San Fernando Valley State College

PHASE AND COMPOSITION ANALYSIS OF CHROMIUM HYDRIDE

A thesis submitted in partial satisfaction of the
requirements for the degree of Master of Science in

Chemistry

by

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To my parents
and to Carol

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ABSTRACT

PHASE AND COMPOSITION ANALYSIS OF CHROMIUM HYDRIDE

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The electrodeposition of chromium hydrides was carried out using various solution compositions and current densities. The work was performed in order to characterize phases, phase transitions, and chemical compositions for the composition range CrH_0 to CrH_2 .

The face-centered and hexagonal chromium hydride phases were prepared and immediately examined with X-rays and analyzed for hydrogen. The inability to prepare the face-centered phase with a hydrogen to chromium atom ratio greater than one (1) is explained by the thermal instability of this phase.

The cell parameters of both the hexagonal hydride and the face-centered hydride were found to be independent of the hydrogen concentration.

CHAPTER I

INTRODUCTION

This research was performed to characterize the chromium hydride phases and phase transformations for the composition range CrH_0 to CrH_2 , and to resolve the several contradictions previously reported in the literature. The different phases were obtained by adjustment of solution compositions and other plating factors.

Insufficient study of the absorption of hydrogen during electrochemical deposition of chromium has resulted in discrepancies in reported cell parameters, phase transitions, and chemical compositions. Huttig and Broadkorb¹ were first to observe the low solubility of hydrogen (about 0.45 weight percent hydrogen) in cathodic chromium. Later Guichard² and then Makareva and Biryukov³ found a slightly higher solubility of hydrogen in plated chromium. In 1926, Ollard and Bradley⁴ reported a hexagonal crystal structure for electro-deposited chromium. X-ray studies of chromium plates produced under special conditions⁵ confirmed the existence of the hexagonal phase. By using refrigerated chromic acid solutions partially reduced with sugar, Wood⁶ was able to produce plates with the hexagonal crystal structure which, when heated above 130°C , changed to a body-centered cubic arrangement which is the normal atomic structure of metallic chromium. For many years the hexagonal phase was treated as an

allotropic modification of chromium, and no explanation was offered for the large difference in the diameters of the chromium atoms in the two structures -- $2.71\text{\AA}$ for the atom in the hexagonal structure, and $2.49\text{\AA}$ for the atom in the body-centered cubic structure.

In 1947, Snavely⁷ reported that the supposed allotropic modification of chromium was in fact a hexagonal hydride phase; he also identified a second hydride phase having a face-centered cubic arrangement of chromium atoms. Snavely was able to prepare these hydrides by electrolyzing chromic acid solutions and adjusting the temperature, solution composition, and current density. The hydrides originally were identified as CrH for the hexagonal hydride and CrH₂ for the face-centered hydride by analogy with existing hydrides and structures. More recently,⁸ the existence of both hydrides has been confirmed, and the hexagonal phase has been found to be approximately CrH₁, but the composition CrH₂ has not been confirmed for the face-centered cubic phase. Since all the structural studies were carried out using X-rays, the results are with respect to the chromium atoms only.

By analogy with other metallic hydrides Snavely then suggested a zinc blende structure for the hexagonal phase with hydrogens occupying half the tetrahedral sites. By filling the remaining tetrahedral sites with hydrogen, a smooth transition to the face-centered fluorite (CrH₂) structure could be explained. Albrecht, et al.,⁹ however, using neutron diffraction techniques, showed that the structure postulated by Snavely for the hexagonal phase was

incorrect. They found that the structure was not a zincblende type structure, but rather an anti-NiAs structure (Figure 1) with hydrogens in the octahedral sites.

Figure 1. -- Anti-nickel Arsenide Structure

The shaded spheres represent the chromium atoms, and the unshaded spheres represent the hydrogen atoms.

