The Crystal Structure of a M_3B_2-Type Double Boride

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Two isomorphous borides extracted from different superalloys possess a double boride structure, involving metal atoms of varying size. The structure is tetragonal with $c/a = 0.54$ and belongs to space group $P4/mbm$. It consists of larger metal atoms located at the vertices of directly stacked $3^2.4.3.4$ semi-regular-tessellation layers with smaller metal atoms at the centers of square prisms and boron at the centers of triangular prisms. Boron atoms occur in isolated bonded pairs.

Experimental

A new boride structure has been found in alloys HS–88 and Incoloy 901, each with around 0·1% boron addition. The borides were extracted electrolytically from unaged specimens and examined by X-ray powder analysis. Small amounts of TiC were also present in both extracts. Incoloy 901 without boron does not produce this structure.

In Incoloy 901 the boride goes into solution between 2200 and 2400 °F. It exists as morphologically isotropic particles of a few microns in diameter distributed in strings along the worked direction in both Incoloy 901 and HS–88; this is typical of the more refractory secondary phases, such as TiN and NbC.

The powder data of the Incoloy 901 extract can be indexed on a tetragonal lattice of unit-cell dimensions

$$a = 5.783, \quad c = 3.134 \text{ Å}, \quad c/a = 0.542 .$$

Comparison of the observed and calculated $\sin^2 \theta$ values is shown in Table 1. The data from the HS–88 extract index similarly with unit-cell dimensions

$$a = 5.72, \quad c = 3.11 \text{ Å}, \quad c/a = 0.543 .$$

An extract from Incoloy 901 was spectrographed quantitatively for boron, aluminum, silicon, titanium, chromium, iron, nickel and molybdenum. The specimen was diluted to 10% and again to 1% in spectrographically pure graphite, and intensities were calibrated with Spex-Mix standards. Molybdenum and titanium were the most concentrated elements and there was some doubt about their readings; therefore, these two elements were also determined colorimetrically after chemical separation.

As already mentioned, there was also some TiC in the extract, which made the titanium determination too high. TiC has the NaCl structure with $a=4.327$ Å. The integrated intensities of the (220) line of TiC and the (002) line of the boride were determined by measuring the peak areas on the diffractometer chart with a planimeter, taking averages of 20 readings each. All atoms scatter in phase for these two lines, and they

Table 1. *Tetragonal indexing of X-ray lines of Incoloy 901 extract*

Cu $K\alpha$ radiation

| d (Å) | | | Incoloy 901 | |
HS–88	Incoloy 901	*hkl*	Observed $\sin^2 \theta$	Calculated* $\sin^2 \theta$
3·11	3·14	001	0·0602	0·0605
2·86	2·89	200	0·0709	0·0711
2·554	2·586	210	0·0885	0·0889
2·465	2·490	111	0·0955	0·0960
2·108	2·124	201	0·1313	0·1316
2·021	2·043	220	0·1420	0·1422
1·979	1·994	211	0·1491	0·1493
1·810	1·828	310	0·1774	0·1777
1·556	1·564	002	0·2421	0·2420
1·390	1·403	410	0·3022	0·3021
—	1·364	330	0·3203	0·3199
1·333	1·338	212	0·3309	0·3308
—	1·313	401	0·3440	0·3448
—	1·296	420	0·3546	0·3554
1·271	1·277	411	0·3624	0·3626
1·240	1·247	331	0·3810	0·3804
	1·245	222	0·3832	0·3841
1·181	1·190	312	0·4198	0·4197
1·059	1·067	511	0·5227	0·5225
1·037	1·043	412 003	0·5443	0·5441 0·5444

* $a = 5.783, \quad c = 3.134$ Å.

are separated only by $1\frac{1}{2}°$ in 2θ. Assuming the metallic composition of the boride to be that indicated by the chemical analysis but with somewhat less titanium, the relative intensities indicated that there were 2·33 times as many unit cells of boride as of TiC. The boride structure determination given below shows that there are 6 metal atoms per unit cell of the boride, or 14 metal atoms of boride to every 4 titanium atoms in TiC. This knowledge provided the subtraction of titanium due to TiC from the chemical analyses. Measurement of the (200) and (220) intensities of TiC and the resulting calculation of the (111) intensity also provided its subtraction from the (111) intensity of the boride, with which it coincides.

