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INTERFACIAL REACTIONS AND WETTING BEHAVIOR
OF GLASS-IRON SYSTEMS

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ABSTRACT

Interfacial reactions and enhanced wetting or spreading of $\text{Na}_{2-x}\text{FeSi}_2\text{O}_{5+x}$ and $\text{Na}_{2-2x}\text{FeSi}_2\text{O}_5$ glasses on substrate of high purity iron (Marz) and commercial iron (Armco) were observed at 1000°C at low partial pressures of O_2 and Na vapors. Reactivity increased with increase of the oxygen/silicon ratio in the glass and purity of iron, and with decrease of the gas pressures.

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I. Introduction

Glass to metal maximum adherence has been shown to occur when the glass at the interface is saturated with the oxide of the lowest valence cation of the substrate metal.¹⁻⁸ Such equilibrium compositions at the interface lead to a balance of attractive forces exerted by the glass and metal on oxygen and metal ions in the interfacial region. A continuous transition zone is thus established between the metallic bonding in the substrate and the ionic-covalent bonding in the glass, which represents primarily a chemical rather than van der Waals type of bonding.

Saturation with the substrate metal oxide and the associated chemical bonding at the interface is lost by chemical interdiffusion into the bulk glass if the glass is not in equilibrium with the interfacial zone. Chemical reactions can then occur at the interface as the system attempts to maintain saturation or achieve saturation if it did not exist.^{9,10} The present investigation was undertaken to study the nature of possible reactions and the conditions under which they occur. Sessile drop experiments provided a convenient configuration for reaction studies since specimens could be cross-sectioned for examination of the interface. Information on wetting behavior and interfacial tensions was also provided. The experimental systems were iron substrates and sodium silicate glasses containing iron oxide in atmospheres of low partial pressure of oxygen.

II. Experimental

(1) Materials

The glasses prepared for this study are indicated on the FeO-Na₂O-SiO₂ ternary system shown in Fig. 1.* One composition series ranged from NS₂(Na₂Si₂O₅) along the NS₂-FeO join up to saturation with FeO at 1000°C (0, 2.9, 6.0, 9.1, 16.1, 28.0 and 44.5 w/o FeO). A second series was formed by increasing amounts of FeO (0, 7.2, 11.3, 14.5, 17.3 and 19.2 w/o) replacing Na₂O up to saturation with respect to SiO₂ which lie on a line from NS₂ and approximately parallel to the Na₂O-FeO join up to the 1000°C isotherm. The former series thus has an increasing O/Si ratio and the latter, a constant O/Si ratio of 2.5.

All of the glasses containing iron oxide were prepared from NS₂ powder (Philadelphia Quartz Co.) and Fe, Fe₂O₃, and SiO₂ powders (Baker's reagent grade). These were dry mixed, packed into iron crucibles, and heated in a Kanthal wire wound mullite tube resistance furnace for 24 h at 1000°C with a flowing mixture of 1 part CO and 1 part CO₂ which maintained an oxygen pressure of 5×10^{-15} atm. Liquid glasses resulted containing FeO which was formed by reaction (9). The glass colors were bluish and greenish-blue, indicating that some ferric ions were still present in the latter glasses. NS₂ glass specimen disks were cut from glass rods (Corning Glass Works).

Two sources of iron specimens were used: Marz grade (Materials Research Corp., Orangeburg, N.Y.) in 1/2 in. squares cut from 20 mil thick foils, and Armco (American Rolling Mills Co.) in 1/8 in. thick

*Redrawn by Robert B. Langston, this laboratory, based on data of Carter and Ibrahim^{11a} and Schairer, et al.^{16b}

disks cut from 5/8 in. diameter rods. The principal impurities in Marz iron were: 8.0 ppm C, 7.2 ppm O, 7.0 ppm N, 8 ppm Mg. A typical analysis of Armco iron is 0.015% C, 0.0285% Mn, 0.995% P, 0.025% S, 0.003% Si; precipitates of wüstite (FeO) are also present.

