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Physico-chemical properties of chromium sesquisulphide

K. N. STRAFFORD, A. F. HAMPTON*
Department of Materials Science, Newcastle upon Tyne Polytechnic, Newcastle upon Tyne, UK

The range of stoichiometry and defect structure of chromium sesquisulphide, "Cr_2S_3", have been determined for a range of temperature (1123 to 1273K) and sulphur pressure (1.06×10^{-1} to 1.77×10^{4} N m^{-2}) employing chemical analysis, marker and thermoelectric power measurement techniques. It has been shown that the upper limit of stoichiometry corresponds to $CrS_{1.54}$, while the lower limit extends to at least $CrS_{1.30}$. The conditions (temperature and sulphur pressure) under which the compound is stable at compositions intermediate to these values have been determined for S/Cr ratios at intervals of 0.02.

It has been established that "Cr_2S_3" is an *n*-type metal-excess compound within these composition limits, containing unassociated trivalent chromium interstitials and/or trivalent chromium interstitials associated with one quasi-free electron, as the predominant mobile defect species.

1. Introduction

In order to understand fully the nature of the corrosion behaviour of materials in gaseous environments at elevated temperatures with a view to improving their corrosion behaviour, and developing new corrosion resistant alloys, it is essential that data pertaining to the principle physico-chemical properties of the reaction products being formed or likely to be formed, are available. In particular, it is well known that the reaction mechanism(s) which are operative are primarily governed by the defect structure of the reaction product(s), provided that the thermodynamic conditions for spontaneous corrosion to occur are first satisfied [1].

Probably, one of the most aggressive conditions likely to be experienced by materials commonly in use for high temperature applications is a sulphur-containing atmosphere, where interaction between the material with the ambient atmosphere results in the formation of a metal sulphide reaction product. Unfortunately, interpretation and understanding of such reactions are often hampered by the lack of data relating to the physico-chemical properties of most metallic sulphides; this situation can be contrasted with the corresponding data which are mostly available for many of the metal oxides which are formed during high-temperature oxidation.

The current prominent use of chromium-containing alloys in many high-temperature applications, where corrosion, particularly sulphidation, is a major problem [2-14], has resulted in much interest in the chromium/sulphur system, and the physico-chemical properties of chromium sulphides. In the present studies, some of the physico-chemical properties of chromium sesquisulphide, nominally Cr_2S_3 have been investigated. Although this compound, or one with a composition close to Cr_2S_3, is known to form as a corrosion product on Cr and Cr-bearing alloys, when they are contained in sulphur-rich atmospheres at elevated temperatures [5, 8, 11], virtually nothing is known about its range of stoichiometry and defect structure at elevated temperatures.

Preliminary sulphidation studies [18] on chromium coupons in various H_2S/H_2 gas mixtures in the temperature range 1123 to 1273K indicated that formation of a scale of reaction product consisting solely of "Cr_2S_3" took place. These studies suggested a convenient method whereby the pure compound could be prepared, by complete sulphidation of Cr sheet, and on which the desired physico-chemical measurements could be subsequently made.

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*Present address: Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio, USA.

Consideration was first given to an assessment of the range of stoichiometry exhibited by chromium sesquisulphide corresponding to a wide range of sulphur partial pressures, within the temperature range 1123 to 1273 K involving gravimetric and chemical analysis studies. The nature of the defect structure of the compound has also been investigated by thermoelectric measurements and marker studies.

2. Experimental

2.1. The sulphidation apparatus

2.1.1. Thermobalance assembly

The experimental conditions (exposure time, and temperature) necessary for the preparation of samples of chromium sesquisulphide "Cr_2S_3" by the complete sulphidation of coupons of chromium, and their subsequent equilibrium with various H_2S/H_2 gas mixtures to allow assessment of the range of stoichiometry of the sulphide, were determined by gravimetric studies using a quartz spring thermobalance. The main features of the thermobalance have been described in the literature [15]. The overall accuracy of the spring/cathetometer arrangement permitted weight changes in the sample (Cr or Cr_2S_3) to be measured to within $\pm 3 \times 10^{-8}$ kg. H_2S/H_2 gas mixtures, dried with calcium chloride, were admitted at the bottom of the balance and exhausted at the top. Gas flows were monitored with the aid of a glass flowmeter. The temperature of the electrical resistance furnace was controlled so that the maximum possible overall variation in temperature within the hot zone (3×10^{-2} m in length) was $\pm 3°$ C.

2.1.2. Operating procedure

After sealing a prepared sample of Cr* in the thermobalance extension tube, the whole system was evacuated and the furnace brought to the required reaction temperature. The balance was then isolated from the vacuum pumps and a fast stream of high purity argon was passed through the balance and the sample was lowered into the hot zone of the furnace tube. The flow rate of the argon was then quickly, but steadily, reduced to zero whilst at the same time the appropriate H_2S/H_2 gas mixture was introduced into the balance, its flow rate being correspondingly progressively increased.

Immediately after stopping the flow of argon, the flow rate of the H_2S/H_2 mixtures was maintained at 1.5×10^{-6} m^3 sec^{-1} for about 1.20×10^2 sec to flush out traces of residual argon, before being reduced to a flow rate of 5.83×10^{-7} m^3 sec^{-1} for the duration of the experiment. Preliminary experiments indicated that the sulphidation rate of pure chromium was independent of gas flow rate, within the limits 1.67×10^{-7} and 1.5×10^{-6} m^3 sec^{-1}. The commencement of the sulphidation reaction was taken as being the instant that the H_2S/H_2 gas mixture was introduced into the balance.