The results of the chemical analysis with titanium

due to TiC subtracted are given here in atomic proportions normalized to a total of 5 atoms:

B	Si	Cr	Fe	Ni	Mo	Ti	Al
1·98	0·01	0·59	0·39	0·21	1·01	0·59	0·22

This indicates 3 metal to 2 boron atoms.

The extract from HS–88 was not chemically analyzed. A qualitative X-ray spectrum indicated, however, that there was an abundant supply of tungsten in addition to the elements listed above.

Structure determination

The only systematic absences apparent from the X-ray powder data are $(0kl)$ with odd k, limiting the possible space groups to $P4bm$, $P\bar{4}b2$ and $P4/mbm$. An arrangement has been found in $P4/mbm$ which packs a plausible combination of metal and boron atoms in familiar atomic coordinations and gives relative X-ray intensities in satisfactory agreement with those observed. Lacking data whereby the number of atoms per unit cell could be independently determined, one cannot prove rigorously that this is the only solution to the diffraction data; however, a multiplicity of geometrically plausible solutions in a unit cell of this size is extremely unlikely.

The arrangement corresponds to the atomic ratio $M_2M'B_2$, where M and M' designate respectively 'large' and 'small' metal atoms. Taking Mo, Ti and Al as large atoms, the chemical results given above indicate this ratio approximately. Two $M_2M'B_2$ groups may fit into the unit cell as follows:

Space group $P4/mbm$:

4 M in (g):

$u, \frac{1}{2}+u, 0$; $\bar{u}, \frac{1}{2}-u, 0$;

$\frac{1}{2}+u, \bar{u}, 0$; $\frac{1}{2}-u, u, 0$; with $u = 0{\cdot}183$.

4 B in (h):

$v, \frac{1}{2}+v, \frac{1}{2}$; $\bar{v}, \frac{1}{2}-v, \frac{1}{2}$;

$\frac{1}{2}+v, \bar{v}, \frac{1}{2}$; $\frac{1}{2}-v, v, \frac{1}{2}$; with $v = 0{\cdot}394$.

2 M' in (b):

$0, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

The positional parameter u was chosen so that the M atoms within a layer lie at the vertices of a perfect $3^2.4.3.4$ semi-regular tessellation (network of Fig. 1). These layers are stacked in direct coincidence with corresponding layers above and below. The M atoms thus form columns of regular triangular and square prisms; the boron atoms lie at the centers of the triangular prisms and the M' atoms at the centers of the square prisms. This assumed arrangement gives:

$$u = \tfrac{1}{4}(\sqrt{3}-1), \quad v = \tfrac{1}{2}-\tfrac{1}{3}u\sqrt{3}.$$

The X-ray intensities were measured from flat powder specimens with a diffractometer. One-hundred-second counts were read for each peak of the Incoloy 901 extract, using a 0·3° detector slit. Intensities ranged from 70 to 2,100 counts sec.$^{-1}$ above a background of 700 counts sec.$^{-1}$. Intensities for the HS–88 extract were the estimated peak areas of a diffractometer chart.

Structure factors, $F(hkl)$, were calculated for the above-described structure approximating the atomic
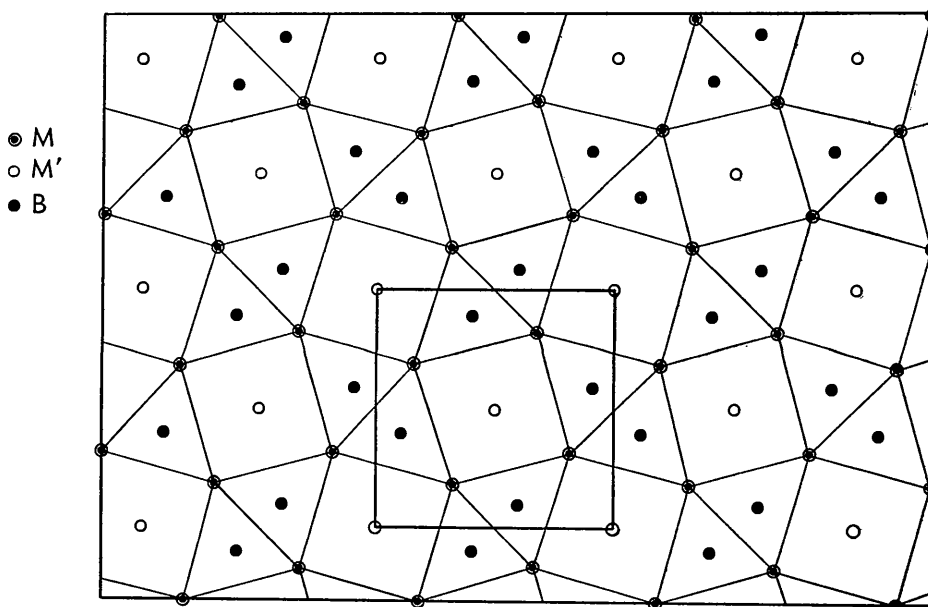

