253. *Liquid Metals. Part XI.*[1] *The Wetting of Chromium, Molybdenum, and Tungsten by Liquid Sodium.*

By C. C. Addison and E. Iberson.

Receding contact angles for liquid sodium on molybdenum and tungsten surfaces in an argon atmosphere have been studied as a function of time and temperature. Each metal shows a critical wetting temperature of 160°, below which contact angles remain above 90°. Above 160° complete wetting occurs, and the rate of wetting increases in a regular manner with increasing temperature. Qualitative observations at a chromium surface indicate similar behaviour. The results are consistent with a mechanism in which the surface film of oxide (Cr_2O_3, MoO_2, or WO_3) is reduced to the metal by liquid sodium.

In Part V[2] experiments were described in which plates of iron, cobalt, or nickel were partly immersed in liquid sodium, within an argon atmosphere. The metal plates were first abraded to a high gloss in air, and the variations of contact angle with time and temperature were interpreted satisfactorily on the basis of two assumptions: (*a*) that when no surface film was present, pure sodium would always spread, ultimately, to give a zero contact angle, θ, on a pure solid metal; and (*b*) that the variations in θ resulted directly from the rate and the nature of the chemical reaction between liquid sodium and the oxide film. The oxides present as films on these metals (Fe_2O_3 and Fe_3O_4, Co_3O_4 and CoO, and NiO) are all reduced to the metal by liquid sodium at the temperatures at which complete wetting occurs. Furthermore, each metal has a critical wetting temperature (140, 190, and 195°, respectively) below which no wetting occurs, and below which it is believed that reduction of the oxide film to metal cannot occur.

Similar experiments are now described for molybdenum and tungsten; the results support the interpretations of wetting phenomena advanced for iron, cobalt, and nickel.

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[1] Part X, Addison, Pulham, and Roy, *J.*, **1965**, **116**.

[2] Addison, Iberson, and Manning, *J.*, **1962**, **2699**.

Chromium metal was not available in the form of thin plates, and only qualitative observations could be made.

EXPERIMENTAL

Sodium and argon were purified as already described.[2] The preparation of the molybdenum and tungsten plates (*ca.* 4 × 2 × 0·05 cm.), and measurement of contact angles by the vertical-plate method, were carried out as described in Part V.[2] The plates were kindly supplied by A.E.R.E. Harwell. Molybdenum was 99·98% pure (main impurity: Fe <0·01%). Tungsten was 99·90% pure (main impurity: Fe, 0·02—0·05%).

After each experiment the metal plates were washed free from sodium, dried, and weighed. In no case was any weight change observed. The metal surfaces showed no signs of attack on microscopic examination, and qualitative analysis of the sodium gave no positive test for molybdenum or tungsten.

RESULTS AND DISCUSSION

The variation in receding contact angle with time at various temperatures is shown for molybdenum in Fig. 1, and for tungsten in Fig. 2. The behaviour of the two metals is very similar. In each case the contact angle reached zero at all temperatures above 160°, at a rate which increased with increasing temperature. Wetting occurs immediately at temperatures above 300°. There is a critical change in wetting behaviour at 160°; below 160°, the contact angle remained above 90°. This type of wetting behaviour closely resembles that found for iron, cobalt, and nickel, and we consider it to be characteristic of oxide films which are reduced to the metal by liquid sodium at temperatures above the critical temperature.

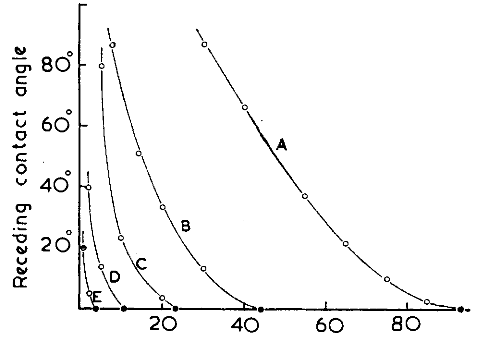

FIG. 1.

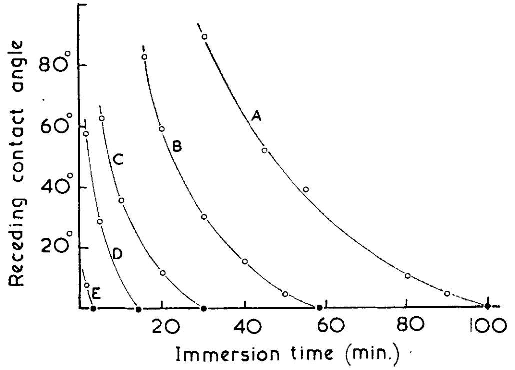

FIG. 2.

FIG. 1. Receding contact angles for liquid sodium at a molybdenum surface (A, 160°; B, 180°; C, 200°; D, 230°; E, 270°).

FIG. 2. Receding contact angles for liquid sodium at a tungsten surface (A, 160°; B, 180°; C, 200°; D, 230°; E, 280°).

