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CHEMICAL REACTIONS OF METAL POWDERS WITH ORGANIC AND INORGANIC LIQUIDS DURING BALL MILLING

Alan Arias

Lewis Research Center
Cleveland, Ohio 44135

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1975

5.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TN D-8015		

4. Title and Subtitle	5. Report Date
CHEMICAL REACTIONS OF METAL POWDERS WITH ORGANIC AND INORGANIC LIQUIDS DURING BALL MILLING	September 1975
	6. Performing Organization Code
7. Author(s)	8. Performing Organization Report No.
Alan Arias	E-8369
	10. Work Unit No.
9. Performing Organization Name and Address	505-01
Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135	11. Contract or Grant No.
	13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address	Technical Note
National Aeronautics and Space Administration Washington, D. C. 20546	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

On milling chromium powder in 3 metal chlorides and either chromium or nickel powders in 10 organic liquids representative of 9 different functional groups, the powders always reacted with the liquid and became contaminated with elements from them. The milled powders had specific surface areas ranging from 0.14 to 37 m^2/g, and the total contamination with elements from the milling liquid ranged from 0.01 to 56 weight percent. In most milling runs, compounds resulting from substitution, addition, or elimination reactions formed in or from the milling liquid; and in most runs with organic liquids H_2, CH_4, and CO_2 were generated.

17. Key Words (Suggested by Author(s))

Synthesis — Powder metallurgy
Catalysis — Comminution

18. Distribution Statement

Unclassified - unlimited
STAR Category 23 (rev.)

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	27	$3.75

* For sale by the National Technical Information Service, Springfield, Virginia 22161

CHEMICAL REACTIONS OF METAL POWDERS WITH ORGANIC AND INORGANIC LIQUIDS DURING BALL MILLING

by Alan Arias

Lewis Research Center

SUMMARY

This investigation was conducted to determine the nature of the reaction products resulting from ball milling chromium and nickel metal powders in organic and inorganic liquids. To meet this objective, 3 milling runs with chromium in 3 liquid metal chlorides and 17 milling runs with either chromium or nickel in 10 organic liquids representative of 10 different functional groups were made.

In all milling runs the solid phases (milled powders) became contamainated with chemical elements from the milling liquid. The solid phases had total contaminations from these elements ranging from 0.01 to 56 weight percent and specific surface areas ranging from 37 to 0.14 square meters per gram.

In most runs the liquid phases (milling liquids after milling) contained compounds formed by reaction of the milling liquids with the bare metal surfaces formed during milling. Some of the most significant reactions and reaction products were as follows:

On milling chromiun in titanium tetrachloride, stannic chloride, or silicon tetrachloride, these chlorides were reduced to lower valence states and chromium chlorides formed. Milling chromium or nickel in n-heptane yielded alkanes of higher boiling point than n-heptane. Milling chromium in methyl or ethyl alcohols yielded compounds believed to be organometallic. Milling chromium or nickel in acetone yielded diacetone alcohol. Milling chromium in butyraldehyde yielded organic compounds and water. (Some of these compounds were α-β unsaturated aldehydes and apparently present in monomeric and polymeric forms.) Milling chromium or nickel in carbon tetrachloride yielded hexachloroethane. Milling chromium or nickel in benezene and chromium in toluene yielded compounds of higher boiling point than benzene or toluene; the infrared spectra of these compounds resembled that of polystyrene.

During most milling runs with organic liquids, hydrogen, methane, and carbon dioxide were generated. In runs with nickel in either ethyl alcohol or benzene, oxides of nitrogen were also generated.

From the results of this investigation it is concluded that metal powders cannot be comminuted in organic or inorganic liquids without becoming contaminated with the elements making up the milling liquid. However, it should be possible to select milling liquids that produce either low levels of contamination or contaminants that may be removed by simple reduction procedures.

INTRODUCTION

In a previous investigation (ref. 1) it was found that, after ball milling chromium in a variety of organic liquids, the milled powders were contaminated with elements (carbon, oxygen, and hydrogen) from the organic liquids. Similarly, nickel powders milled in ethyl alcohol with a variety of additives showed an increase in carbon, oxygen, and nitrogen contents (ref. 2). Although it was surmised that these contaminations (particularly carbon and hydrogen) were caused by the reaction of the chromium or nickel powders with the organic liquids during milling, the exact nature of the reaction products was unknown. The presence of contaminating elements in the milled powders could have been due to absorbed or chemisorbed milling liquid as well as to chemical reactions.

As a rule, contaminating elements, particularly carbon and oxygen, are undesirable in chromium and nickel as well as in other metal powders intended for the production of either dispersion strengthened alloys or superalloys. Oxygen and carbon from the milling liquid are undesirable mainly because, during consolidation of the powders into high temperature alloys, the oxygen and carbon form very difficult to reduce oxides and carbides. Even in cases where reduction of oxides and carbides is possible, the high reduction temperatures usually required may well alter some desirable attribute of the alloy such as grain size or uniformity of dispersoid. Thus, it is highly desirable to mill metal powders intended for powder metallurgy applications in liquids (or in other environments) that cause either tolerably low contamination or readily removable contaminants. To this end, it is necessary to understand the nature of the reactions that can occur between the metal powder and the milling liquid.

The objective of the present investigation was to determine the nature of the reaction products resulting from the reaction of chromium and nickel metal powders with organic and inorganic liquids during ball milling. To accomplish this objective, chromium powder was ball milled in three different metal chlorides and in several organic liquids. These organic liquids were selected so as to determine the effects of the most common organic functional groups on reactivity. In addition, nickel powder was also ball milled in some of these organic liquids to compare the reaction behavior of this less reactive metal with that of chromium.

In order to determine the nature of the reaction products, the three phases present in the ball mill (solid metal powder, milling liquid, and head space gases) were chemically analyzed. After each milling run, the solid phase (milled metal powder) was analyzed for elements present in the milling liquid, and its surface area determined. After most milling runs, the resulting liquid phase (milling liquid after ball milling) was analyzed for soluble reaction products, and their nature determined as far as feasible. Also, during or after most milling runs the gas phase (head gases) was analyzed either by gas chromatography or by mass spectrometry.

The findings of this investigation have significance to at least two distinct fields of endeavor: powder metallurgy and chemical synthesis.

MATERIALS

The materials used in this investigation were chromium and nickel powders, 3 liquid-metal chlorides, and 10 organic liquids. These materials are listed and characterized in table I.

EQUIPMENT

The metal powders were ball milled in gas tight ball mills provided with pressure gages to monitor the ball mill pressure and with vacuum type valves for evacuating the ball mills and pressurizing them with helium. These stainless-steel ball mills were similar to the one described in reference 1, except that in some milling runs the mills used in the present investigation had either nickel or molybdenum liners. The inside diameter of the mills was 10 centimeters (4 in.). The ball charges used in the various ball milling runs were as follows: 3400 grams of 1.27-centimeter (1/2-in.) diameter stainless-steel balls, with stainless-steel mills; 3500 grams of nickel shot, 1.27 to 0.63 centimeter (1/2 to 1/4 in.) in diameter, with nickel lined ball mills; and 3200 grams of 0.95-centimeter (3/8-in.) diameter chromium balls, with the molybdenum lined ball mill.

PROCEDURES

The flow diagram for milling chromium (Cr) in liquid metal chlorides is shown in figure 1. Most of the operations described in figure 1 were carried out in a dry box because of the hygroscopic or toxic nature of the liquid metal chlorides used. The flow diagram for milling either Cr or nickel (Ni) in organic liquids is shown in figure 2. Attempts were made to make the procedures shown in figures 1 and 2 as uniform as possible. Thus, all milling runs either in organic or in inorganic liquids were for 384 hours at 100 rpm in ball mills pressurized with helium. However, to minimize contamination of the milled powders with material from the balls and mills (pickup), different types of balls and mills were used for milling Cr and Ni powders. In addition, because of the corrosive nature of the acetic acid used in one of the runs with Cr powder, Cr balls in a molybdenum lined mill were used. Unfortunately, the Cr balls became available too late in the program for use with all the milling runs with Cr.

