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Sulfur in Chromia

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The solubility of sulfur in chromia has been studied in H_2–H_2O–H_2S tagged with ^{35}S at 973 and 1173 K at low oxygen and sulfur partial pressures typical for coal gasification-systems. For monocrystalline samples, it has been shown that sulfur-containing species are only present adsorbed on the surface of the specimens and can be removed by ultrasonic cleaning in acetone. The surface coverage after 4 weeks of exposure to H_2–H_2O–H_2S was between 2.8 and 19.3% of a monolayer. In polycrystalline chromia, sulfur was located only in pores and cracks of the sample. In dense, compact areas of the specimens the solubility of sulfur was below the detection limit of autoradiography, which was estimated to be better than 0.17 ppm.

KEY WORDS: Sulfur; chromia; tracer; sulfur solubility; adsorption; pores.

INTRODUCTION

In several industrial processes, like coal gasification, petrochemistry or gas-turbine applications, Fe- or Ni-base alloys with high Cr- or Al-contents are used. These materials are exposed to gas atmospheres characterized by low-oxygen and high-sulfur activities. The major problem under these conditions is the attack by sulfur and the formation of fast-growing sulfides or of eutectics with low melting points (Fe–FeS: 1258 K, Ni–NiS: 918 K).[1-7] In most operating atmospheres, the oxygen pressure is high enough to allow the formation of Cr_2O_3 and Al_2O_3, due to H_2O, SO_2, or CO_2 as gas compounds. In coal-gasification atmospheres, however, the oxygen pressure is too low to allow the formation of Fe- and Ni-oxides.

On Cr-containing alloys, the formation of a dense, continuous chromia layer by preoxidation under conditions where only Cr_2O_3 can be formed

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leads to good sulfidation resistance.[8-11] After long-term exposure to the sulfidizing/oxidizing gas atmosphere, however, even a chromia layer eventually fails. External sulfidation can be observed on top of the chromia scale under conditions where chromia, as well as the sulfides MnS, FeS, and nickel sulfides are stable.[6,8,11-15] But even without external sulfidation, failure of chromia scales on Fe–Cr and Fe–Cr–Ni alloys was observed.[9,10,16]

Stringer[9] assumed that sulfur penetrates through the chromia scale and that a "critical microstructure" of sulfides rich in chromium is built up at the oxide grain boundaries. When these chromium sulfides are oxidized, free sulfur is formed and can further penetrate into the alloy. Especially when the alloy is depleted of chromium, sulfides of Fe or Ni can be formed.

Another mechanism was proposed by Stott.[10] He observed Cr-rich sulfides on top of the chromia layer which were connected to zones of internal sulfidation by sulfide ducts. These sulfide ducts serve as fast-diffusion paths for the outward diffusion of the base metals. Stott proposed that degradation of the chromia scale is initiated by penetration of sulfur-containing species into the oxide along certain favored paths. After diffusion of these species to the chromia-alloy interface, internal sulfides will form first. But there is no experimental evidence for these initially-formed internal sulfides. Along the penetration paths sulfide ducts will be formed. The nature of the favored paths for sulfur penetration is unclear. Stott assumes that they are micropores in the chromia layer.

Penetration of sulfur through chromia scales may be possible by (i) dissolution of sulfur in chromia and diffusion through the bulk or along grain boundaries to the oxide/metal interface, and (ii) transport of sulfur-containing molecules like H_2S or SO_2 through physical defects in the oxide scale like pores and cracks.

If internal sulfides are formed according to mechanism (i), sulfur must be soluble in chromia. The sulfur activity at the oxide/metal interface must reach the necessary values for sulfide formation. For sulfur diffusion to occur, a gradient of sulfur activity across the oxide scale is necessary as a driving force. Therefore, only such internal sulfides can be formed which have a formation pressure lower than the sulfur pressure in the gas phase.

In contrast, internal sulfidation according to mechanism (ii) is possible even if the sulfur partial pressure in the gas phase is lower than the formation pressure for those sulfides. This can be the case in atmospheres with SO_2: as $p(O_2)$ decreases from the chromia-gas interface to the metal–chromia interface, $p(S_2)$ increases due to the equilibrium

$$SO_2 = 1/2\ S_2 + O_2 \qquad p(S_2) = K[p(SO_2)/p(O_2)]^2$$

There are several studies of solubility and diffusion of sulfur in oxides. The solubility of sulfur in FeO was investigated by Kor and Turkdogan[17] at

1523 K in Ar–H_2–CO_2–SO_2 gas mixtures. They found a solubility in FeO of 0.01 mass%. Flatley and Birks[18] found higher values of 0.03–0.4% sulfur in FeO and 0.03% in Fe_3O_4 by investigating iron samples after exposure to Ar–SO_2 with microprobe analysis. Yang and Whittle[19] investigated the solubility of sulfur in FeO at 1143 K in H_2–10%H_2S ($p(S_2) = 10^{-5}$ bar) after a very short exposure of 1 to 2 min. By AES it was shown that sulfur was present only at grain boundaries of the oxide. They estimated the diffusion coefficient of S in FeO to be at least 10^{-4} cm^2 s^{-1}, but questioned, if this high value originates from penetration of gaseous species through small pores in the oxide instead from grain-boundary diffusion.