Although the structural types for the chromium hydrides are now well established, there are several contradictory results for the chemical compositions of the hexagonal hydride and the face-centered hydride. Knoedler⁸ claims that the hexagonal hydride phase exists as a single phase only in the composition range $\text{CrH}_{0.95-1.00}$. Roy and Gibb¹⁰ claim that only the hexagonal phase is present in the range $\text{CrH}_{1.0-1.5}$, and they assert that Snavely's scheme of adding hydrogen would predict an equal concentration of hexagonal and face-centered cubic phases at $\text{CrH}_{1.5}$ and that beyond $\text{CrH}_{1.5}$ only the face-centered phase should appear. The discrepancies concerning the chemical composition of the face-centered phase may be reconciled by considering the stability of this hydride phase. Proskurnikov and Krylov¹¹ have investigated the preparation and properties of chromium hydrides and concluded that when the current is switched off a considerable amount of hydrogen is liberated from the deposit in a very short time. The highest concentration of hydrogen in a chromium hydride was reported by Snavely to be $\text{CrH}_{1.7}$.^{7,12} An attempt was made by Proskurnikov and Krylov to prepare $\text{CrH}_{1.7}$ by duplicating Snavely's plating conditions. Analysis of their chromium hydride deposit by vacuum extraction ten minutes after the current was switched off gave 1.032 g-atom of hydrogen, which is much less than Snavely's result. Evidence of rapid decomposition was confirmed by the transformation of the cathode deposit from a compact, dark grey material to a cracked and blistered surface whereupon layers separated. Evidently the electrocrystallization of a hydride with a hydrogen content much greater than 1 g-atom is very possible, but

when the current is switched off considerable hydrogen is liberated very rapidly from the deposit.

Listed below are the published unit cell parameters for the hexagonal and face-centered chromium hydrides.

<u>HEXAGONAL</u>	<u>FACE-CENTERED</u>	<u>AUTHOR</u>
$a_o = 2.717\text{\AA}, c_o = 4.418\text{\AA}$	$a_o = 3.850\text{\AA}$	Snively ¹²
$a_o = 2.722\text{\AA}, c_o = 3.441\text{\AA}$	$a_o = 3.861\text{\AA}$	Mackay ¹³
$a_o = 2.717\text{\AA}, c_o = 4.418\text{\AA}$	$a_o = 2.878\text{\AA}$	Roy and Gibb ¹⁰

Snively¹² and Mackay¹³ did not give chemical compositions for their chromium hydrides, while Roy and Gibb¹⁰ gave $\text{CrH}_{1.0}$ for the hexagonal phase. The discrepancies are most likely printing errors.

This research clarifies and establishes the phases, cell parameters, and compositions for the chromium-hydrogen system for $0 < \text{H/Cr} < 1.1$.

CHAPTER II

DISCUSSION

Chromium hydride is classified as a nonstoichiometric interstitial hydride, based on X-ray, neutron diffraction, and magnetic susceptibility experiments. X-ray diffraction analysis clearly shows that structural changes occur with the formation of the hydride phase, and neutron diffraction shows the positions of the hydrogens in the hydride phase. Magnetic susceptibility experiments indicate that the amount of physical adsorption due to van der Waals' forces is negligible compared to chemisorption with the formation of a chemical bond between the hydrogen and chromium atoms. Measurement of the magnetic susceptibility, χ_g , for pure Cr and CrH shows them both to be paramagnetic, and as the hydrogen concentration increases, the magnetic susceptibility increases. The measured values of the magnetic susceptibility at 193-295°K can be used to calculate the magnetic moment of chromium in CrH. The value found, $1.77 \mu_B$, corresponds to one unpaired electron.¹¹ The theoretical magnetic moment, calculated on the assumption that only the spin moment is free and the orbital moment is 'frozen,' would be $1.73 \mu_B$. This corresponds to the experimental result, thus indicating that hydrogen gives up its electron to the chromium and forms a bond. The bonding mechanism for the chromium hydrides is not well understood; however, some light was shed on this mechanism from a series of investigations

aimed at increasing the plating efficiency in chromium deposition.^{7,14,16}

It is generally recognized that the deposition of Chromium takes place not through a simple reduction, but through an intermediate step-cathode film.⁷ The stability of this film depends on the current density and temperature, and this film can exist only within a well-defined range of these two factors. The cathode film in a CrO_3 and H_2SO_4 plating solution consists of Cr (III), Cr (VI), and SO_4^{-2} . Its stability decreases with increasing temperature and sulfuric acid concentration. Although this film contains no metallic chromium, it can be reduced in a very short time by a cathodic treatment. Evidence that chromium is deposited in the chromic acid bath directly from the hexavalent and not the trivalent form has been provided by measurements made by F. Ogburn and A. Brenner¹⁵ using a radioactive tracer. The tracer was ^{51}Cr , which is a soft gamma ray emitter with a half-life of 26.5 days. Their final results demonstrated that the chromium originally present in the bath in the hexavalent state was deposited, while the chromium present in the trivalent state was not deposited. The exact manner in which the hexavalent ion is reduced at the cathode is still obscure, and it is not known whether this is by electronic interchange or by a process involving atomic hydrogen. Snively presented evidence which suggested that the reduction of Cr (VI) to the pure metallic body-centered state could only occur in a narrow cathode pH range. According to Snively, increasing the pH near the cathode surface leads to the formation of the unstable hexagonal hydride and at still

