JOURNAL OF MATERIALS SCIENCE 13 (1978) 421–426

The transfer of titanium and boron to aluminium master alloys via Na_2TiF_6 and $NaBF_4$

J. D. DONALDSON, C. P. SQUIRE
Department of Chemistry, Chelsea College, University of London, Manresa Road, London, UK

F. E. STOKES
Laporte Industries Limited, General Chemicals Division, Moorfield Road, Widnes, UK

Na_2TiF_6 and $NaBF_4$ are studied as alternatives to their potassium equivalents for use in aluminium master alloy manufacture and the transfer efficiencies of B and Ti in various systems reported. The compositions of the slags formed in the reactions are used, along with the phase diagrams for the $KF–AlF_3$ and $NaF–AlF_3$ systems, to discuss the nature of the reactions between the fluorides and aluminium.

1. Introduction

Sodium hexafluorotitanate (Na_2TiF_6), sodium tetrafluoroborate ($NaBF_4$) and their admixtures have been assessed as alternatives to the currently used potassium equivalents for the manufacture of aluminium master alloys containing boron and/or titanium. The sodium salts offer possible advantages over the potassium salts because the difference in the atomic weights of sodium and potassium means that proportionately less sodium salt is needed to introduce the same weight of boron or titanium to the alloy. Also the slag produced would be a sodium cryolite derivative, which might have more commercial value than a potassium cryolite. The sodium salts have the same high wettability with molten aluminium as the potassium salts and similar handling properties in being crystalline, non-hygroscopic and stable.

In a series of laboratory scale (200 g) melts the transfer efficiency of Ti and B (the weight of Ti and/or B found in the melt over the weight contained in the salt, expressed as a percentage) from their complex fluorides into aluminium was determined for the systems $NaBF_4–Al$, $Na_2TiF_6–Al$ and $NaBF_4–Na_2TiF_6–Al$. The results are compared with those obtained from melts made using the potassium salts. A smaller series of larger scale (2 kg) melts was made and the results obtained confirmed the trends indicated by the results from the laboratory scale melts. The quantities of salts added were such as to give a theoretical level of titanium and boron, for both single and double salt systems, of the order of 4% and 1% respectively as these levels are commonly used by alloy manufacturers.

2. Experimental

The laboratory scale melts were made by heating approximately 200 g of high purity (99.98%) aluminium, contained in an unlined crucible, to 800° C in a muffle furnace. The salts or mixtures of salts were then added to the metal surface, as aluminium foil wrapped packets, whilst the melt was still in the furnace. The reaction was allowed to become quiescent after each addition. After the last addition the melt was removed from the furnace, stirred with an alumina rod, and allowed to cool.

The resulting specimens were paraboloid, measuring some 1.5 in. diameter at the widest point and being some 2 in. in length. After removal of slag a centre core sample of the melt was taken by drilling a $\frac{3}{8}$ in. hole through the vertical centre. The turnings so produced were collected and analysed to determine the "average" titanium and/or boron levels. After drilling the samples were cut in half down the vertical centre and one of the faces so produced milled near the top and near the bottom with a $\frac{1}{4}$ in. cutter. The millings were collected and analysed to determine whether the titanium and boron was segregating in the melt.

The large scale melts were made in a similar manner. About 2 kg of high purity aluminium, contained in an unlined plumbago crucible, was heated to 800° C, in an electric furnace, the temperature being monitored by a thermocouple placed in the melt. As before, the salts were added as aluminium foil wrapped packets to the melt surface, and the melt allowed to become quiescent after each salt addition prior to the next. After the last addition the pot was removed from the furnace, the slag scraped off the surface of the melt and the latter then chill-cast into a cylindrical mould to give a product some 8 in. long by 3.5 in. diameter.

Each ingot was cut down the longitudinal centre. In one of the faces so produced, $\frac{1}{2}$ in. wide trenches were cut along the longitudinal edges as well as through the centre along the lateral edges and across the middle of the melt. The millings from the six trenches were retained for analysis.