After alteration of either the composition of the gas mixture (H_2S/H_2 ratio), or the temperature, the resultant change in weight of the sample was followed using the cathetometer. The sample was allowed to equilibrate for a period of ~ 12 h until the new condition of constant weight had been attained. The exposure conditions were then altered and the process of re-equilibration followed. This procedure was carried out until the equilibrium compositions of the "Cr_2S_3" corresponding to the various sulphur pressures (see Table I) had all been determined. The conditions in the environment surrounding the sample were in fact changed in one of two alternative ways, either (1) by altering the composition of the H_2S/H_2 gas mixture at a fixed temperature, or (2) by altering the temperature of the atmosphere, but keeping the composition of the gas mixture constant.

At the termination of an experimental run the flow rate of the gas mixture was progressively reduced as argon was re-introduced into the gas stream, until the sulphur-containing gas had

TABLE I Calculated sulphur pressure (N m^{-2}), derived from various H_2S/H gas mixtures at various temperatures as used in the stoichiometry studies*

Gas composition %H_2S/% H_2 (by volume)	Equilibration temperature (K)		
	1123	1198	1273
4/96	1.06×10^{-1}	3.46×10^{-1}	9.55×10^{-1}
20/80	3.77	1.26×10	3.75×10
30/70	1.12×10	3.75×10	1.09×10^2
43/57	3.45×10	1.15×10^2	3.43×10^2
57/43	1.07×10^2	3.57×10^2	1.04×10^3
65/35	1.97×10^2	6.57×10^2	1.93×10^3
85/15	2.01×10^3	6.55×10^3	1.77×10^4

*Calculated from available thermodynamic data [24].

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*For surface preparation details see under materials sub-section.

been flushed out of the balance. The sample was then rapidly winched out of the hot zone of the balance into the extension unit and immediately removed from the apparatus, and allowed to cool.

2.2. Materials

The composition and particulars of the high purity chromium sheet, used in the preparation of Cr_2S_3 have been given in an earlier paper [15], as have the compositions of the constituent hydrogen and hydrogen sulphide gases used to prepare the gas mixtures and the composition of the high purity argon gas used for flushing the thermobalance assembly.

Small rectangular coupons of approximate dimensions $5 \times 3 \times 1 \times 10^{-3}$ m and weighing 2×10^{-4} kg were cut from the chromium sheet using a jewellers saw. A small hole (2.8×10^{-4}m diameter) was drilled through the metal coupons to allow their easy suspension from the quartz spring by a thin platinum wire. All six faces of individual samples were successively ground down to 600 grade silicon carbide paper and then washed in carbon tetrachloride. Samples were then individually wrapped in tantalum foil and annealed for 2h at 1273K in vacuum (1.33×10^{-2} N m^{-2}). Finally, all surfaces were lightly abraded with 600 grade paper, and degreased in carbon tetrachloride. They were then loaded individually into the thermobalance ready for sulphidation, i.e. for conversion to Cr_2S_3.

2.3. Thermoelectric power measurements

Here a specimen of Cr_2S_3, prepared by complete sulphidation of pure Cr strip, was contained in a controlled atmosphere furnace such that a temperature gradient was impressed on the specimen. The sample was suspended on thin Pt and Pt/Rh wires contained in a multibore silica tube (see Fig. 1). The Seebeck voltage generated across the specimen was measured with a vernier potentiometer, the smallest discrimination on which was 10^{-7} V.

The details of the experimental techniques used to determine the thermoelectric power of "Cr_2S_3" are as follows. A chromium platelet ($3.0 \times 0.5 \times 0.1 \times 10^{-2}$m) was prepared as described above, except that two 2.5×10^{-4}m holes were drilled through the platelet, one at either end. Two pure platinum wires, 2.5×10^{-4}m in diamter, were then put through the holes, and, on the opposite side of the platelet, each of the platinum wires was joined to a Pt-13% Rh wire, also 2.5×10^{-4}m diameter, using a small oxy-acetylene torch. In this manner two thermocouple junctions were formed, one at each end of the specimen, which could be used to measure the temperatures at each end of the specimen, and hence provide a measure of the temperature gradient along the sample. The four wires were led out of the apparatus through quadruple bore capillary quartz tubing and used to suspend the specimen in a constant temperature gradient within the vertical furnace.

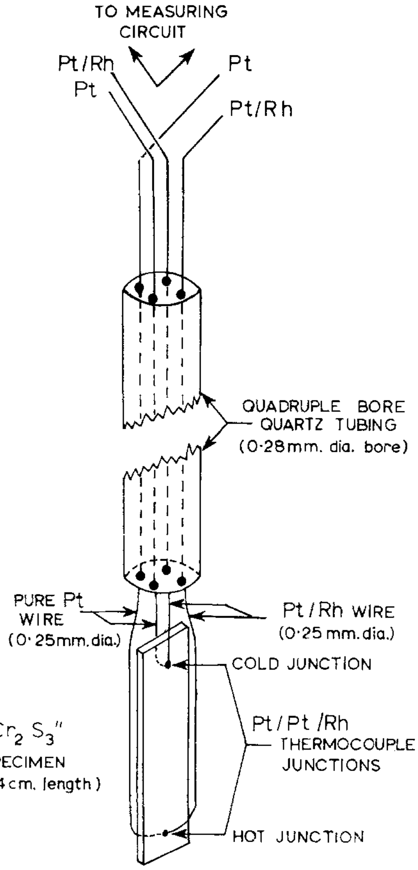

Figure 1 Specimen holder and assembly for thermoelectric power studies.

