic structure (space group: $Pm3m$, $Z = 1$). The microhardness of this phase increases with increasing boron content. The oxidation onset temperature indicated by the TG-curves also increases with boron content. The mechanical strength and chemical stability of this phase are strongly dependent on the boron content. Ab initio calculations show excellent agreement with experimental lattice parameter. A decrease in the lattice parameter tends to increase the bulk modulus.

Acknowledgements

This study was performed under the Interuniversity Cooperative Research Program of the Laboratory for Advanced Materials (LAM), Institute for Materials Reseach (IMR), Tohoku University. V.K. thankfully acknowledges hospitality at IMR, Tohoku University. We are grateful to the staff of the Center for Computational Science of IMR, Tohoku University for allowing the use of the Hitachi RS-8000/64 super computing facility and their kind support.

References

[1] F. Galasso, Perovskites and High-Tc Superconductors, Gordon and Breach, London, 1990.
[2] H. Iwahara, M. Balkanski, T. Takahashi, H.L. Tuller (Eds.), Solid State Ionics, Elsevier, Amsterdam, 1992.
[3] N. Kamegashira, J. Meng, T. Murase, K. Fujita, H. Satoh, T. Shishido, T. Fukuda, 10th International Ceramics Congress—Part A, P. Vincenzini (Ed.), Techna Srl, 2003, p. 181.
[4] K. Oikawa, T. Kamiyama, S. Ikeda, T. Shishido, S. Yamaguchi, Solid State Ionics 154–155 (2002) 641.
[5] P. Rogl, L. Delong, J. Less-Common Met. 91 (1983) 97.
[6] T. Shishido, J. Ye, T. Sasaki, R. Note, K. Obara, T. Takahashi, T. Matsumoto, T. Fukuda, J. Solid State Chem. 133 (1997) 82.
[7] T. Shishido, J. Ye, S. Okada, K. Kudou, T. Sasaki, S. Ishida, T. Naka, M. Oku, I. Higashi, H. Kishi, H. Horiuchi, T. Fukuda, J. Alloys Compd. 280 (1998) 65.
[8] T. Shishido, S. Okada, K. Kudou, K. Iizumi, M. Oku, Y. Ishizawa, T. Amano, S. Kohiki, Y. Kawazoe, K. Nakajima, J. Alloys Compd. 354 (2003) 198.
[9] T. Shishido, J. Ye, K. Kudou, S. Okada, K. Iizumi, M. Oku, Y. Ishizawa, A. Yoshikawa, M. Tanaka, S. Oishi, N. Kamegashira, S. Kohiki, Y. Kawazoe, K. Nakajima, Jpn. J. Appl. Phys. 42 (8) (2003) 5213.
[10] H. Holleck, J. Less-Common Met. 52 (1977) 167.
[11] T. Shishido, J. Ye, S. Okada, K. Kudou, T. Sasaki, S. Isida, T. Naka, M. Oku, I. Higashi, H. Kishi, H. Horiuchi, T. Fukuda, J. Alloys Compd. 309 (2000) 107.
[12] M. Oku, T. Shishido, T. Shinohara, T. Fukuda, Q. Sun, Y. Kawazoe, K. Wagatsuma, J. Alloys Compd. 339 (2002) 317.
[13] H. Sumiya, S. Uesaka, S. Satoh, J. Mater. Sci. 35 (2000) 1181.
[14] B.A. Cook, J.L. Harringa, T.L. Lewis, A.M. Russell, Scripta Mater. 42 (2000) 597.
[15] K. Kudou, S. Okada, T. Mori, T. Shishido, T. Tanaka, I. Higashi, K. Nakajima, P. Rogl, Y.B. Anderson, T. Lundstrom, Jpn. J. Appl. Phys. 41 (2002) L928.
[16] S. Okada, K. Kudou, T. Mori, T. Shishido, P. Rogl, T. Lundstrom, Trans. Kokushikan Univ., Fac. Eng. 36 (3) (2003) 11.
[17] L.C. Pauling, The Nature of Chemical Bonding and Structure of Molecules and Crystals, An Introduction to Modern Structural Chemistry, Cornell University Press, Ithaca, NY, 1940.
[18] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
[19] P.E. Bloechl, Phys. Rev. B 50 (1994) 17953.
[20] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558;
G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251.
[21] G. Kresse, J. Furthmuller, Phys. Rev. B 55 (1996) 11169.
[22] G. Kresse, J. Hafner, J. Phys. Condens. Matter. 6 (1994) 8245.
[23] M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, J.D. Joannopoulos, Rev. Mod. Phys. 64 (1992) 1045.
[24] J.P. Perdew, in: P. Ziesche, H. Eschrig (Eds.), Electronic Structure of Solids '91, Akademie Verlag, Berlin, 1991.
[25] M. Oku, T. Shishido, M. Arai, K. Wagatsuma, K. Nakajima, J. Alloys Compd. 390 (2005) 202.