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Effect of Ni and Co Additives on Phase Decomposition in TiB_2–WB_2 Solid Solutions Formed by Induction Field Activated Combustion Synthesis

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Solid solutions of TiB_2–WB_2 were densified and annealed simultaneously to cause the decomposition into the phases $(Ti,W)B_2$ and $(W,Ti)B_2$. Ni and Co were added to solid solutions formed by induction field activated combustion synthesis. The presence of these metals as additives markedly enhanced the kinetics of the subsequent decomposition process. With these additives, decomposition to the two phases occurred within minutes (360 s) in contrast to hours when the solutions did not include the additives. The phases resulting from decomposition, $(Ti,W)B_2$ and $(W,Ti)B_2$, were identified by X-ray to have the hexagonal AlB_2 and W_2B_5 structures, respectively. The precipitated phase, $(W,Ti)B_2$, occurred as elongated grains with aspect ratios of as high as about 10 in samples containing Ni as the additive.

I. Introduction

Interest in the diborides of transition metals has been motivated by several attractive properties, including high melting point, hardness, and electrical and thermal conductivity.[1] In addition, many of these borides form extensive solid solutions, which when annealed at lower temperatures decompose to give rise to unusual microstructures containing the second phase in the form of highly oriented precipitates. Such microstructures are qualitatively similar, but on a much finer scale compared to fiber-reinforced composites. In the case of solid solutions of TiB_2 and WB_2, the phases resulting from decomposition are $(Ti,W)B_2$ and $(W,Ti)B_2$, which have the AlB_2 and W_2B_5 structures, respectively.[2] The latter phase occurs as a highly oriented phase. Such a microstructure is believed to give rise to improvements in the mechanical properties (e.g., fracture toughness).

Solid solutions of TiB_2–WB_2 have been produced by the annealing of the two borides at high temperatures[2–4] or by field-activated synthesis using elemental reactants in a spark plasma synthesis (SPS) apparatus.[5,6] In the latter approach, synthesis and densification were accomplished simultaneously and samples with relative densities as high as 94% have been prepared. The decomposition of these solutions to two phases has been found to be kinetically slow. Moreover, it was found that the addition of other elements (e.g., Cr) enhances the decomposition.[3,4] In a recent investigation, the present authors prepared TiB_2–WB_2 solid solutions by induction field activated combustion synthesis (IFACS), again using elemental reactants. It was shown that solid solutions could be synthesized in about 2 min,[7] in sharp contrast to the long annealing time required in the conventional (furnace) method. In the IFACS method rapid heating is achieved by the induced current,[8,9] which has been shown to be effective in the synthesis of compounds with low heats of formation, a decided advantage over conventional combustion synthesis.[10,11] In the previous IFACS work the solid solution products were loose powders and required a densification step which was accomplished in an SPS apparatus. The relative density of the TiB_2–WB_2 solid solutions after this step was ~86%.

As indicated above, the decomposition of the solid solutions is slow and additives have been incorporated to enhance this process. In the present work, we investigated the effect of the addition of nickel and cobalt powders on the decomposition of the TiB_2–WB_2 solid solutions formed by the IFACS method.

II. Experimental Procedure

High-purity powders of Ti, W, and B were used as reactants in this study. The titanium powders were 99.5% pure and had an average particle size of about 22 μm (Sumitomo Sitix, Inc., Amagasaki, Japan). The tungsten powders were 99.9% pure with an average particle size of about 8 μm (Kojundo Chemical Laboratory, Inc., Sakaido, Japan) and the crystalline boron powders were 99% pure with a particle size of less than 45 μm (Kojundo Chemical Laboratory, Inc., Sakaido, Japan). The additive powders were 99.9% pure nickel with an average particle size of about 2–3 μm and 99% pure cobalt with an average particle size of about 5 μm. Both the Ni and Co powders were obtained from the Kojundo Chemical Laboratory, Sakaido, Japan. Powders of titanium, tungsten, and boron were weighed out in mole ratios of Ti/W/B = 1/1/4.6 to give a composition of $(Ti,W)B_{2.3}$ and were dry-mixed in an automatic agate mortar for 1 h. Excess boron was used because of previous experience indicating the loss of this element (due to the evaporation of its oxide) during synthesis.[7]

The mixed powders were packed into a cylindrical carbon sheet, ~0.7 mm in thickness and 40 mm in diameter and 10 mm long. The packing density of each powder compact was about 50%. Each sample was placed in commercial casting sand inside a silicon nitride crucible of 70 mm inside diameter, 140 mm outside diameter, and 70 mm depth. That crucible was then placed in the IFACS equipment.[7] Details of the experimental setup were provided in recent publications.[7–9] The reaction in the sample was initiated by induction under the conditions of 85 V, 170 A, 70 kHz,

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and 120 s. The powders of the resulting TiB_2–WB_2 solid solutions were crushed by ball milling using a silicon nitride jar and balls until an average particle size of 2 μm was obtained.

