CCLXXIV.—*Intermetallic Actions. The System Aluminium–Arsenic.*

By QASIM ALI MANSURI.

THE action of arsenic on aluminium appears to be mentioned only in *Compt. rend.*, 1900, **130**, 1391, where it is stated that arsenic combines with aluminium at high temperatures, but nothing is recorded about the exact nature of the compounds. To throw further light on this problem, it was therefore considered necessary to make a complete investigation of this system. Aluminium of 99·6 per cent. purity, as determined by the hydrogen method, and resublimed arsenic were used.

EXPERIMENTAL.

Preliminary Work.—The chief experimental difficulty met with was due to the volatile nature of arsenic. Attempts were therefore made to prepare the alloys in sealed glass tubes, under a seal of molten potassium sulphate (in which the crucible containing a mixture of aluminium and arsenic was dipped, and the sulphate was allowed to freeze on top of it to form a seal), and by blowing or passing arsenic vapour through or over molten aluminium heated at a high temperature.

It was noticed that no action takes place between arsenic and aluminium up to about 600°. Even at about 750° the metals do not react with each other if the pressure of arsenic vapour is too high (about one atmosphere). At low pressure and high temperature, probably yellow arsenic is formed, and it is this which reacts with aluminium. At about 800° and at low pressure, this action is more marked, the yellow arsenic forming a brown compound, Al_3As_2, with aluminium which does not melt at that temperature nor dissolve in molten aluminium. At atmospheric pressure, this action takes place at about 900°, with the same result.

The view that it is yellow arsenic which reacts chemically with aluminium, and not the black variety, is supported by the fact that whilst, in the favourable circumstances mentioned above, no black arsenic was left, there was always a little yellow coating in the upper part of the tubes. Again, the product of the dissociation of the compound is yellow arsenic. The inner surfaces of the stoppered bottles in which the alloys were stored were always found covered with a deposit of yellow arsenic, which turned to the brown variety after exposure to light for some time. The brown compound is stable at high temperatures, for when freshly formed it does not give off arsenic vapour even at 1000°, but when it is cooled and kept for some time and heated again, it begins to evolve arsenic vapour at about 500°. Also, when freshly prepared, the compound dissolves almost completely in dilute hydrochloric acid, but after keeping for some time at room temperature, it becomes darker, and on treatment with dilute hydrochloric acid there is always a black residue of almost pure arsenic. These facts show that the compound is stable at high temperatures, but breaks up at low temperatures.

Systematic Investigation of the System.—After the preliminary observations, mentioned above, for the determination of the *liquidus* at the aluminium end of the equilibrium diagram, it was necessary to heat the brown compound isolated, with aluminium at a very high temperature out of contact with air, as at low temperatures the solid compound separated out from molten aluminium almost completely. It is possible that at very high temperatures the compound may melt and may then be miscible with molten aluminium, but this suggestion could not be tested owing to lack of suitable heating apparatus. However, to throw some light on this point, work was started in sealed hard-glass tubes.

Thermal Analysis.—As hard-glass tubes become porous to arsenic vapour at about 650°, a platinum couple could not be used. After testing several base-metal couples, the author found a couple made of two chrome–nickel wires of different compositions most suitable for working with arsenic alloys, as it was not easily contaminated with arsenic and could be used satisfactorily up to about 1100°. The two wires (No. 25 *B.S.G.*), containing different percentages of chromium, formed a couple about twice as sensitive as a platinum–rhodium couple. Two chrome–nickels differing even more in composition should form a still more sensitive couple.

Close contact of the hot junction of the couple with the outside of the glass tubes in which the alloys were prepared, was made by means of purimachos cement. Used in this way, the couple was quite sensitive, and all thermal changes in the alloys could be easily detected.

As the alloys were heated by means of a gas tube-furnace, the heating could not be made very regular and therefore the heating curves of the alloys could not be obtained.