All milling and drilling was done dry to avoid contamination of the turnings by lubricating fluid. The laboratory scale melts were also sectioned without lubricating fluid, but with the larger scale melts fluid was necessary and care was taken to remove it from the surfaces prior to sampling.

Titanium content was determined using an adaptation of the standard hydrogen peroxide colorimetric technique and boron content by the carminic acid colorimetric method [1]. In both cases the absorbance was measured on a Unicam SP500 spectrometer. The turnings were coned and quartered to appropriate sample size.

Samples of the slag from each melt were analysed by X-ray and chemical methods. X-ray diffraction powder photographs were taken, on a Phillips 11.64 cm diameter camera using Ni filtered Cu$K\alpha$ radiation, and from these the crystalline content of the slag was identified as being either potassium or sodium cryolite derivatives, according to the salt used. Slag samples were subsequently analysed for sodium or potassium, aluminium and fluorine. The alkali metal content was determined (in hydrochloric acid) by atomic absorption spectroscopy using a Perkin–Elmer 103 spectrophotometer. Fluorine content was determined by an adaptation of the Willard and Winter [2] distillation method and aluminium by EDTA titration using the method of Culp [3] on the mother liquor from the fluoride distillation. The mother liquor Al was in an uncomplexed form since the fluorine was removed in the distillation.

3. Results and discussion

3.1. Analysis of melts

In all of the laboratory scale melts the titanium and boron segregated towards the bottom of the melt. It was thus apparent that the rate of cooling was too slow to prevent the denser titanium- and boron-containing phases from settling out under gravity. In the binary systems these phases have been identified as $TiAl_3$ [4–7] and AlB_2 [5–8], and from crystallographic data [9, 10] their calculated densities are 3.35 and 3.18 g cm^{-3} respectively, which are high compared to 2.70 g cm^{-3} for aluminium. In the tertiary system $TiAl_3$ is recognized [4–7] as being present as a discrete phase, but there is some confusion as to whether boron is present as AlB_2, TiB_2 or $(TiAl)B_2$. The density, calculated from crystallographic data [9], of TiB_2 is 4.53 g cm^{-3} and thus all the phases that could be present have a density higher than that of aluminium.

Because of this segregation effect the figures in Table I relating to the transfer efficiency of titanium and boron must be viewed as trends rather than precise figures. For the sodium salt systems the figures represent the average of one analysis from each of seven melts and for the potassium salt systems the average of one analysis from each of three melts.

The segregation effects noticed with the laboratory scale melts did not occur on the larger scale and a homogenous distribution of boron and titanium was found. This is most probably due to good mixing in the melt when it was poured prior to a rapid chill-cast freezing. The exchange efficiencies found for titanium and boron in the

TABLE I Titanium and boron transfer efficiencies for laboratory scale melts.

Melt system	Ti transfer efficiency (%)	B transfer efficiency (%)
$NaBF_4$–Al	–	35
KBF_4–Al	–	65
Na_2TiF_6–Al	85	–
K_2TiF_6–Al	95	–
Na_2TiF_6–$NaBF_4$–Al	95	65
K_2TiF_6–KBF_4–Al	100	100

TABLE II Titanium and boron exchange efficiencies for large scale melts.

Melt system	Ti transfer efficiency (%)	B transfer efficiency (%)
$NaBF_4$–Al	–	15
$NaBF_4$–Na_2TiF_6–Al	80	54
KBF_4–K_2TiF_6–Al	80	89

larger scale melts are given in Table II. Only one melt was made of each system. The figures represent the average of the six analyses on each melt.