To the powders of the TiB_2–WB_2 solid solutions, powders of nickel or cobalt were added at levels of 0.5 and 1.0 wt%, respectively, and were dry-mixed in an automatic agate mortar for 30 min. From these mixed powders, cylindrical compacts, ~16 mm in diameter and 10 mm long, were formed by cold isostatic pressing at 250 MPa. The packing density of the powder compact was ~60%. To effect a decomposition of the solid solutions, annealing experiments were conducted by induction heating. The powder compact was placed in a cylindrical carbon sheet, ~47 mm in diameter and 17 mm long. The carbon crucible was made of several tens of carbon sheets, 0.7 mm in thickness, with a hole 16 mm in diameter and with lids also made of carbon sheets. The carbon crucible with the compact was placed in commercial casting sand inside the silicon nitride crucible described above. The crucible was placed inside the induction coil. The heat treatment was performed by passing a current induced in the carbon sheet (85 V, 170 A, 70 kHz) under atmospheric pressure of air. The sample, being embedded in the carbon sheet, experienced a reducing environment. Temperatures were measured with a W–5%Re/W–25%Re thermocouple using a data acquisition recorder as described in previous publications.[7–9]

After the annealing period, the products were analyzed by X-ray diffraction (RAD-C system, Rigaku of Tokyo, Inc., Tokyo, Japan) using Cu*K*α radiation. Microstructural and elemental analyses were conducted on cross sections of the annealed samples using scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) (JSM-330, JEOL of Tokyo, Inc., Tokyo, Japan).

III. Results and Discussion

The induction current through the carbon sheet heated the sample. The temperature increased at a rate of 700°C·min^{-1} in the initial stages, and then increased smoothly (with a decreasing rate) to a maximum of 1840°C after 300 s. The temperature was then held constant for an additional 60 s. This treatment was used for all samples.

X-ray diffraction patterns of products annealed in the induction furnace under atmospheric pressure (air) are shown in Figs. 1(a) through (c). Figure 1(a) depicts the XRD results for a sample that had no additive, Fig. 1(b) shows the pattern for a sample which contained 0.5 wt% Ni, and Fig. 1(c) shows the pattern for the sample with 1.0 wt% Co. The peaks of the product without additives were those belonging to the $(Ti,W)B_2$ solid solutions which corresponded closely to the diffraction peaks of TiB_2. (hexagonal AlB_2 structure, *P*6/*mmm*). In contrast, the patterns of the sample with the Ni and Co additives contained peaks belonging to the solid solution phases $(Ti,W)B_2$ and $(W,Ti)B_2$; the latter has the hexagonal W_2B_5 structure ($P6_3/mmc$). Examining the X-ray diffraction peaks of the samples with Ni and Co shows a shift to lower 2θ values for the (001) peak (at $2\theta = 28.00$ for the sample without additives). In view of the dependence of the lattice parameters on composition in the solid solution,[7,12] this observation is consistent with the decrease in the W content of the solid solution as a result of the precipitation of the second phase. Results of EDS analyses on the $(Ti,W)B_2$ and $(W,T)B_2$ phases indicated that the former contained less tungsten.[13] For example, in the case

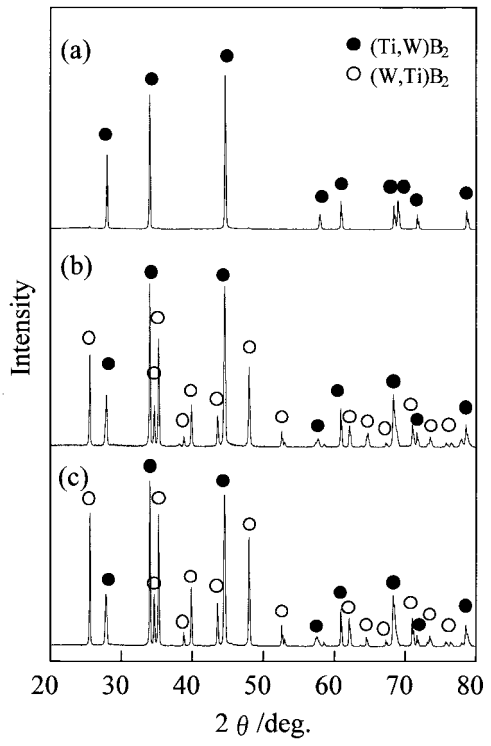

Fig. 1. X-ray diffraction patterns of the products annealed by induction: (a) $(Ti,W)B_{2.3}$ with no additive, (b) $(Ti,W)B_{2.3}$ + 0.5 wt% Ni, (c) $(Ti,W)B_{2.3}$ + 1.0 wt% Co.