The solubility of sulfur in NiO was investigated by Pope and Birks[20] at 1173 K and 1273 K in CO–CO_2–SO_2 gas mixtures. The highest observed sulfur concentration at 1273 K was 0.026%. J. B. Wagner and coworkers[21,22] investigated the diffusion of ^{35}S in NiO single crystals and polycrystalline NiO. They determined diffusion coefficients of 5.4 10^{-13} cm^2 s^{-1} in NiO single crystals and of 1.0 10^{-11} cm^2 s^{-1} in polycrystalline NiO. After corrosion of Ni in Ar-10%SO_2 at 1073 K Wootton and Birks[23] observed very high sulfur concentrations of 5% in the oxide scale.

There are only a few studies of the solubility and diffusion of sulfur in chromia. Hocking and Vasantree[24] studied chromia scales grown in 2:1 SO_2:O_2 at 1173 K. They found sulfur concentrations of 9% in the scale, caused by chromium–sulfide particles in the scale.

Diffusion of S in hot-pressed Cr_2O_3 was investigated by Seybolt[25] at 1273 K in H_2–H_2S gas mixtures with $p(S_2) = 7 \times 10^{-3}$ bar. The diffusion coefficient of sulfur was found to be 1.5×10^{-10} cm^2 s^{-1}, a much higher value than the diffusion coefficients for oxygen in chromia.[26, 27] Due to the high-sulfur partial pressure, formation of chromium sulfides cannot be ruled out. Additionally, the residual porosity of hot-pressed chromia samples must be taken into account.

Chang *et al.*[28] estimated diffusion coefficients of ^{35}S in hot-pressed chromia at temperatures between 973 and 1373 K to range from 5.1×10^{-11} cm^2 s^{-1} to 5.2×10^{-10} cm^2 s^{-1}. This study suffers from the same problems as those of Seybolt.[25]

Romeo *et al.*[29] oxidized chromium in oxygen at 1173 K or 1273 K in pure oxygen and exposed the preoxidized samples to a mixture of $H_2 - 10\%H_2S$ at 1173 K. On both sides of the chromia, chromium sulfide was formed. The reaction in H_2–H_2S followed a linear rate law. The rate constant increased with increasing sulfur partial pressure. Romeo *et al.* speculate that sulfur changes the defect structure of chromia and, therefore, the diffusion of chromium in chromia. In another paper,[30] they report a sulfur concentration in chromia of 0.5 at. % But they do not consider the formation of chromium sulfides which would give rise to fast-diffusion paths in the oxide. The diffusion coefficients found by these authors are probably not characteristic for pure chromia.

Benlyamani *et al.*[31] measured the solubility of sulfur in Cr_2O_3 at 1273 K in $CO-CO_2-SO_2$ at various oxygen- and sulfur partial pressures, using chromia in powdered form with 5–10 μm particle size. The sulfur content of Cr_2O_3 was determined by the neutron-activation technique. Assuming that all measured sulfur was dissolved in the bulk, they report a sulfur solubility between 93 ppm and 16 ppm.

In order to verify whether the adsorption of SO_2 on the Cr_2O_3 surface was an important factor, the sulfur levels were compared between normal specimens and specimens of extra-fine particles obtained by further grinding of the starting materials. The difference in particle sizes is not reported, however. The authors claim that the results of these tests show essentially the same levels of sulfur at equilibrium as with the coarse starting materials.

In addition, Benlyamani *et al.*[32] investigated the diffusion of sulfur in polycrystalline and monocrystalline Cr_2O_3 between 1173 K and 1373 K using radioactive ^{35}S. The polycrystalline-chromia samples were prepared by sintering, leading to a density greater than 99%. The radiotracer sulfur was applied to each sample in the form of sulfuric-acid solution which was subsequently evaporated. Additional nonradioactive sulfur was added in a benzene solution. The sample was encapsulated in a quartz tube in air. The resulting value of $p(SO_2)$ was calculated to be 10^{-2} atm and $p(O_2)$ from 0.90 to 1.10 atm. The reactions possible between the specimens and chemicals used in this process were not considered, however. The authors report volume-diffusion coefficients between 1.07×10^{-13} and 5.0×10^{-13} cm^2 s^{-1}, the grain-boundary diffusion coefficients were found to be about five orders of magnitude higher. Problematic in the investigation of such polycrystalline samples is again the residual porosity of about 1%. Diffusion into pores and microcracks will lead to inaccurate values.