3.2. Slag systems

3.2.1. KBF_4–K_2TiF_6–Al

X-ray diffraction powder photographs of the slag from this system show only $KAlF_4$ and K_3AlF_6 to be present with the ratio somewhere in the region of 10:1 in favour of $KAlF_4$. This ratio is confirmed by the chemical analysis of slag samples from this system which yielded a potassium content of 30.0%, an aluminium content of 18.6% and a fluorine content of 51.5%. These figures are consistent, within the limits of the analytical methods, with the composition of a 10:1 mixture of $KAlF_4$ and K_3AlF_6; potassium 30.28%, aluminium 17.68% and fluorine 52.04%.

Consideration of the phase diagram [11] for the KF–AlF_3 system, Fig. 1, shows that for a ratio of $KAlF_4$:K_3AlF_6 of 10:1 – corresponding to 54 mol % KF and 46 mol % AlF_3 – the melting point is just under 600° C and this is the melting point found for the slag. A powder photograph of the slag at room temperature would be expected to reveal a mixture of K_3AlF_6 and cubic $KAlF_4$. In fact tetragonal $KAlF_4$ is identified, together with K_3AlF_6. It was found, from the large melt, that the percentage transfer of Ti was about 80% and of B about 90%. Assuming that the mole ratio of K_2TiF_6:KBF_4 is about 1:1, giving a ratio of 4.2:1 by weight of Ti to B, and that the loss of B and Ti occurs as BF_3 and TiF_4 respectively, then the melt reactions may be represented by:

$$9KBF_4 + 9Al \longrightarrow 9(KF \cdot AlF_3) + 9B$$
$$KBF_4 \longrightarrow KF + BF_3$$

and

$$9K_2TiF_6 + 12Al \longrightarrow 9(KF \cdot AlF_3) + 3(3KF \cdot AlF_3) + 9Ti$$
$$2K_2TiF_6 \longrightarrow 4KF + 2TiF_4.$$

The ratio of KF:AlF_3 in the slag is 32:21 but a mixture of $KAlF_4$ and K_3AlF_6 gives a 13:11 ratio of KF:AlF_3. The molten slag, however, does decompose with some loss of AlF_3 and this process would bring the ratio nearer to that observed. Moreover, it is not unreasonable to assume that some reaction occurs between the components of the slag, i.e. KF and AlF_3, and molten aluminium. The study of such a reaction has not yet been reported in the literature but that of the corresponding Na system has [12]. Assuming that the KF–AlF_3 system reacts with the aluminium in the same manner as the NaF – AlF_3 system we have:

A $\quad AlF_3(\text{melt}) + 2Al(l) \longrightarrow 3AlF(g)$

B $\quad 6KF(\text{melt}) + Al(l) \longrightarrow 3K_2F(g) + AlF_3\ (\text{melt}).$

The authors [12] found that, for the sodium

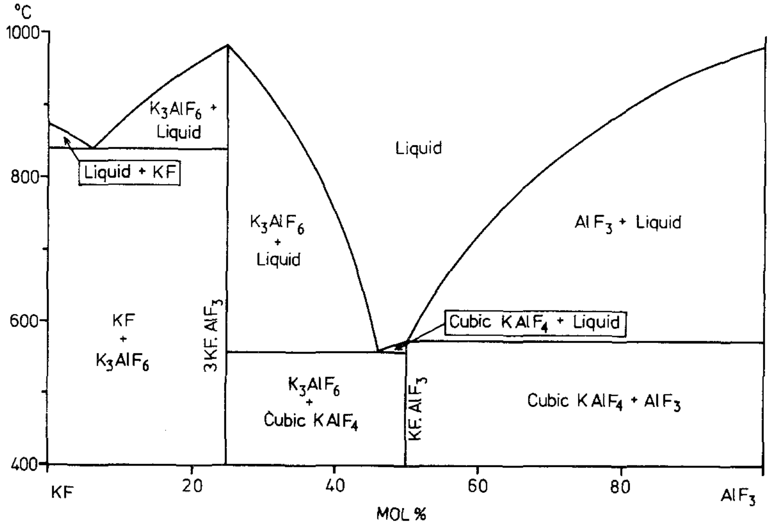

Figure 1 Phase diagram for the KF–AlF_3 system.

system, these reactions occurred in the approximate ratio of 1:2 for A:B. If this is followed for the potassium system then the net result is that for the loss of 12 moles of KF from the slag 1 mole of AlF_3 is formed. It would thus only require a small percentage of the slag to undergo reaction with the aluminium to result in a final ratio of KF:AlF_3 of 13:11.