Loading Mills

In all milling runs with Cr, 150 grams of -20 mesh Cr powder and 750 milliliters of liquid milling liquids were used. Except for the run involving chromium with acetic acid (run 14, table II) already mentioned, all other milling runs with Cr powder were carried out in stainless-steel mills loaded with stainless-steel balls. The head space of these mills was about 420 milliliters.

The Ni milling runs were carried out in Ni lined ball mills loaded with Ni shot. In all cases, 200 grams of Ni powder and 500 milliliters of organic milling liquid were used. The head space of these mills was about 500 milliliters.

For milling Cr with metal chlorides (runs 1 to 3, table II), the mills were loaded inside a dry box and then pressurized with helium to a gage pressure of about 69 kilonewtons per square meter (10 psi) before starting the milling run. In all other milling runs involving either Cr or Ni, after loading the mills in a fume hood they were evacuated to about 17 kilonewtons per square meter (2.5 psi) absolute pressure and then back filled with helium to about 69 kilonewtons per square meter (10 psi) gage pressure. This evacuation - back filling procedure was repeated two more times, and the run started.

Gas Analyses

Mill pressures during the run were recorded. In some of the runs the mill pressure was released either to obtain gas samples for analysis or to release a pressure buildup caused by gases evolved during ball milling. The gas phase (mixture of He, reaction gases, residual gases, and vapor of the milling liquid) was analyzed by mass spectrometry either during or at the end of most runs. These analyses were carried out beyond the molecular weight of the milling liquid. In one case, gas chromatography was used to analyze the reaction gases as a function of milling time.

Handling of Slurries

After each run the slurries resulting from milling were separated from the balls by sieving. Slurries of organic liquids and metals were either centrifuged or filtered to separate the milled powder (solid phase) from the organic liquid (liquid phase). The still wet solid phase was washed twice with about 500 milliliters per washing of the same liquid used for milling, except for the runs with butyraldehyde and with acetic acid (runs 13 to 15, table II) in which anhydrous ethyl alcohol had to be used. These operations were carried out in a fume hood in air. The slurries resulting from milling Cr powder in

metal chlorides (runs 1 to 3, table II) were loaded in gas tight containers in a glove box, and the liquid and solid phases separated by centrifuging. The same procedure was used for separating the metal chloride wash liquids from the solid phases.

Liquid Phases

Because of their obnoxious and toxic nature, the liquid phases resulting from milling in metal chlorides were discarded after visually examining them for the presence of reaction products. In most cases the organic liquid phases were examined by gas chromatography at temperatures programmed from 100° to 200° C. This examination was carried out to determine whether volatile liquids or solids other than the milling media were present in the liquid phase. To determine whether low volatility liquids or solids were present, about 50 milliliters of the liquid phase were evaporated to dryness. Attempts were then made to separate some of the compounds thereby known to be present in some of the liquid phases, either by evaporation of the more volatile components or by fractional distillation. Some of these compounds were then identified by infrared spectroscopy and in some cases also by nuclear magnetic resonance (NMR) spectroscopy and by direct chemical analyses.

Solid Phases

The solid phases resulting from milling Cr in metal chlorides were dried by heating to about 100° C in an evacuated dry box. These dry solid phases were subsequently handled in air. The dry solid phase resulting from milling Cr powder in titanium tetrachloride (run 1, table II) contained relatively large amounts of reaction products visibly different from the very large, shiny flakes of Cr. The solid reaction product was easily washed out of the solid phase with water. The water washings were then dried to recover the reaction product for analysis. The rest of the solid phase was again vacuum dried at about 100° C.

The solid phases resulting from milling either Cr or Ni powders in organic liquids were dried by heating at about 100° C in vacuum.

In all cases the solid phases were chemically analyzed for the elements in the chemical formula of the milling liquid and for oxygen even if not in the formula. The specific surface area of the solid phases was determined by the Brunauer, Emmet, and Teller (BET) method.

RESULTS AND DISCUSSION

A list of ball milling runs together with the main results of this investigation are shown in table II. It is clear from the chemical analysis of the reaction products shown in this table that in all cases a chemical reaction occurred between the metal powder and the ball milling liquid. The reaction products are distributed among three distinct and separable phases: a solid, a liquid, and a gas phase. In all cases there is a solid phase or milled metal powder which is contaminated with elements (C, H, etc.) from the milling liquid. Also, in the majority of cases the liquid phase contains soluble reaction products. Finally, in all runs where gas analyses were performed, there were reaction gases in the gas phase. The results of all the gas analyses were normalized so that the reaction gases added up to 100 volume percent.

In what follows, the results shown in table II are presented and explained in greater detail. First, the solid phases are described together because they have features that are common for all the runs. Then, the liquid and gas phases are described together for each run or for each group of runs with Cr and Ni in the same milling liquid.

Solid Phases

Under the heading "Solid phase, Powder recovered, percent" in table II a figure of 100 indicates that practically all the powder loaded in the mill was recovered after ball milling; a figure of less than 100 indicates that during milling some of the powder welded itself to the balls and ball mill and could not be either shaken or scraped loose. In most instances there was a small amount of material lost by the balls; that is, ball material was picked up by the solid phase powder. If the pickup is significant it will be indicated in the discussion of the particular run involved.

The chemical analysis shows that in all the runs, to a greater or lesser extent, the solid phases were contaminated with elements from the ball milling liquids. The analyses shown in table II were corrected for the amounts of these elements present in the raw materials. The only element which may not have come from the milling medium is oxygen, since the powders were all handled in air. It has been expected that milled Cr powders from runs in milling liquid bearing no oxygen (runs 1 to 4, 16, 18, and 20, table II) would have about the same oxygen-specific surface ratios, due to contamination with atmospheric oxygen. Similar results had been expected for the equivalent Ni runs. It can be seen from the oxygen-specific surface ratios in table II that these expectations were not realized. However, some trends are apparent from these ratios. Thus, except for the nickel-carbon tetrachloride (Ni-CCl_4) run, Ni is much more contaminated with

oxygen (from all sources) than Cr. Also, a low ratio may indicate a protective coating of reaction products. This may be the case in run 2 in which the solid phase had a whitish-gray color quite unlike that of any other solid phase.

It had also been hoped that the hydrogen to carbon ratios shown in table II would offer a clue as to the nature of the reaction products in or on the solid phase. Thus a hydrogen-carbon ratio close to that in the milling medium might indicate either milling medium trapped between welded powder particles or residual organic reaction products in the powder. These expectations were not realized for any of the runs as these ratios always were found to be low. Taking into account the relative accuracy of the chemical analysis, the results from pyrolysis of powders by gas chromatography, and the fact that the powders were vacuum dried at temperatures of at least 100° C, it is surmised that, at most, only a small fraction of the contamination in the solid phases resulting from milling in organic liquids is in the form of organic compounds that are removable as such.

In connection with the contaminations of the solid phases with carbon, oxygen, chlorine, and hydrogen shown in table II, it should be noted that these contaminations do not necessarily make the powders unsuitable for dispersion strengthening applications. In many instances the contamination may be reducible to harmless levels by well known reduction techniques. Thus, for instance, carbon and oxygen in Ni can be readily reduced by heating the powders in hydrogen at about 350° C. Similarly, chlorine in Cr can be removed by heating in hydrogen at temperatures below about 650° C.

Liquid and Gas Phases

Run 1: chromium-titanium tetrachloride (Cr-$TiCl_4$). - The liquid phase resulting from the Cr-$TiCl_4$ run was purple. The material removed from the solid phase by washing with water (and mentioned under Procedures) proved to be hydrated chromium chloride ($CrCl_3 \cdot 6H_2O$). Considering that titanium trichloride ($TiCl_3$) is violet, it is clear that the following, thermodynamically feasible reaction (ref. 3) occurred during ball milling:

$$Cr + 3TiCl_4 \rightarrow \underset{\left(\begin{smallmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{smallmatrix}\right)}{CrCl_3} + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{liquid}\\ \text{phase}\end{smallmatrix}\right)}{3TiCl_3}$$

The relatively low residual chlorine in the water washed Cr powder may indicate that for some reason the chromic chloride ($CrCl_3$) formed during the reaction did not remain on

the Cr surface. With nothing on the surface to prevent it, the Cr particles weld to each other during ball milling, as indicated by the relatively low specific surface area (0.14 m^2/g). No increase in ball mill pressure was noted during the run, and the gas phase was not analyzed.