higher pH, to the formation of the unstable face-centered hydride. He suggested that the relationship between surface deposit and pH is as shown in Figure 2. The actual pH value at the cathode surface could not be measured, but results suggested that the hydride is deposited in the pH 3 to pH 6 range.

Figure 2. -- Schematic representation of the relation between cathode film pH and the structure of the plate produced in the chromium plating process.

In the light of Snively's proposed phase diagram for chromium hydride, we shall discuss our results beginning with the body-centered cubic phase.

Body-Centered Cubic Chromium Metal
Containing Dissolved Hydrogen

Solution composition and other plating factors were adjusted so as to deposit chromium metal with the body-centered cubic crystal arrangement. X-ray analysis of these deposits agreed well with reliable measurements on samples of relatively high purity reported by the authors given below:

<u>CELL PARAMETER</u>	<u>AUTHOR</u>
$2.8848\text{\AA}$ 20°C	Fine, et al. ¹⁶
$2.8847\text{\AA}$ 20°C	Sully, et al. ¹⁷
$2.8844\text{\AA}$ 18°C	Pearson ¹⁸
$2.8840\text{\AA}$ 25°C	This work
$\sigma = 0.0006\text{\AA}$	

We found that hydrides with low hydrogen concentrations had the same body-centered crystal lattice as chromium metal except that the unit cell parameter was somewhat expanded as the hydrogen concentration was increased; for example:

<u>FORMULA</u>	<u>CELL PARAMETER</u>	
Cr	$2.884\text{\AA}$	
$\text{CrH}_{0.05}$	$2.884\text{\AA}$	$\sigma = 0.0008\text{\AA}$
$\text{CrH}_{0.08}$	$2.888\text{\AA}$	

The body-centered chromium phase also existed at $\text{CrH}_{0.12}$; however, a mixture of body-centered and hexagonal hydride phase appeared at $\text{CrH}_{0.45}$. We estimate the phase boundary between body-centered cubic hydride and hexagonal plus body-centered cubic hydrides to be at approximately $\text{CrH}_{0.15}$.

It is natural to inquire into the possibility that the body-centered cubic form of chromium may be a hydride. The largest interstices in the body-centered cubic atomic arrangement are those on the face-centered positions. In the chromium lattice the smallest of these almost spherical openings are $1.58\text{\AA}$ in diameter. It is concluded that these face-centered interstices could not be occupied by hydrogen atoms as such, since they have a diameter of only $0.74\text{\AA}$. An interstitial atom must be sufficiently large to contact all surrounding atoms if a stable or even a metastable interstitial solid solution type of structure is to be established. It is therefore concluded that the hydrogen present in body-centered cubic chromium deposit is occluded as molecular hydrogen in voids somewhat larger than the crystal lattice interstices. Apparently, much of the hydrogen of hydride forms does not escape when the hydrides decompose, but is occluded in the body-centered cubic decomposition product.⁷ Thus, the claimed synthesis^{19,20} of a black, solid chromium hydride, CrH_3 , by the reduction of an ether suspension of chromium trichloride with a phenyl Grignard reagent in the presence of hydrogen gas is probably finely divided chromium metal on which considerable amounts of hydrogen have been occluded or physically adsorbed. It is indeed

difficult to distinguish such systems from nonstoichiometric hydrides by purely chemical means.