After the specimen was completely sulphidized and the resulting sulphide "Cr_2S_3" equilibrated with a particular chosen H_2S/H_2 gas mixture at 1000° C, the Seebeck emf was measured. Further similar measurements were made after allowing equilibrium to be systematically re-attained with gas mixtures of differing composition at different temperatures. Thus the Seebeck emf was determined for "Cr_2S_3" corresponding to a wide range of stoichiometry. The Seebeck coefficient, Q, relative to pure platinum was calculated according to

$$Q = \mathrm{emf}/T$$

where T is the temperature difference along the specimen. The sign of Q was taken as negative when the specimen was n-type [16]. This occurs when the hot end is positive with respect to the cold end, i.e. when the electron current flows from the cold to the hot end of the sample via the external conductor circuit.

The compositions and temperatures of the various atmospheres (H_2S/H_2 mixtures) used to prepare "Cr_2S_3" specimens of known variable degrees of stoichiometry (determined in these studies) upon which thermoelectric power measurements were made are given in Table II.

TABLE II Sulphur pressures ($N\ m^{-2}$) and corresponding sulphide compositions (in parentheses) expressed as S/Cr ratios, derived from various H_2S/H_2 gas mixtures at various temperatures, as used in the thermoelectric power studies

Gas mixtures $\%H_2S/\%H_2$ (by volume)	Temperature (K)		
	1123	1198	1273
4/96	1.06×10^{-1} (1.37)	3.46×10^{-1} (1.34)	9.55×10^{-1} (1.31)
30/70	1.12×10 (1.45)	3.75×10 (1.44)	1.09×10^{2} (1.40)
85/15	2.01×10^{3} (1.54)	6.55×10^{3} (1.54)	1.77×10^{4} (1.54)

2.4. Marker experiments

Two types of marker experiment were used. In the first method a narrow band of pure platinum was coated on to the prepared main faces of chromium coupons and then the samples were allowed to sulphidize in a H_2S/H_2 atmosphere for various standard exposure times at 1273K. In order to obtain such a band of platinum, platinum past was mixed with white spirit until reasonably viscous, and was then painted on to the faces of the specimen. The coated sample was then fired at a temperature of 800°C in order to drive off the volatile binding agents and solvent. This firing operation was of very short duration and no visible contamination of the specimen with oxide (Cr_2O_3) occurred. The coating and firing procedure was repeated several times until a band of platinum of reasonable thickness ($\sim 1.0 \times 10^{-5}$m) was built up.

The coated specimens were then sulphidized for various exposure times using the apparatus and techniques described earlier in this paper. The sulphidized specimens were mounted and prepared for metallographic examination in section techniques described elsewhere [15, 17, 18]. The position of the platinum markers was noted and photographed. In order to confirm that the Pt marker band was not hindering scale growth or modifying the growth mechanism, the thickness and the morphology of the scales formed after simultaneous exposure of coated and uncoated coupons of chromium were compared and found to be the same.

The second series of marker-type experiments involved scratching the main surface of prepared Cr specimens to standard depths of 5×10^{-6} and 1.3×10^{-5}m. This was achieved using a scribing tool held in a vertical Vernier stage on a workshop lathe. Scratched samples were then isothermally sulphidized for various successively increasing exposure periods. The faces of the sulphidized coupons were first examined macroscopically. Samples were then mounted and prepared for microscopic examination in section. The depth of the scratch in the metal substrate and the observed corresponding dip produced at the outside surface of the sulphide scale were measured as a function of exposure time.

2.5. Chemical analysis methods

2.5.1. Analysis of chromium sulphides

The following methods of chemical analysis were adopted for the determination of the sulphur and chromium contents in the prepared sulphides.

Sulphur determination Sulphur was determined directly by combustion of the chromium sulphide in oxygen to form the oxide (Cr_2O_3) and sulphur dioxide according to the equation:

$$Cr_2S_3 + \frac{9}{2}O_2 \rightarrow Cr_2O_3 + 3\,SO_2\,\cdot \qquad (1)$$

The sulphide sample was first crushed in a pestle and mortar, and a known weight placed in a small alumina boat. The sample was then oxidized at 1273K in oxygen to constant weight. The decrease in the weight of a sample of sulphide when converted in this way to the oxide provided a measure of the amount of sulphur originally present in the sample. On complete combustion of 5×10^{-4}kg of a CrS_x sample it was possible (weighing to ± 5 × 10^{-8}kg) to determine a change in stoichiometry equivalent to a change in "x" of ± 0.005. For the purposes of calculation the departure from stoichiometry of Cr_2O_3 was assumed negligible [19].

Chromium determination A volumetric method [20, 21] was adopted, involving the fusion of the chromic oxide with sodium peroxide, followed by leaching with water in order to obtain the chromium metal in solution. The solution was then filtered, acidified and made up to 250 ml. A 50 ml aliquot was removed, a known excess of standard ferrous ammonium sulphate solution was added, and the excess of ferrous salt was titrated with standard potassium dichromate solution using *N*-phenylanthranilic acid as indicator.