3.2.2. KBF_4–Al

The powder photographs of the slag from this system show that it consists of $KAlF_4$ together with trace amounts of K_3AlF_6. The chemical analysis of the slag (K, 26.5%; Al, 20.4% and F, 53.3%), are consistent, within the limits of the analytical methods, with the composition of $KAlF_4$ (K, 27.52%; A, 19.00% and F, 53.48%). The effect of a trace amount of K_3AlF_6 would not noticeably affect the analytical figures.

Examination of the phase diagram, Fig. 1, for the KF–AlF_3 system shows that this slag system is represented by a region a little to the left of the 50% mole ratio line (KF · AlF_3).

From the series of small scale melts, it was found that the transfer efficiency of boron was about 65% and assuming that the loss of boron occurs as BF_3, then the melt reactions may be represented by:

$$2KBF_4 + 2Al \longrightarrow 2(KF \cdot AlF_3) + 2B$$
$$KBF_4 \longrightarrow KF + BF_3$$

The ratio of KF:AlF_3 is 3:2 and for pure $KAlF_4$ this ratio is 1:1. With the slag containing a trace amount of K_3AlF_6 the KF:AlF_3 ratio would be slightly in favour of KF. Assuming some loss of AlF_3 from the slag by volatilization or that the slag reacts with the aluminium in the same way as described for the KBF_4–K_2TiF_6–Al system then the final ratio of KF:AlF_3 predicted would be closer to the observed value of 3:2.

3.2.3. K_2TiF_6–Al

The powder photographs of the slag from this system show that it consists of $KAlF_4$ and K_3AlF_6 in an estimated ratio of 3:1. No chemical analyses were performed on the slag since the system was examined only on the small scale and the amount of uncontaminated slag produced was very small.

Examination of the phase diagram, Fig. 1, shows that this slag system must be represented by a region to the right of the 25 mol % AlF_3 line (3KF · AlF_3). It cannot be to the left of this line otherwise the powder photograph would reveal the presence of KF. If the ratio of $KAlF_4$:K_3AlF_6 is taken as 3:1 then this region will be near to a line going through 40 mol % AlF_3.

From the series of small scale melts it was found that the transfer efficiency of titanium is about 95%. Assuming that loss of titanium occurs as TiF_4 then the melt reactions may be represented by:

$$18K_2TiF_6 + 24Al \longrightarrow 6(3KF \cdot AlF_3) + 18(KF \cdot AlF_3) + 18Ti$$
$$K_2TiF_6 \longrightarrow 2KF + TiF_4.$$

The ratio of KF:AlF_3 is 38:24 or 1.6:1 and for a 3:1 mixture of $KAlF_4$ and K_3AlF_6 this ratio is 1.5:1. As in the two previous systems it would seem that some loss of AlF_3 or slag reaction with the aluminium occurs.

3.2.4. $NaBF_4$–Na_2TiF_6–Al

Powder photographs of the slag from this system show only $Na_5Al_3F_{14}$ to be present and this is confirmed by the chemical analyses which show the composition to be Na, 24.3%; F, 57.1%; and Al, 17.7%. The theoretical composition of $Na_5Al_3F_{14}$ is Na, 24.88%; F, 57.59%; and Al, 17.53%.

Consideration of the phase diagram [15] for the NaF–AlF_3 system, Fig. 2, shows that this slag must be represented by a region very close to the 55 mol % AlF_3 line (5NaF · 3AlF_3) since appreciable deviation from this line would result in the presence of Na_3AlF_6 or AlF_3 which would be revealed on the powder photographs.