(2) Experimental Conditions

Four experimental arrangements with 3 furnaces provided different atmospheric test conditions at the experimental temperature of 1000°C. Furnace I* consisted of a resistance heated graphite tube surrounded by a vacuum chamber, which has already been described.¹² A specimen was placed on an alumina "dee" tube which was inserted into the graphite tube. Temperatures were monitored and controlled by means of a Pt-Pt 10% Rh thermocouple located next to the specimen. Contact angle measurements were made with a telescope fitted with a protractor with movable cross hairs by sighting along the alumina tube through fused silica windows incorporated into the vacuum chamber. Total pressures of 10^{-8} to 10^{-9} atm were attained at the test temperature. The low heat capacity of the furnace and high current flow through the graphite heating element made use of the zirconia oxygen probe[†] inaccurate. The P_{O_2} in this set up, taking into account leakages, was estimated to be less than about 10^{-20} atm due to the presence of carbon and to be proportional to the total

*Furnaces will be referred to in the text by the designated numeral.

†The probe consists of a zirconia tube filled with a mixture of NiO and Ni in which a Pt wire is imbedded and extended through a sealed top. A second Pt wire is extended along the outside of the tube and wrapped around the tip. The e.m.f. established between the two wires is a function of the difference of the unknown oxygen pressure outside the tube and known pressure inside the tube at temperature.

pressure in the furnace.

Furnace II consisted of a tantalum wire wound alumina tube inside of which was an alumina "dee" tube, surrounded by a vacuum bell jar. The total pressure at 1000°C was about 10^{-7} atm. The P_{O_2} was estimated to be approximately 10^{-10} atm.

Furnace III was a Kanthal wire wound mullite tube with glass fittings joined to either end of the tube as shown in Fig. 2. The procedure consisted of evacuating the system, sealing it off and backfilling with the desired gaseous atmosphere which was then passed through the furnace during the entire experiment. With a flowing 10/1 CO/CO₂ atmosphere, the measured P_{O_2} was 9.6×10^{-17} atm at 1000°C. With flowing argon, an additional graphite tube, within which the specimens were held, was placed inside the mullite tube. The measured P_{O_2} , which was controlled by reactions of oxygen with the carbon and which was dependent on the flow rate of argon, varied from 4 to 7×10^{-19} atm.

(3) Analysis of Experiments

The specimens were sectioned, polished and subjected to optical and electron microprobe analysis. Photomicrographs, X-ray fluorescence photos and backscattered electron photos were taken of selected interfacial regions.

III. Results

(1) Na₂FeSi₂O_{5+x} Glasses

Sessile drop contact angles of this series on Marz iron after 2 h at 1000°C are shown in Fig. 3. In Furnace I with a total pressure of 10^{-8} atm, the contact angles ranged from 55 to 10° for 0 to 6.0 w/o FeO,

and spreading occurred for glasses with 9.1 w/o FeO and higher. Retardation in spreading for the glass with 44.5 w/o FeO occurred, however, because of increase of viscosity due to formation of reaction precipitates. Corresponding angles in Furnace II ranged continuously from 60 to 27° for 0 to 44.5 w/o FeO (Fig. 3). It is expected that γ_{sl} decreased with the development of a chemical bond^{4,6} and γ_{lv} increased¹³ with increase of FeO content. On the basis of Young's relationship (Eq. 1)

$$(\gamma_{sv} - \gamma_{sl}) = \gamma_{lv} \cos \theta \quad (1)$$

where γ_{sv} is the solid/vapor surface tension, γ_{sl} --solid/liquid, and γ_{lv} --liquid/vapor, the observed decrease in contact angle with increase of FeO must then be attributed to a greater decrease in γ_{sl} than the corresponding increase in γ_{lv} . Spreading occurred when an additional contribution of the free energy of a reaction between the metal and glass to the driving force for wetting ($\gamma_{sv} - \gamma_{sl}$) was sufficiently large to exceed γ_{lv} .¹⁴

Occurrence of reactions was verified by a deposition of Na in the cold parts of the vacuum chamber with a subsequent appearance of precipitates in the glass when the reaction was allowed to continue. For example, an electron microprobe of the 9.1 w/o FeO glass on Marz iron for 2 h in Furnace I indicated a loss of about half of the Na₂O, and an increase of FeO to 25 w/o at the edge of the drop and 17 w/o in the center; SiO₂ precipitates were also present around the edge (Fig. 4). In Furnace II, the contact angle for this specimen was 45°, and these

reaction indicators were not observed. However, when a few pieces of carbon were placed in the hot zone with the specimen, the contact angle was approximately 5° after about 30 min. and SiO_2 began to precipitate out of the glass after about 1 h. This effect can be associated with the dissociation of a chemically adsorbed oxygen layer on the exposed metal surface and a resulting increase of γ_{sv} as discussed later. Glasses with higher contents of FeO, after reaction in Furnace I, showed precipitates of fayalite (Fe_2SiO_4 , referred to subsequently as F_2S).