Kim *et al.*[33] investigated the effect of sulfur on chromia scales grown on Fe–25Cr at 1173 K in $H_2-H_2O-H_2S$. The samples were then examined with SEM, STEM, and EDX. They measured the sulfur concentration across grain boundaries in the chromia and found increased sulfur X-ray intensities within 2, 5 nm of grain boundaries. The authors conclude that there is strong segregation of sulfur to grain boundaries. The experiments were performed at a sulfur partial pressure higher than the formation pressure of chromium sulfide and an oxygen pressure above the formation pressure of chromia. Under such conditions oxide and sulfide can grow simultaneously until equilibrium of the sample surface with the gas phase is achieved. [6,34] This period, often called "transient state," can last very long when sulfides are formed, due to the high diffusivities of cations in sulfides. Therefore sulfide formation cannot be excluded in this study. Even the preoxidation treatment, carried out by the authors, of 1 or 10 hr before H_2S is added to the gas mixture, does not solve this problem, because chromium–sulfide formation has been shown to occur even after 150 hr preoxidation in H_2–H_2O.[12,34]

This review of the literature shows that the experimental results on the solubility of sulfur in chromia vary quite considerably, depending on the quality of the chromia samples and on the composition of the gas phase. The major problems are the possibility of sulfide formation and the residual porosity in the sintered or hot-pressed-chromia samples. In addition, adsorption of sulfur on surfaces and solubility of sulfur in chromia have to be distinguished carefully.

The present work was carried out to determine the sulfur solubility in chromia at oxygen and sulfur partial pressures, which are typical for coal-gasification systems. The results contribute to a better understanding of the breakdown of chromia scales under these conditions.

EXPERIMENTAL METHOD

To investigate the solubility of sulfur in chromia, two types of samples have been used. In some studies chromium or chromium-containing alloys have been oxidized to form a chromia scale, in other studies compact chromia samples have been used. The use of chromium as a base material for oxidation is problematic because even after a preoxidation treatment of more than 100 hr, chromium sulfide formation has been observed,[10,12,34] even though these sulfides were not in equilibrium with the gas phase. As sulfur is very surface active, chromia in powdered form, with a very high surface area, is also unsuitable.

To avoid possible sulfide formation due to the reaction of metallic chromium and sulfur or H_2S, in the present study compact chromia samples were used, both monocrystalline and polycrystalline samples. The chromia monocrystals were provided by Ingenierbuero Bert Scholz (Grafrath, Germany). These samples were 4–5 mm in diameter and 1 mm thick. Polycrystalline chromia samples were prepared by KFA Jülich (Institut für Reaktorentwickelung) by a HIP-Process. Chromia powder (Merck, purity >99%) was densified at 1873 K in Ar 5.7, the polycrystalline samples obtained had a diameter of 12 mm and a thickness between 2 and 6 mm.

Penetration of sulfur into the chromia samples was studied in radioactive H_2–H_2O–H_2S atmospheres tagged with ^{35}S. The gas mixtures were chosen according to a thermochemical stability diagram (Fig. 1).

Since the defect structure of chromia is dependent on temperature and oxygen pressure, the samples were preannealed in H_2–H_2O for 3 weeks at the same temperature and oxygen pressure as in the H_2–H_2O–H_2S atmospheres used later (see Table I). For the investigation of the solubility of

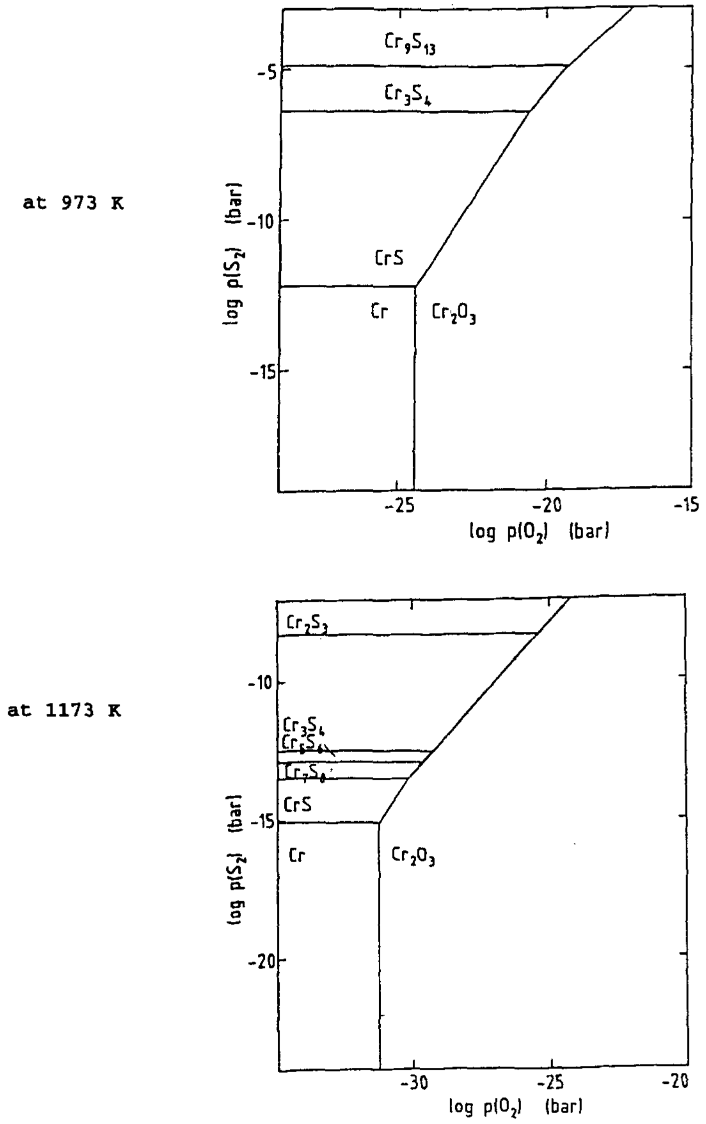

Fig. 1. Two-dimensional thermochemical stability diagrams for the system Cr–O–S at 973 and 1173 K.

