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# THE RELEASE OF HYDROGEN ON BALL MILLING CHROMIUM IN WATER

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## ABSTRACT

On ball milling, chromium powder reacted with the water used as the grinding medium, and hydrogen was evolved. A film composed of $Cr_2O_3$ and $CrO_2$ formed on the powder surface during this reaction. This film was calculated to be about 6.7 Å (0.00067 $\mu$m) thick. Although the specific surface area of the powder continuously increases, a large proportion of the particles also became welded to each other during the milling process. The welding sandwiched the oxide films between the powder particles. For this reason, the ratio of oxide formed to measured surface (and apparent thickness of the film) increase with ball-milling time.


STAR Category 20

# THE RELEASE OF HYDROGEN ON BALL MILLING CHROMIUM IN WATER

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## SUMMARY

Ball milling of high-purity, coarse chromium powder in water released hydrogen, and a chromium oxide film formed on the chromium particles at the same time. This oxide film was calculated to be about 6.7 Å (0.00067 $\mu$m) thick and was composed of chromic oxide ($Cr_2O_3$) with small amounts of chromium dioxide ($CrO_2$).

As judged from surface area measurements, the chromium powder continuously decreased in size during ball milling. After 768 hours of ball milling, the average particle size of the powder was about 300 Å (0.03 $\mu$m). The ball-milled chromium particles ended up as flakes with a length to thickness ratio of about 10.

The surface area of the ball-milled powders continuously increased with ball-milling time. Yet, it is surmised that during the milling many fine particles became welded together sandwiching the oxide films between them. For this reason, the ratio of oxide formed to measured surface area of ball-milled powders increased with milling time. Because of the sandwiching process, it may be difficult to reduce the oxides in these ball-milled metal powders.

## INTRODUCTION

Ultrafine chromium powder is not commercially available at the present time. This type of chromium powder is needed for various research projects (including dispersion strengthening) which are underway or contemplated for the future. For this reason, a program to produce ultrafine chromium powder was undertaken at the NASA Lewis Research Center. This program included making fine chromium powder by ball milling in various liquid media. On grinding chromium with some of these liquids, it was observed that the pressure of gas within the ball mill increased. The writer and other workers in the field have noted pressure buildups on ball milling other metals in a variety of liquids. Generally, this pressure increase is relatively slight and has been attributed to a temperature increase during ball milling. On ball milling chromium in

water, however, the writer observed an unusually high pressure increase. This pressure increase was so large that it could not possibly be attributed to temperature effects. For this reason a preliminary investigation of this phenomenon was conducted. It involved installing a pressure gage in the ball mill to determine the pressure buildup and analyzing the gases evolved in the mill by mass spectrometry. Ball-mill pressures in excess of 10 atmospheres ($10.13 \times 10^5$ N/m$^2$) were observed. The gas evolved during ball milling was mostly hydrogen. To the writer's knowledge, hydrogen release during ball milling of metals has not been described previously in the literature.

It was surmised that hydrogen evolution was caused by the reaction of chromium with water. This suggested that chromium oxide could be formed at the same time on the surface of chromium. Since most liquids contain water as an impurity, it follows that grinding of chromium in many of these media would probably also cause it to oxidize. In addition, the water may also modify the grinding characteristics of the milling media. The same would be true when using grinding aids containing water of hydration. Whatever the origin of the water, its reaction with the chromium powder could modify the properties of the powder. For these reasons, it was decided to look further into the reaction of chromium with water.

The main purpose of this investigation was to study in more detail the reaction which occurs on ball milling chromium with water. It was also intended to attempt to correlate quantitatively the pressure buildup (due to hydrogen release) with the oxide content of the chromium.

The experimental work consisted in ball milling chromium in water in gas tight ball mills. The pressure of the hydrogen released was determined, with a pressure gage in the mill, as a function of ball-milling time. From these data, the amount of oxygen reacted with the chromium was calculated. The nature of the oxide formed by the reaction was determined by X-ray diffraction. From the data so obtained, the thickness of the chromium oxide layer was calculated. For comparison purposes, the oxygen content of the ball-milled powders was also determined by chemical analyses.

## MATERIALS, EQUIPMENT, AND PROCEDURES

The only materials used in this investigation were chromium metal and water. The starting raw chromium was high-purity-flake chromium. The chemical analyses of this chromium is given in table I. The coarse chromium powder used as mill feed material was prepared from this raw flake chromium.