Fig. 1. Double boride structure as viewed along the c axis. M' and B atoms lie on planes midway between semi-regular tessellations of M atoms. Heavy square outlines unit-cell.

number ratio $M:M'$ as 1·5. Calculated intensities were determined by the formula:

$$I \sim p|F(hkl)|^2 \frac{(1+\cos^2 2\theta)}{\cos \theta \sin^2 \theta} \,,$$

where p is the multiplicity and θ the Bragg angle. Diffractometer geometry provides a constant absorption factor; a temperature factor was not determined. The observed and calculated relative intensities were normalized on the (002) reflection, for which scattered X-rays from all atoms are in phase regardless of position parameters. These are compared in Table 2.

Table 2. *Comparison of calculated and observed X-ray intensities*

Cu $K\alpha$ radiation

hkl	Calculated	Observed Incoloy 901	Observed HS–88
110	3	—	—
001	26	31	28
200	13	10	13
210	75	81	78
111	33	42	44
201	114	101	95
220	29	20	31
211	99	104	95
310	37	39	52
221	1	—	—
320	5	—	—
311	0	—	—
002	20	20	20
112	0	—	—
400	0	—	—
321	1	—	—
410	22	14	24
202	2	—	—
330	4	4	—
212	16	19	17
401	2	4	—
420	3	3	—
411	28	28	28
331	25 ⎫	20	24
222	10 ⎭		
421	2	—	—
312	17	13	17
430	1	—	—
510	0	—	—
322	3	—	—
431	3	—	—
520	1	—	—
511	13	5	11
402	0	—	—
412	18 ⎫	10	11
003	1 ⎭		

The general agreement indicates that the atomic arrangement of the metallic framework is correct, and the boron atoms are located unambiguously by space considerations.

Discussion

The atomic coordinations are listed in Table 3. The M–B distances are similar to those for Mo–B, W–B and Ti–B listed by Kiessling (1950). The tessellated layers of M atoms provide, as shown in Fig. 1, that pairs of triangular prisms be joined on common prism

Table 3. *Atomic coordinations*

Central atom	Neighbors	Interatomic distances (Å) Incoloy 901 extract	Interatomic distances (Å) HS–88 extract
M	5 M	2·99	2·96
M	2 M	3·13	3·11
M	4 M'	2·63	2·61
M	6 B	2·33	2·31
M'	8 M	2·63	2·61
M'	4 B	2·36	2·34
B	6 M	2·33	2·31
B	2 M'	2·36	2·34
B	1 B	1·73	1·71

faces, and through these faces pairs of boron atoms are closely spaced at typical boron–boron distances (Kiessling, 1950). The rhombic prisms formed by the triangular pairs have the same configuration as the unit cells of the hexagonal diborides; e.g., TiB_2 (Kiessling, 1950) and MoB_2 (Bertaut & Blum, 1951).

The environment of the M' atom is similar to that in the ordered body-centered cubic (CsCl) structure, pertinent examples being TiNi and TiFe (Laves & Wahlbaum, 1939). The 'cubes' in this case are tetragonally distorted by a 5 % elongation.

Kiessling (1950) has discussed the tendency for self-bonding among boron atoms, noting that with increasing boron concentrations the boron atoms occur as: (a) isolated atoms, as in M_2B; (b) zigzag chains, as in MB; (c) two-dimensional nets, as in MB$_2$; and (d) three-dimensional frameworks at higher boron/metal ratios. The double boride structure, M_3B_2, introduces still another type; namely, isolated pairs.

References

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