Run 2: chromium-stannic chloride (Cr-$SnCl_4$). - The liquid phase obtained from the Cr-$SnCl_4$ milling run was colorless. However, a whitish gray reaction product coated the solid phase. On analysis the solid phase showed 23.14 weight percent tin and 33±3 weight percent chlorine. From these results, from the fact that stannous chloride ($SnCl_2$) and chromous chloride ($CrCl_2$) are both white colored solids, and from consideration of free energies of formation (ref. 3), it is clear that the following ball mill reaction occurs:

$$Cr + SnCl_4 \rightarrow CrCl_2 + SnCl_2$$
$$\begin{pmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{pmatrix}\begin{pmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{pmatrix}$$

No increase in pressure was noted during the run, and the gas phase was not analyzed.

Run 3: chromium-silicon tetrachloride (Cr-$SiCl_4$). - The liquid phase from the Cr-$SiCl_4$ run was colorless. No coating was noted on the dark gray solid phase which on analysis showed 0.32 weight percent silicon and 1.6±0.2 weight percent chlorine. Experiments showed that temperatures over 500° C in flowing hydrogen were required to remove the chlorine from the solid phase. This showed that the silicon and chlorine analyses were not due to $SiCl_4$ adsorbed on the solid phase powder. From these facts and from free energy data (ref. 3), it is probable that the following reaction took place during ball milling:

$$Cr + 2SiCl_4 \rightarrow CrCl_2 + Si_2Cl_6$$
$$\begin{pmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{pmatrix}\begin{pmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{pmatrix}$$

Thermodynamically, both $CrCl_2$ and $CrCl_3$ are possible reaction products, but the exact oxidation state of Cr in the reaction products was not determined. No increase in pressure was noted during the milling run, and the gas phase was not analyzed.

Runs 4 and 5: chromium - n-heptane (Cr - n-C_7H_{16}) and nickel - n-heptane (Ni - n-C_7H_{16}), respectively. - The liquid phases resulting from milling either Cr or Ni in n-C_7H_{16} were colorless. Gas chromatography of the liquid phases showed only n-C_7H_{16}. Evaporation of the liquid phases yielded viscous, colorless residues. These residues were 0.0133 weight percent for the Cr run and 0.011 weight percent for the Ni run. The infrared spectra of both residues were identical and indicated an alkane or mixtures of alkanes. Considering the viscosity of the liquid residues, it is surmised that these alkanes have 12 to 14 carbon atoms. These alkanes may have formed from free radicals, such as $C_6H_{13}\cdot$ or $C_7H_{15}\cdot$, created by reaction of n-C_7H_{16} with the metal surfaces.

The total mill pressure developed during the Cr milling run was 382 kilonewtons per square meter (55.5 psi). A gas phase sample taken in the interval from 159 to 384 hours in the run showed that the reaction gases were mainly hydrogen with much smaller amounts of methane (CH_4) and trace amounts of carbon dioxide (CO_2). (See table II.)

The total ball mill pressure developed during the Ni run was much smaller than that for the Cr run and amounted to 20.7 kilonewtons per square meter (3.0 psi). An analysis of a gas sample taken towards the end of the milling run showed mainly hydrogen with much smaller amounts of CH_4 and CO_2. (See table II.)

In addition to hydrogen, CH_4, and CO_2, small amounts of nitrogen, argon, and sometimes oxygen were detected in this gas phase as well as in most of the other gas phases analyzed in this investigation. These were residual atmospheric gases not completely removed by evacuation of the mill, and probably also gases dissolved in the milling liquid or adsorbed on the metal powders. In addition, varying amounts of the vapor of the milling liquids were also revealed in the analysis. None of these gases are included in table II because they are not considered to be reaction gases.

Hydrogen and methane are obviously formed by reaction of the milling medium with bare metal surfaces formed during ball milling. The exact reaction mechanism is not known, but it could involve a cracking process on the metal surface followed by reaction of the fragments; for example,

$$CH_3(CH_2)_5CH_3 \xrightarrow{Ni, Cr} CH_3(CH_2)_5\cdot + \cdot\dot{\underset{\cdot}{C}}\cdot + H_2\uparrow + H\cdot$$

Then,

$$CH_3(CH_2)_5\cdot + \cdot(CH_2)_5CH_3 \rightarrow CH_3(CH_2)_{10}CH_3$$

$$\cdot\dot{\underset{\cdot}{C}}\cdot + 4H\cdot \rightarrow CH_4\uparrow$$

$$\cdot\dot{\underset{\cdot}{C}}\cdot \rightarrow C(\text{in solid phase})$$

$$H\cdot \rightarrow H(\text{in solid phase})$$

The dots in the reaction products indicate unshared valence electrons. From another point of view and if CH_4 formation is regarded as side-reaction cracking, the n-heptane may be assumed to react by a Wurtz reaction (ref. 4) as follows:

$$C_7H_{16} + Cr(\text{surface}) \rightarrow C_7H_{15}Cr + \frac{1}{2}H_2\uparrow$$

Then,

$$2C_7H_{15}Cr \rightarrow C_{14}H_{30} + 2Cr(\text{surface})$$

The CO_2 in the gas phases for these as well as for other runs is probably formed by reaction of active carbon with oxides on the powder surfaces and/or on the balls and mill walls. This view appears to be supported by the fact that (as will be shown in the section discussing run 9) the amount of CO_2 generated at the beginning of the milling run is much larger than later on in the run. In addition, milling runs (see table II), where comparison is possible, show that Ni runs generate relatively more CO_2 than Cr runs. This would be expected under the proposed reaction mechanism, since chromic oxide (Cr_2O_3) is more stable than nickel oxide (NiO). The same relation would hold on the assumption that CO_2 is formed by reaction of carbon with Fe_2O_3 (or $FeO\cdot Cr_2O_3$) on the balls and mill surfaces. However, the formation of CO_2 could also be due to reaction of carbon with adsorbed, dissolved, or residual oxygen.

Runs 6 and 7: chromium-methyl alcohol ($Cr\text{-}CH_3OH$) and ni-methyl alcohol ($Ni\text{-}CH_3OH$), respectively. - The liquid phase resulting from the $Cr\text{-}CH_3OH$ run was brown but that from the $Ni\text{-}CH_3OH$ run was colorless. In both cases, the gas chromatograms of the liquid phases were the same as that of the original CH_3OH.

After evaporation of the CH_3OH, the liquid phase from the $Cr\text{-}CH_3OH$ run yielded 0.248 weight percent of a brown solid. Analysis of this brown solid showed 37.6 weight percent oxygen, 7.01 weight percent carbon, and 3.94 weight percent hydrogen. Spectrographic analysis indicated 18.5 weight percent chromium, 14.5 weight percent iron, and 2 weight percent nickel. (The Fe and Ni were due to pickup, as indicated later.) The infrared spectrum of this brown compound (or compounds) resembled that of metal

formates. Thus, both chemical analysis and the infrared spectrum indicate some kind of organometallic compound. However, there is not enough information at present to identify this brown material.

The Cr-CH_3OH run produced the unusually high pickup of about 45 weight percent (total powder weight basis) as compared with less than 2 weight percent for most other runs with stainless-steel balls and mills. This may be due to the relatively high reactivity of alcohols, particularly methyl alcohol, toward metals with the formation of metal alkoxides (ref. 4).

After evaporation of the CH_3OH, the liquid phase from the Ni-CH_3OH run yielded 0.05 weight percent residue. The residue was not analyzed.