The cooling curves were obtained by means of a water-drop curve tracer. In this arrangement, a suspended mirror-galvanometer throws a spot of light on a glass screen, which is moved vertically by means of a simple water-dropping arrangement. The spot of light moves horizontally as the temperature changes, and thus a curve is traced, by means of a soft pencil, on a paper mounted on the glass screen. A millivoltmeter was arranged in series with the galvanometer, so that when a break occurred on a curve on the tracer, a reading corresponding with it could be taken on the millivoltmeter. The couple was calibrated by means of tin, lead, zinc, aluminium, commercial antimony, m. p. 622°, levol, and copper.

Cooling curves of the alloys were traced from about 750°. Alloys containing up to 5 per cent. of arsenic melted satisfactorily, but when 7 per cent. of arsenic had been added, the pieces of aluminium did not fuse together, but remained separate, and were coated with the brown compound; nevertheless, a thermal arrest occurred at the freezing point of aluminium. It seems that in these alloys the brown compound forms a strong and hard envelope round the aluminium which holds molten aluminium within it and does not allow it to run together even although the tubes are well shaken.

In alloys containing up to 10 per cent. of arsenic no thermal arrest could be detected at the higher temperatures. The only thermal arrest observed was at the freezing point of aluminium and therefore the determination of the *liquidus* had to be postponed.

In order to find the composition of the compound thermally, 12 grams of aluminium turnings and 1·5 grams of arsenic were heated at 750° in a sealed, evacuated (about 15 mm. pressure) hard-glass tube. (It was noticed in preliminary work that in a glass tube about 6 inches in length and half an inch in diameter about 2 grams only of arsenic could be converted at one time to yellow arsenic, under the experimental conditions, and made to combine with aluminium.) The aluminium turnings, thus coated with the compound, were again mixed with 1·5 grams of arsenic and again heated in another glass tube to the same temperature. In this way, the compound could be gradually prepared. Each time a cooling curve was also taken. The only thermal arrest observed in all these cases was at the freezing point of aluminium, and this became smaller and smaller, in accordance with and proportional to the eutectic times law, until, with the alloy containing about 64 per cent. of arsenic, it could no longer be detected.

An attempt was next made to prepare alloys containing higher percentages of arsenic in the same way by the gradual addition of arsenic to the compound, but without success; arsenic separated in the upper part of the glass tube, and the brown compound remained in the lower part. This result showed that the compound did not alloy even with arsenic and that no other compound of a higher composition was formed. Had the brown compound alloyed with arsenic and formed a eutectic, a thermal arrest should have been observed at some temperature up to 750°.

When aluminium turnings were heated at about 900° with arsenic vapour in an atmosphere of nitrogen, an alloy containing at most about 69 per cent. of arsenic was formed. This alloy also did not melt and appeared similar to the brown compound prepared by the other methods.

Chemical Analysis.—The arsenic in alloys rich in aluminium was estimated iodometrically by Hefti's method ("Analytical Chemistry," Treadwell and Hall, 1905, II, p. 214).

The solution of aluminium chloride having been filtered to remove the small residue of silica, the aluminium in the filtrate was estimated gravimetrically as Al_2O_3.

In the alloys rich in arsenic, it seems that the compound breaks up on keeping at low temperatures, and the black arsenic formed is not attacked by dilute hydrochloric acid. The arsenic in these alloys was therefore first converted to arsenic acid and then estimated by Williamson's method.

For the estimation of aluminium, 100 c.c. of the solution remaining after the estimation of arsenic were filtered, so boiled with concentrated hydrochloric acid and potassium bromide as to ensure removal of arsenic, and the aluminium was then estimated gravimetrically as above.

These methods gave good results, as is shown by the duplicates recorded below :

(*a*) Filings obtained from the outer surface of the alloy containing 5 per cent. of arsenic : Found, Al = 91·74; As = 7·85; SiO_2 = 0·27 per cent.