The flake chromium was first crushed in a stainless-steel mortar and pestle. The crushed chromium was then pulverized in a small stainless-steel hammer mill until it passed a 30-mesh sieve. This coarse chromium powder was used for the ball-milling

TABLE I. - CHEMICAL AND PARTICLE SIZE ANALYSES OF AS-RECEIVED AND AS-MILLED CHROMIUM

| Processing conditions | Chemical analysis[a] | | | | | | Surface area (by BET method[b]), $m^2/g$ | Particle size[b, c], μm |
|---|---|---|---|---|---|---|---|---|
| | Oxygen, percent | Nitrogen, ppm | Carbon, ppm | Sulfur, ppm | Iron, percent | Other, percent | | |
| As-received chromium | [d]0.0050 | 50 | 94 | 730 | [d]0.001 | [d]Si, 0.003<br>[d]H, 0.001 | (e) | (Chunks approx. 15 by 15 by 4 mm) |
| Crushed and hammer-milled chromium | .0086 | 83 | (e) | (e) | .33 | (e) | 0.125 | 4.94 |
| Run 1: milled in water for 48 hr | .454 | (e) | (e) | (e) | (e) | (e) | 1.23 | .452 |
| Run 2: milled in water for 112 hr | 1.25 | (e) | (e) | (e) | (e) | (e) | 3.62 | .153 |
| Run 3: milled in water for 384 hr | 7.19<br>[b]9.21 | 214 | 1180 | (e) | 4.54 | (e) | 9.65 | .057 |
| Run 4: milled in water for 768 hr | [b]18.46 | 146 | 790 | (e) | 6.46 | (e) | 17.97 | .031 |

[a]Unless indicated otherwise, all chemical analyses were done by a commercial laboratory.
[b]In-house analyses.
[c]Particle size was obtained from the surface area S and the density of chromium (7.2 g/cu cm) by the following formula: Particle size (μm) = 4/(7.2)S (ref. 6).
[d]Supplier's analysis.
[e]Not determined.

experiments. The preparation of the coarse chromium powder was performed entirely inside a gas-tight, argon glove box. During this work, the argon glove box was evacuated at regular intervals and refilled with high-purity argon so as to keep the oxygen level below 100 ppm.

After hammer milling, the chromium powder was kept in gas tight containers until ready for use. Samples of this powder were packed into tin capsules for oxygen analysis. The chemical analysis of coarse chromium powder is included in table I.

The water used as the ball-milling medium was distilled water processed to remove dissolved gases. A gas tight vessel provided with a vacuum valve was used for the gas removal. The vessel was partly filled with the distilled water and then evacuated with a mechanical vacuum pump until the water boiled. After the water boiled for about 5 minutes, the vacuum valve was closed and the vessel placed in the argon glove box where the mills were to be loaded.

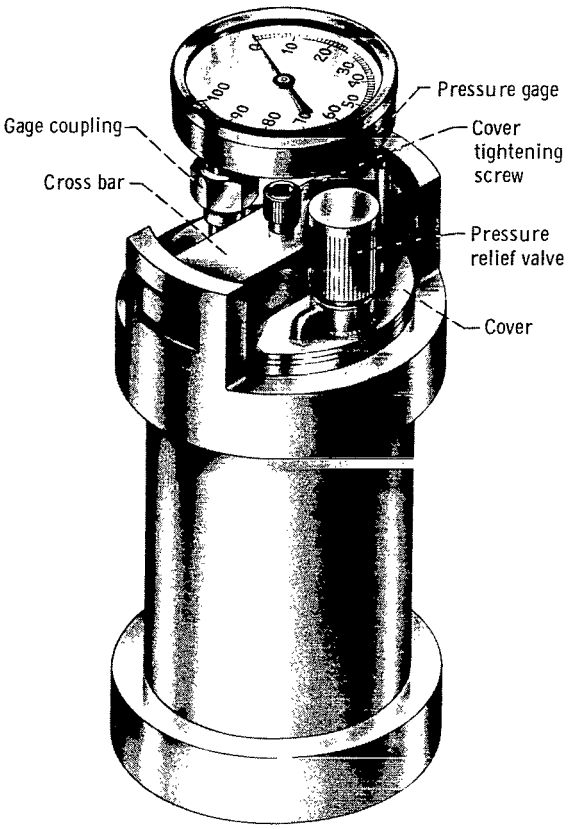


Figure 1. - Gas tight ball mill with pressure gage.

The type of ball mill used in this work is shown in figure 1. The ball mills were made from 410 stainless steel. These mills have an inside diameter of 10.2 centimeters and a volume of 1580 cubic centimeters. The covers for these mills have an O-ring gasket to provide a gas tight seal. These mills can withstand up to about 20 atmospheres ($2.03 \times 10^5$ N/m$^2$) absolute pressure without leaking. In order to monitor the pressure developed by the hydrogen released on ball milling, the covers are provided with 7.5-centimeter-diameter pressure gages. These gages were calibrated before installation in the cover. The accuracy of these gages is better than 1/2 percent of the maximum gage reading. The mills also have a vacuum type valve for the release of pressure or for taking samples of the gases generated during ball milling.

The balls used for ball milling were 12.6 millimeter nominal diameter and made from type 440 stainless steel. In all runs, 400 of these balls weighing about 3220 grams were used.

The mills were loaded in the argon glove box. In all runs, 150.00 grams of chromium powder and 750±2 cubic centimeters of water were used. The free volume (head space) of the mills was calculated to be 402 cubic centimeters (including pressure gage

volume). Four identical mills were loaded in this manner. All four mills were run simultaneously at 100 rpm. Run 1 was stopped after 48 hours of milling time. Pressure readings were continued for 48 hours after the mill was stopped. Run 2 was stopped after 112 hours, run 3 after 384 hours, and run 4 after 768 hours of milling time. The pressure readings for run 4 were continued for about 100 hours. The mills were opened in the argon glove box, and the milled chromium powders dried under argon. Samples of powders were taken for surface area determinations and for chemical analyses. Tin capsules were filled with the powders for oxygen analyses. The hydrogen-pressure - milling-time data and the oxygen-pickup - milling-time data used in this investigation were obtained entirely from run 4.