The total increase in ball mill pressure during the Cr run was 1133 kilonewtons per square meter (164.4 psi) as compared with 121 kilonewtons per square meter (17.5 psi) for the Ni run. As for the other milling runs, the higher increase in pressure in the Cr run reflects its higher reactivity, as compared with Ni. In both runs the gas phases (see table II) were mainly composed of hydrogen with smaller amounts of CH_4 and CO_2.

On the basis of these results, the overall ball mill reaction on milling either Cr or Ni in CH_3OH may be represented by the following unbalanced equation:

$$M + CH_3OH \rightarrow H_2\uparrow + CH_4\uparrow + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{liquid}\\ \text{phase}\end{smallmatrix}\right)}{\text{Organometallics}} + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{smallmatrix}\right)}{C} + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{smallmatrix}\right)}{H}$$

where M is either Cr, Ni, or Fe (from balls and mill).

Runs 8 and 9: chromium-ethyl alcohol (Cr-C_2H_5OH) and nickel-ethyl alcohol (Ni-C_2H_5OH), respectively. - The liquid phase from the Cr-C_2H_5OH run had a light reddish brown color, whereas that from the Ni-C_2H_5OH run was colorless. The gas chromatograms of the liquid phases were the same as that of the original C_2H_5OH.

On evaporation to dryness, the liquid phase from the Cr run yielded 0.0211 weight percent of a red-brown, solid residue. Paper chromatography of this residue indicated that it was made up of a red-brown compound and a much smaller amount of a yellow colored compound. The infrared spectrum of the mixture resembled that of an acetate. In this regard it is to be noted that, when the ball mill was first opened, the liquid phase appeared colorless; the red-brown coloration developed gradually on exposure to air. This suggests that the red-brown compound may have resulted from the oxidation of an organometallic compound, possibly an alkoxide.

On evaporation to dryness, the liquid phase from the Ni run yielded 0.005 weight percent residue, and no attempt was made to identify it.

The 993-kilonewton-per-square-meter (144-psi) pressure increase during the Cr run is about five times the 207-kilonewton-per-square-meter (30-psi) increase during the Ni run. Both gas phases are composed mainly of H_2 and smaller amounts of CH_4 and CO_2. In addition, the gas phase from the Ni run showed the presence of relatively small amounts of oxides of nitrogen (NO_2, N_2O, and NO). Because of this unexpected development, an additional Ni-C_2H_5OH run (not included in table II) was made. This run was for the sole purpose of determining the analysis of the gas phase as a function of milling time. After each analysis, the ball mill was evacuated and then pressurized with pure helium. The results of the analyses are shown in figure 3. In addition to the NO_2 shown in the figure, small amounts (<1 percent total) of N_2O and NO were noted at the beginning of the run. As also shown in figure 3, CH_4, CO_2, and NO_2 predominate at the beginning of the run then gradually decrease while hydrogen increases to become the main gas evolved.

It is surmised that the oxides of nitrogen are formed by the catalyzed reaction of nitrogen and oxygen (present as residual, dissolved, or adsorbed gases). This reaction may be of interest for the catalytic fixation of nitrogen but the pursuit of this matter is beyond the scope of the present investigation.

From the results presented, the overall ball mill reaction may be represented by an equation similar to that stated for the runs with methyl alcohol (runs 6 and 7).

Run 10: chromium-ethyl ether (Cr-$(C_2H_5)_2O$). - The liquid phase resulting from the Cr-$(C_2H_5)_2O$ run was colorless. Gas chromatography of this liquid phase revealed only $(C_2H_5)_2O$. No significant residue remained after evaporation.

As shown in table II, the total pressure increase during ball milling was 648 kilonewtons per square meter (94 psi). The gas phase was predominantly composed of hydrogen with smaller amounts of CH_4 and CO_2.

The relatively high CO_2 content (for a Cr run) together with the relatively high oxygen to specific surface ratio in the solid phase suggests that the oxygen in $(C_2H_5)_2O$ reacted with the Cr.

From these results, the unbalanced equation for the ball mill reaction could be written:

$$(C_3H_5)_2O + Cr \rightarrow H_2\uparrow + CH_4\uparrow + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{smallmatrix}\right)}{C} + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{smallmatrix}\right)}{H} + Cr_2O_3\ (\text{on Cr})$$

Runs 11 and 12: chromium-acetone ($Cr\text{-}CH_3COCH_3$) and nickel-acetone ($Ni\text{-}CH_3COCH_3$), respectively. - The liquid phases resulting from milling either Cr or Ni in CH_3COCH_3 were yellow, although in the case of the Ni run, the color of the liquid phase did not become noticeable until it was concentrated to about 1/10 of its original volume.

Gas chromatography of the liquid phase from the Cr run showed (in addition to acetone) the presence of two compounds representing about 1.6 percent of the liquid. Evaporation of the volatile components in the liquid phase yielded about 1.5 percent of a red-brown, oily liquid. This liquid was identified as diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) from its infrared and NMR spectra.

The liquid phase from the Ni run showed the same kind of chromatogram as that from the Cr run. After evaporation, the liquid phase yielded 0.022 percent of an oily, reddish-brown liquid. The infrared spectrum of this liquid was identical to that of the diacetone alcohol from the Cr run. Therefore, it was concluded that it was also diacetone alcohol. Quite probably the diacetone alcohol was formed by aldol condensation catelyzed by the bare Cr or Ni surfaces.

Spectrographic analysis of the residue showed the liquid phase from the Ni run to contain about 0.07 ppm of all detected metals, including <0.00013 ppm Ni in solution. Thus, if the yellow color of the liquid phases is due to metal ions, the amounts of metal ions involved are very small.

The pressures developed during either ball milling run were relatively small (table II). Only the gas phase for the Ni run was analyzed. In this case the predominant gas species is CH_4 with small amounts of CO_2 and hydrogen. Considering the results shown in figure 2 the high CH_4 at low ball mill pressures is not considered relevant, just another instance of the same effect in a Ni run. In these two runs the unbalanced equation for the ball mill reaction may be written as follows (where M = Cr or NI):

$$CH_3COCH_3 + M \rightarrow CH_4\uparrow + H_2\uparrow + CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{C}=O + C + H$$

(in liquid phase) (in solid phase) (in solid phase)

Run 13: chromium-butyraldehyde ($Cr\text{-}CH_3(CH_2)_2CHO$). - The liquid phase resulting from the $Cr\text{-}CH_3(CH_2)_2CHO$ milling run had a very dark red-brown color. The gas

chromatogram of this liquid phase is shown in figure 4. This chromatogram shows a large number of different compounds (many unresolved) with some of them in relatively high yields. The liquid phase was separated into five fractions by fractional distillation. The first fraction (74^{o} to 78^{o} C at atmospheric pressure) was a mixture of butyraldehyde (~40 percent of the liquid phase) and water (~2 percent). The yellow colored second fraction (100^{o} to 122^{o} C at atmospheric pressure) represented about 24 percent of the liquid phase. The infrared and NMR spectra of this second fraction indicated an α-β unsaturated aldehyde. This aldehyde was tentatively identified as 2-ethyl-2-hexenal.

The yellow colored third fraction was obtained by vacuum distillation at 90^{o} to 145^{o} C and represented about 9 percent of the liquid phase. Its infrared spectrum was the same as that of the second fraction, despite the obvious difference in boiling points. More will be said about this later.

The yellow colored fourth fraction was obtained by vacuum distillation at 140^{o} to 170^{o} C and represented about 19 percent of the liquid phase. Its infrared spectrum shows strong absorption bands at 5.75 micrometers (C=O stretch) and 8.41 micrometers (C—O—C stretch) indicating an ester, possibly a butyrate.

The fifth fraction was the dark colored pot fraction which boiled at about 240^{o} C at atmospheric pressure and could not be distilled any further with the available equipment. This pot fraction represented about 6 percent of the liquid phase. The infrared spectrum of this fraction was the same as that of the second and third fractions, again, despite the large difference in boiling points.