This series of glasses on Armco iron in Furnace I generally did not wet or react as readily as on Marz iron. For example, the 9.1 w/o FeO glass showed a contact angle of 32° after 2 h, and after 4 h, the angle approached zero and SiO_2 precipitates were observed. Armco iron, after annealing at 1100°C for 20 h in Furnace I, however, showed similar reaction behavior to Marz iron.

The 44.5 w/o FeO glass on Armco iron after 2 h in Furnace I did not wet as readily as on Marz iron but reactions occurred immediately. In both cases bubbling ceased in 2 to 3 min.; the reaction, however, continued resulting in a decrease of wüstite dendrites, growth of fayalite crystals and increase in interfacial roughening, as observed at room temperature (Fig. 5). As before, the reaction was associated with Na loss.

(2) $\text{Na}_{2-2x}\text{Fe}_x\text{Si}_2\text{O}_5$ Glasses

Sessile drop experiments of this series on Marz iron after 2 h in Furnace III with flowing 10/1 CO/CO_2 showed contact angles of about 55° . No precipitates were observed, but the NS_2 glass was slightly bluish

indicating some reaction with the iron. Similar experiments were repeated in Furnace III with flowing argon for 2, 5 and 44 h using both Marz and Armco irons. The contact angles were about 55 to 60° and the NS₂ glass was slightly blue. In these cases, the essentially constant contact angle can be attributed to counterbalancing decreases of γ_{sl} and corresponding increases of γ_{lv} . The glass specimens with more than 14.5 w/o FeO showed precipitates of metallic iron at the liquid/vapor interface after 2 h; with more than 7.2 w/o FeO, after 5 h.

The series repeated in Furnace I with a total pressure of 10^{-9} atm on Marz iron showed contact angles of about 30° for about 30-45 min., and then spreading occurred with bubbling of the glass and subsequent appearance of SiO₂ precipitates (after shorter times with increasing FeO in the glass). On Armco iron, acute contact angles of about 50° were retained for 2 h; in an experiment with NS₂ glass, the angle was retained for 20 h with SiO₂ precipitates occurring in the region of the glass/vapor interface.

IV. Discussion

The oxidation of the Fe substrate at the solid/glass interface by reduction of Na⁺ in the glass was the principal reaction observed in this study, as previously reported.^{9,10} The structure of glass is complex and individual molecular species do not exist within its structure, but it is convenient to express this net electrochemical reaction for any of these glasses in the following form:

A replacement of 2Na^+ in the glass by Fe^{++} occurs with no change in the O/Si ratio and thus with a shift of an overall composition point, in the $\text{Na}_2\text{O}-\text{SiO}_2-\text{FeO}$ phase diagram (Fig. 1), approximately parallel to the $\text{Na}_2\text{O}-\text{FeO}$ join. The figure also shows the isothermal section for 1000°C . By inspection, it can be seen that all of the glasses of the $\text{Na}_{2-2x}\text{Fe}_x\text{Si}_2\text{O}_5$ series and the $\text{Na}_2\text{Fe}_x\text{Si}_{2+5x}\text{O}_{5+x}$ series with a starting amount of FeO up to about 15 w/o, upon continued reaction with Fe, become saturated with SiO_2 ; with further reaction, the glass also becomes saturated with Fe_2S ; and if the reaction were carried to completion, the liquid composition would remain constant until the liquid is consumed with the final composition being Fe_2SiO_4 and SiO_2 . The $\text{Na}_2\text{Fe}_x\text{Si}_{2+5x}\text{O}_{5+x}$ glasses with more than about 15 w/o FeO would follow the same pattern but would be first saturated with Fe_2S and then also with SiO_2 . Glasses close to saturation with FeO upon reaction with Fe would become saturated with and result in precipitates of FeO, followed by precipitates of Fe_2S with continued reaction. The complete reaction can be represented by Eq. (3).