From the large scale melts it was found that the average percentage transfer is about 80% for Ti and about 54% for B. Making the same assumptions as for the potassium system, i.e. that the mole ratio of $NaBF_4$:Na_2TiF_6 is about 1:1 and that the loss of boron and titanium occurs as BF_3 and TiF_4 respectively, then the melt reactions may be represented by:

$$6NaBF_4 + 6Al \longrightarrow 6(NaF \cdot AlF_3) + 6B$$
$$5NaBF_4 \longrightarrow 5NaF + 5BF_3$$

and

$$9Na_2TiF_6 + 12Al \longrightarrow 9(NaF \cdot AlF_3) + 9Ti$$
$$2Na_2TiF_6 \longrightarrow 4NaF + 2TiF_4.$$

The ratio of NaF:AlF_3 is 33:18 but for $Na_5Al_3F_{14}$ the ratio is 5:3. This is indicative of some loss of AlF_3 or reaction between slag and aluminium.

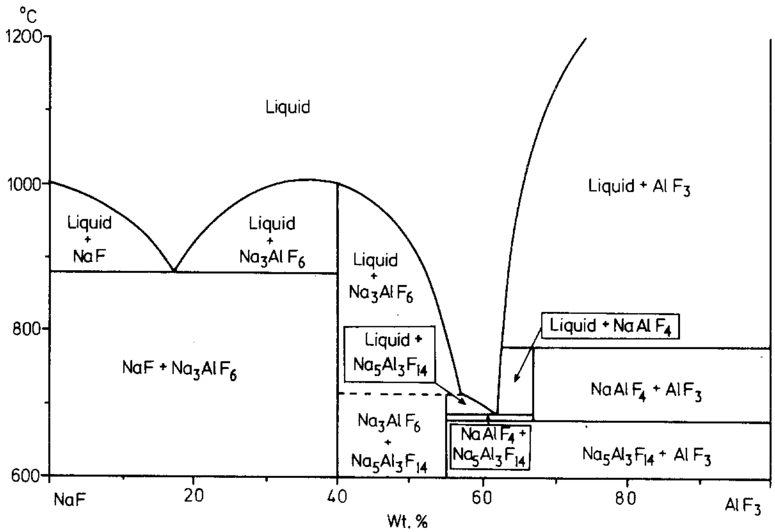

Figure 2 Phase diagram for the $NaF-AlF_3$ system.

Snow and Welch [12], who studied the reaction of aluminium with molten cryolite, have proposed:

A $AlF_3(melt) + 2Al(l) \longrightarrow 3AlF(g)$

B $6NaF(melt) + Al(l) \longrightarrow 3Na_2F(g) + AlF_3$ (melt),

with the reactions occurring in the approximate ratio of 1:2 for A:B. The net result is that for the loss of 12 moles of NaF from the slag 1 mole of AlF_3 is formed.

3.2.5. $NaBF_4$–Al

The powder photographs of the slag from this system show the presence of $Na_5Al_3F_{14}$ and Na_3AlF_6 in an estimated ratio of 1:1. No chemical analyses were performed on the slag from this system since it was not possible to obtain an uncontaminated sample of adequate size from either the large scale or small scale melts.

Examination of the phase diagram, Fig. 2, shows that this slag system must be formed in the region representing the co-existence of $Na_5Al_3F_{14}$ and Na_3AlF_6. If the ratio of these two compounds is 1:1 then this region will be near to the 50 wt% AlF_3.