The volume of ferrous solution which was oxidized by the dichromate originating from the chromic acid was calculated, and from this the weight of chromium determined.

$$1 \text{ ml N-Fe}^{3+} \equiv 1 \text{ ml N-}K_2Cr_2O_7 \equiv 2.534 \times 10^{-5} \text{ kg } Cr_2O_3 \equiv 1.734 \times 10^{-5} \text{ kg Cr.}$$

The probable accuracy of this determination was such that for a sample of sulphide, composition Cr_yS (where $y = 0.67$ for nominal "Cr_2S_3") the error in this would be ± 0.002.

2.6. X-ray analysis of Cr_2S_3

Confirmatory identification of Cr_2S_3 as the sulphide formed over the complete range of experimental conditions imposed during the stoichiometry studies was obtained using the Debye-Scherrer technique. Comparison of the patterns was made with ASTM data cards. Most satisfactory results were obtained using a copper target and nickel filter.

3. Results

3.1. Investigation of the range of stoichiometry of "Cr_2S_3"

The range of stoichiometry of chromium sesquisulphide (nominally Cr_2S_3) was investigated by studying the variation in chemical composition of the compound in terms of the S/Cr ratio (determined gravimetrically), over the temperature range 1123 to 1273K and a wide range of sulphur pressure (1.06 × 10^{-1} to 1.77 × 10^4 N m^{-2}). The equilibration stoichiometric studies for a set of exposure conditions (i.e. at one particular temperature and in one gas mixture) were repeated on four separate coupons; thus operating at three reaction temperatures and employing seven different gas mixtures, a total of eighty-four individual experimental runs were performed. The results are summarized in Fig. 2 where the equilibrium compositions (calculated from spring extension, then checked by chemical analysis) of the chromium sesquisulphide, expressed as the S/Cr ratio, are plotted as a function of the logarithm of the corresponding equilibration sulphur pressures for the three equilibrium temperatures. Although there is some scatter in the results it is, nevertheless, clear that there is an approximately linear relationship between these variables at all three temperatures, over a wide range of sulphur pressure. At high sulphur pressure, however, the S/Cr ratio becomes approximately constant, i.e. the composition of the "Cr_2S_3" becomes approximately constant.

The straight lines drawn through each of the

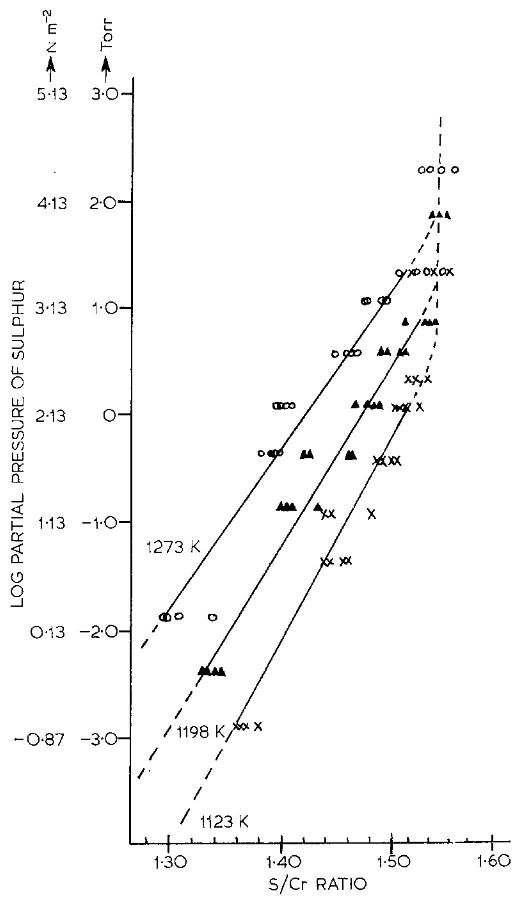

Figure 2 The composition of chromium sesquisulphide, in terms of S/Cr ratio, as a function of the log of equilibrium partial pressure of sulphur at temperatures of 1123, 1198 and 1273 K.

sets of experimental points determined at the three temperatures have been fitted by adopting the least square criteria. The degree of correlation of the individual set of points about the fitted least-square line was assessed by the so-called product moment correlation coefficient, r [22]. The values of the correlation coefficient for the three straight lines shown in Fig. 2 are: at 1273 K, $r = 0.97$; at 1198 K, $r = 0.98$; and at 1123 K, $r = 0.96$ indicating a very satisfactory degree of correlation about the fitted line, since $r = 1$ corresponds to a perfect functional relationship [22].

It is clear from Fig. 2 that there is a large range of stoichiometry in Cr_2S_3, extending (under the present experimental conditions) from about $CrS_{1.30}$ to $CrS_{1.54}$. This latter value is clearly approximately the upper stoichiometric limit for "Cr_2S_3"; the minimum S/Cr ratio for which the "Cr_2S_3" phase is still stable has clearly not been established or reached under the present conditions. It should be emphasized that the sole presence of the "Cr_2S_3" phase over the entire range of experimental conditions imposed was confirmed by powder diffraction techniques.