Hexagonal Chromium Hydride

The hexagonal chromium hydride phase was prepared by electrolysis of CrO_3 in dilute acid, with high CrO_3 concentration, high current density, and temperatures in the range 2-4°C. This hydride was produced as either bright, or grey, or black plates in thin layers. Although the hexagonal hydride phase appeared at the composition $\text{CrH}_{0.45}$, the body-centered cubic phase still predominated for this composition. This was evident from the relative intensities of the lines on the X-ray pattern. In general, the unit cell parameters remained constant for the hexagonal hydride phase as the hydrogen concentration was increased; however, in all hexagonal preparations the body-centered cubic phase was also present. As the hydrogen to chromium ratio approached one (1), the relative amount of body-centered phase decreased to only a trace. Listed below are the cell parameters for the hexagonal hydride phase as reported by various investigators.

<u>HEXAGONAL HYDRIDE</u>	<u>FORMULA</u>	<u>AUTHOR</u>
$a_o = 2.717\text{\AA}, c_o = 4.418\text{\AA}$	Not given	Snively ⁷
$a_o = 2.722\text{\AA}, c_o = 3.441\text{\AA}$	Not given	Mackay ¹³
$a_o = 2.717\text{\AA}, c_o = 4.418\text{\AA}$	$\text{CrH}_{1.0}$	Roy and Gibb ¹⁰
$a_o = 2.722\text{\AA}, c_o = 4.433\text{\AA}$	$\text{CrH}_{1.0}$	This work
$\sigma = 0.0001\text{\AA}$		

Mackay's c_0 value for the hexagonal hydride, $3.441\text{\AA}$, is undoubtedly a misprint and should be $4.441\text{\AA}$.

The surface structures of the cathode deposits, which were from one to several thousandths of an inch in thickness, were usually examined with an X-ray diffractometer within an hour after plating. The hexagonal hydride was found to decompose slowly at room temperature to the body-centered cubic metal; therefore, minimal delay in obtaining the X-ray and analytical data was necessary. Samples which required storage were sealed under argon in a glass vial and maintained at 2°C , at which temperature they appeared to be stable indefinitely.

The first layer of many of the hexagonal cathode deposits was studied by dissolving off the brass base metal disk with cold nitric acid and X-raying the surface of the plate formerly in contact with the brass surface. In all cases, this rear surface was found to be predominantly body-centered cubic, even though the front surface was hexagonal. This is in agreement with Snavely's conclusion that deposits produced at low pH, before the cathode film reaches an equilibrium at the higher pH value, are always body-centered cubic in structure. Although Snavely's experimental conditions for preparing the pure hexagonal phase were duplicated, a mixture of body-centered and hexagonal hydride always resulted. Since the body-centered phase occurred only in trace amounts at $\text{CrH}_{1.0}$, it is felt that this composition is metastable and the small amount of body-centered phase resulted from decomposition of the hexagonal phase. The fact that

lower hydrogen concentrations -- that is, $\text{CrH}_{0.4}$ to $\text{CrH}_{0.9}$ -- produced larger proportions of body-centered phase as determined from relative line intensities indicates that either the cathode film for this composition range remained at a low pH value for a relatively long period of time before reaching equilibrium at higher pH values, or very unstable hexagonal hydrides were formed in which much decomposition to body-centered cubic phase occurred while the plating was in progress. Many of the plates produced in this composition range ($\text{CrH}_{0.4}$ - $\text{CrH}_{0.9}$) were found to separate into two layers. A thin layer sometimes remained on the base metal. The surface of the overlying plate which separated from this base as a disc was always entirely body-centered cubic, bright to dull white, and extremely hard. Thus, there is evidence that the body-centered phase plates out initially and is followed by the hexagonal phase. Many of the deposits which had compositions in the range $\text{CrH}_{0.4}$ to $\text{CrH}_{0.9}$ did contain cracks, which perhaps indicates the formation of unstable hydrides. Snively⁷ has discussed cracks in chromium deposits and their relationship to the stability of the deposited hydrides. He concluded that the length of the cracks is indicative of, but not an absolute measure of, the thickness of the plate in which hydride decomposition proceeded at any given time during the plating process.

The "α-Manganese" Modification of Chromium

Numerous plating conditions were tried; however, we were unable to prepare the cubic structure reported by K. Sasaki and S. Sekito.²¹ They reported a structure which was isomorphous with α-manganese,

having a lattice constant of 8.717 kX units and a calculated specific gravity of 7.48. This structure was reported to change completely to the body-centered form on standing for 230 days at room temperature. Sasaki and Sekito are the only investigators who have reported this structure.

