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TRANSPORT OF METALS BY GASEOUS CHLORIDES AT ELEVATED TEMPERATURES

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The purpose of these experiments was to determine the transport of several metals by chlorides at elevated temperatures. The subhalides back react at lower temperatures to deposit the metal and to regenerate a normal halide. For example, when aluminum chloride is passed slowly over metallic aluminum at 800° and 0.001 atmosphere, 50% of the $AlCl_3$ reacts to form AlCl.[1] The AlCl vapor back reacts in a cooler zone of the reaction tube to deposit aluminum and regenerate $AlCl_3$. The effect of these reactions is to transport aluminum from a hot zone to a cold zone. The transported aluminum can be purified by this process.

In the work to be reported, reduced pressures were used to avoid the relatively high temperatures required at atmospheric pressure. Two types of reactions were investigated: (1) a metal with its anhydrous gaseous chloride, and (2) a metal with a dissimilar anhydrous gaseous chloride.

Most of the anhydrous chlorides (Table I) were prepared from the metal and chlorine immediately before use. Silicon tetrachloride was purchased from Fisher Scientific Co. The tantalum chloride listed in Table I was not used in the distillation experiments.

TABLE I

PREPARATION OF CHLORIDES OF $M + Cl_2$

Metal	Temp., °C.	Probable product	How identified
Cb	1000	$CbCl_5$	Orange salt
Cr	1000	$CrCl_3$	Light lavender salt
Fe	925–1050	$FeCl_2$	Purple salt
Ga	675	$GaCl_2$	M.p. 160–170°
Ge	800	$GeCl_4$	M.p. approx. −50°
Mn	900–1070	$MnCl_2$	Pink salt
Ni	1010	$NiCl_2$	Yellow salt
Ta	730	$TaCl_5$	Pale yellow salt
Ti	1250	$TiCl_4$	M.p. approx. −30°
W	950	WCl_6	Deep purple salt
Zr	1250	$ZrCl_4$	White salt

In the preparations chlorine gas was passed over an Alundum boat containing the metal surrounded by a quartz tube. Temperature was raised until a reaction took place. The salts condensed on the cold wall of the quartz tube and were removed in a dry air room.

When chlorine gas was passed over metallic tungsten in an Alundum boat at 950°, most of the Alundum boat was volatilized and the condensate was a pinkish-orange colored salt. This reaction may have taken place

$$3W + Al_2O_3 + 9Cl_2 \longrightarrow \frac{3WOCl_4}{\mathrm{Red}} + \frac{2AlCl_3}{\mathrm{White}}$$

The boiling points of the two salts are not too far separated: $WOCl_4$, b.p. 227.5° and $AlCl_3$ b.p. 178°. A mixture of the salts could give the pinkish orange color. A subhalide reaction may also have occurred to a small extent since 0.5% Al (as determined by hydrogen evolution) was condensed in one portion of the salt. Tungsten was contained in a graphite boat to produce the chloride.

The conditions for Type 1 reactions are given in Table II. The metal chlorides were passed slowly over a heated Alundum boat containing the metal. The transported metal and salts were condensed on an air-cooled silica tube and tube walls.

TABLE II

REACTIONS OF $M' + M'Cl$

Metal	Chloride	Temp., °C.	Pressure, mm.	Metal product
Cb	$CbCl_5$	1000	0.4	No reaction
Cr	$CrCl_3$	1250	0.2	Cr
Cr	$CrCl_2$	1250	0.2	Cr
Fe	$FeCl_2$	1300	2.3	Fe
Ga	$GaCl_2$	800	0.2	Ga
Ge	$GeCl_4$	1250	5.0	Ge
Mn	$MnCl_2$	1000	0.1	No reaction
Ni	$NiCl_2$	1010	0.05	No reaction
Si	$SiCl_4$	1000	3.0	Si
Ti	$TiCl_4$	1300	2.5	Ti
Ti	$TiCl_3$	1250	1.5	Ti
Zr	$ZrCl_4$	1225	0.2	Zr

In each of these reactions, the transported metal product was separated and identified by appearance and chemical analysis. Although Gross[2,3] reported subhalides of manganese (MnF) and nickel (NiBr, NiCl), there was no evidence of metal under the conditions of these experiments.

Appreciable amounts of metallic condensed products resulted when chlorides of iron, gallium, silicon and zirconium reacted with the corresponding metals. $CrCl_2$ produced a larger yield of chromium than $CrCl_3$, and $TiCl_3$ produced a larger yield of titanium than $TiCl_4$. The yield of germanium was very small at 1250°. $CrCl_3$, $GeCl_4$ and $TiCl_4$, on the basis of color and appearance, appeared to form the lower valence chlorides $CrCl_2$, $GeCl_2$ and $TiCl_3$, while in all other experiments the deposited chloride appeared to be the same as the starting material.

The conditions and products for Type 2 reactions are given in Table III.

X-Ray analysis of the deliquescent chlorides condensed on the cold region of the reactor tube were not conclusive. The elements in the chlorides were verified by analysis.

A Ga–Al alloy free from salt was produced in the heated boat when $GaCl_2$[4] vapor was passed over aluminum. The aluminum in the alloy increased from 35.3% at 800° to 68.3% at 1000°. Results

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(3) P. Gross, U. S. Patent 2,470,305–6 (to International Alloys Ltd.) May 17, 1949.