Considering the readiness with which some unsaturated aldehydes such as acrolein undergo polymerization (ref. 5), it is surmised that the third and fifth fractions are oligomers (dimer and trimer, probably) of the monomeric compound in the second fraction.

The 2-ethyl-2-hexenal monomer mentioned probably formed by aldol condensation followed by dehydration, thus:

$$2CH_3CH_2CH_2CHO \xrightarrow[\text{surface}]{\text{metal}} CH_3CH_2CH_2CHOHCHCHO \xrightarrow{-H_2O} CH_3CH_2CH_2CH{=}CCHO$$

(the C_2H_5 group is attached to the CH of $CH_3CH_2CH_2CHOHCHCHO$ and to the C of $CH_3CH_2CH_2CH{=}CCHO$)

A remarkable feature of this reaction is the presence of free water in the reaction products, in view of the fact that a very reactive Cr surface is available during milling. This suggests that the dehydration step and the subsequent polymerization of 2-ethyl-2-hexenal may have occurred on heating during distillation.

The (assumed) butyrate may have formed from butyraldehyde in the presence of atmospheric oxygen during distillation.

The increase in pressure during milling was less than 7 kilonewtons per square meter (1 psi). The gas phase was not analyzed.

Runs 14 and 15: chromium-acetic acid (Cr-CH_3COOH) and nickel-acetic acid (Ni-CH_3COOH), respectively. - The liquid phase resulting from milling Cr in CH_3COOH was brown and yielded 2.82 weight percent of a brown solid on evaporation. The infrared spectrum of this brown solid corresponds to that of chromium acetate.

The liquid phase resulting from the Ni-CH_3COOH run was green. Gas chromatography of this liquid phase showed two compounds eluting before and two compounds eluting after the CH_3COOH. The total amounts of these compounds is estimated at 0.5 weight percent of the liquid phase. No attempt was made to identify them. On evaporation the liquid phase yielded 3.5 weight percent of a green solid. This green solid was identified as nickel acetate from its infrared spectrum.

The total pressure increase during the Cr run was 371 kilonewtons per square meter (53.8 psi) as compared with 328 kilonewtons per square meter (47.5 psi) for the Ni run. The analyses of the gas phases showed that the main gas evolved in either case was hydrogen with smaller amounts of CH_4 and CO_2.

This pair of runs represent the only instance noted in this investigation where the reactivity of Ni, as measured by yields of reaction products, was higher than that of Cr.

The unbalanced equation for the ball mill reaction may be represented by

$$CH_3COOH + M \rightarrow H_2\uparrow + CH_4\uparrow + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{liquid}\\ \text{phase}\end{smallmatrix}\right)}{M(OOC\ CH_3)_n} + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{smallmatrix}\right)}{C} + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{smallmatrix}\right)}{H}$$

where M is either Cr or Ni and n = 2 or 3.

Runs 16 and 17: chromium-carbon tetrachloride (Cr-CCl_4) and nickel-carbon tetrachloride (Ni-CCl_4), respectively. - The liquid phases resulting from milling either Cr or Ni in CCl_4 were red (although not the same hue). On evaporation, the liquid phase from the Cr run yielded 0.29 weight percent and that from the Ni run 0.14 weight percent of dark red, gummy residues. Both residues evolved white fumes on heating at about 350° C, leaving a black residue. Infrared spectra and direct comparison with commercially obtained samples showed that the condensate obtained from the white fumes was hexachloroethane (C_2Cl_6) in both runs. The black residues were about 60 weight percent carbon. From spectroscopic analysis of the dark red residues, it was established that the liquid phase from the Cr-CCl_4 run contained about 41 ppm of all detected metals, and that from the Ni-CCl_4 run contained about 4 ppm of all detected metals.

Attempts were made to determine how the chlorine and carbon are associated in the solid phase. X-ray diffraction analysis showed only the metals. After heating the powders at 420° C for 90 minutes in vacuum, the chlorine and carbon contents remained practically the same as in the original solid phase. From this it is deduced that the chlorine is tied up in metal chlorides and not in organic compounds. It is not known how the carbon is associated in the solid phase.

No changes in ball mill pressures were noted during ball milling. The gas phases were not analyzed.

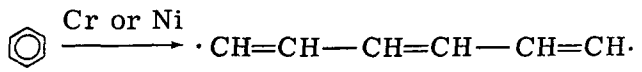
Considering these results, the unbalanced equation for the ball mill reaction may be written as

$$CCl_4 + M \rightarrow \underset{\left(\begin{smallmatrix}\text{in}\\ \text{liquid}\\ \text{phase}\end{smallmatrix}\right)}{C_2Cl_6} + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{smallmatrix}\right)}{MCl_n} + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{smallmatrix}\right)}{C}$$

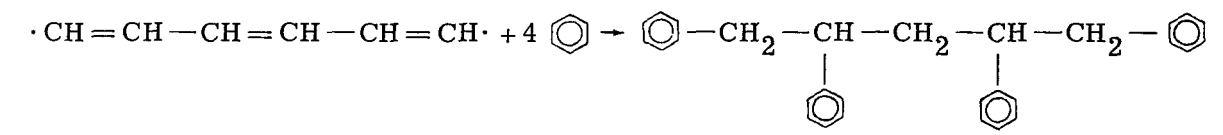
where M is either Cr or Ni and n = 2 (for Ni) or 3 (for Cr).

It is surmised that milling a metal in halogenated compounds such as CCl_4 should prove a useful method of obtaining anhydrous (and perhaps even oxygen free) metal halides such as $AlCl_3$, AlI_3, $SnCl_2$, etc. This method would entail either milling until all the metal reacted or else milling followed by recovery of the metal halide by distillation or by solvent extraction.

Runs 18 and 19: chromium-benzene (Cr-C_6H_6) and nickel-benzene (Ni-C_6H_6), respectively. - The liquid phases from both the Cr-C_6H_6 and the Ni-C_6H_6 appear colorless on separation from the solid phases. On evaporating them to about $1/20^{th}$ of their original volumes, however, the liquid phases are yellow colored. Gas chromatography of the liquid phases showed only C_6H_6. On evaporating the liquid phase from the Cr run, 0.03 weight percent of a yellow, viscous liquid was obtained. Similarly, the liquid phase from the Ni run yielded 0.014 weight percent of a yellow-tan, viscous liquid. Paper chromatography showed only one compound in each of the residues. The infrared spectra of both residues were similar and had many of their absorption bands coinciding with those of polystyrene. It is surmised that the residues may be oligomers brought about by break up of the benzene ring followed by addition of benzene to the unsaturated carbon bonds, for example,



then



Spectrographic analysis of the yellow residue from the Cr run indicated that the liquid phase had 0.04 ppm of all detected metals in solution.

The total pressure increase during the Cr milling run was only 11 kilonewtons per square meter (1.6 psi), and the main gas evolved was CH_4 with smaller amounts of CO_2 and hydrogen. The pressure increase during the milling run was about 1.2 kilonewtons per square meter (0.18 psi) and was deduced from the gas analysis. The gases evolved during this run were mainly hydrogen with smaller amounts of CH_4 and oxides of nitrogen. As in the case of the Ni-C_2H_5OH run, the oxides of nitrogen are probably due to the catalyzed reactions of residual atmospheric gases.

From the stated results the overall unbalanced equation for the ball mill reactions may be written as

$$C_6H_6 + M \rightarrow CH_4\uparrow + H_2\uparrow + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{liquid}\\ \text{phase}\end{smallmatrix}\right)}{\text{Polymer}} + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{smallmatrix}\right)}{\text{C}} + \underset{\left(\begin{smallmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{smallmatrix}\right)}{\text{H}}$$

where M is either Cr or Ni.

Run 20: chromium-toluene (Cr-C_6-H_5CH_3). - A yellow colored liquid phase resulted from the Cr-$C_6H_5CH_3$ run. Gas chromatography of the liquid phase showed only $C_6H_5CH_3$. Evaporation of the liquid phase to dryness yielded 0.094 weight percent of a reddish-brown, viscous residue. The infrared spectrum was similar to that of polystyrene. It is surmised that this polymer (oligomer, most likely) was formed by a process similar to that described under the Cr-C_6H_6 run.