A Metastable Chromium Phase

From our investigations we have found a phase transition in electrodeposited chromium. A hexagonal hydride of composition $\text{CrH}_{0.93}$ and dimensions $a_o = 2.720\text{\AA}$ and $c_o = 4.435\text{\AA}$ was prepared and then decomposed to the body-centered phase by heating for 1.2 hours at 80°C . After heating at 143°C for another 1.2 hours, a face-centered cubic phase appeared in addition to the body-centered phase. This new phase remained along with the body-centered phase after the sample was cooled to 24°C . The diffraction lines were not well defined, and thus only an approximate unit cell parameter of $3.7\text{\AA}$ was determined. No attempt is made to explain what stabilizes this face-centered phase, but it probably corresponds to the face-centered cubic modification of chromium metal (β - Cr) with a unit cell parameter of 3.76 kX, which is reported to occur when chromium metal is heated to 1850°C .²²

Face-Centered Chromium Hydride

The final composition range for the chromium hydride system which we investigated was $\text{CrH}_{1.0}$ to $\text{CrH}_{2.0}$. Unfortunately, we were

unable to prepare hydrides with a hydrogen to chromium ratio much greater than one (1). An attempt was made to prepare $\text{CrH}_{1.7}$ by duplicating Snively's plating conditions; however, our results were similar to those of Proskurnikov and Krylov¹¹ in that a considerable amount of hydrogen gas was liberated from the deposit immediately after the plating ceased. Rapid decomposition was also evident from the texture of the cathode deposit, since it was cracked and blistered. Although we were unable to prepare hydrides with a hydrogen to chromium ratio much greater than one (1), the conditions we employed did produce the same face-centered cubic phase which was first identified by Snively. In general, the face-centered phase is favored over the hexagonal phase by high concentrations of CrO_3 and high current densities. High current density promotes a high hydrogen concentration which thereby favors the face-centered phase. A decrease in temperature should also favor a greater hydrogen concentration and thus favor the face-centered phase. In order to minimize the number of variables, however, we carried out all hydride preparations at the same temperature of 3°C . The face-centered phase was also favored by the presence of Cr (III), and thus it appears that a partial reduction of the chromic acid bath is necessary to produce this phase. It has been reported^{23,24} that this hydride structure is independent of the particular reducing agent used although sugar generally has been used.

Listed below are the unit cell parameters from various authors for the face-centered hydride phase at room temperature.

<u>FACE-CENTERED</u>	<u>AUTHOR</u>
$a_o = 3.850\text{\AA}$	Snively ⁷
$a_o = 3.861\text{\AA}$	Mackay ¹³
$a_o = 2.878\text{\AA}$	Roy and Gibb ¹⁰
$a_o = 3.8605\text{\AA}$	Redden ²⁵
$a_o = 3.853\text{\AA}$	This work
$\sigma = 0.0005\text{\AA}$	

Our unit cell parameter agrees well with all the reported values except for that of Roy and Gibb's value. We suspect that their value was misprinted and should actually be $3.878\text{\AA}$. Snively's value of $3.85\text{\AA}$ is probably for the composition $\text{CrH}_{1.7}$ although he did not explicitly state that the composition $\text{CrH}_{1.7}$ was determined for the cell parameter given above. The other three authors do not give any composition for their hydrides; however, our composition for the value given above was $\text{CrH}_{1.01}$.

No unusual phase transitions occurred when the face-centered cubic phase was heated and decomposed. Samples were heated to 147°C at which temperature the face-centered cubic phase decomposed directly to the body-centered cubic phase with no intermediate phases appearing.

Summary of Experimental Results

Table 1 tabulates the results of our current research. In summary, no pure hexagonal phase could be prepared. When the composition of the deposit was $\text{CrH}_{0.45}$, both hexagonal and

body-centered cubic phases were present. The hexagonal phase was present throughout the composition range $\text{CrH}_{0.45}$ to $\text{CrH}_{1.00}$ with similar unit cell parameters for all deposits within this range.