In all four runs, the hydrogen generated on ball milling was released at regular intervals inside the argon glove box. During run 4 (the longest), samples of the gas generated in the mill were taken at regular intervals. These gas samples were analyzed by mass spectrometry. The pressure data from run 4 were used for the calculations and plots in this report.

The surface areas of all the milled powders were determined by the BET method (ref. 1).

Both X-ray diffraction and X-ray fluorescence analyses were performed on the powder from run 4. To prevent contamination of the powder used for X-ray diffraction, the powder was loaded in a capillary tube in the argon glove box and the tube was sealed.

The powders from run 4 were also examined with the electron microscope to determine the shape of the powder particles and as a check on the surface areas (or particle sizes) obtained by the BET method.

# RESULTS

## Chemical and Surface Area Analyses of Milled Powders

Unless indicated otherwise, the data in table I will be used for the description of the results of chemical and surface area analyses that follow.

Both the as-received and the as-hammer-milled chromium have a relatively low oxygen content. Some iron was picked up by the milled chromium powder from the stainless-steel crusher and hammer mill. There is no reason to believe that the iron pickup, the sulfur in the as-received chromium, or the other impurities could have any effect on hydrogen evolution or on the oxidation of the chromium during ball milling.

The oxygen content of the ball-milled chromium powders increases with milling time. The 18.46 weight percent oxygen content of the powder ball milled for 768 hours represents 58.56 weight percent of $Cr_2O_3$. It appears that if ball milling were continued

long enough, all the chromium metal would be oxidized.

The iron content of the ball-milled chromium powder increases continuously with ball-milling time. The iron is in the stainless steel picked up by the chromium powder from the crusher, mills, and balls. This stainless steel contains carbon and a small amount of nitrogen. Hence, these two elements appear in larger quantities in the ball-milled chromium than in the original chromium. However, as the analyses for runs 3 and 4 show, the amounts of these two elements are not proportional to the iron pickup.

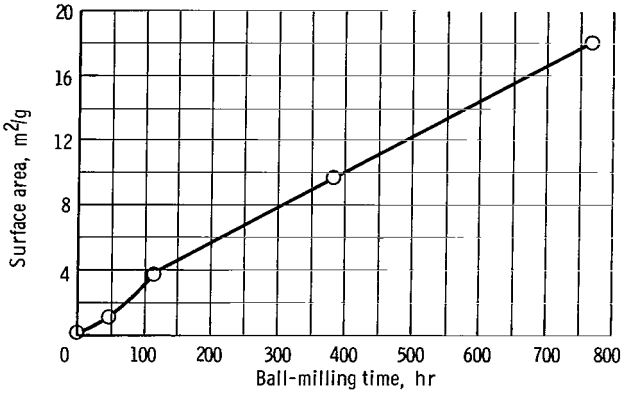


Figure 2. - Surface area (by BET method) of ball-milled chromium powder as function of ball-milling time.

The surface areas of the ball-milled powders increase (or the particle sizes decrease) with ball-milling time, as shown both in table I and in figure 2. The average particle size of the powders ball milled 768 hours is 310 Å (0.031 $\mu$m). By powder metallurgy standards, this is a very fine powder. This size of powder would be well suited for dispersion strengthening purposes, were it not for its high oxygen content.

## Evolution of Gases During Ball Milling

Table II shows the chemical analyses of the gases taken from the ball mill at the times shown both in this table and in figure 3.

The argon shown in all the analyses comes from the atmosphere in the argon glove box in which the gas samples were taken or the ball-mill pressure was released. For comparison purposes, a typical analysis of the argon used in the glove box is included in table II.

Table II shows that hydrogen represents more than 99 percent of the gases other than argon. It is surmised that the oxygen, nitrogen, and carbon dioxide appearing in all the analyses either came from the argon used in the glove box or are the result of leakage of

TABLE II. - ANALYSIS OF GASES TAKEN FROM RUN 4 AT VARIOUS MILLING TIMES AND TYPICAL ANALYSIS OF ARGON BOX ATMOSPHERE

| Gas source | Chemical analysis[a], percent | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Argon | Helium | Hydrogen | Oxygen | Carbon monoxide | Carbon dioxide | Nitrogen | Methane |
| Argon box (typical) | Balance | 0.027 | 0.052 | 0.003 | 0.031 | 0.014 | 0.043 | 0 |
| From ball mill, 48 hr of milling (sample 1, fig. 3) | Balance | .051 | 43.5 | .024 | .007 | .014 | .062 | .085 |
| From ball mill, 161 hr of milling (sample 2, fig. 3) | 7.72 | 0 | 90.4 | .001 | .123 | .009 | .754 | .060 |
| From ball mill, 387.4 hr of milling (sample 3, fig. 3) | .945 | 0 | 98.84 | 0 | .0135 | .0051 | .0224 | .0303 |
| From ball mill, 576 hr of milling (sample 4, fig. 3) | .445 | 0 | 99.3 | .033 | 0 | .002 | .145 | .036 |

[a]Mass spectrometric method.