Spectroscopic analysis indicated that there were only 6 ppm of all detected metals in solution in the liquid phase.

The pressure built up during the milling run was only about 4.3 kilonewtons per square meter (0.62 psi), as calculated from gas analysis. Analysis of the gas phase showed mainly H_2 and smaller amounts of CH_4 and CO_2.

The unbalanced equation for the overall ball milling reaction may be written as

$$C_6H_5CH_3 + Cr \rightarrow H_2\uparrow + CH_4\uparrow + \underset{\begin{pmatrix}\text{in}\\ \text{liquid}\\ \text{phase}\end{pmatrix}}{\text{Polymer}} + \underset{\begin{pmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{pmatrix}}{\text{C}} + \underset{\begin{pmatrix}\text{in}\\ \text{solid}\\ \text{phase}\end{pmatrix}}{\text{H}}$$

Color of the Liquid Phases

Repeated references have been made to the color of the liquid phases or to their residues. The colors observed may be due to the presence of transition metal ions, to compounds with unconjugated double bonds, to colloids, or to other causes. In some instances, such as in Cr or Ni acetates, the color of these reaction products is obviously due to the presence of Cr and Ni ions. In most cases the amounts of metals detected in the liquid phases were too small to establish whether the color observed was due to metal ions. However, indirect evidence gathered from an extra milling run with aluminum in acetone suggests that this is the case for at least some of the liquid phases. In this instance the (abundant) reaction products were colorless; in contrast, the diacetone alcohol obtained by milling Cr or Ni in acetone was red-brown in color. Consequently, it is possible that some of the reactions observed in the present investigation may have been brought about by mechanisms involving organometallic compounds. Considering that in most cases the amounts of metal involved are very small, investigations of the kind reported herein may be useful in the field of catalysis. The pursuit of these matters, however, is beyond the scope of the present investigation.

Reactivity of Bare Metal Surfaces

Benzene and n-heptane (as well as all the other alkanes) are among the most inert organic compounds toward active metals. For this reason it was extremely interesting that they would react at all with metals like Cr and Ni. This reactivity is due in great part to the fact that during ball milling the powder's bare metal surface is exposed to chemical attack by the liquid in contact with it. It may well be, however, that other factors besides bare surfaces may influence reactivity. One of these factors is the strain energy associated with the heavily cold worked metal particles. As discussed in reference 1, this strain energy should, and most likely does, enhance reactivity, since strain energy increases the free-energy change associated with the chemical reaction. Another factor that possibly has an effect on reactivity are localized heat effects at the points of impact in the particles. The fact that "fragments" such as CH_4, hydrogen, and perhaps

even colloidal carbon appear among the reaction products suggests that pyrolytic or cracking processes, which in turn are indicative of heat effects, occur during ball milling. Whatever factors may enhance the reactivity of bare metal surfaces, however, the undeniable fact is that these surfaces are capable of bringing about a large variety of chemical reactions in many different organic and in some inorganic liquids. The effect of metal surfaces on reactivity would also apply to organic gases and to organic solids dissolved in suitable liquids. It follows that these bare metal surfaces, whether created by ball milling or otherwise, should prove a useful tool in organic synthesis. The usefulness of these bare metal surfaces in organic synthesis or in catalysis stems not only from their ability to allow substitution reactions (as in the formation of Cr and Ni acetates) or addition reactions (such as formation of diacetone alcohol from acetone) but mostly from their apparent ability to create free radicals. These free radicals are capable of further reaction with neutral molecules or among themselves. Such radicals are formed both in n-heptane and in benzene as already indicated.

Under normal conditions both benzene and n-heptane (as well as other alkanes) are unreactive towards active metals; nevertheless, these liquids react with Cr and Ni during ball milling. The bare surfaces of Cr and Ni were also shown to bring about reactions involving many different functional groups. Now, the great majority of organic compounds may be regarded as combinations of aliphatic and aromatic compounds together with a limited number of functional broups. Further, the alkanes are about the least reactive among the aliphatic compounds and benzene is about the least reactive among the aromatic compounds. From this it follows that bare surfaces of suitable metals should be capable of bringing about reactions in very many organic compounds when brought in contact with these surfaces. A corollary to these observations is that most metal powders cannot be comminuted in organic compounds without contamination; at the very least, this should be the case for metals of higher reactivity than Ni. To judge from their oxidation potentials this includes most of the metals in the periodic table.

Comminution and chemical synthesis are not the only examples of phenomena brought about by bare metal surfaces; galling and wear of bearings due to inadequate lubrication may be cited as additional examples. The bare metal surfaces formed either during galling or due to wear of bearings should be capable of reacting either with the lubricant or with atmospheric gases. For this reason it is surmised that the findings of this investigation may find applications in the field of lubrication.

CONCLUDING REMARKS

It is clear from the results of the present investigation that, although the objective stated in the INTRODUCTION was accomplished, none of the milling runs yielded the

hoped for "clean," milled metal powders. However, the results obtained may allow a judicious selection of milling liquid on the basis of what kind and amount of contaminant is either tolerably low or reducible to negligible levels by well known techniques. In addition, a novel method of synthesizing organic and inorganic compounds by reactions on bare metal surfaces has been developed as part of this investigation. As regards this synthesis of chemical compounds, the results reported herein seem meager when compared with the possibilities. Considering the many metals and the thousands of organic and inorganic compounds available, there appears to be ample opportunity for exploration and discovery in the area of reactivity of bare metal surfaces. Besides their application in organic synthesis there is reason to believe that investigations of the type reported herein may find applications in other fields such as in catalysis and in lubrication.

SUMMARY OF RESULTS

This investigation was conducted to determine the nature of the reaction products resulting from the reaction of metal powders with organic and inorganic liquids during ball milling. The results obtained will be summarized in three sections dealing with solid phases (milled powders), liquid phases (ball milling liquid), and gas phases (ball mill head gases) as follows:

Solid Phases

1. Ball milling chromium powders in inorganic liquids and either chromium or nickel powders in organic liquid produced solid phases (milled powders) that were always contaminated with the chemical elements making up the ball milling liquid.

2. The solid phase powders resulting from ball milling had total contaminations from elements in the milling liquid ranging from 0.01 to 56 weight percent and specific surface areas ranging from 0.14 to 37 square meters per gram. As a rule, the larger the specific surface area of the powder, the greater its contamination.

3. The solid phase powder resulting from milling nickel in n-heptane had the lowest contamination among the powders resulting from the nickel milling runs. This powder was contaminated with 0.169 weight percent oxygen, 0.456 weight percent carbon, and 0.0297 weight percent hydrogen. The oxygen was due to atmospheric contamination after milling.

4. The solid phase powder with the minimum contamination of 0.01 weight percent chlorine resulted from milling chromium in titanium tetrachloride.

Liquid Phases

1. The liquid phases (ball mill liquids) resulting from milling either chromium or nickel powders in a variety of organic and inorganic liquids contained compounds formed by the chemical reaction of the milling liquid with the bare metal surfaces created on the powders during ball milling. The reactions noted and the compounds detected were too numerous to adequately describe them all in this section. Only the most significant reactions or reaction products are mentioned.

2. On milling either chromium or nickel powders in n-heptane, an alkane of higher boiling point than n-heptane was formed in the liquid phase.

3. On milling chromium powder either in methyl or in ethyl alcohols, compounds believed to be organometallic formed in the liquid phase. Probably, similar compounds formed on milling nickel in the same liquids.

4. On milling chromium or nickel in acetone, diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) formed in the liquid phases.

5. On milling chromium in butyraldehyde, a large number of organic compounds (some in high yields) and water formed in the liquid phase. Some of these compounds were α-β unsaturated aldehydes and apparently result from just one aldehyde present both in monomeric and polymeric forms.