TABLE 1

FORMULAS AND CELL PARAMETERS
FOR CHROMIUM HYDRIDE

FORMULA	CELL PARAMETER	COMMENTS
$\text{CrH}_{0.05}$	Body-centered cubic $a_o = 2.884\text{\AA}$ $\sigma = 0.0008$	Only body-centered cubic present. The grey-white deposit chipped off cathode leaving shiny surface on brass.
$\text{CrH}_{0.08}$	Body-centered cubic $a_o = 2.888\text{\AA}$ $\sigma = 0.0006$	Deposit was chipped off and examined with X-rays on the deposit and brass sides. No difference in line intensity was observed.
$\text{CrH}_{0.12 \pm 0.02}$	Not determined.	Only body-centered cubic was present. Sample annealed at 500°C for one hour and compared with original room temperature X-ray photograph showed no difference in line intensity for the deposit and brass side.
$\text{CrH}_{0.45 \pm 0.01}$	Hexagonal $a_o = 2.723\text{\AA}$ $c_o = 4.444\text{\AA}$ $\sigma = 0.0001$	Two phases were present. The body-centered cubic predominated as deduced from the relative strengths of lines on the X-ray pattern.
$\text{CrH}_{0.81}$	Hexagonal $a_o = 2.725\text{\AA}$ $c_o = 4.436\text{\AA}$ $\sigma = 0.0001$	Hexagonal and body-centered cubic phases were present, but the hexagonal phase was the major part of the deposit. Only three lines for body-centered cubic appeared, and they were of low intensity.

TABLE 1 -- Continued

FORMULA	CELL PARAMETER	COMMENTS
CrH _{0.81} (continued)		No shiny surface remained after chipping off top surface of cathode.
CrH _{0.90±0.02}	Hexagonal a _o = 2.721 ^o Å c _o = 4.434 ^o Å σ = 0.0004	Deposit was grey-white with only one body-centered cubic line appearing.
CrH _{0.93±0.03}	Hexagonal a _o = 2.720 ^o Å c _o = 4.435 ^o Å σ = 0.0001	Grey-white deposit chipped off top surface leaving no shiny surface on the brass. Sample was heated and observed to change from a mixture of hexagonal and body-centered cubic to pure body-centered cubic and a new face-centered cubic phase.
CrH _{1.00±0.01}	Hexagonal a _o = 2.722 ^o Å c _o = 4.433 ^o Å σ = 0.0001	These grey crystals were crushed and stored in a vial at 3°C for one year under argon with no appreciable decomposition. Trace amounts of body-centered cubic.
CrH _{1.01±0.02}	Face-centered a _o = 3.853 ^o Å σ = 0.0005	Blistered grey deposit was easily chipped off brass and left some silver color on the brass. Heating the sample to 147°C showed that face-centered cubic hydride decomposes directly body-centered cubic chromium metal with no intermediate phases. No hexagonal phase present at this composition.

TABLE 1 -- Continued

FORMULA	CELL PARAMETER	COMMENTS
$\text{CrH}_{1.02 \pm 0.01}$	Face-centered $a_o = 3.854\text{\AA}$ $\sigma = 0.0003$	Pitted shiny grey-brown deposit was easily chipped off brass cathode leaving shiny surface on brass.
$\text{CrH}_{1.02 \pm 0.01}$	Hexagonal $a_o = 2.724\text{\AA}$ $c_o = 4.440\text{\AA}$ $\sigma = 0.0001$	Hexagonal and trace body-centered cubic phases were present. The sample was heated to 93°C and the hexagonal phase was still present without much decomposition.

No hexagonal phase could be prepared in which the composition was greater than $\text{CrH}_{1.02}$, and it was confirmed that the hexagonal hydride phase decomposes to body-centered cubic metal upon being heated to 143°C . A novel face-centered cubic phase was found to exist at room temperature after heating one hexagonal hydride sample to 143°C , although no report of the existence of this phase in chromium deposits can be found in the literature. Face-centered cubic hydride was also prepared corresponding to $\text{CrH}_{1.02}$, but attempts to prepare face-centered hydrides with hydrogen concentrations greater than 1.02 were not fruitful. The face-centered hydride began to decompose at 65°C and was completely decomposed to body-centered cubic chromium metal at 143°C .