The line fitted by the least mean squares method gives only the best estimate of the value of the parameters in question. The degree of uncertainty in this estimate can be assessed by calculating the limits within which the points plotted, at a particular reaction temperature, are contained. The points at all three temperatures are of the order 3 to 5% of the estimated value represented by the fitted line.

3.2. Thermoelectric power measurements

Thermoelectric power measurements indicated that under the stated conditions "Cr_2S_3" is a n-type material, having a negative Seebeck coefficient relative to pure platinum. The voltage developed by the imposition of a temperature gradient along the specimen was significantly larger than the residual voltage at zero-temperature gradient. The values of the coefficient ($V° C^{-1}$) relative to platinum are summarized in Table III. The same data are plotted as a function of the log of the corresponding sulphur partial pressure in Fig. 3.

In Fig. 4, the absolute thermoelectric power values, after correction for Q_{Pt} [23], are plotted as a function of the reciprocal of the corresponding absolute temperatures. These curves of Q (absolute) versus $1/T$K in the two gas mixtures of lowest H_2S/H_2 ratio appear to be approximately linear; however, in the H_2S-rich gas mixture, H_2S/H_2-85/15, the function is more of a curved nature. The material exhibited n-type conduction at all temperatures up to 1273 K, but the value of the Seebeck coefficient decreased with increasing temperature. Thus the possibility of a transition from n-type to p-type conduction might be expected at higher temperatures.

Confirmation of the n-type conduction behaviour of the material was obtained by comparing the signals with those obtained after the coupon of chromium sesquisulphide was completely oxidized to Cr_2O_3 in atmosphere of pure oxygen [24]. Chromic oxide is known to be p-type material below 1523 K [25] and in fact the sign of the signal was opposite to that previously obtained with the chromium sesquisulphide.

The barrier energy for charge carriers attempting to enter the conduction band of the n-type semiconducting chromium sesquisulphide, i.e. activation energy for conduction, can be expressed [23, 26] in terms of the absolute thermoelectric power, Q_{abs}, as follows,

$$-Q_{abs}T = (E_C - E_F) + 2kT$$

where E_C is the conduction band energy, E_F is the Fermi level and k is Boltzmann's constant.

For a plot of Q_{abs} versus $1/T$K, Fig. 4, the slope of the curve is equal to the activation energy for conduction in the material ($E_C - E_F$). Despite the non-linearity of the curves, especially for the sulphur-rich gas mixture, a straight line has been drawn in order to estimate the activation

TABLE III Seebeck coefficients, Q ($V °C^{-1}$), of chromium sesquisulphide as a function of temperature in various H_2S/H_2 gas mixtures

Gas mixtures % H_2S/% H_2 (by volume)	Temperature (K)		
	1123	1198	1273
4/96	-2.70×10^{-4}	-2.65×10^{-4}	-2.50×10^{-4}
30/70	-3.50×10^{-4}	-3.35×10^{-4}	-3.00×10^{-4}
85/15	-5.10×10^{-4}	-4.05×10^{-4}	-3.60×10^{-4}

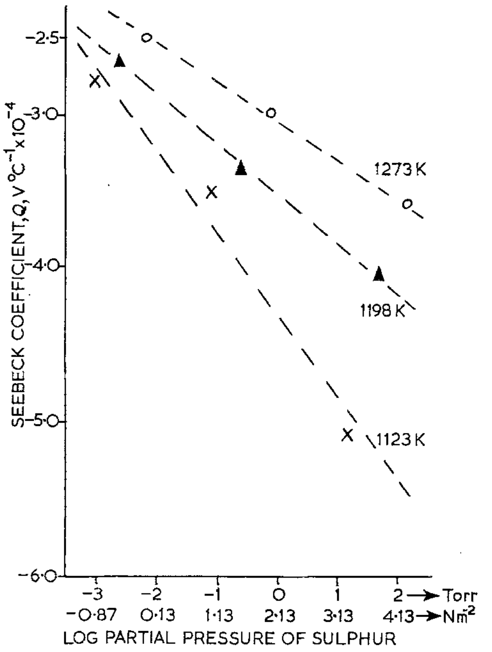

Figure 3 Observed Seebeck coefficient (thermoelectric power coefficient) of chromium sesquisulphide as a function of the logarithm of partial pressure of sulphur at various temperatures.

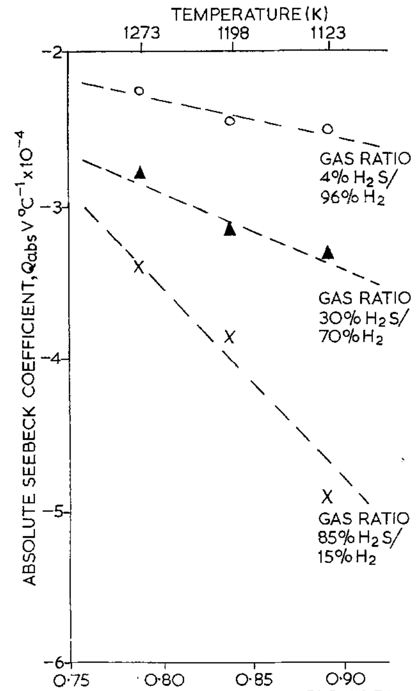

Figure 4 Absolute Seebeck coefficient of chromium sesquisulphide as a function of the reciprocal of absolute temperature in various H_2S/H_2 gas mixtures.

energy for conduction. The energies calculated from the slopes of the three curves are given in Table IV.