6. On milling chromium or nickel in benzene and chromium in toluene, a compound or compounds of higher boiling point than either benezene or toluene and whose infrared spectra resembled that of polystyrene formed in the liquid phases.

7. On milling either chromium or nickel powders in carbon tetrachloride, hexachloroethane (C_2Cl_6) formed in the liquid phases.

Gas Phases

In most milling runs involving either chromium or nickel powders milled in organic liquids, hydrogen, methane, and carbon dioxide gases were generated as a result of chemical reactions between metal powders and the milling liquid. In the runs involving nickel in ethyl alcohol and in benzene, oxides of nitrogen were also generated and were probably due to the catalyzed reaction of residual atmospheric gases.

CONCLUSIONS

From the results of the present investigation, the following conclusions can be drawn:

1. Metal powders cannot be comminuted in organic or inorganic liquids without becoming contaminated with the elements making up the milling liquid. It is surmised that the same holds true for milling in gases.

2. The results reported herein should make it possible to select milling liquids that produce either low levels of contamination or contaminants that may be removed by simple reduction procedures.

3. Reactions of bare metal surfaces, whether produced by milling or otherwise, with organic and inorganic compounds should prove useful in the synthesis of other chemical compounds.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 13, 1975,
505-01.

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TABLE I. - CHARACTERIZATION OF RAW MATERIALS

Material		Form	Grade	Purity	Manufacturer's specifications or chemical analysis
Name	Chemical formula				
Chromium	Cr	Powder (-20 mesh)	(a)	99.5 (min.)	Oxygen, 134 ppm; carbon, 97 ppm; nitrogen, 83 ppm; hydrogen, 5 ppm; iron, 0.33 wt. %. Specific surface area, 0.11 m^2/g
Nickel	Ni	Powder (1.2 μm)	(b)	99.7	Oxygen, 0.170 wt. %; carbon, 980 ppm; hydrogen, 41 ppm; iron, 80 ppm. Specific surface area, 0.37 m^2/g
Silicon tetrachloride	$SiCl_4$	Liquid	Tech.	(b)	Fuming, clear liquid; Fisher Scientific S-165
Stannic chloride	$SnCl_4$		(b)		Anhydrous; Fisher Scientific T-140
Titanium tetrachloride	$TiCl_4$		Purified		Fisher Scientific T-308
n-Heptane	C_7H_{16}		(b)		Boiling range, 98.38-98.49° C; specific gravity, 0.683 (20/20); residue after evaporation, 0.0031 percent
Methyl alcohol	CH_3OH		Reagent	99.5	Anhydrous; Mallinckrodt No. 3016; residue after evaporation, 0.005 percent
Ethyl alcohol	C_2H_5OH		Style F	(b)	Nitrogen, 17 ppm; anhydrous; residue after evaporation, 0.0012 percent
Diethyl ether	$(C_2H_5)_2O$		Reagent	(b)	Anhydrous; Fisher Scientific E-138
Acetone	CH_3COCH_3		Reagent	(b)	Residue after evaporation, 0.001 percent; aldehyde, 20 ppm; methanol, 50 ppm; water, 0.5 percent
n-Butyraldehyde	C_3H_7CHO		(b)	(a)	Eastman No. 440
Acetic acid	CH_3COOH		Reagent	99.7	Glacial; Fisher Scientific A-38
Carbon tetrachloride	CCl_4			99	Fisher Scientific C-570
Benzene	C_6H_6			(b)	Residue after evaporation, 0.001 percent; Fisher Scientific B-411
Toluene	$C_6H_5CH_3$			(b)	Residue after evaporation, 0.0002 percent; Fisher Scientific T-324

[a] High purity.
[b] Unknown.

TABLE II. - LIST OF MILLING RUNS AND COMPOSITION OF PHASES RESULTING FROM BALL MILLING

Run	Reactants		Reaction products															
			Solid phase								Liquid phase		Gas phase					
	Metal powder	Milling liquid	Powder recovered, percent	Oxygen ppm	Carbon, ppm	Hydrogen, ppm	Other, wt.%	Powder surface, m^2/g	Ratios		Color of liquid	Main reaction products	Total pressure increase in ball mill during run, kN/m^2 (psia)	Gas analysis (normalized)				
									Oxygen, ppm / Surface, m^2/g	Hydrogen to carbon ratio, moles/mole				Milling time interval for analysis, hr	Hydrogen, vol.%	Methane, vol.%	Carbon dioxide, vol.%	Other gases, vol.%
1	Cr	$TiCl_4$	100	(a)	(a)	(a)	Cl, 100 ppm[b]	0.14	(a)	(a)	Purple	$TiCl_3$	~0	(a)	(a)	(a)	(a)	----------
2	↓	$SnCl_4$	100	1 126	158	(a)	Sn, 23.14; Cl, 33±3	3.21	351	(a)	Colorless	(a)	~0	(a)	(a)	(a)	(a)	----------
3		$SiCl_4$	100	4 900	336	(a)	Si, 0 32; Cl, 1.6	4.12	1 189	(a)	↓	(a)	~0	(a)	(a)	(a)	(a)	----------
4	↓	C_7H_{16}	70	5 680	827	240	----------	1.56	3 641	3.16		Higher molecular weight alkanes	382 (55.5)	159 - 384	97.2	2.79	0.030	----------
5	Ni	C_7H_{16}	40	1 690	4 560	297	----------	.19	8 894	.777	↓	Higher molecular weight alkanes	20.7 (3.0)	223 - 384	98.9	.71	.36	----------
6	Cr	CH_3OH	100	45 700	11 080	1310	----------	37.0	1 235	1.41	Brown	Organo metallic compound	1133 (164.4)	233 - 305	95.7	4.29	.039	----------
7	Ni	CH_3OH	60	2 620	4 720	197	----------	.20	13 100	.497	Colorless	(a)	121 (17.5)	0 - 384	99.1	.073	.790	----------
8	Cr	C_3H_5OH	100	1 236	208	15	----------	.90	1 373	.858	Red-brown	Organo metallic compound(s)	993 (144)	342 - 384	99.6	.395	.041	----------
9	Ni	C_2H_5OH	56	1 600	5 850	158	----------	.26	6 154	.322	Colorless	(a)	207 (30)	0 - 384	86.8	9.15	.544	NO_2, 2.28; N_2O, 0.855; NO, 0.387
10	Cr	$(C_2H_5)_2O$	80	5 790	6 403	440	----------	1.23	4 707	.818	Colorless	(a)	648 (94)	31 - 189	93.7	5.58	.687	----------
11	Cr	CH_3COCH_3	100	6 420	3 030	124	----------	2.03	3 162	.488	Yellow	Diacetone alcohol	<7 (1)	----------	(a)	(a)	(a)	----------
12	Ni	CH_3COCH_3	↓	7 970	13 870	229	----------	.96	8 302	.188	Yellow	Diacetone alcohol	6.2 (0.90)	0 - 384	8.39	80.4	11.2	----------
13	Cr	$CH_3(CH_2)_2CHO$		4 320	4 360	88	----------	.99	4 360	.242	Red-brown	H_2O + higher molecular weight aldehydes + other compounds	<7 (1)	----------	(a)	(a)	(a)	----------
14	Cr	CH_3COOH		8 610	12 400	662	----------	2.40	3 588	.636	Brown	Cr acetate	371 (53.8)	0 - 384	97.3	1.94	.760	----------
15	Ni	CH_3COOH		13 020	11 270	706	----------	2.25	5 786	.746	Green	Ni acetate	328 (47.5)	0 - 384	90.9	7.06	2.04	----------
16	Cr	CCl_4		(a)	15 700	(a)	Cl, 18.27	6.64	(a)	(a)	Red	C_2Cl_6	~0	----------	(a)	(a)	(a)	----------
17	Ni	CCl_4		3 600	9 020	(a)	Cl, 7.45	30.5	118	(a)	Red	C_2Cl_6	~0	----------	(a)	(a)	(a)	----------
18	Cr	C_6H_6	↓	17 500	17 900	205	----------	6.59	2 655	.137	Yellow	Polymer resembling polystyrene	11 (1.6)	0 - 384	6.15	75.1	18.7	----------
19	Ni	C_6H_6	58	1 830	10 000	149	----------	.26	7 038	.177	Greenish yellow	Polymer resembling polystyrene	1.2 (0.18)	0 - 384	94.5	4.77	0	NO_2, 0.43; N_2O, 0.30
20	Cr	$C_6H_6CH_3$	100	4 000	9 100	342	----------	1.37	2 920	.448	Yellow	Polymer resembling polystyrene	4.3 (0.62)	0 - 384	90.8	7.06	2.08	----------

[a]Not determined.