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TABLE III

REACTIONS OF M′ + M″Cl

Metal	Chloride	Temp., °C.	Pressure, mm.	Metal product	Deposited chlorides
Al	$GaCl_2$	800–1000	0.2	Ga–Al	Ga + Al
Ga	$AlCl_3$	800–1000	0.2	Ga–Al	Ga + Al
Al	$GeCl_4$	1000	2.0	Ge–Al	Al
Ge	$AlCl_3$	1000	0.5	Thin mirror	Al
Fe–Al	$FeCl_3$	1000	1.0	Fe–Al	Al
Fe	$AlCl_3$	1100	4.0	Al–Fe	Al + Fe
Si	$AlCl_3$	1000	0.7	Si	Al
Al	$SiCl_4$	1000	3.0	Si–Al	Al
Ti	$AlCl_3$	1250	0.4	Ti–Al	Al + Ti
Al	$TiCl_4$	1000	3.0	Al–Ti	Ti + Al
Fe + Al + Si + Ti	$TiCl_3$	1000	3.0	Al–Si	Al + Ti

were similar when $AlCl_3$ vapor was passed over gallium metal, except that in this case the Ga–Al alloy was in small globules mixed throughout the chlorides of gallium and aluminum. The metal deposit contained 66% germanium and 30% aluminum when $GeCl_4$ vapor was passed over aluminum. A very thin metallic mirror was produced when $AlCl_3$ vapor was passed over metallic germanium. Metallic iron and $AlCl_3$ were the chief products of passing $FeCl_3$ vapor over a ferro-aluminum alloy. An Fe–Al alloy and chlorides of both iron and aluminum were the result of passing $AlCl_3$ vapor over metallic iron. Elemental silicon was distilled when $AlCl_3$ vapor was passed over silicon. In contrast with this behavior, a 50-50% Si–Al alloy was distilled when $SiCl_4$ vapor was passed over aluminum. This reaction is similar to that for $AlCl_3$ vapor passed over germanium except that more silicon was condensed, possibly because of the difference in temperature. When $TiCl_4$ vapor was passed over aluminum, an alloy of 70% Al–30% Ti was transported. In this reaction the $TiCl_3$ must have been partially reduced to $TiCl_2$ evidenced by black crystals mixed with purple crystals. The percentage of aluminum and titanium was reversed when $AlCl_3$ vapor was passed over titanium. Aluminum and silicon were preferentially distilled when $TiCl_3$ vapor was passed over an alloy of 70.8% silicon, 10.1% iron, 9.0% titanium and 1.4% aluminum.[5-9]

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SURFACE TENSION AT ELEVATED TEMPERATURES. IV. SURFACE TENSION OF Fe–Se AND Fe–Te ALLOYS

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Experimental data have previously been reported[2-4] giving the surface tension of pure iron and the effect of various surface active agents in solution. Among the most active surface active additives are oxygen and sulfur. In the present work, these studies have been extended to investigate the surface activity of selenium and tellurium in liquid iron.

Experimental

The sessile drop method which has been described in detail previously[2-4] was employed to determine surface tension of the liquids in contact with aluminum oxide. Maximum experimental deviations in measured values for a given composition vary between 1 and 3%.

High purity vacuum-melted iron (Vacuum Metals Corporation Ferrovac E ingot) was employed as the base material. This metal has the following impurities: 0.003 C, 0.007 O, 0.0005 N, 0.005 S, 0.01 Si, < 0.003 Al, <0.006 Co, <0.001 Cu Mn, < 0.01 Ni Pb, < 0.0005 Sn, < 0.003 Mo. Samples were prepared by melting this material with additions of high purity selenium and tellurium in purified helium after outgassing at red heat *in vacuo,* using pure aluminum oxide crucibles. The resulting ingots were cut up to provide samples which were used for experimental measurements.

After placing in the furnace and leveling, the system was heated to 1000° under vacuum (0.01 μ) and then heated to 1570° for measurements in 0.5 atm. of helium. Hospital grade helium was purified with a liquid nitrogen cold trap, Cu_2O at 400° to oxidize reduced gases, Mg chips at 400° and Ti at 1000° to remove oxidized gases, and activated charcoal at −200°.

Samples were analyzed for O, Se and Te after carrying out the surface tension determinations at 1570°. Results are given in Table I.

TABLE I

SURFACE TENSION MEASUREMENTS

Composition, %			Surface tension
Oxygen	Selenium	Tellurium	
0.020	0.03	..	1000
.010	0.10	..	740
.023	..	0.04	1325
.025	..	0.10	1300
.008	..	..	1632[3]
.020	..	..	1541[3]

Discussion

Surface tension is plotted as a function of log weight per cent. addition in Fig. 1. The oxygen content of the liquids makes for some difficulty in interpretation. In the case of tellurium, which is least surface active, it is reasonable to assume that the surface tension lowering due to the oxygen content is independent of the tellurium content. Experimental data have been adjusted in this way (open points) in Fig. 1 for the oxygen content. For the case of selenium, which is much more surface active, this assumption is not as satisfactory—the required correction being somewhat less due to selenium adsorption at the surface. We have indicated the maximum correction to be expected by open points on Fig. 1. Since selenium is strongly surface active, the general interpretation of the results is not affected by errors in this assumption.

Both selenium and tellurium additions decrease the surface tension of liquid iron, indicating a concentration at the surface. The excess surface

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