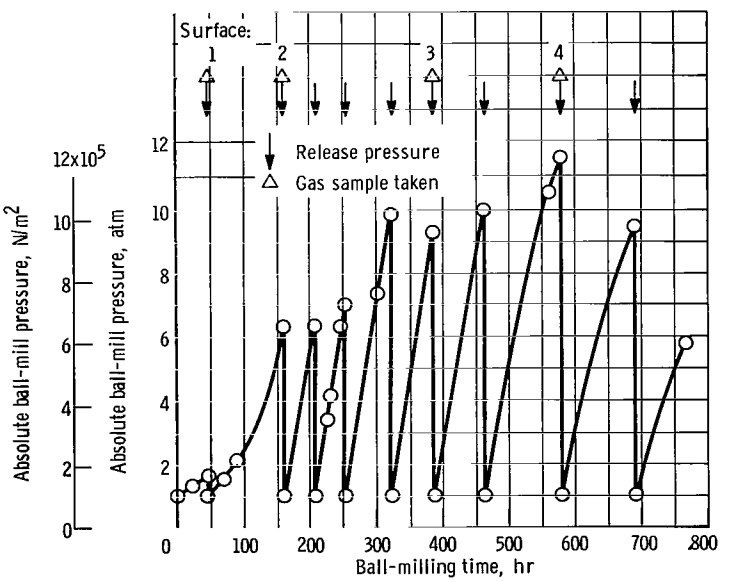


Figure 3. - Pressures developed on ball milling of chromium in water as function of time for run 4.

atmospheric air into the gas sampling bottles. The carbon monoxide content varied from one analysis to another without any definite pattern. This carbon monoxide probably came from the argon in the glove box and varied because the carbon monoxide content of the argon used also varied.

The methane shown in table II was undoubtedly evolved during ball milling. The amounts of methane in the last two analyses in the table are almost the same. Hence, it may be stated that, within the limits of analytical accuracy, the methane decreases with ball-milling time. It is surmised that this methane was produced by the reaction of (nascent) hydrogen with the carbides on the surface of the stainless-steel powder picked up during ball milling. Since the rate of pickup decreases with milling time, so does the methane. In short, only hydrogen and traces of methane are evolved on grinding chromium in water.

The pressure that built up as a function of time during the grinding of chromium (run 4) is shown in figure 3. The breaks in the curve are a result of the releases of ball-mill pressure and of the withdrawal of gas samples from the mill. The release of pressure was necessary to prevent leakage of gas from the mill.

For runs 1 (48 hr of milling) and 4 (768 hr of milling) the pressure that built up was monitored after stopping the ball mills. The first showed an additional pressure increase of 0.003 atmosphere (304 $N/m^2$) in 48 hours. The second showed a pressure increase of approximately 0.05 atmosphere (5066 $N/m^2$) in 100 hours. In either case, the pressure increases represent less than 1 percent of that obtained by ball milling for the same period of time. For this reason, this effect is neglected in the data shown in this report.

## X-ray Analyses of Ball-Milled Powders

The X-ray diffraction analysis of the powder ball milled for 768 hours shows chromium (Cr), chromic oxide ($Cr_2O_3$), and (weak) chromium dioxide ($CrO_2$). No iron oxide lines were detected in the diffraction pattern. Both chemical analysis (table I) and X-ray fluorescence analysis show that this powder contains iron. As already indicated, this iron is in the stainless steel picked up from the equipment used for crushing and milling.

The X-ray diffraction pattern also showed broadening of the lines. This line broadening is accounted for by the small particle size of the powder.

## Electron Photomicrographs

A transmission electron photomicrograph of the powder from run 4 is shown in figure 4. Other samples of the same powder were shadowed and electron photomicrographs


Figure 4. - Transmission electron photomicrograph of chromium powder after ball milling in water for 768 hours.

(not shown) taken. From the transmission photomicrographs of shadowed particles, it was determined that the powder particles are flake shaped and have an average length to thickness ratio of about 10. The surface area of this sample was calculated (from the particles shown in fig. 4) to be about 20 square meters per gram. This value agrees quite well with the 18 square meters per gram obtained by the BET method.

## DISCUSSION OF RESULTS

### Hydrogen Evolved During Ball Milling

A reaction between chromium and water was shown to occur during ball milling. This reaction was evidenced by the increase in pressure in a gas tight ball mill due to hydrogen evolution. The reaction of chromium with water to form chromium oxides with the release of hydrogen can be shown to be thermodynamically feasible.

For the room-temperature reaction,

$$2Cr\ (s) + 3H_2O\ (\ell) = Cr_2O_3\ (s) + 3H_2\ (g) \qquad (1)$$

the free energy change is (ref. 2)

$$\Delta F = -253\ 150 + 0 - (0 - 3 \times 56\ 720)$$

$$= -82\ 990 \text{ cal } (-347\ 000 \text{ J})$$

Similarly, for the room-temperature reaction

$$Cr\ (s) + 2H_2O\ (\ell) = CrO_2\ (s) + 2H_2\ (g) \qquad (2)$$

the $\Delta F$ is -16 560 calories (-69 400 J) (ref. 2).