The free energy equation for reaction (2) under nonequilibrium conditions is

$$\Delta F = \Delta F^\circ + RT \ln \frac{a(\text{FeO})_{\text{gl}} (P_{\text{Na}})^2}{a(\text{Na}_2\text{O})_{\text{gl}}} \quad (4)$$

The standard free energy, ΔF° , at 1000°C (with Na gas at 1 atm pressure, liquid Na_2O and solid $\text{Fe}_{0.95}\text{O}$ as standard states) is +9340 cal/mol. It is expected that, if data were available to use the standard states for Na_2O reflecting its structure in a given glass, the ΔF° would be less positive with increase of O/Si ratio--making reaction (2) correspondingly more feasible. ΔF° for reaction (3) is considerably larger. In any case, ΔF° for the redox reaction regardless of the standard states chosen is always positive because the oxidation potential for Na is larger than for Fe. Reaction (2) thus does not occur spontaneously; its occurrence depends on the activity quotient in Eq. (4) being sufficiently less than 1 to result in an overall negative ΔF . Borom and Pask in a reaction study of the Fe-- $\text{Na}_2\text{Si}_2\text{O}_5$ system showed that it was reaction-controlled, i.e., the reaction rate was slower than the diffusion rate.¹⁰ The reaction is dependent on a low P_{Na} but also on a low activity of FeO and a high activity of Na_2O at the glass interface (i.e., a decrease in the $a(\text{FeO})_{\text{gl}}/a(\text{Na}_2\text{O})_{\text{gl}}$ ratio). It is expected that the increased reactivity of $\text{Na}_2\text{Si}_2\text{O}_5$ glasses with increasing additions of FeO, as indicated by spreading (Fig. 3) and appearance of precipitates, resulted from an increase of the $a(\text{Na}_2\text{O})_{\text{gl}}$ with the increase of the O/Si ratio of the glass. Likewise, a comparison of the two series of glasses indicates that for a given molar content of FeO a decrease of the activity ratio occurred with an increase of Na_2O content and a corresponding increase of the O/Si ratio.

With the formation of an interface, the first step in the reaction is an equilibration of the activities of FeO in the interfacial

transition zone:

$$a(\text{FeO})_{\text{metal interface}} = a(\text{FeO})_{\text{glass interface}} \quad (5)$$

In most cases, the $a(\text{FeO})_m$ at the interface is one or close to one since the usual P_{O_2} is above the equilibrium P_{O_2} for FeO at 1000°C of approximately 2×10^{-15} atm; and the $a(\text{FeO})_{gl}$ is considerably less than one. A diffusion flux of oxide then proceeds from the metal to the glass. As a consequence, the $a(\text{FeO})_m$ at the interface will remain high for a limited time period since the diffusivity of FeO (oxygen) in γ -Fe at 1000°C, which has been reported to be 6.67×10^{-7} cm²/sec,¹⁵ is slightly higher than the diffusivity of Fe²⁺ in $\text{Na}_2\text{Fe}_x\text{Si}_{20-x}\text{O}_{5+x}$, which has been reported to be from 6 to 12×10^{-8} cm²/sec depending on the glass composition.¹⁶ When this equilibrium for the system is reached, however, the $a(\text{FeO})$ at the interface will be essentially the same as the $a(\text{FeO})$ in the bulk of the glass because of the relative solubilities of FeO: in γ -Fe, approximately 40 ppm¹⁵ and in glass, 20 to 44 w/o depending on the O/Si ratio.¹⁶ This equilibration process then takes longer with Armco iron because it has inclusions of iron oxide particles; as a result, its $a(\text{FeO})_m$ at the interface is at or close to 1 for a longer time.

The most critical factor for reaction (2) to take place is the magnitude of the pressure of the Na gas formed at the interface. The Na gas can emerge from the glass surface as a bubble nucleated at the interface or by atomic diffusion through the glass. In the former case, the internal pressure of Na at the interface must exceed the pressure of

the ambient atmosphere; this can be represented by

$$p - p_o = 2\gamma_{lv}/r \quad (6)$$

where p_o is the external pressure on the liquid and r is the radius of the bubble (assuming the radius is relatively large). The bubble formation mechanism then should be the most difficult in Furnace III which has ambient pressures of about 1 atm. If the Na leaves the interface by diffusion to the glass/vapor interface, the nature of the ambient atmosphere and the thickness of the glass layer, i.e., the length of the diffusion path, will be controlling factors. The magnitude of the p_{Na} in the atmosphere and the ambient total pressure will affect the emergence of the Na from the glass which is necessary to achieve and maintain a low P_{Na} at the interface.