From the large scale melt the percentage transfer for boron is found to be about 15%. Assuming that the loss of boron occurs as BF_3 then the melt reactions may be represented by:

$$NaBF_4 + Al \longrightarrow NaF \cdot AlF_3 + B$$
$$6NaBF_4 \longrightarrow 6NaF + 6BF_3.$$

The ratio of NaF:AlF_3 is 7:1 whereas in a mixture of 1:1 $Na_5Al_3F_{14}$ and Na_3AlF_6 it is 2:1. It is thus apparent that the loss of volatile AlF_3 and or the reaction between slag and aluminium must be considerable to result in a final ratio of 2:1 of NaF:AlF_3.

3.2.6. Na_2TiF_6–Al

The powder photographs of the slag from this system show the presence of only $Na_5Al_3F_{14}$. No chemical analyses were performed on the slag since the system was examined only on the small scale and the amount of uncontaminated slag produced was inadequate.

Examination of the phase diagram, Fig. 2, shows that this slag system, like the $NaBF_4$–Na_2TiF_6–Al slag system, must be represented by a region very close to the 55 wt% AlF_3 line since any appreciable deviation from this line would result in the presence of Na_3AlF_6 or AlF_3 which would be revealed on the powder photographs.

From the series of small scale melts it was found that the percentage transfer of titanium is about 85%. Assuming that the loss of Ti occurs as TiF_4 then the melt reactions may be represented by:

$$9Na_2TiF_6 + 12Al \longrightarrow 9(NaF \cdot AlF_3) + 3(3NaF \cdot AlF_3) + 9Ti$$
$$2Na_2TiF_6 \longrightarrow 4NaF + 2TiF_4.$$

The ratio of NaF:AlF_3 is 11:6 whereas in $Na_5Al_3F_{14}$ it is 5:3. Thus a comparatively small loss of AlF_3 from the system is required to give an experimental ratio of 10:6.

Conclusions

In all of the melt systems investigated sodium fluorotitanate, Na_2TiF_6, is a viable alternative to its potassium counterpart, K_2TiF_6. Sodium fluoroborate, $NaBF_4$, is considerably less efficient than potassium fluoroborate, KBF_4, in the single salt systems and its use in such systems does not seem advantageous. In the double salt systems, where the boron transfer is increased due to its combination with both titanium and aluminium, the level of transfer efficiency for $NaBF_4$ is substantially increased, yet still remains appreciably below that for KBF_4. The use of the mixed Na_2TiF_2–$NaBF_4$ might, however, still be a viable economic proposition particularly if its slag product, a sodium cryolite derivative, has a resale value without the need for prior processing.

Acknowledgements

We are grateful to Laporte Industries Limited for the supply of materials used on this work and for a maintenance grant to CPS.

References

1. F. D. SNELL and C. L. HILTON, "Encyclopaedia of Industrial Chemical Analysis", Vol. 5 (Interscience, New York, 1966), p. 122.
2. H. H. WILLARD and O. B. WINTER, *Ind. Eng. Chem., Anal. Ed.* 5 (1933) 7.
3. S. L. CULP, *Chemist Analyst* **56** (1967) 29.
4. L. BACKERUD, *Jernknot. Ann.* **155** (1971) 422.
5. I. MAXWELL and A. HELLAWELL, *Met. Trans.* 3 (1972) 1487.
6. J. A. MARCANTONIO and L. F. MONDOLFO, *ibid* 2 (1971) 465.
7. I. G. DAVIES, J. M. DENNIS and A. HELLAWELL, *ibid* 1 (1970) 275.
8. K. H. WIEDEMANN, *Metallwissenschaft und Technik* 15 (1961) 221.
9. U. DEUTHER, *Freiberger Forschunschaft* **B112** (1966) 201.
10. E. J. FELTEN, *J. Am. Chem. Soc.* 78 (1956) 5977.
11. B. PHILLIPS, C.M. WARSHAW and I. MOCKRIN, *ibid* 49 (1966) 633.
12. R. J. SNOW and B. J. WELCH, *J. Electrochem. Soc.* **115** (1968) 1170.
13. G. MESROBIAN, Thesis, Lyon University, No. 704 (1971).

Received 11 May and accepted 17 June 1977.