Table I. Experimental Conditions for the Investigation of the Solubility of Sulfur in Chromia

Condition number	Temperature (K)	log $p(S_2)$ (bar)	log $p(O_2)$ (bar)	Carrier gas	Exposure time
1	1173	-5.25	-16.55	He/H_2	4 weeks
2	1173	-7.25	-17.88	H_2	4 weeks
3	973	-8.00	-22.57	H_2	4 weeks
4	973	-10.00	-23.91	H_2	4 weeks

sulfur in chromia, the stability of chromia under the experimental conditions must be maintained. This leads to the requirement of a minimum $p(O_2)$ of the Cr–Cr_2O_3-equilibrium to avoid reduction of the oxide. In addition, sulfide formation has to be avoided. Therefore, depending on the choice of $p(S_2)$, $p(O_2)$ must be raised further to stay in the stability field of chromia (see Fig. 1). The experimental conditions are shown in Table I. One polycrystalline and one monocrystalline chromia sample were exposed to each condition in Table I.

H_2S tagged with ^{35}S was provided by Amersham/Buchler with a specific activity of about 25 mCi/mmol H_2S. The chromia samples were encapsuled in quartz ampoules using the apparatus shown in Fig. 2. The apparatus consists of two parts: a non-radioactive part and a radioactive part. At first, the H_2S, tagged with ^{35}S, was distributed among the four quartz ampoules (c) which contained the samples, as follows: the radioactive part of the apparatus was first evacuated, after which all valves were closed. The glass membrane enclosing the radioactive H_2S (d) (about 5 ml) was broken using a quartz-covered magnet (e) which could be moved from the outside with the help of another magnet. The four different required $p(H_2S)$ were established by successive dilution into the evacuated ampoules (c) and evacuated quartz vessels (f). In each step, one ampoule with a sample and one quartz vessel were opened. The required $p(H_2S)$ was determined by the volume of the quartz vessel. The vessels also served as H_2S-reservoirs for the next dilution step. Between the dilution steps the pipelines were flushed with helium to remove residual H_2S and were then evacuated.

The H_2S was trapped by a solution of $CuSO_4$ before the exhaust. After that, a mixture of H_2–H_2O or H_2–H_2O–He was added to each ampoule (c). These gases had been premixed and filled into vials (a), which could be exchanged in the inactive part of the apparatus. The amount of the gas mixture added to each of the ampoules with the radioactive H_2S was controlled by the pressure decay in the inactive part of the apparatus (b).

The ampoules were sealed at a pressure of 0.30 or 0.25 bar, in order to reach 1 bar at the temperature of 973 K or 1173 K, respectively, during the heat treatment. After the exposure, the samples were stepwise polished parallel to the surface. Before and after each polishing step, the activity of ^{35}S on

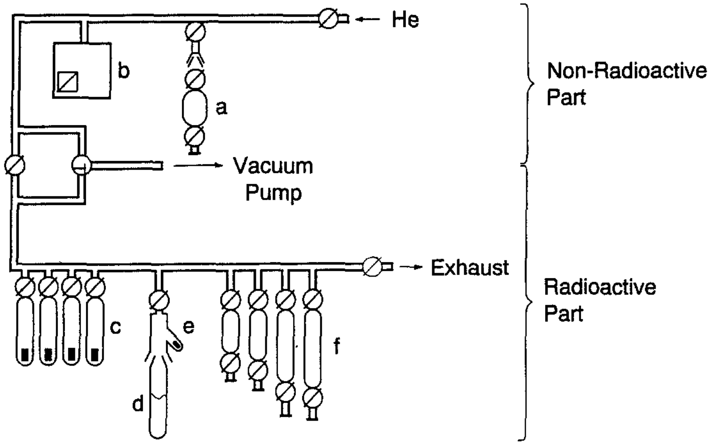

Fig. 2. Schematic diagram of the apparatus used to fill ampoules with H_2-H_2O-H_2S tagged with ^{35}S: (a) exchangable vial containing premixed H_2-H_2O, (b) pressure-measuring device, (c) reaction ampoules, containing the chromia samples, (d) ampoule with H_2S, tagged with ^{35}S, (e) magnet, covered with quartz, to break the glass membrane enclosing the radioactive H_2S, and (f) quartz vessels.

the surface of the sample was measured using a methane-flow counting tube. The thickness of each layer removed was measured using a thickness gauge (+/−1 μm) and by microbalance.

RESULTS AND DISCUSSION

Some of the results for the polycrystalline chromia samples have been published previously.[34] Figure 3 shows an optical micrograph of a polycrystalline chromia before the experiments. The grain size ranges from 20 to 200 μm.

Figure 4 shows a SEM micrograph of a polycrystalline chromia sample after exposure to H_2-H_2O-H_2S at 973 K under condition 3 (Table I); pores can be seen on the surface, and no sulfur was detectable by EDX on the surface. This surface is typical of all polycrystalline samples.

