

of the hydrogen-ordered material measured from Kikuchi lines with $B = \langle 10\bar{1}0 \rangle$ is 0.808\AA compared with 0.805\AA determined by X-ray powder techniques.

On the basis of the results of Margolin and Portisch⁸ on Ti-Al alloys, hydrogen would be expected to occupy tetrahedral interstices in Ti_3Sn . However, the absence of ordering reflections other than (0001) and $\{1121\}$ implies that the unit cell has not changed. Thus, using the Ti_3Sn unit cell, structure factors have been calculated for the common reflections assuming a single hydrogen atom per unit cell in all possible tetrahedral interstices and using values for the electronic scattering amplitudes of Ti, Sn, and H taken from Smith and Burge.⁹ The structure factors are given in Table I for one case.

A hydrogen concentration in solution of 11 at. pct or 2000 ppm by weight is necessary to enable each Ti_3Sn unit cell to contain one hydrogen atom. This is not unreasonable for a titanium alloy; indeed it has been shown that a Ti-8 Al-1 Mo-1 V alloy contains 800 ppm hydrogen in solid solution before hydride precipitation occurs.¹⁰ Furthermore, Ti-12.5 Al can absorb ~ 4400 ppm hydrogen, of which at least 2700 ppm is thought to be dissolved in the Ti_3Al phase, without forming hydrides.⁸ In the former alloy hydride formation during electropolishing has been reported.¹

It is instructive to consider the distortion arising from the hydrogen ordering process in terms of the observed domain boundary planes. For hydrogen atoms in tetrahedral interstices the distortion in the c direction is the same across the domain boundary and the fringe contrast arises from the component of distortion in the basal plane. This is consistent with the observed extinction of all fringe images with $g = (0002)$. Assuming distortion in the basal plane along $\langle 11\bar{2}0 \rangle$, *i.e.* a_1, a_2, a_3 , Fig. 4 shows each type of domain wall separating domains with different a_1 and a_2 distortions. All three planes are coherent twin planes although only $(1\bar{1}00)$ and $(11\bar{2}0)$ are compound twins. Both $(1\bar{1}00)$ and $(11\bar{2}0)$ will be low energy domain boundaries because the strain is symmetrically oriented with respect to the boundary plane¹¹ whereas $(1\bar{1}01)$ will have a higher energy because of the strain asymmetry.

It is concluded that the model of one hydrogen atom in a tetrahedral interstice per unit Ti_3Sn cell accounts for the presence of the extra reflections in the diffraction patterns and that the domain boundaries are on coherent twin planes. Further the hydrogen concentration required is reasonable in terms of that reported in solution in other titanium alloys.

The authors wish to acknowledge financial support for this work from the Tin Research Institute, England.

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The Mutual Solubilities of Titanium and Boron in Pure Aluminum

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THE mutual solubilities of titanium and boron in Al-Ti-B ternary melts were determined over the temperature range 700° to 1300°C and the results interpreted in terms of the assumption (for which there is considerable evidence¹) that the solubilities of these elements are limited by their reaction together to form titanium diboride (TiB_2) probably containing aluminium diboride. In the method used, ternary melts were sampled at progressively lowered temperature levels after allowing time for titanium diboride precipitated to settle out.

10 kg melts were made from super purity aluminium (99.99 pct) and Al-3.6 pct Ti and Al-1 pct B master alloys. Impurity levels for the hardener addition alloys are listed in Table I.

Stepwise reductions in temperature were made daily and samples for analysis were taken near the surface after gentle skimming. A minimum period of 21 h quiescence was allowed at each temperature. Stirring during and after settling was avoided as it would have disturbed precipitated titanium diboride particles at the bottom of the crucible and thus resulted in high nonequilibrium titanium and boron concentrations in the samples taken for analysis. Stirring before the stepwise temperature reductions was not considered necessary. Titanium and boron additions were made at temperatures in excess of the temperature of the first analytical sample and well stirred into the melt. Alumina-coated clay-graphite crucibles were used in an electric resistance furnace. Temperatures were measured by a fused alumina-sheathed platinum/platinum-rhodium thermocouple to $\pm 2^\circ\text{C}$, and were continuously monitored. Melt temperatures were controlled to $\pm 5^\circ\text{C}$ or less.