Our research confirms Knoedler's⁸ claim that the hexagonal phase exists in the composition range $\text{CrH}_{0.95}$ to $\text{CrH}_{1.00}$, but his claim that this range should consist of only the hexagonal hydride

phase is questionable since we found trace amounts of body-centered cubic phase even at $\text{CrH}_{1.0}$. Roy and Gibb's¹⁰ claim that only the hexagonal phase is present in the range $\text{CrH}_{1.0}$ to $\text{CrH}_{1.5}$ seems to be in error since we were able to prepare face-centered cubic chromium hydride with a composition $\text{CrH}_{\sim 1.0}$. Figure 3 shows the zincblende and fluorite structures given by Snively^{7,12} for the face-centered cubic hydride phase. We were not able to reproduce his preparation of a face-centered cubic phase having a $\text{CrH}_{1.7}$ composition. The highest hydrogen concentration which we could prepare in this work for this phase was $\text{CrH}_{1.0}$, corresponding to the zincblende structure.

Snively's cell parameter values for face-centered hydride, $a_0 = 3.85\text{\AA}$, and for hexagonal hydride, $a_0 = 2.717\text{\AA}$ and $c_0 = 4.418\text{\AA}$, were in agreement with our results. One value published recently¹³ for the ' c_0 ' of the hexagonal hydride and Roy and Gibb's ' a_0 ' value for the face-centered hydride appear to be misprints. From experimental evidence, the cell parameters of the hexagonal hydride and the face-centered hydride remain constant for each phase even though the hydrogen concentration is varied. A slight expansion of the cell parameter was observed as metallic chromium absorbs hydrogen gas. The resulting phases with a hydrogen to chromium ratio greater than or equal to one (≥ 1) do not depend on composition, but rather on the method of preparation. It is felt that the irregularities in the phase diagram for the chromium hydride system have resulted from the variety of preparation techniques and the examination of the resulting hydrides under nonequilibrium conditions.

Zincblende Structure Fluorite Structure

Figure 3. -- Zincblende and Fluorite Structures

The shaded spheres represent the chromium atoms, and the unshaded spheres represent the hydrogen atoms.

CHAPTER III

EXPERIMENTAL

General

All X-ray photographs were obtained with a General Electric X-ray Diffractometer, Model XRD-5. Powder photographs were taken with a General Electric XRD-5 powder camera and with a Seemann heat camera with 0.5 mm quartz capillaries.

A FORTRAN IV program was written for the General Electric 415 computer which assigned Miller indices and computed best cell parameters from a least squares procedure.

Procedures

Plating Apparatus

The electrodeposition apparatus consisted of a Forma constant temperature bath, a one-liter crystallizing dish containing the CrO_3 solution, and a simple plastic fixture for holding the anode and the sample (Figure 4). The plating solution was stirred during deposition, and the temperature was maintained at $3 \pm 1^\circ\text{C}$. The plating fixture was constructed of methyl methacrylate sheet with a one-square-inch platinum sheet anode electrically connected through a platinum wire. The cathode consisted of brass disks 1.27 cm in diameter held in a

Plastic fixture for holding
anode and sample

Figure 4. -- Electrodeposition Cell

countersunk hole 1.27 cm in diameter. The brass disk was wedged into the countersunk hole against the platinum wire, thus masking the back of the cathode while holding it at the bottom of the hole.

Preparation of Hexagonal Hydride Phase

Using a plating solution containing 400 g/l CrO_3 , 400 g/l $\text{Na}_2\text{Cr}_2\text{O}_7$, and 4 g/l H_2SO_4 , and a current density of 15 A/dm^2 at 3°C , a hexagonal hydride phase of composition $\text{CrH}_{1.0}$ was produced after plating for 24 hours. $\text{CrH}_{0.93}$ was prepared by using 587 g/l CrO_3 , 2.9 g/l H_2SO_4 , and 10 g/l sugar, and a current density of 9 A/dm^2 . The sugar inhibited the formation of the chromium plate, so 48 hours were required before enough material was plated out to carry out the necessary analysis. $\text{CrH}_{0.45}$ was prepared from a bath containing 200 g/l CrO_3 and 2 g/l H_2SO_4 and having a current density of 63 A/dm^2 . $\text{CrH}_{0.12}$ was prepared by reducing the current density to 50 A/dm^2 and using 200 g/l CrO_3 and 2 g/l H_2SO_4 . In general, high current densities, low temperatures, and high concentrations of CrO_3 favored high hydrogen concentrations. Intermediate hydrogen concentrations were thus prepared by adjusting these variables in the appropriate direction. In all cases the solutions were stirred with a magnetic stirrer.