The probable reason that either of these reactions have not been observed before is that chromium is normally covered with a protective layer of its own oxide. Ball milling either flattens or breaks up chromium particles. Flattening of a particle causes an increase of its surface area. Breakage of a particle also creates new surfaces. In either case, clean chromium surfaces are exposed and these can react with water. Hence, during ball milling, the reaction of chromium with water continues as long as new surfaces are formed.

As already indicated, the reaction rate of chromium with water immediately after stopping the ball mill is less than 1 percent of that during ball milling. Only a slight after-ball-milling reaction would be expected since no new surfaces are formed and the gas evolution could result only by surface diffusion of chromium atoms to the water - chromium oxide interface. This diffusion would be time dependent. If only a monomolecular layer of oxide were formed on the chromium, the slight (1 percent) after-ball-milling reaction would be expected to be almost instantaneous. It is shown later in this report that the oxide film formed on chromium during ball milling was thicker than a monomolecular layer.

It can be shown thermodynamically that the maximum hydrogen pressures that can be allowed to build up in the mills could not reverse the reaction. If high hydrogen pressures were generated by the reaction and could be contained, the equilibrium equations (eqs. (1) and (2)) would be reversible. From thermodynamic considerations, the hydrogen pressure required to reverse the first reaction is greater than

$$P = \exp(-\Delta F/3RT)$$

$$= \exp(46.8)$$

$$= 2.24 \times 10^{20} \text{ atm } (2.27 \times 10^{25} \text{ N/m}^2)$$

This value is obviously too high for any known container. Similarly, pressures for the reversal of the second reaction are calculated to be greater than $1.02 \times 10^6$ atmospheres ($1.034 \times 10^{11}$ N/m$^2$), again too high to be contained. The highest hydrogen mill pressure reached in this investigation was 11.6 atmospheres ($11.7 \times 10^5$ N/m$^2$). This pressure is deemed to be too low to affect the reaction rate of chromium with water appreciably. Since thermodynamics shows this reaction to be feasible, similar behavior can be expected on ball milling other metals if water is present.

## Oxidation of Chromium During Ball Milling

As the equilibrium equations (eqs. (1) and (2)) indicate, the amount of chromium oxide formed is proportional to the amount of hydrogen evolved. The amount of hydrogen evolved can be approximately determined from the pressure buildup in the mill by use of Boyle's law. Boyle's law is valid only for ideal gases at constant temperature. These requirements are believed to have been closely approached in this investigation.

The constant temperature requirement of Boyle's law was met because, although there was a slight temperature increase in the mill during grinding, the mill was allowed to cool for 2 hours (to room temperature) before taking pressure readings. Normal variations in atmospheric temperatures and pressures were estimated to affect the pressure readings by less than 1 percent. Finally, because of the low critical temperature of hydrogen (33.1° K) it can be reasonably assumed that, in the pressure range reached in the mills, the hydrogen behaves as an ideal gas (ref. 3).

The moles of hydrogen generated were obtained from the known free volume of the mill $V$ ($V = 402$ cm$^3$ at the beginning of the run) and the increase in pressure $\Delta P$ in the mill, as follows:

$$\text{Moles of } H_2 \text{ generated} = \frac{\Delta P \text{ (atm)} \times V \text{ (liter)}}{22.4 \left(\text{atm} - \frac{\text{liter}}{\text{mole}}\right)}$$

For every mole of hydrogen generated, 16 grams of oxygen react with the original 150-gram charge of chromium. Hence, the moles of hydrogen generated multiplied by 16/150 gives the oxygen pickup in grams per gram of original chromium. The results for the oxygen pickup so obtained are plotted in figure 5. The data points plotted in this figure were corrected for the increase in free volume $V$ of the mill with ball-milling time. This increase is

$\Delta V$ = Volume of water reacted - (Volume of chromium oxide formed

- Volume of chromium converted to chromium oxide)

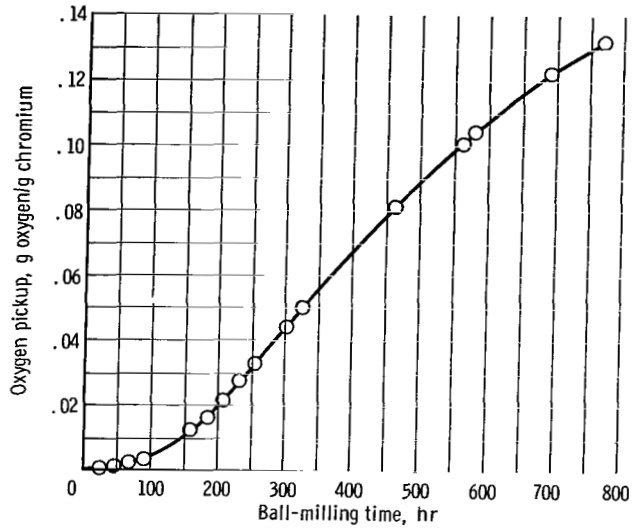


Figure 5. - Oxygen picked up by chromium on ball milling in water as function of ball-milling time for run 4 (calculated from data in fig. 3).