Melts sampled in this way had nominal titanium:boron ratios of 5:1 and 2.2:1 (the stoichiometric ratio for titanium diboride). In the case of the 5:1 ratio alloys the solubility products for the three lowest temperatures examined were not calculated because the boron concentrations were lower than the limit of the analytical method (< 0.0002 wt pct). The results are given in Table II together with results obtained from other work.^{2,3} A 1:2 ratio series was also included originally, but all the titanium concentrations were lower than the limit of the analytical method (< 0.002 wt pct) and these results have therefore been omitted.

The results are shown in Fig. 1 as a logarithmic plot of the weight-percent solubility product, (Ti)

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Manuscript submitted April 18, 1972.

$\times (B)^2$, against the reciprocal of temperature (K). The line shown in this graph has the relationship:

$$\log K = 5.22 - \left(\frac{1.62 \times 10^4}{T} \right)$$

This relationship is based only on results obtained in the present tests at temperatures greater than 1000°C, at which concentrations of titanium and boron were not at the extreme limits of the analytical methods used and the accuracy was greater than at lower temperatures.

The form of the relationship is partial confirmation of the assumption that titanium and boron are mainly present as diboride, rather than, for example, a mixture of $TiAl_3$ and AlB_2 . The amounts of titanium and boron coprecipitated indicate a solid solution or mixture of TiB_2 and excess boron presumably as AlB_2 .

The results agree closely with those from other work^{2,3} and these are included in Table II and Fig. 1.

To indicate the requirements for removing titanium from high-conductivity aluminum without excess boron, Fig. 2 shows the solubilities of titanium and boron for

Table I. Impurity Levels in Al-B and Al-Ti Master Alloys

Element	Impurities, Wt Pct	
	Al-B Alloy	Al-Ti Alloy
Fe	0.05	0.04
Si	0.04	0.04
Mg	0.007	0.003
Mn	0.01	0.002
Cu	0.006	0.03
Ni	n.d. <0.005	n.d. <0.005
Pb	tr. ~0.01	n.d. <0.01
Cr	n.d. <0.01	n.d. <0.01
Zn	tr. ~0.01	n.d. <0.01
Sn	n.d. <0.01	~0.05

Table II. Solubilities of Titanium and Boron in Ternary Al-Ti-B Melts

Nominal Initial Ti:B Ratio and Composition, Wt Pct	Temperature at Which Sample Taken		Analyzed Composition, Wt Pct		Solubility Product $(Ti) \times (B)^2$ Wt Pct	$10^4 T, K$
	K	°C	Ti	B		
5:1 (0.14 Ti, 0.027 B)	1573	1300	0.17	0.0090	1.38×10^{-5}	6.37
	1481	1208	0.16	0.0024	9.2×10^{-7}	6.76
	1391	1118	0.16	0.0016	4.1×10^{-7}	7.19
	1249	976	0.15	0.0002	6.0×10^{-9}	8.00
	1174	901	0.15	<0.0002	—	—
	1051	778	0.16	<0.0002	—	—
	996	723	0.16	<0.0002	—	—
2.2:1 (0.06 Ti, 0.027 B)	1568	1295	0.055	0.011	6.7×10^{-6}	6.37
	1531	1258	0.049	0.009	3.97×10^{-6}	6.54
	1333	1060	0.044	0.002	1.76×10^{-7}	7.52
	1303	1030	0.042	0.001	4.2×10^{-8}	7.69
	1235	962	0.043	0.0008	2.76×10^{-8}	8.06
	1168	895	0.040	0.0004	6.4×10^{-9}	8.54
	1073	800	0.038	0.0002	1.52×10^{-9}	9.34
2.3:1 ² (0.023 Ti, 0.010 B)	1023	750	0.003	0.0002	10^{-10}	9.8
1.7:1 ² (0.0065 Ti, 0.0037 B)	973	700	0.0004	0.0004	5.0×10^{-11}	10.2
Not quoted, probably approximately	1373	1100	Not quoted	Not quoted	6×10^{-8}	7.28
	1243	970	Not quoted	Not quoted	1×10^{-8}	8.05
	2.2:1 ³	1123	850	Not quoted	Not quoted	2×10^{-9}