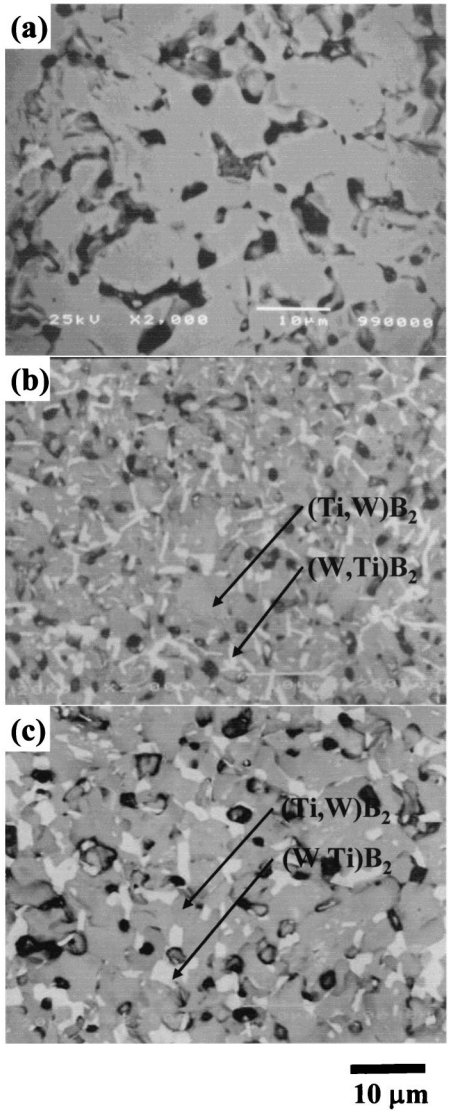

Fig. 2. Scanning electron micrographs of cross sections of annealed products (annealing time 360 s): (a) $(Ti,W)B_{2.3}$ without additive, (b) $(Ti,W)B_{2.3}$ + 0.5 wt% Ni, and (c) $(Ti,W)B_{2.3}$+ 1.0 wt% Co.

of a solution with a nominal composition of 50 mol% WB_2, the concentration of W in $(Ti,W)B_2$ after decomposition was equivalent to less than 40 mol% WB_2.

Scanning electron micrographs (backscattered electron images) of cross sections of annealed samples are shown in Figs. 2(a) through (c). Figure 2(a) is for a solid solution without additive, Fig. 2(b) is for a sample with 0.5 wt% Ni, and Fig. 2(c) is for a sample with 1.0 wt% Co. Figure 2 (a) shows the presence of the solid solution only, indicating that the precipitation of the second phase did not take place, while Fig. 2(b) shows the presence of the two phases $(Ti,W)B_2$ (darker gray phase) and $(W,Ti)B_2$ (lighter gray phase). Similar general results were obtained in samples containing Co as an additive. However, in this case, regions of the second phase are less numerous and are larger in size in comparison to the case of the Ni-containing samples. Identification of the phases was done by EDS measurements. As can be seen from Figs. 2(b) and (c), the $(W,Ti)B_2$ phase precipitated in an elongated form. The rodlike grains were ~1 μm thick and 5 μm long.

The observed size of the $(W,Ti)B_2$ grains in this study was much larger than was observed in previous studies by Telle and co-workers[3] and by Kaga *et al.*[6] in the same binary system but with Cr as additive. In the previous studies, the precipitate was in the form of very small platelets, which were nanometric in size. The presence of Ni and Co appeared to have an enhancing influence on the growth of the $(W,Ti)B_2$ phase. It has been reported that during annealing small particles of residual WB_2 initiate the growth of platelets along the grain boundaries of the host crystals.[3] But this condition may not have been met in the present study, where elemental powders were used in contrast to the use of the borides as starting materials in the work of Telle and co-workers.

It is clear from the present results that the presence of Ni and Co enhanced the decomposition of the solution. In general, the nucleation of the second phase from a TiB_2–WB_2 solid solution required an incubation period longer than 2 h. But, as seen above, with Ni and Co, a second phase formed in 6 min. As in the case of Cr additive,[3] the role of Ni and Co in the enhancement of the decomposition is not totally clear. It may be related to the possible interaction between the borides and Ni or Co. Nickel and iron have been reported to form borides when added to TiB_2.[14,15] The increased mobility of boron associated with its interaction with Ni or Co may enhance the decomposition of the solid solution. Related to this proposed explanation is the finding that the addition of 1.0 wt% CoB markedly accelerates the densification of TiB_2.[16]

IV. Conclusion

The effect of Ni and Co additives on the phase separation of TiB_2–WB_2 solid solutions formed by induction field activated combustion synthesis was investigated. The product decomposed from the $(Ti,W)B_2$ single phase to $(Ti,W)B_2$ and $(W,Ti)B_2$ phases within 360 s, in contrast to hours when the solution did not include additives. The $(W,Ti)B_2$ phase that formed from the decomposition had an elongated grain structure but with grain sizes on the scale of micrometers as contrasted to the nanometric scale precipitates when Cr was used as an additive. The formation of borides of Ni and Co is suggested as playing a role in the enhancement of the decomposition of the solid solution.

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