In the sessile drop experiments, the magnitude of the contact angle determines the thickness of the glass layer, the thickness being less around the edge of the drop and for smaller contact angles; a decrease is realized with an increase of the driving force for wetting around the periphery of the drop.¹⁴ Wetting is strongly dependent on the magnitude of γ_{sv} which can increase to about 2000 dynes/cm at a very low P_{O_2} .¹³ An increase of P_{O_2} has a marked effect on the lowering of γ_{sv} ; when the $a(FeO)_m$ approaches 1, a continuous chemisorbed oxygen layer will form and the γ_{sv} should approach the value for iron oxide. It would then be expected that the γ_{sv} of Marz iron in Furnace I with an ambient pressure of 10^{-9} atm would be greater than at a pressure of 10^{-8} atm (contact

angle of 30 vs 55° for NS₂). The thinner glass layer results in accelerated reactions around the edge of the drop; the associated smaller $a(\text{FeO})_m$ at the metal interface also contributes to the rate of the reaction. This type of explanation also applies to the reaction of 9.1 w/o FeO glass with Marz iron in Furnace II in the presence of a few pieces of carbon. The high contact angles in Furnace III can be attributed to relatively low values of γ_{sv} because of surface adsorption of CO gas from the flowing atmosphere.

Another reaction that can change the details of the electrochemical reaction (2) is the loss of Na₂O at the liquid glass/vapor interface by the reaction

Taking the standard states as liquid Na₂O, and Na and O₂ gases at 1 atm pressure, ΔF° for the reaction at 1000°C is +52,000 cal/mol. Under non-equilibrium conditions the free energy equation is

$$\Delta F = +52,500 + RT \ln \frac{(P_{\text{Na}})^2 (P_{\text{O}_2})^{1/2}}{a(\text{Na}_2\text{O})_{gl}} \quad (8)$$

This reaction is thus favored by a high $a(\text{Na}_2\text{O})_{gl}$ and low pressures of Na and O₂ in the atmosphere. Figure 6 is an equilibrium plot of $a(\text{Na}_2\text{O})_{gl}$ vs P_{Na} at a number of P_{O_2} 's. The effect of Na₂O loss on the composition change of a glass can be shown on the phase diagram by an extension of the join between Na₂O and the starting glass composition.

The NS₂ glass with 9.1 w/o FeO can be used as an example: if the glass only lost Na₂O by vaporization, then the percentage FeO content would increase to 12 w/o when SiO₂ precipitates appear; if Na was lost only by replacement of 2Na⁺ by Fe²⁺, then the FeO would reach ~30 w/o. The experimentally measured amount of 28 w/o suggests that both reactions took place with the electrochemical one being dominant.

Na₂O loss by vaporization from the NS₂ glass with 44 w/o FeO during its reaction with both Marz and Armco iron must have also taken place as indicated by the rapid growth of F₂S crystals in the liquid glass. A loss and replacement of about 5 w/o Na₂O at 1000°C brings the overall glass composition into the 3-phase region of FeO, F₂S and liquid (Fig. 1); with continued reaction the FeO content drops and F₂S increases. Since the specimens are analyzed at room temperature, some of the observed FeO precipitates are formed due to supersaturation of the liquid with FeO on cooling. The similar reactivity for both iron specimens in this case was due to the $a(\text{FeO})$ being essentially one in the interfacial zone because the $a(\text{FeO})_{\text{gl}}$ was one.

Two other reactions have also been observed with glasses containing iron oxide: one an equilibration with the atmosphere and the other, with the substrate metal. If the P_{O_2} in the atmosphere is low enough, decomposition of the iron oxide dissolved in the glass can occur with the precipitation of Fe at the glass/vapor interface; e.g. using solid FeO as the standard state, at 1000°C the equilibrium P_{O_2} is 1.5×10^{-15} atm at an $a(\text{FeO}) = 1.0$, 1.5×10^{-17} at 0.10, 1.5×10^{-19} at 0.01. Kinetically, this reaction is slow. If Fe³⁺ is present in the glass, then reaction (9)

will proceed readily at 1000°C because its ΔF° is -12 kcal/mol. This reaction can contribute to the delay of the reactions associated with the evolution of Na vapor.