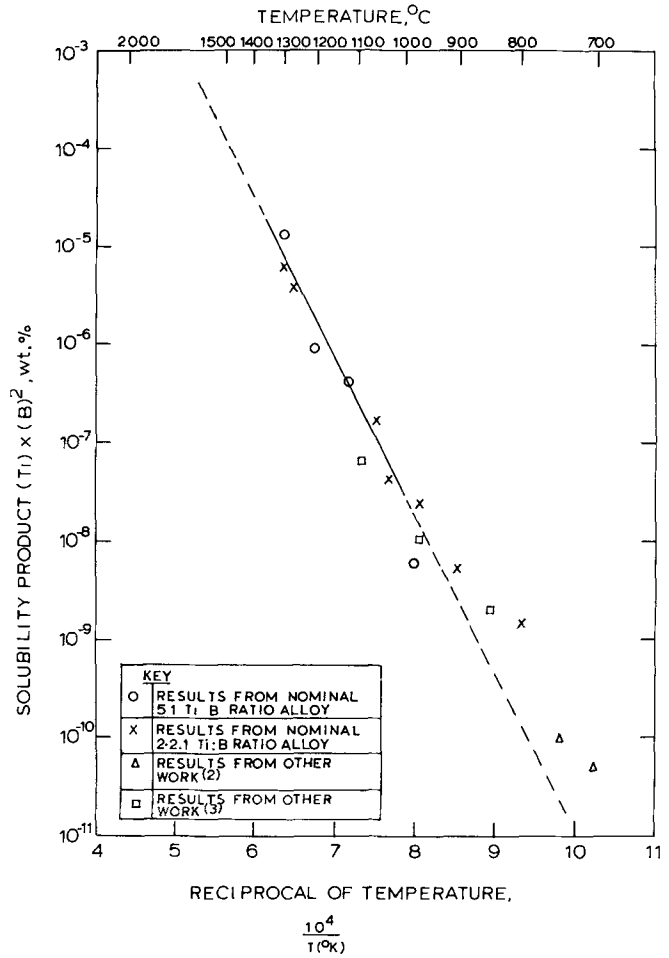


Fig. 1—Logarithmic plot of solubility product against reciprocal of temperature. Line based only on results obtained at temperatures >1000°C (*i.e.* upper seven points).

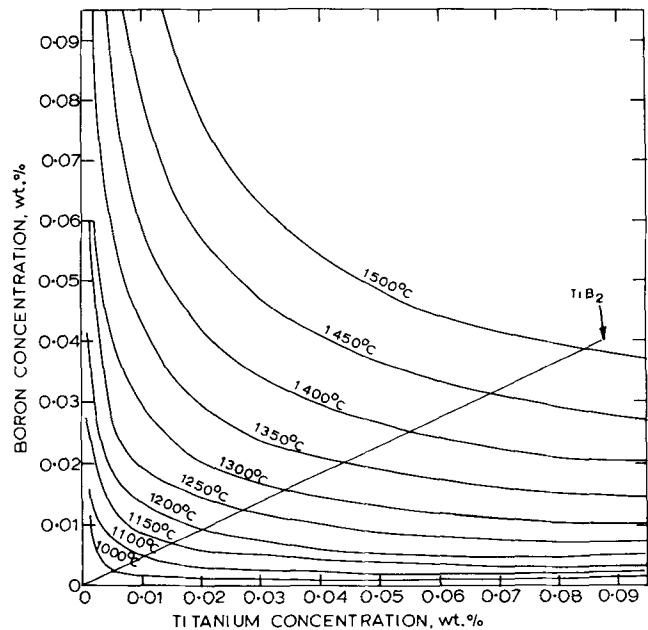


Fig. 2—Predicted solubilities of titanium and boron in Al-Ti-B ternary melts at various temperatures.

various temperatures and compositions, as predicted by the relationship obtained from the solubility determinations. The curves indicate that melts become saturated with respect to TiB_2 at very low concentrations of titanium and boron. For example at $1300^\circ C$ the solubility limit was 0.035 pct Ti, 0.016 pct B, equivalent to 0.051 pct TiB_2 .

The author is indebted to London and Scandinavian Metallurgical Co. Limited, by whom the work was fully supported, for permission to publish this communication.

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Abnormal Grain Growth at the Curie Point During Hot-Pressing of Iron

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DURING hot-pressing experiments on iron powder, it was observed that extensive grain growth occurred near the Curie point. These experiments consisted in heating 4N iron powder at the constant rate of $7^\circ C/min$ from room temperature to $1000^\circ C$ in a vacuum hot-pressing apparatus with a 1200 psi uniaxial pressure applied on the powder. The compaction rate was continuously recorded.