TABLE IV Approximate activation energies for conduction evaluated during thermoelectric power studies on chromium sesquisulphide for the temperature range 1123 to 1273 K in various H_2S/H_2 gas mixtures

Gas mixtures % H_2S/% H_2 (by volume)	Activation energy for conduction (eV)
4/96	0.25
30/70	0.47
85/15	1.36

3.3. Marker studies

In the first set of experiments involving exposure of prepared sample of Cr coated with a thin narrow band of platinum paste to the H_2S/H_2 atmosphere for increasing exposure periods at 1273 K, the main features revealed on a microscopic examination of the scales formed, in cross-section, are shown in Fig. 5. It will be evident that the marker is located at, or close to, the metal/scale interface.

In the second set of experiments where several prepared samples of pure Cr were scratched to known standard depths and then sulphidized, several interesting observations were made. Firstly, it was clear from macroscopic observations that the scratches were progressively buried under the growing scale as the period of sulphidation increased. The actual change in the depth of the scratch with increasing exposure time was also examined and measured by means of a Vernier microscope. The results of these measurements are summarized in Fig. 6 where the depth of the scratch is plotted as a function of exposure time. The apparent scratch depth appears to decrease as a parabolic function of the exposure period.

Finally, Fig. 7a to c shows the scale formation on three identically scratched specimens but sulphidized for different exposure periods; it is clear that the scratch depth is significantly less the longer exposure period.

4. Discussion

The present studies of the stoichiometry of chromium sesquisulphide, nominally "Cr_2S_3", show that the compound exists over a wide range of composition under the experimentally im-

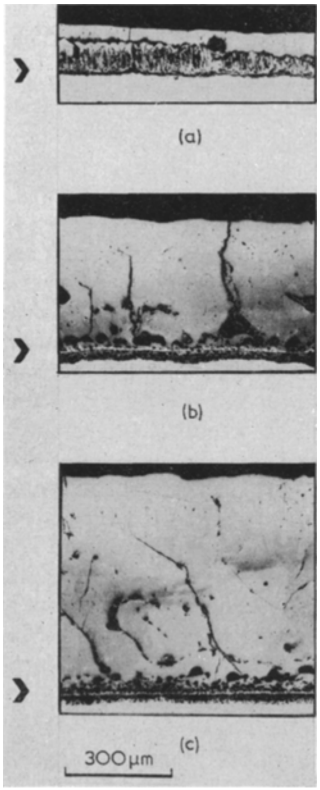

Figure 5 Location of platinum markers within a chromium sesquisulphide scale formed on pure chromium after sulphidation at (a) 600, (b) 3600 and (c) 7200 sec. Arrowhead indicates marker location.

posed conditions in keeping with a large group of chalcogenides [27, 28]. Considering the composition of the sulphide in terms of the S/Cr ratio, the upper composition limit is apparently reached at S/Cr = 1.54, no further increase in the ratio being observed over several higher orders of sulphur partial pressure. The minimum S/Cr ratio observed was 1.30 and it would appear that the phase boundary between the chromium sesquisulphide and the adjacent phase in the Cr-S system, probably Cr_3S_4, has not quite been reached under the present experimental conditions. The lower limit of the range of stoichiometry is given by Hauffe [29] as S/Cr = 1.22.

Such a wide range of stoichiometry is also in keeping with similar trends in many metallic sulphides; for example Ni_3S_2 is reported to exist from $Ni_3S_{1.95}$ to $Ni_3S_{2.40}$ above 700°C [30], whilst Cu_2S is stable over the range $Cu_{1.65}S$ to $Cu_{2.00}S$ [30]; the monoclinic sulphide of chromium, and the most stable sulphide of chromium

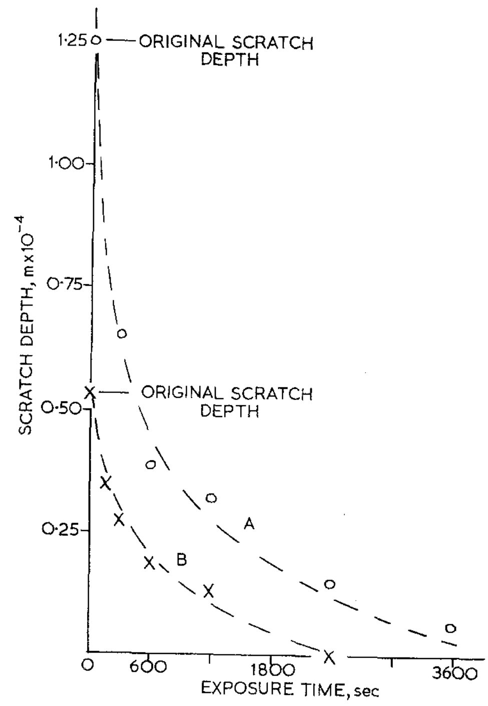

Figure 6 Residual scratch depth in metal substrate as a function of period of sulphidation at 1273 K.

at room temperature, CrS has a reported stoichiometric range of $Cr_{1.00}$ to $CrS_{1.17}$.