The X-ray diffraction pattern of the chromium powder ball milled for 768 hours showed no iron oxides. The significance of this fact is that the iron picked up during the processing of the chromium powder was not oxidized. Thus, iron pickup did not contribute to the hydrogen released during the ball milling of chromium.

Considering the various sources of error already discussed (gage accuracy, temperature and pressure variations, etc.) the overall accuracy of the data in figure 5 is estimated to be better than 5 percent. The accuracy of the correlation between the as-analyzed oxygen content and the as-calculated oxygen content is discussed later.

The monitoring of hydrogen pressure during the ball milling of chromium could be used to study ball-milling variables such as the effect of ball size, ball charge, mill speed, etc., on grinding speed.

## Thickness of Chromium Oxide Film

For a better understanding of the phenomena that occur during ball milling, it was felt that a calculation of the thickness of the oxide layer formed by the reaction of chromium with water would be helpful. The average, hypothesized, or apparent, oxide layer thickness can be calculated with the aid of figures 2 and 5 if the following assumptions are made.

(1) All the chromium oxide formed on the chromium surface is $Cr_2O_3$. This assumption can be made because the X-ray diffraction pattern for $CrO_2$ is very weak.

(2) The ball-milled powders have no preferred orientation, since the widening of the X-ray diffraction pattern lines may be accounted for by the small size of the powder particles.

To aid in the calculations, the data at low ball-milling times (up to 160 hr) from figures 2 and 5 were replotted in figure 6. From the density and molecular weight of $Cr_2O_3$, the molar volume was calculated. From the molar volume and Avogadro's number, it was calculated that a "randomly oriented" monomolecular layer of 1 mole of

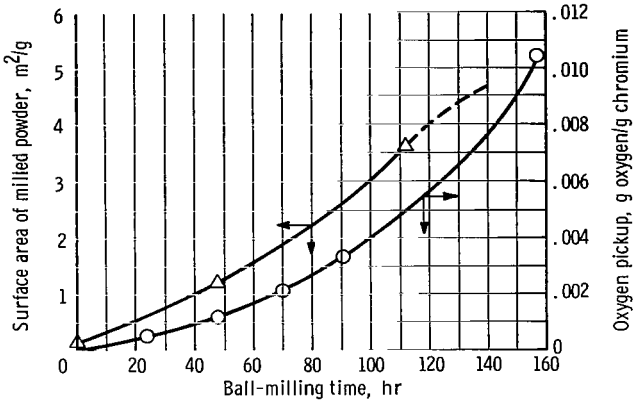


Figure 6. - Calculated oxygen pickup and surface area (by BET method) of chromium powder as function of ball-milling time. (Data from figs. 2 and 5 enlarged to show early stages of ball-milling run.)

$Cr_2O_3$ would cover an area of 79 800 square meters (see appendix for detailed calculations and comments). This is equivalent to 1669 square meters per gram of oxygen (in $Cr_2O_3$). If a powder has a surface area of S square meters per gram and W grams of oxygen per gram of chromium, the number of apparent monomolecular oxide layers N will be (approximately) 1669 W/S. An equivalent expression that gives the number of monomolecular oxide layers for surfaces formed between two milling time intervals is

$$N = 1669 \frac{\Delta W}{\Delta S}$$

The number of monomolecular layers N calculated in the manner described previously for run 4 is shown in table III and in figure 7. The data for these calculations were obtained from figures 2, 5, and 6. From the data in table III and in the appendix, the thickness of the oxide layer at the early stages of the ball-milling run (up to 48 hr) is calculated to be 6.7 Å (0.00067 $\mu$m). Although the number of monomolecular layers N

TABLE III. - APPARENT NUMBER OF MONOMOLECULAR CHROMIC OXIDE LAYERS AT VARIOUS TIME INTERVALS DURING BALL-MILLING RUN 4

| Milling time intervals, hr | Increase in oxygen (g/g of Cr), $\Delta W$ | Increase in surface area ($m^2$/g of Cr), $\Delta S$ | Apparent average number of $Cr_2O_3$ monomolecular layers, N |
|---|---|---|---|
| 0 to 24 | 0.00055 | 0.535 | 1.71 |
| 24 to 48 | .000631 | .56 | 1.88 |
| 48 to 112 | .00373 | 2.42 | 2.57 |
| 112 to 384 | .0593 | 6.03 | 16.38 |
| 384 to 768 | .0698 | 8.32 | 14.0 |

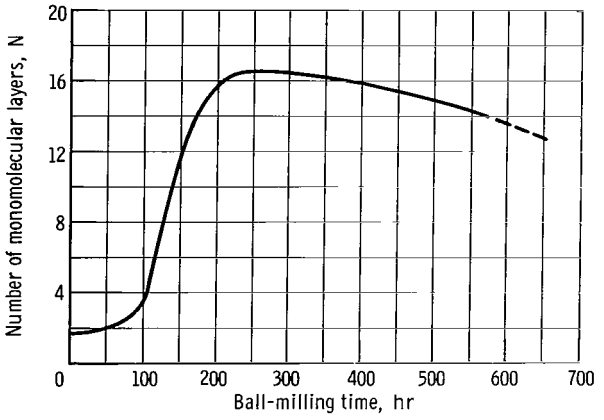


Figure 7. - Apparent number of monomolecular layers of chromic oxide formed on chromium as function of ball-milling time. (Data from figs. 2 and 5.)

apparently increases with additional milling, the actual oxide layer thickness is believed to have remained at 6.7 Å (0.00067 $\mu$m), as discussed later.