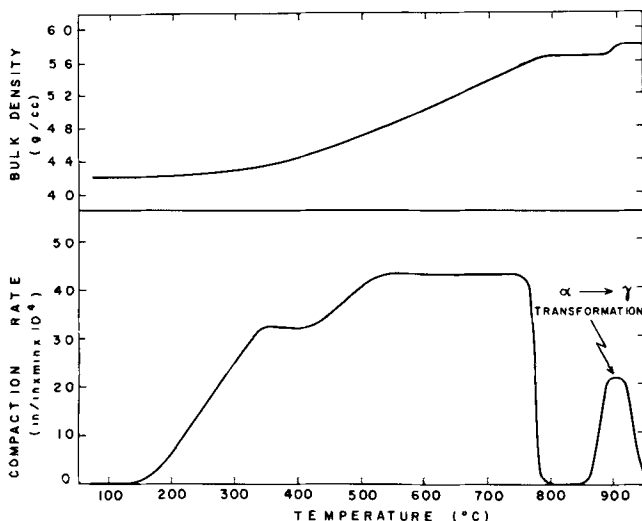


Fig. 1—Compaction rate and bulk density vs temperature during hot-pressing of 4N iron powder.

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Manuscript submitted April 3, 1972.

At about $775^\circ C$, the compaction rate decreased sharply, Fig. 1. To investigate this decrease, the microstructures of specimens hot-pressed up to temperatures just below and just above the Curie point (determined as $775^\circ C$ by DTA analysis) were studied. The results of this metallographic study are illustrated by the microstructures of Figs. 2 and 3 for powder specimens pressed respectively up to 750° and $825^\circ C$. It can be seen that, between 750° and $825^\circ C$, the grains grow from about 8 to 80μ diam. This abnormal growth coincides with the abrupt decrease in the compaction rate at $775^\circ C$.

The extensive grain growth at the Curie point can be explained by assuming that, below the Curie temperature, each grain or powder particle is a distinct magnetic domain. This assumption is reasonable since

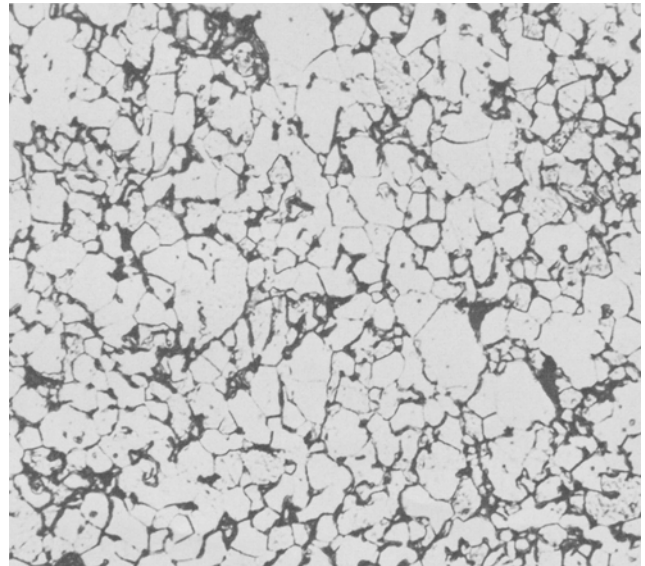


Fig. 2—Microstructure of a specimen hot-pressed from room temperature to $750^\circ C$. (Black areas are pores; density is 5.6 g/cc.) Magnification 500 times.

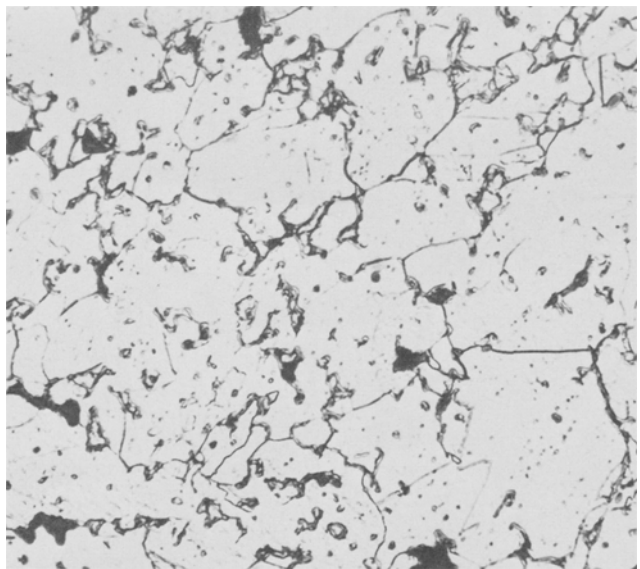


Fig. 3—Microstructure of a specimen hot-pressed from room temperature to $825^\circ C$. (Black areas are pores; density is 5.7 g/cc.) Magnification 500 times.