The thermoelectric power measurements indicated unequivocally that over a large range of sulphur pressure for the temperature range 1123 to 1273 K "Cr_2S_3" is an *n*-type semiconductor containing quasi-free electrons. The present findings are in fact in broad agreement with similar but more limited electrical property measurements made by Radzkovakaya and Oganesyan [31]. These authors measured both the thermoelectric power and the electrical resistance of stoichiometric chromium sesquisulphide pellets (prepared by powder metallurgy methods) as a function of temperature between 473 and 1173 K. To minimize oxidation of the samples these measurements were carried out under vacuum. The problem of oxidation of Cr_2S_3 is in fact a very real one, as demonstrated by Strafford and Hampton [24]. It was shown that the values of the thermoelectric power became negative at a temperature of 473 K and remained negative at temperatures up to 1173 K indicating that the predominant charge carriers were quasi-free electrons. However, at temperatures below 473 K the sign of the coefficient was

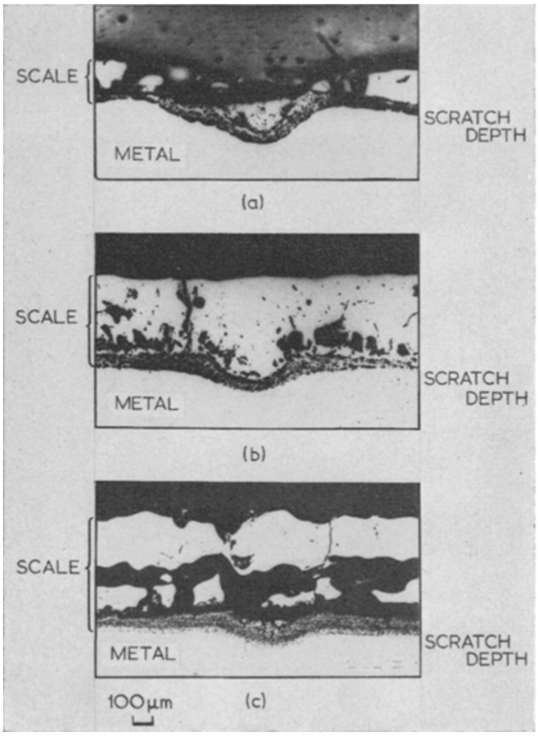

Figure 7 Sections of chromium sesquisulphide scales formed on chromium specimens, marked on main faces with a standard depth of scratch after sulphidation at 1273 K for times of (a) 3 × 10^2 (b) 1.8 × 10^3 and (c) 3.6 × 10^3 sec.

positive, indicating conduction apparently by electron holes. The resistivity measurements showed the same trend.

Accepting that "Cr_2S_3" is an *n*-type semiconductor containing quasi-free electrons, the question arises as to the nature of the associated defects, i.e. whether excess cations or anion vacancies. The results of the marker experiments all strongly suggest that the chromium ion is mobile in the "Cr_2S_3" lattice, sulphidation of Cr to form Cr_2S_3 taking place as a result of outward diffusion of the cation, the possibility of an inward diffusion of the sulphur anion being essentially excluded.

The use of markers to investigate the mobility of anions and of cations during sulphidation of metals has been discussed by Strafford [1], where appropriate attention was drawn to the limitations and difficulties in interpretation of results. In the marker experiments attempted in these studies, great care was taken to ensure that the marker location was a true representation of the diffusion processes occurring during the reaction mechanism. Thus comparison of reaction rates and scale morphology of coated and uncoated specimens and assessment of the general reproducibility of the experimental observations suggested that confidence could be placed on these observations and their subsequent interpretation [15].

The results of the scratch marker studies also substantiate the interpretation that cations must be the predominant diffusing species in the sulphide in view of the observation that the topology of the underlying metal surface (containing the scratch) was not reproduced or impressed on the outer surface of the growing sulphide scale, both the visible presence of the scratch on the growing sulphide scale (as shown by the depression in the sulphide surface) and the depth of the scratch remaining in the metal substrate decreasing with increasing exposure time. The progressive disappearance of these features according to a parabolic function with exposure time (Fig. 6) would be expected for a metal displaying parabolic corrosion kinetics. The present observations are to be compared with the opposite results noted during the formation of oxide scales on titanium [32] and titanium alloys [33, 34] and on tantalum and niobium [35, 36] where it is known that scale growth occurs via outward diffusion of the anion, scratches and other surface defects being retained on the outer surface of the scale.

Interestingly it should be noted that such a defect model for Cr_2S_3 is also confirmed by other observations made by Strafford and Hampton [15] concerning the relative rates of parabolic sulphidation of chromium and some dilute chromium molybdenum alloys. Here, it was noted that small additions of molybdenum in the range 0.01 to 1 wt % progressively reduced the rate of sulphidation of chromium, which would be anticipated if the parent scale of Cr_2S_3 was being doped by Mo^{4+} leading to a decrease in defect concentration in accordance with Wagner-Hauffe theory.

On the other hand Mrowec and Zastawnik [37] came to the conclusion that Cr_2S_3 was a *p*-type material after studying the sulphidation of chromium and some chromium-nickel alloys (containing 18 and 37 wt % Ni). However, these observations were made at a higher sulphur pressure (1.014 × 10^5 N m^{-2}) than the present work; perhaps "Cr_2S_3" undergoes a transition to *p*-type under these conditions. However, possibly equally important is that one suspects that the rigorous conditions implicit in the Wagner-Hauffe doping model [1] are not being fulfilled in such nickel-rich alloys and, therefore, scales.