V. Conclusions

$\text{Na}_2\text{Fe}_x\text{Si}_{20-5+x}\text{O}_{5+x}$ and $\text{Na}_{2-2x}\text{Fe}_x\text{Si}_2\text{O}_5$ glasses were observed to react with iron at 1000°C with the evolution of Na vapor according to Eq. (2); the reactions are more feasible and faster primarily when the P_{Na} at the interface is low and also when the $a(\text{FeO})_{\text{interface}}/a(\text{Na}_2\text{O})_{\text{glass}}$ ratio at the glass-metal interface is small. The results indicate that this activity ratio must remain favorable and that the ΔF° for the reaction becomes less positive with an increase of the O/Si ratio of the glass. Continued reaction results in the precipitation of SiO_2 , fayalite (Fe_2SiO_4), or FeO depending on the O/Si ratio of the glass.

Maintenance of a low P_{Na} at the interface requires the removal of reduced Na either by diffusion or by Na bubble nucleation and movement to the surface from where its emergence is dependent upon the nature of the ambient atmosphere. Bubble nucleation is dependent upon the Na reaction pressure being higher than the atmospheric pressure above the drop; it was thus favored in Furnace I. Sodium elimination by diffusion is dependent upon the length of the diffusion path, i.e., the thickness of the glass, and the P_{Na} and the total pressure of the atmosphere. Low P_{O_2} in the atmosphere results in a higher γ_{sv} and a lower $a(\text{FeO})$ at

the metal interface, which is favorable for a reaction at the interface; these factors lead to lower contact angles and also spreading of the sessile drop resulting in thinner glass layers.

Armco iron is less reactive than Marz iron because of its higher iron oxide content. The $a(\text{FeO})$ at the interface thus remains high even when $a(\text{FeO})$ in the bulk glass is low until equilibration of $a(\text{FeO})$ throughout the interfacial zone is achieved.

Low P_{Na} and P_{O_2} in the atmosphere causes loss of Na_2O at the glass/vapor interface. Decomposition of FeO can also occur at a low P_{O_2} . The resulting change in the overall glass composition affects the rates of reactions with the substrate iron.

Any reactions involving the iron substrate increase the Fe^{2+} , or FeO , content of the glass at the interface. This composition change is desirable for attaining or maintaining interfacial compositions approaching saturation with iron oxide, i.e., a high $a(\text{FeO})_{\text{int}}$, that is necessary for realizing maximum chemical bonding at the glass/metal interface.

Acknowledgments

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Figure Captions

- Fig. 1. $\text{FeO-Na}_2\text{O-SiO}_2$ phase diagram showing 1000°C isothermal section and experimental glass compositions.
- Fig. 2. A schematic drawing of tube furnace designated as Furnace III in text.
- Fig. 3. Contact angles vs. FeO content in $\text{Na}_2\text{Fe}_x\text{Si}_{25+x}\text{O}_{5+x}$ series of glasses in Furnace I at total pressure of 10^{-8} atm and Furnace II.
- Fig. 4. Electron microprobe oscilloscope traces of a cross-section of glass with 9.1 w/o FeO on Marz iron after 2 h at 1000°C in Furnace I indicating SiO_2 precipitates: (left) Fe radiation, and (right) Si radiation (640X).
- Fig. 5. Electron microprobe oscilloscope traces of a cross-section of glass with 44.5% FeO on Armco iron after 10 min. at 1000°C in Furnace I indicating F_2S and FeO precipitates: (top) back-scattered, (middle) Fe radiation, and (bottom) Si radiation. (700X).
- Fig. 6. Equilibrium activity of Na_2O vs. equilibrium P_{Na} at several P_{O_2} at 1000°C for reaction (7).

Fig. 1

XBL 709-6646

Fig. 2

Fig. 3

XBB 697-4572

Fig. 4

XBB 709-4033

Fig. 5

XBL 709-6643

Fig. 6

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