(*b*) Filings obtained from the same alloy after filing off about 1 mm. of the outer surface : Found, Al = 99·29; As = 0·31; SiO_2 = 0·22 per cent.

(*c*) Alloy containing 7·5 per cent. of arsenic, after filing off the outer surface : Found, Al = 98·95; As = 0·58; SiO_2 = 0·19 per cent.

(*d*) Alloy heated with the compound in the oxy-hydrogen flame; after filing off the outer surface : Found, Al = 98·01; As = 1·11; SiO_2 = 0·29 per cent.

(*e*) The compound Al_3As_2 as prepared in glass tubes, after powdering and passing through a 120-mesh sieve : Found, Al = 34·81, 34·93; As = 64·57, 64·39; SiO_2 = 1·2, 0·9 (theoretically, As = 64·88 per cent.).

(*f*) The same alloy, without powdering : Found, Al = 35·00; As = 63·64; SiO_2 = 1·03 per cent.

(*g*) The compound Al_3As_2 as prepared by submitting aluminium filings to the action of arsenic vapour in an atmosphere of nitrogen at about 900° : Found, Al = 31·21, 30·74; As = 69·00, 69·17; SiO_2 = 0·23, 0·21 per cent.

Micrographic Analysis.—As the compound Al_3As_2 did not melt at the temperature of the experiments, it was simply mixed with aluminium in all the alloys and was in an amorphous, powdery condition. Such heterogeneous alloys were very difficult to polish and even on polishing they did not show any uniform and regular structure except where the compound had been acted upon by moisture and decomposed, making a few blow-holes. No successful photomicrographs of the alloys could therefore be taken.

Conclusions.

1. Aluminium and arsenic combine to form the compound Al_3As_2—as shown by thermal and chemical analysis. The action commences at about 750° and a low pressure, where yellow arsenic is formed and acts upon the aluminium.

2. The compound Al_3As_2 is stable at high temperatures, but begins to break up at lower temperatures. When the compound breaks up, yellow arsenic is first formed.

3. The compound Al_3As_2 is a brown, amorphous powder which looks like iron rust and does not melt up to the temperature of fusion of silica (about 1600°).

4. It is very reactive and evolves arsenic trihydride freely when exposed to moisture. For this reason, the alloys were always stored in stoppered bottles, and all polishing, etc., was done in fume chambers.

5. When heated in air, the compound oxidises to alumina and arsenious oxide.

6. The solid compound does not seem to dissolve in molten aluminium to any appreciable extent, but separates from it almost completely at its freezing point, nor does it alloy with arsenic to form a eutectic. The equilibrium diagram of the system is probably like that of the system aluminium–antimony investigated by Tammann (*Z. anorg. Chem.*, 1906, **48**, 53). It attains an abnormal or a flat (showing immiscibility) maximum at very high temperature and has for its *solidus* the horizontals corresponding to the melting points of aluminium and arsenic, respectively.

7. It is interesting to note that most of the compounds of arsenic with other metals are also of the type M_3As_2, as, for example, Cd_3As_2 (*Z. Metall.*, 1913, **4**, 228), Hg_3As_2 (*Arch. Pharm.*, 1899, **237**, 126), Sn_3As_2 (*Gazzetta*, 1912, **42**, I, 274; *Atti R. Accad. Lincei*, 1911, [vi], **20**, 593), Fe_3As_2 (*Metallurgie*, 1907, **4**, 131), Zn_3As_2 (*Z. anorg. Chem.*, 1921, **118**, 264), Mn_3As_2 (*Metallurgie*, 1911, **8**, 727), Co_3As_2 (*ibid.*, 1908, **5**, 150), Ni_3As_2 (*ibid.*, 1907, **4**, 207), and Mg_3As_2 (compound obtained by Parkinson in 1867).

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Goldsmiths' Research Laboratory,
The University, Cambridge.

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