The surfaces of the monocrystalline samples appeared flat in the SEM after exposure to the sulfur-containing gas atmospheres. No sulfur was detected by EDX on these samples, too. To determine the sulfur-concentration profile from the residual radioactivity measured before and after every polishing step, the attenuation of the β-radiation in chromia must be considered. Figure 5 shows a profile of a sample with a layer of thickness h, which is removed in one polishing step. I_0 characterizes the ^{35}S radioactivity measured before removal of this layer, i.e., includes the radiation from the

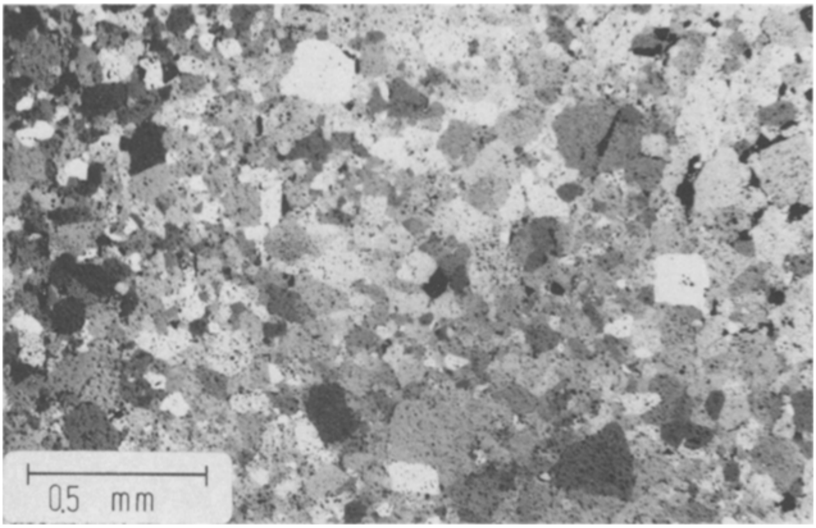

Fig. 3. Optical micrograph of a polycrystalline chromia sample.

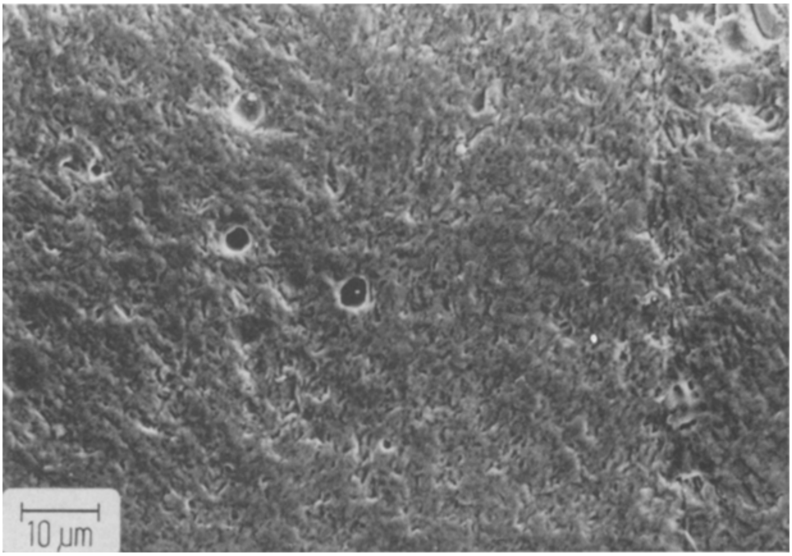

Fig. 4. Scanning electron micrograph of a sintered chromia sample (No. 3, see Table I) after exposure to H_2–H_2O–H_2S.

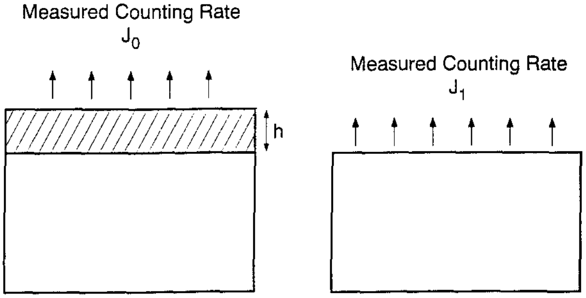

Fig. 5. Profile of a sample with a layer of thickness *h* removed in a polishing step. I_0 = radioactivity measured on the surface of the sample with a counting tube before removal of the layer, and I_1 = radioactivity measured on the surface of the sample after removal of the layer.

