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Abstract

Full Text

CHEMISTRY

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ON RHENIUM BORIDES

(Presented by Academician N. I. Chernyaev, 20 IX 1957)

Information on compounds of rhenium with boron is practically absent from the literature, unless one counts the cursory mention in the work of Heine and Moers ⁽¹⁾ of the possibility of obtaining alloys of rhenium with boron by heating rhenium with BBr_3 . These compounds are of interest primarily because they should possess features in common both with the stable, refractory, and hard borides of tungsten ⁽²⁾, and with the unstable borides of manganese ⁽³⁾.

In this connection, in the present work the phase composition was investigated of alloys of rhenium with boron, prepared with the aim of obtaining chemical compounds existing in the systems of metals close in electronic structure and properties to rhenium, i.e., in the boron systems of tungsten, molybdenum, and manganese: Re_4B , Re_2B , Re_3B_2 , ReB , Re_3B_4 , Re_2B_3 , ReB_2 , and Re_2B_5 .

The alloys were prepared by sintering pressed mixtures of rhenium and boron powders in a vacuum laboratory furnace ⁽⁴⁾ on a substrate of hot-pressed boron carbide at a temperature of 1900° for 0.5-2 h. The starting powder contained 99.966% Re and insignificant amounts of impurities: 0.008% K; 0.006% Na, 0.013% Ca; 0.003% Fe; 0.001% Al; 0.001% Cu; 0.003% Ni. The boron powder was obtained by vacuum purification of magnesiothermic amorphous boron and contained 99.8% B.

X-ray diffraction patterns of the specimens were taken in copper radiation in an RKD camera of diameter 57.3 mm by the powder method. Cylindrical specimens 0.8 mm in diameter were prepared with a paraffin binder to prevent interaction with the atmosphere ⁽⁵⁾.

The X-ray diffraction patterns of the alloys are shown in Fig. 1. An attempt was made to identify the alloys obtained by comparing the positions of lines on the X-ray diffraction patterns with theoretically calculated line positions for analogous known phases in other systems, the value of the atomic radius of rhenium being taken as 1.373 \AA ⁽⁶⁾. In doing so, no satisfactory correspondence of the structures of the phases obtained with known boride phases was obtained.

Beginning with the composition Re_4B , a gradual rearrangement of the rhenium lattice is observed. Along with the rhenium lines, which are considerably broadened, a certain number of additional weak lines appear, also broadened in character. With a further increase in the boron content to 33 at.% these lines

Fig. 1. X-ray diffraction patterns of alloys of the Re-B system. Boron content, in percent: a-0, b-20, c-33.3, d-40, e-50, f-57.1, g-60, h-66.6, i-71.3

Figure 1: Fig. 1. X-ray diffraction patterns of alloys of the Re-B system. Boron content, in percent: a-0, b-20, c-33.3, d-40, e-50, f-57.1, g-60, h-66.6, i-71.3

become sharper. In an attempt to index this γ -phase with the aid of Hull curves, most of the lines can be indexed in the tetragonal system with lattice constants: $a = 5.47$ and $c = 4.73$ Å. A further increase in the boron content is also accompanied by a gradual change in the appearance of the X-ray diffraction patterns. Beginning with 50 at.% boron, the X-ray diffraction patterns of all specimens are almost identical. Despite the absence of significant structural changes in going from one alloy to another, a noticeable difference is observed between the X-ray diffraction patterns of specimens of compositions far apart from one another. It should be noted that there is a closer similarity

Fig. 1. X-ray diffraction patterns of alloys of the Re-B system. Boron content, in percent:

a-0, b-20, c-33.3, d-40, e-50, f-57.1, g-60, h-66.6, i-71.3.

X-ray diffraction patterns of alloys within the composition ranges 20-35 at.% B and 40-80% B than between these ranges. This gives grounds to assume the presence in the Re-B system of two phases: γ in the region 20-35 at.% B and γ' in the region of alloys containing more than 40 at.% boron; moreover, the γ' phase, with increasing boron content, also undergoes some rearrangement of its lattice and passes into a phase with a slightly altered structure. It has not yet been possible to identify this phase. An alloy with 33.3 at.% boron, immediately after sintering, revealed a structure corresponding to the ε -phases Me_2B_5 , with lattice constants $a = 2.97$ and $c = 13.8$ Å, which after prolonged exposure in air (for one month) transformed into the structure of the γ' -phase.

The thermoe.m.f. of the alloys in a pair with copper was measured. In all cases the sign of the thermoe.m.f. proved to be negative. The magnitude of the thermoe.m.f. in alloys with a boron content of 30-40 at.% is 6-7 $\mu\text{V}/\text{deg}$, and for alloys with a boron content of 60-66 at.% it is 3-4 $\mu\text{V}/\text{deg}$. The change in thermoe.m.f. may be connected with the transition from the γ - to the γ' -phase, apparently a more ordered one, which agrees with the character of the X-ray diffraction patterns.

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