## Welding of Particles During Ball Milling

Table III (and fig. 7) shows that the calculated "apparent" number of monomolecular layers N generally increased as ball-milling time increased; N goes from about 2 at the beginning to about 15 toward the end of the ball-milling run. This increase in N with ball-milling time could be the result of one or more of three causes.

(1) The surfaces newly created on the ball-milled chromium continue to react with water for a long time after they are formed.

(2) The chromium oxide formed on the chromium particles spalls off the surface during ball milling. Hence, the same surfaces can react several times with water.

(3) The finer particles weld with each other or onto larger ones during ball milling. Since these particles already have an oxide film, this film is (partially) sandwiched between the welding particles.

It has already been mentioned that, after ball milling is stopped, the amount of hydrogen generated is less than 1 percent of that generated by ball milling during the same period of time. Hence, although it occurs, the continued reaction of the newly created surfaces with water cannot be the reason for the observed increase in N with ball-milling time.

The well-known resistance of chromium to oxidation is the result of the toughness and adherence of its own oxide film. If repeated temperature cyclings fail to spall off its thick oxide film, it is highly unlikely that ball milling can spall off a thin film in a very small particle. The reasons why this is unlikely are, first, that thin oxide films are more pliable than thicker ones and, second, that under stress (either mechanical or thermal) small particles are less likely to lose coherence with their oxide film than larger ones. Hence, cause (2) for the increase in N with ball-milling time is deemed to be improbable.

Cause (3) for the increase in N with ball-milling time appears to be the most logical of the three and, in addition, is supported by work described in the literature (to be discussed later). If the oxide weight increase or the N value (apparent number of monomolecular layers) increased linearly with S, the ratio of calculated oxide pickup to S would be approximately constant. However, the increase in these values is linear only during the first 48 hours or so of the ball-milling run. These values increased very rapidly when the surface area increased beyond about 3.6 square meters per gram (i.e., ball-milling times greater than about 100 hr), as shown in table III and figure 7.

The increase in N while chromium continues to oxidize with increasing ball-milling time means that while new, smaller particles are being formed by comminution of larger ones, other large particles are being formed by welding of smaller ones. The surface area between the welded particles is not measured by the BET method of surface area analysis. The net effect is that the ratio of oxygen to surface area increases with ball-milling time and so does N. The author believes that water can also be trapped between the welded particles.

The idea that particles both decrease and increase in size during ball milling is not new. That this is correct has been experimentally verified. In reference 4 it is shown that fine fractions of ground sand can be made to weld into larger ones by grinding. The same phenomenon has been reported for nickel ball milled in a variety of liquid media

(ref. 5). The ball-milling reactions may be better understood with the aid of figure 7 and the following hypothesized explanations:

(1) Up to about 100 hours of ball-milling time, the predominant mechanism is that large particles of chromium are flattened into large single flakes and welding of particles is minimal. The ratio $\Delta W/\Delta S$, and hence N, remains approximately constant.

(2) As the predominantly single flakes become thinner and are broken into smaller flakes, the welding rate of particles increases and agglomerates of welded particles increase in number. The increased welding of particles causes an increase in the $\Delta W/\Delta S$ ratio. This explains the sharp rise in the curve for N against time (fig. 7) between about 100 and 200 hours.

(3) As the single flakes disappear to form agglomerates by welding, the agglomerates become flattened into new flakes and these flakes are (eventually) fractured. However, these flakes have now more oxide in them than the original ones, since the oxide film formed by reaction with water remained on the particles. Hence, the new surfaces created on the agglomerates by flattening and by fracturing react with less water and N decreases.

This explanation of the data from this investigation indicates that a large proportion of the oxygen picked up by the chromium powder may be sandwiched between chromium particles. It is surmised that the same may be true for other ball-milled metal and alloy powders. Hence, it may be more difficult to reduce the oxides formed in some milled metal powders than in the pure oxide powders.

## As-Calculated and As-Analyzed Oxygen Content of Milled Powders

As shown by the analyses in table I, the oxygen content of the ball-milled powders is invariably larger than that calculated from the hydrogen generated during ball milling (fig. 5). (Note that in table I the oxygen is in percent basis, while in figure 5 it is in grams per gram of original chromium.) Correlation of the data was surprisingly good to 384 hours, but the added samples were done at another source and higher values obtained at 384 and 768 hours of ball-milling time. The reasons for the higher values given by the chemical analyses from the latter source are not clear at this time.