By examining the observed systematic variations of the S/Cr ratios in Cr_2S_3 as a function of sulphur pressure at various temperatures, and comparing these variations with anticipated behaviour, it is possible to put forward some tentative conclusions regarding the degree of association of electronic and ionic defects in "Cr_2S_3". Thus assuming that the predominant ionic defects in the chromium sesquisulphide crystal lattice are indeed chromium interstitials, then depending on the degree of association between ions and electrons and the state of ionization of the chromium the following defect equilibria may be written, using the notation of Kröger [38]:

$$Cr_2S_3 \rightleftharpoons 2\,Cr_i^{3+} + 6e + \frac{3}{2}S_2 \qquad (2a)$$

$$Cr_2S_3 \rightleftharpoons 2\,Cr_i^{2+} + 4e + \frac{3}{2}S_2 \qquad (2b)$$

$$Cr_2S_3 \rightleftharpoons 2\,Cr_i^{+} + 2e + \frac{3}{2}S_2 \qquad (2c)$$

$$Cr_2S_3 \rightleftharpoons 2\,Cr_i^{\times} + \frac{3}{2}S_2 \qquad (2d)$$

From these expressions the theoretical dependence of the concentration of cation interstitials on the sulphur pressure may be deduced:

$$(Cr_i^{3+}) \propto (P_{S_2})^{-3/16} \qquad (3a)$$
$$(Cr_i^{2+}) \propto (P_{S_2})^{-3/12} \qquad (3b)$$
$$(Cr_i^{+}) \propto (P_{S_2})^{-3/8} \qquad (3c)$$
$$(Cr_i^{\times}) \propto (P_{S_2})^{-3/4}\,. \qquad (3d)$$

A measure of the actual variation of isothermal defect concentration with sulphur pressure can be obtained by analysis of the slopes of the line shown in Fig. 8. The plots in this Figure have been obtained from the equilibration studies of "Cr_2S_3" with various H_2/H_2S atmosphere (see Fig. 2). Here $\Delta\ w/w$ is the change in weight of the "Cr_2S_3" samples associated with re-equilibration, divided by the original weight of the sample corresponding to initial equilibration in the lowest sulphur-containing gas mixture (H_2S/H_2 = 4%96%) at 1273 K, i.e. the lowest composition limit (minimum S/Cr ratio) observed.

The slopes of these lines (in terms of defect concentration) are compared with the foregoing theoretical slopes (or exponents) in Table V. It is clear that only the tri- and divalent ionic species are apparently relevant to the defect structure of Cr_2S_3. In particular, the possible existence of univalent interstitial chromium ions (i.e. Cr_i^{3+} associated with two electrons) can be discounted.

However, the evidence does suggest there might be a transition from the unassociated trivalent chromium interstitial, Cr_i^{3+}, to Cr_i^{3+} associated with one electron, as the predominant species, as the temperature increases from 1123 to 1273 K. However, one would expect that if such a transition in the degree of association of the defect species was to occur, the higher valency or unassociated cation would be present at the higher temperature. In view of this, no definitive conclusion regarding the exact degree of association of the chromium interstitials can be made, other than that the species involved are Cr^{3+}

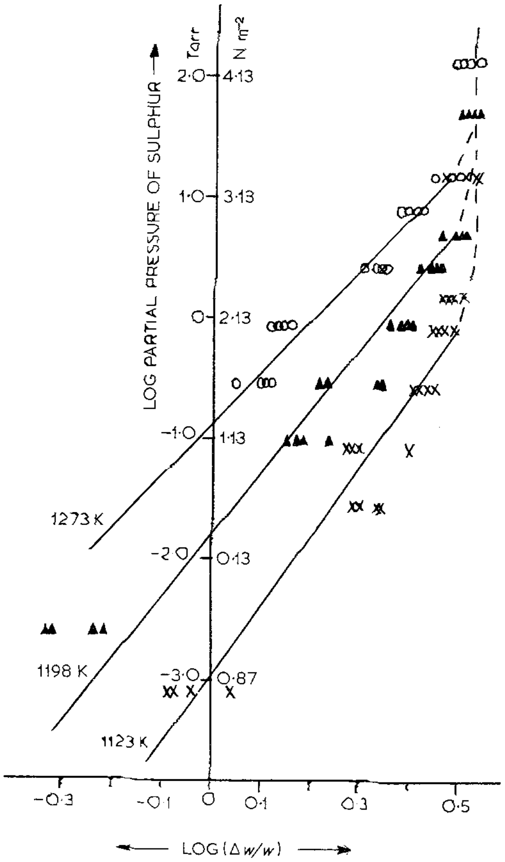

Figure 8 The logarithm of ($\Delta\ w/w$) as a function of the logarithm of partial sulphur pressure at various temperatures.

TABLE V Theoretically evaluated exponents for the dependence of the concentrations of chromium interstitial defects in "Cr_2S_3" on the ambient sulphur partial pressure, and the sulphur pressure exponents observed experimentally at 1273, 1198, and 1123 K

Nature of lattice defect	Theoretical pS_2 exponents	Temperature (K)	Experimentally determined pS_2 exponents, ± 6%
Cr_i^{3+}	– 0.19	1273	– 0.25
Cr_i^{2+}	– 0.25	1198	– 0.20
Cr_i^{+}	– 0.37	1123	– 0.17
$Cr_i^{\times}$	– 0.75		

interstitials unassociated and/or associated with one free electron.

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