layer and the sample beneath. I_1 characterizes the measured activity after removal. The contribution of I_1 to I_0 is attenuated by the factor $e^{-\mu h}$ with $\mu = ln2\,\delta/d_{1/2}$, $d_{1/2} = 0.0033\,\mathrm{g\,cm^{-2}}$ (for ^{35}S), $\delta = 5.21\,\mathrm{g\,cm^{-3}}$ (for chromia), and h= height of the removed layer. The radioactivity from ^{35}S located in the removed layer is therefore $I_0 - I_1\,e^{-\mu h}$. A uniform sulfur distribution was assumed in the removed layer. The attenuation of the radioactivity of the tracer located in the removed layer is then described by

$$I_s = \int_0^h I/h\; e^{-\mu x}\,dx = I/\mu h\;(1 - e^{-\mu h})$$

with I_s = intensity measured on the surface of a layer of thickness h with uniform sulfur distribution, and I = intensity that would be measured on the surface of the sample without absorption of radiation in the sample. The geometry of the counting tube and the absorption of radiation in air and in the counting-tube window have to be taken into account as well. For a point source, the geometric factor, i.e., the fraction of β-particles, which are counted by the counting tube, can be described by[35]: $G = 0.5\;[1 - a/\sqrt{a^2 + r^2}]$ with a = distance between radiation source and counting-tube window, and r = radius of the counting-tube window. The deviation of the geometric factor[35] of the samples used in this study from that of a point source is less than 5% and was therefore neglected. The geometric factor of the counting tube used in this study has a value of $G = 0.421$. The radiation was attenuated by a factor of 0.625 passing through the air and the counting-tube window. This value already includes the influence of indirect transmission of β-particles from the source to the counting tube. Combining the influence of the geometry and the absorption by air and the counting-tube window, factors give a total attenuation factor of $0.421 \times 0.625 = 0.263$. Hence, the measured count rate was multiplied by 3.8 to obtain the count rate at the surface of the sample.

In the concentration-depth profile, each calculated concentration is plotted at a thickness corresponding to the middle of that removed layer. The thus-obtained, sulfur-concentration profiles for the polycrystalline samples are shown in Fig. 6 from the surface to a depth of 60 μm. It should be stressed that they have been calculated assuming a dense chromia sample and a uniform lateral distribution of sulfur. To check this assumption, autoradiographs were taken before and after several polishing steps. Figure 7 shows autoradiographs of a sample exposed to condition 3 at the surface and after removing layers of 7 and 284 μm, respectively. The autoradiograph is darkened where radioactive radiation has hit the film. It can clearly be seen that the lateral distribution is not uniform. The sulfur is located only in pores and cracks of the samples. Some pores and cracks can be followed from the surface to the depth of 284 μm.

The calculation described above leads to an overestimation of the sulfur concentration, since now we know that some of the sulfur radiation was not attenuated by passing through chromia. This uneven distribution of sulfur

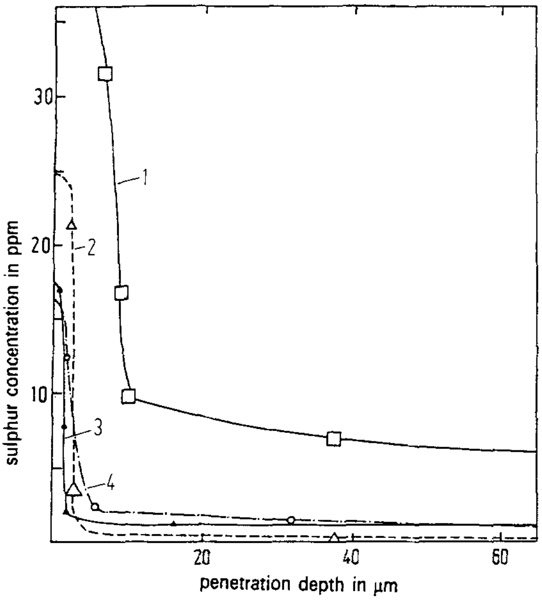

Fig. 6. Sulfur-concentration profiles in sintered chromia (experimental conditions: see Table I).

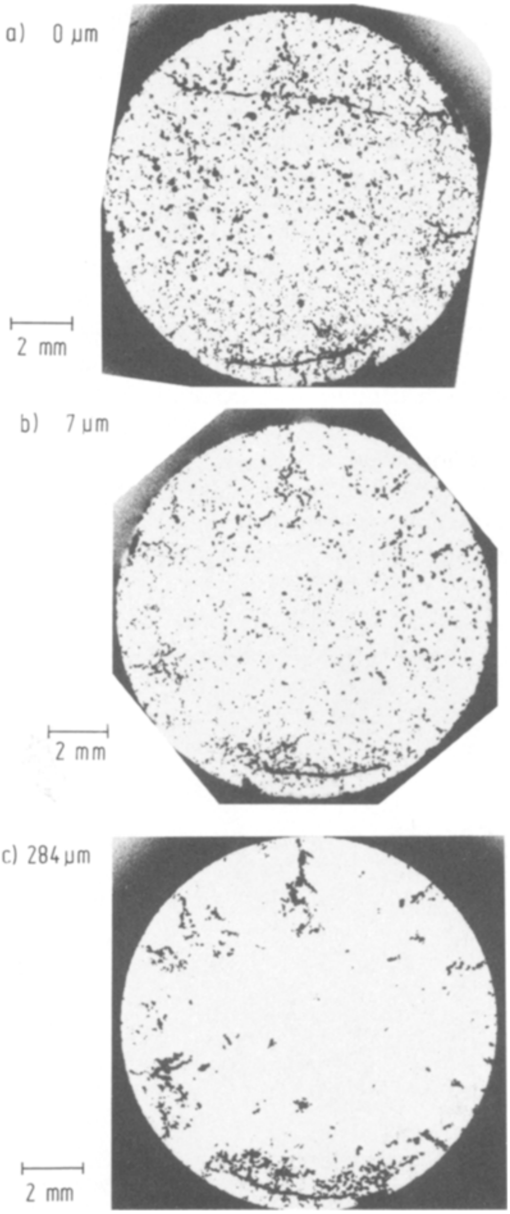

Fig. 7. Autoradiographs of chromia sample No. 3 (see Table I): (a) on the surface, (b) at 7 μm penetration depth, and (c) at 284 μm penetration depth.