A film of the oxide MoO_2 has been identified on the surface of molybdenum metal at temperatures within the range obtaining the present work.[3-5] The presence of MoO_3 is unlikely, since it is formed together with MoO_2 only in films of considerable thickness.[6] On the basis of the $-\Delta G_{298}$ values (MoO_2, 60·5; Na_2O, 89·9 kcal./mole, relative to 1 g.-atom of oxygen [7]) the reduction of the bulk oxide to metal is acceptable, and separate experiments in this laboratory [8] have confirmed that the reaction products do indeed contain

[3] Gulbransen and Hickman, *Trans. Amer. Inst. Min. Met. Engnrs*, 1947, **171**, 344.

[4] Gorbounova and Arslambékov, *J. Chim. phys.*, 1956, **53**, 871.

[5] Zappfe, Warden, and Landgraf, " Metals Tech.," 1948, Vol. 15, Tech. Publn. 2421.

[6] Gulbransen and Wysong, *Trans. Amer. Inst. Min. Met. Engnrs*, 1948, **175**, 628.

[7] Coughlin, U.S. Bureau of Mines, 1954, Bulletin 542.

[8] Addison, Barker, and Pulham, unpublished results.

molybdenum metal. It is probable that reduction of the surface oxide to metal also occurs; the heat of chemisorption of oxygen on molybdenum is of the order of 75 kcal./mole [9] compared with 66·3 kcal./mole for the heat of formation of the bulk oxide.[7] Similar considerations apply to tungsten. In this case the oxide film corresponds to the composition WO_3.[4,6] The values of $-\Delta G_{298}$, $-\Delta H$, and the heat of chemisorption are 60·8,[7] 66·9,[7] and 67 [10] kcal./mole (relative to 1 g.-atom of oxygen), respectively, and the products of the reaction of liquid sodium with tungsten trioxide have been found to contain tungsten metal.[8]

The line relating log T_w (where T_w is the time for complete wetting) and the inverse of T°K is sensitive to any changes in the type of oxide film which may occur as the temperature varies. Thus a straight line is obtained for nickel, since no change occurs in the surface oxide, NiO, whereas pronounced breaks occur in the lines for iron and cobalt at temperatures which correspond to changes in the composition of the oxide film.[2] This relationship is plotted in Fig. 3 for molybdenum and tungsten; the broken line represents results for nickel and is superimposed for comparison. The points for molybdenum lie almost exactly on a straight line. This indicates that the same reaction is responsible for wetting throughout, and that the nature of the oxide film (MoO_2) does not change with temperature within this range. Direct examination of the film has led to the same conclusion.[3-6] The results for tungsten lie on a gentle curve. However, there is no sign of any break in this curve, and these results are again considered to indicate the same wetting process, and the same surface oxide, throughout this temperature range.

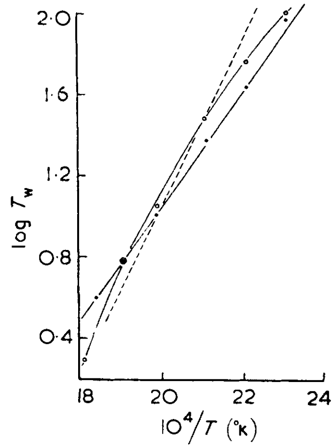

FIG. 3. Influence of temperature on the time for complete wetting (T_w, min.) by liquid sodium.

● ●, molybdenum; o o, tungsten; — — —, nickel.

The Wetting of Chromium. Since thin plates could not be fabricated from pure chromium metal, mild-steel plates were covered with a layer (0·012 cm.) of chromium metal by electrodeposition. Metal surfaces prepared in this way carry a film of the compound constituting the electrolyte; this was removed by abrasion in air in order that the chromium surface should carry an oxide film and be comparable with the molybdenum and tungsten surfaces. This process caused irregularities at the edge of the plates, and uneven wetting at this position. Accurate values for contact angle could not therefore be obtained, but experiments with these plates (by D. H. Kerridge) showed that the wetting behaviour of a chromium surface was similar to that described above. The critical wetting temperature appears to be somewhat higher than for molybdenum and tungsten, and the rate of wetting then increases with increasing temperature. After wetting, the chromium surface showed no sign of attack, and no chromium was detectable in the sodium. This behaviour is

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[9] Hayward, "Chemisorption," Butterworths, London, 1957, p. 101.
[10] Roberts, *Proc. Roy. Soc.*, 1935, *A*, **152**, 445.

consistent with the presence on the metal surface of the oxide Cr_2O_3,[11] for which $-\Delta G_{298}$ is 84·4 kcal./mole, relative to 1 g.-atom of oxygen.[12] Chromium metal has also been identified amongst the products of reaction of liquid sodium with the oxide Cr_2O_3.[8]

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[11] Gulbransen and Andrew, *J. Elektrochem. Soc.*, 1952, **99**, 402.
[12] Kubaschewski, *Z. Elektrochem.*, 1938, **44**, 152.