[b]Excluding ~6 w/o $CrCl_3$ removed with water.

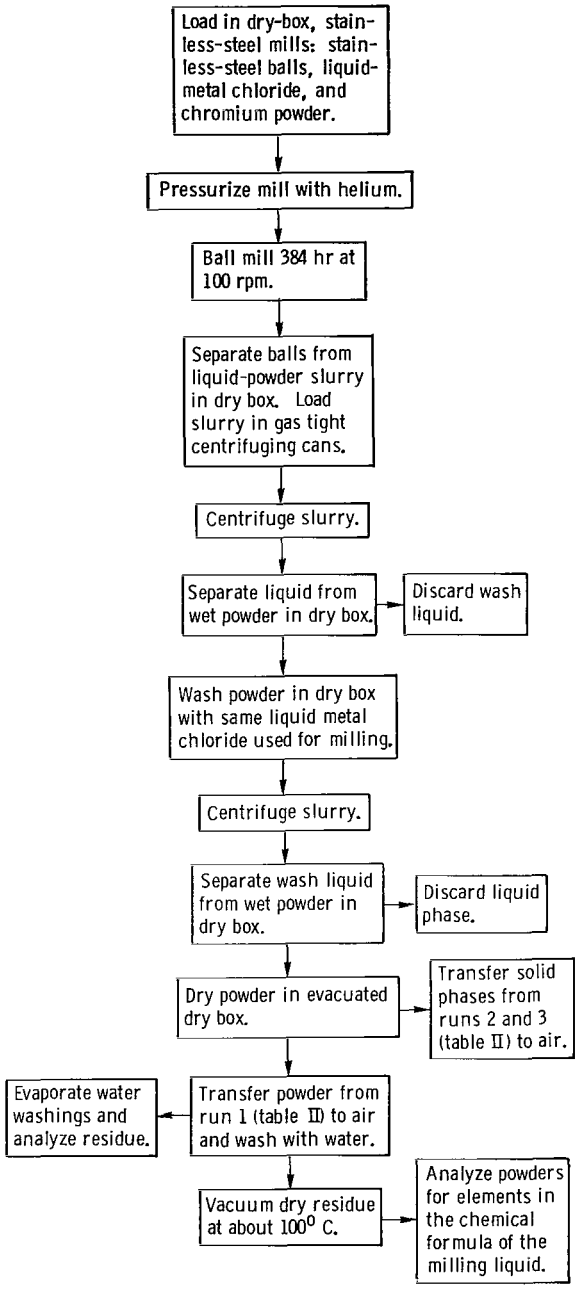

Figure 1. - Flow chart for milling chromium in liquid metal chlorides. (Runs 1 to 3 in table II.)

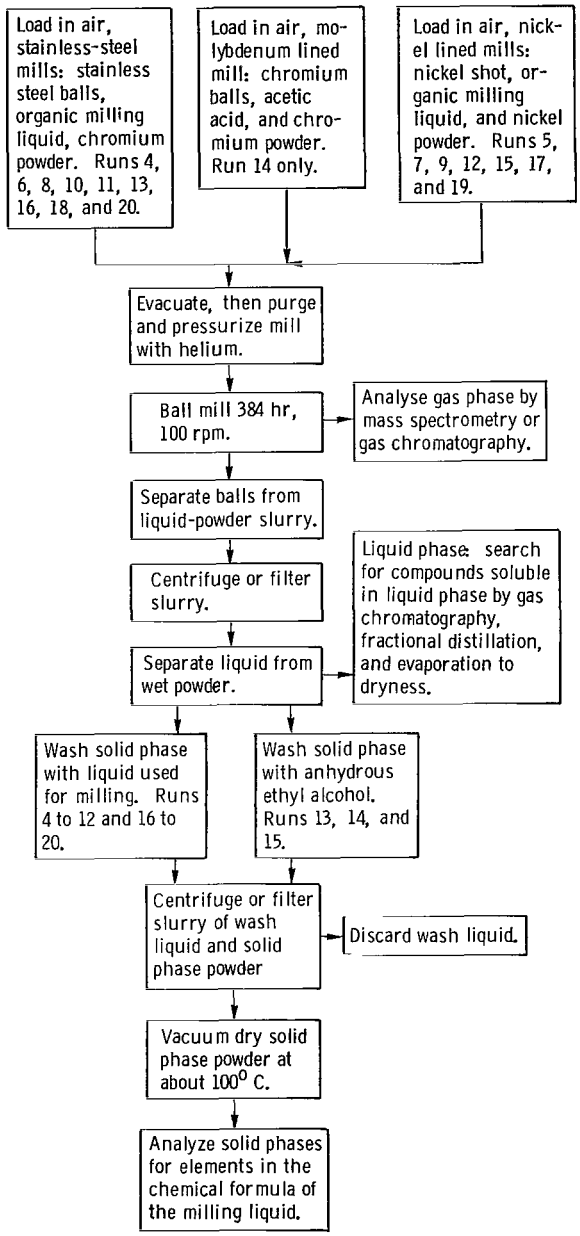

Figure 2. - Flow chart for milling chromium or nickel in organic liquids. (Runs 4 to 20, table II).

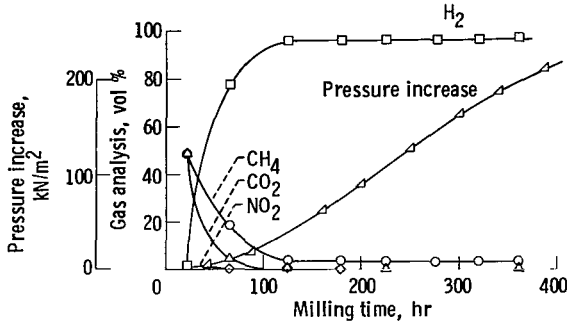

Figure 3. - Chemical composition and pressure increase of gases evolved during ball milling of nickel in ethyl alcohol.

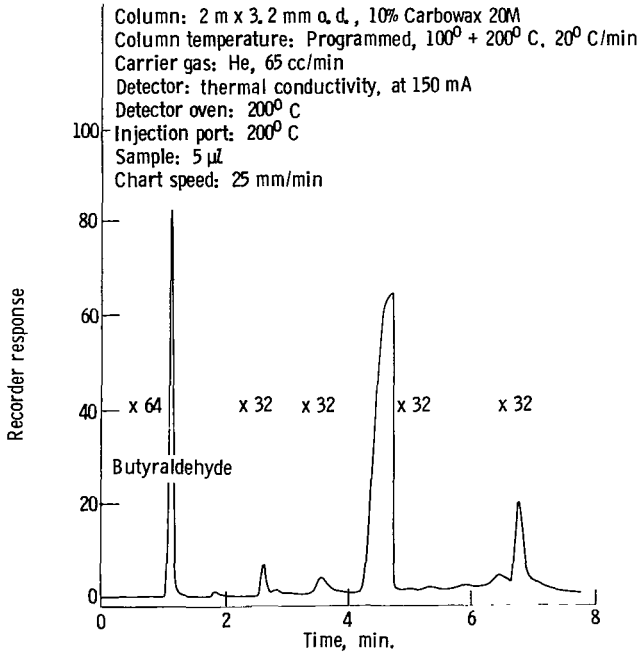

Figure 4. - Gas chromatogram for liquid phase resulting from milling chromium powder in butyraldehyde. (Run 13.)

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