in the chromia samples sheds some doubts on those studies where polycrystalline chromia was used[25,28,32] for estimating the sulfur solubility in chromia, unless a density of chromia of 100% was achieved, which is highly unlikely. In addition, our results show the importance of taking into account the heterogenities in lateral distribution, which were absent in most of the earlier studies.

To determine the solubility of sulfur in chromia only those parts of the samples without pores, micropores, or cracks can be used. Therefore, a method must be applied which combines high sensitivity for sulfur with a high lateral resolution. The autoradiographs taken in this study can be used for a further estimation of the sulfur solubility in polycrystalline samples. On all samples the effect of exposure to radioactive radiation was observed only in areas with pores and cracks. Therefore, the solubility of sulfur in dense, compact regions of the chromia samples must be less than the detection limit of autoradiography.

Since the specific activity of sulfur in the H_2S (25 mCi/mmol) is fairly high, a good sensitivity is achieved. The detection limit depends on the distribution of the radiotracer in the sample. If, for example, a uniform sulfur distribution in a chromia layer with thicknesses of 1 μm, 10 μm, or 50 μm and diameter 12 mm is assumed, the count rate of 1 Imp/min is obtained from weight fractions of 0.0039 ppm, 0.0006 ppm, or 0.0004 ppm, respectively.

This sensitivity will decrease with time due to the decay of ^{35}S. The half life of ^{35}S lasts 87.4 days. With the methane-flow counting tube an increase of 10 Imp/min above the background can be measured, i.e., sulfur, uniformly distributed in a layer 1 μm, can be detected to a concentration of 0.039 ppm.

To measure the sensitivity of the film (AGFA D7) used for the autoradiographs, steel samples with a uniform distribution of ^{14}C were used. As ^{14}C and ^{35}S emit β^- radiation of similar energies, these samples can be used for the calibration.

$$({}^{14}\mathrm{C}: E_{\mathrm{max}} = 0.156\ \mathrm{MeV},\ E_{\mathrm{medium}} = 0.047\ \mathrm{MeV}$$

$${}^{35}\mathrm{S}: E_{\mathrm{max}} = 0.167\ \mathrm{MeV},\ E_{\mathrm{medium}} = 0.049\ \mathrm{MeV})$$

The film was exposed to samples with different surface activities for 288 hr and 65 hr. These exposure times are similar to those used for the chromia samples with ^{35}S. Darkening of the film was detected for all samples with more than 60 Imp/min, as detected by the counting tube.

If the background radiation of about 15 Imp/min is subtracted from this value, counts as low as 45 Imp/min can be detected by autoradiography.

This corresponds to sulfur concentrations of

0.17 ppm in a layer of 1 μm thickness
0.03 ppm in a layer of 10 μm thickness
0.02 ppm in a layer of 50 μm thickness

From the autoradiographs it is therefore concluded that less than 0.17 ppm S are dissolved in the dense, compact areas of the chromia samples.

To study these effects in 100% dense chromia, Cr_2O_3-monocrystals were exposed to the atmospheres given in Table I. After exposure to the ^{35}S-containing gases all samples showed fairly high radioactivities (see Table II). To remove adsorbed sulfur from the surface, the samples were ultrasonically cleaned in acetone at first for 1 min, and then for 30 min. After each cleaning step the residual activity of ^{35}S was measured. The values are given in Table II.

During these measurements, the importance of absolutely clean working procedures became obvious. Each sample was kept in a glass beaker between the cleaning steps. After the first cleaning step (1 min), the samples were returned to the same beakers as before, and then the surface radioactivity was measured again. The samples showed a similar high activity as before cleaning, indicating that a sulfur-containing species diffused from the glass to the sample surface. Further cleaning for 1 min reduced the count rates to low values as measured before. This observation shows how easily artifacts can arise while measuring sulfur solubility and diffusivity.

Additionally, after each measuring step the sample holder and the gold window of the counting tube were wiped to reduce the background count rates. However, since the gold window could not be cleaned ultrasonically after each measuring step, the background count rates were still between 20 and 30 Imp/min during these measurements. The count rates of the chromia monocrystals after 30 minutes cleaning are in the same range.