## CONCLUSIONS

From the results of the present investigation it is concluded that

1. Because of the reaction of chromium with water during ball milling, hydrogen is generated and a chromium oxide film is formed on the chromium particles. It is surmised that the same phenomenon may occur on ball milling of other metals in water.

2. The amount of oxygen reacted with chromium on ball milling can be quantitatively monitored by the increase in pressure due to hydrogen evolution. This monitoring of hydrogen pressure on ball-milling chromium could be used to study ball-milling variables such as the effects of ball size, ball charge, mill speed, etc., on grinding speed.

3. The oxide film formed on chromium during ball milling in water was calculated to be about 6.7 Å (0.00067 $\mu$m) thick. This film is composed of chromic oxide and small amounts of chromium dioxide.

4. Under the conditions used in this investigation, hydrogen was continuously generated, and the surface area of the chromium continuously increased during ball milling. A powder with 300 Å (0.03 $\mu$m) average particle size was obtained on ball-milling chromium in water for 768 hours. It is deduced that welding of the finer particles onto larger ones or with each other was also taking place during ball milling.

5. Because of the welding action taking place concurrently with grinding, a large proportion of the chromium oxide formed may be sandwiched between chromium particles.

6. Since most of the chromium oxide may be at the interface between welded particles, the reduction of this oxide (with hydrogen, carbon, etc.) may prove difficult.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 1, 1968,
129-03-01-05-22.

# APPENDIX - AVERAGE NUMBER OF CHROMIC OXIDE ($Cr_2O_3$) LAYERS ON CHROMIUM POWDER

For the analysis that follows, it will be assumed that only $Cr_2O_3$ is present as an oxide film on chromium and that this film is randomly oriented. It can be imagined that chromium oxide films can be obtained by peeling off monolayers of $Cr_2O_3$ from a "molar cube" (cube shaped molar volume) and building up the oxide film to the required thickness by piling up these monolayers.

The molar volume $V_m$ of $Cr_2O_3$ is

$$V_m = \frac{\text{Molecular weight of } Cr_2O_3}{\text{Density of } Cr_2O_3}$$

$$= \frac{152.02 \text{ g/mole}}{5.21 \text{ g/cm}^3}$$

$$= 29.18 \text{ cm}^3/\text{mole}$$

The "molar cube" has edge $e_m$ given by

$$e_m = V_m^{1/3}$$

$$= 29.18^{1/3}$$

$$= 3.079 \text{ cm}$$

and each of the faces of the molar cube has surface area $s_m$ given by

$$s_m = e_m^2$$

$$= 9.48 \text{ cm}^2$$

The number $n_e$ of $Cr_2O_3$ molecules lying along one edge of the molar cube is

$$n_e = A^{1/3}$$

$$= (6.023 \times 10^{23})^{1/3}$$

$$= 8.45 \times 10^7$$

where $A = 6.023\times10^{23}$ is Avogadro's number. The $n_e$ monomolecular layers (of which the molar cube can be imagined to be made up) each of area $s_m$ can cover a total area $S_m$ given by

$$S_m = n_e s_m$$

$$= \left(8.45\times10^7 \frac{\text{layers}}{\text{mole}}\right)\left(9.48 \frac{\text{cm}^2}{\text{layer}}\right)\left(\frac{1\ \text{m}^2}{10^4\ \text{cm}^2}\right)$$

$$= 80\ 100\ \text{m}^2/\text{mole}$$

Since a mole of $Cr_2O_3$ has 48 grams of oxygen, the area $s_g$ that can be covered with the amount of $Cr_2O_3$ that has 1 gram of oxygen is

$$s_g = \frac{S_m}{48}$$

$$= 1669\ \text{m}^2/\text{g of oxygen (in } Cr_2O_3)$$

A monomolecular layer of $Cr_2O_3$ with $W$ grams of oxygen would cover an area $s_g W = 1669W$ square meters. Now, if a chromium powder has $W$ grams of oxygen per gram of powder and the powder has a surface area of $S$ square meters per gram, the oxide must cover the $S$ square meters of surface with $N$ monomolecular layers

$$N = 1669 \frac{W}{S}$$

If during a ball-milling time interval the oxygen content increases by $\Delta W$ and the surface area of the powder increases by $\Delta S$, the apparent number of monomolecular layers $N$ formed on the surface of powder created in the same time interval is

$$N = 1669 \frac{\Delta W}{\Delta S}$$

and each of these layers has thickness

$$\frac{e_m}{n_e} = \frac{3.079\times10^8\ \text{Å}}{8.45\times10^7}$$

$$= 3.64\ \text{Å}\ (0.000364\ \mu\text{m})$$

The preceding expressions for N are valid only for large particles and/or thin oxide layers for two reasons. The first reason is that the BET method of surface area measurement measures the surface on the outside of the oxide film and not in its mid-thickness, as is required by the equations. The second reason is that the BET method gives the surface area per unit weight of oxide-metal mixture. In this report, the calculated oxygen content is expressed in grams of oxygen per gram of original chromium. With these objections in mind, more accurate expressions for N could have been derived but the ones given suffice for the purposes of this investigation. A more accurate value of N would not have altered the conclusions reached.

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