Preparation of Face-Centered Hydride Phase

Using a bath containing 911 g/l CrO_3 , 3 g/l H_2SO_4 , and 10 g/l sugar, and having a current density of 12 A/dm^2 , a face-centered

cubic hydride of composition $\text{CrH}_{1.0}$ was produced after electrolyzing the solution for 48 hours. This solution was stirred throughout the plating time, and the temperature was maintained at 3°C . The face-centered phase was also prepared without the use of sugar. A bath containing 1000 g/l CrO_3 , 3 g/l H_2SO_4 , and 0.5 g/l $\text{Cr}_2(\text{SO}_4)_3$, and having a current density of 12 A/dm^2 , produced the face-centered phase after 13 hours of plating. This solution was maintained at 3°C and was stirred constantly.

The Chromatographic Analysis of Chromium Hydrides

One- to ten-milligram samples were inserted into the combustion tube of an F&M model 180 carbon hydrogen nitrogen analyzer. After a four-minute burn cycle, the final combustion products, H_2O and traces of CO_2 and N_2 , were passed on to a copper column, having an outside diameter of 6 ft. by $\frac{1}{4}$ in., packed with Porapak Q. The gasses were selectively adsorbed onto the packing material and eluted. The eluent gasses finally were passed out of the oven to an outside copper column, having an outside diameter of 6 ft. by $\frac{1}{4}$ in., packed with one-half Molecular Sieve 4A and one-half Molecular Sieve 13x. The CO_2 and H_2O were irreversibly adsorbed on this column while the N_2 was passed back into the oven through a three-foot column of 4A and 13x Molecular Sieves and through the second detector. All peaks were proportional to percent composition and were inversely proportional to sample weight. The furnace temperature was kept at $940 \pm 1^{\circ}\text{C}$, and the oven temperature was maintained at $85 \pm 1^{\circ}\text{C}$. Approximately four minutes was required for the complete hydrogen analysis following a

four-minute burn cycle with the helium gas flow of 85 ml/min.

Indexing Powder Photographs

A computer program was written which automatically indexes neutron and X-ray powder diffraction photographs of cubic, tetragonal, orthorhombic, and hexagonal crystals. The program was written in FORTRAN IV for the General Electric 415 computer. The input data consisted of one, two, or three initial assignments for the Miller indices along with θ or $\sin \theta$ values. If approximate cell parameters were known, these values were used as input rather than the trial Miller indices. The wavelength, tolerance for the difference between $\sin \theta_o$ (observed) and $\sin \theta_c$ (calculated), and various option parameters were also included in the input. If initial assignments for Miller indices were used as input, approximate cell parameters for the crystal system were calculated using determinants and an approximate relationship; e.g., for the cubic case:

$$\sin^2 \theta = \frac{\lambda^2}{4} \left[\frac{h^2 + k^2 + l^2}{a_o^2} \right] \quad (1)$$

Upon calculating the cell parameters from initial assignments of h , k , and l , all possible values of $\sin^2 \theta$ were generated by varying the Miller indices from zero to the prescribed upper limit; or, if the values of the cell parameters were known, these values were used in the appropriate equation, such as (1), to generate all the $\sin^2 \theta_c$.

A linear function of θ was derived empirically which successfully corrected for absorption even though approximate cell parameters

were used. The function, which was optional within the program, was derived by comparing the computer program assignments of cubic, tetragonal, orthohombic, and hexagonal systems to hkl values which were correctly determined previously. A correction factor for $\sin \theta_c$ was determined such that the difference between $\sin \theta_c$ and $\sin \theta_o$ would be within a weighted tolerance (e.g., according to intensity) while maintaining the 'correct' Miller indices. The empirical function which gave best results for the many structures examined was

$$\text{FUDGE}_i = -5.8 \times 10^{-5} \theta_i + 4.4 \times 10^{-3} \quad (2)$$

where FUDGE_i is the factor for the i^{th} reflection which is to be subtracted from the calculated $\sin \theta_i$.

After all $\sin \theta_c$ values were calculated and corrected for absorption -- if this option was desired -- the difference,

$$\Delta = |\sin \theta_c - \sin \theta_o| \quad (3)$$

was calculated for each reflection. Whenever Δ was within the tolerance, the values of h, k, l, θ , $\sin \theta_c$, $\sin \theta_o$, and Δ were printed out, and the Miller index combination resulting in the smallest Δ value was indicated. This program has recently been published in the Journal of Scientific Instruments.²⁶

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