After repeated polishing and cleaning, the surface radioactivity did not change significantly, indicating that sulfur solubility in chromia monocrys-

Table II: Activity of ^{35}S on Chromia Monocrystals after 4 Weeks Exposure to H_2–H_2O–H_2S Tagged with ^{35}S and After Cleaning Ultrasonically in Acetone

Conditions of the exposures	Activity before cleaning (Imp/min)	Activity after 1 min cleaning (Imp/min)	Activity after 30 min cleaning (Imp/min)
1	1559	201	25
2	548	169	23
3	3699	792	27
4	562	244	24

tals must be lower than the detection limit of the method (as discussed above). The surface coverage with sulfur-containing species can be calculated from the radioactivity of the chromia monocrystals before cleaning. Taking the half life of the isotope ^{35}S into account, the specific activity had a value of 8.037 mCi/mol at the time of measurement. Considering the geometry of the counting tube and absorption of radiation by the air and the counting-tube window this corresponds to a counting rate of 6.8×10^{13} Imp/min per mol sulfur.

Without consideration of the crystallographic orientation of the samples, chromia has an average 8.8×10^{14} Cr-atoms and 1.3×10^{15} O-atoms per cm^2 of surface. Assuming that in a monolayer of S-containing species all Cr-atoms on the surface are occupied, the surface coverage as fraction of a monolayer can be estimated (see Table III).

Only a few measurements of H_2S adsorption on oxides are available for comparison. DeRosset *et al.*[36] found a saturation surface coverage of H_2S on Al_2O_3 to correspond to about 2% of the anionic sites in the temperature range from 533 to 833 K with partial pressures $p(H_2S)$ from 1 mtorr to 4.4 torr in H_2–H_2S gas mixtures, assuming a Langmuir isotherm. The mobility of the adsorbate between the sites was found to be highly restricted.

Thomas and Ullah[37] showed for sulfidized nickel oxide and vanadium pentoxide in H_2S at 773–923 K that the adsorption and desorption characteristics can be explained by a Langmuir isotherm model. Adsorption occurs nondissociatively, i.e., larger quantities of H_2S are adsorbed than S_2. The adsorbed complex was completely mobile. The volume of H_2S occupying a monolayer on either supported NiS or V_2O_5 is only about 1% of the BET capacity estimated by the adsorption of N_2 at 77 K. This implies that chemisorption is only occuring on a small fraction of all surface sites.

Steinbrunn and Lattaud[38] studied the adsorption of H_2S on MoO_3 monocrystals in H_2S and H_2–H_2S at temperatures below 973 K for partial pressures where sulfide formation is possible. The authors explain their results on the initial stages of the sulfidation by dissociative adsorption of H_2S molecules, this is in accord with ESCA results showing the presence of OH and SH groups on the surface. Therefore, the low fraction of surface

Table III. Surface Radioactivity and Surface Coverage of Sulfur on Chromia Monocrystals

Condition	Measured radioactivity	mol S	mol S/cm^2	S-atoms/cm^2	Fraction of a monolayer
1	1559	2.3×10^{-11}	1.2×10^{-10}	7.2×10^{13}	8.2%
2	548	8.1×10^{-12}	4.1×10^{-11}	2.5×10^{13}	2.8%
3	3699	5.4×10^{-11}	2.8×10^{-10}	1.7×10^{14}	19.3%
4	562	8.3×10^{-12}	4.2×10^{-11}	2.5×10^{13}	2.8%

coverage found by us for the adsorption of H_2S on chromia is in agreement with the previous studies of other oxides.

CONCLUSIONS

The sulfur solubility in chromia has been investigated at 973 K and 1173 K at oxygen and sulfur partial pressures typical for coal-gasification atmospheres. In contrast to many earlier studies, the experimental conditions were chosen so that chromium–sulfide formation could not occur.

After equilibration in H_2–H_2O–H_2S for monocrystalline chromia, sulfur is present only on the surface of the specimens. The surface coverage after 4 weeks of exposure was between 2.8–19.3% of a monolayer. The cleaned surfaces can be easily contaminated with sulfur again, which may be due to a high surface mobility of the adsorbed complexes. This leads to difficulties in the measurement of the solubility of sulfur in chromia by successive polishing. As sulfur is located only at the surface, measurements with powdered chromia will lead to a marked overestimation of the values of the sulfur solubility.

In polycrystalline chromia, sulfur was detected in pores and cracks of the samples. In dense, compact areas of the chromia samples the solubility of sulfur was below the detection limit of autoradiography. Therefore, assuming a uniform distribution of sulfur in a layer of at least 1 μm, the solubility is below 0.17 ppm.

This result shows the necessity of using 100% dense chromia samples to estimate the solubility of sulfur in chromia or of using a technique with good lateral resolution to study only areas without residual porosity. Although sulfur solubility in chromia is very low under conditions of low oxygen and sulfur pressures, as they occur in coal-gasification systems, under other experimental conditions, e.g., higher sulfur partial pressures, different results might be obtained. Measurements under conditions where sulfide formation is possible would be particularly useful to clarify this point. Such measurement would, however, require a technique where microscopic sulfides and dissolved sulfur can unequivocally be distinguished.

Since the solubility of sulfur in compact chromia samples is very low under the experimental conditions of coal-gasification atmospheres, the breakdown of chromia scales by internal sulfidation in these atmospheres cannot be explained by solid-state diffusion of sulfur in chromia, but must occur by penetration of sulfur-containing species through pores and cracks of the layer.

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