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Some Experiments on the Formation of an Fe-Al Double Sulfide Compound

Keizo NISHIDA* and Toshio NARITA*

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Abstract

In order to confirm the existence of a special sulfide invariably observed in the scale formed on high Al-ferrous alloys having a good resistance against sulfurization, a double sulfide compound was synthesized with mixed powdered metals of Fe and Al with various ratios in an environment of 1 atm of sulfur vapor and under a pure H_2S gas flow. Then the products were examined by X-ray diffraction and chemical analysis.

The constituents of the products were estimated as $FeAl_2S_4$ in mole by numerous experiments although they were different from each other owing to the lack of a good quality of vessels for preparations.

The crystalline structure of the sulfide was determined to be a hexagonal type by many analytical calculations and its lattice parameters were estimated, but from the recent data of Flahaut the recalculated results were $a_0=3.659\pm0.004$ Å; $c_0=36.16\pm0.03$ Å which were very similar to his calculations.

Accordingly, the above stated sulfide was confirmed to be the same as the present compound and is invariably constant even when the original alloys consisted of various constituents.

1. Introduction

High-temperature sulfurization of iron-based alloys has been carried out and the corrosion mechanism of each process has been elucidated based on the sulfurization kinetics in our laboratory[1)~11)]. The alloying elements indicating an excellent sulfurization resistance were found to be Al[4,5)] and Cr[6,7)]. Especially, Al was a highly effective alloying element against sulfurization of iron.

For example, it was observed from the experimental results, as seen in **Fig. 1**, that all of Fe–Al alloys[4)] and Al-cast irons[5)] showed significantly effective anti-corrosive properties in a higher range of Al content above 6 wt%. Further, in the diffraction patterns of the sulfide scale formed on such alloys some unfamiliar peaks were always recognized, as seen in **Fig. 2**. Of course, there were other peaks from FeS_{1+x} and Al_2S_3 compounds in the same scale. However, it is a question whether the special compound with such uncommon peaks as the present sulfide can be synthesized or not because these peaks in the sulfide are observed in the course of sulfidation of Fe–Al alloys and not in an equilibrated condition. This situation seems very similar to the formation of the $FeCr_2S_4$ compound which is observed in the sulfide scale formed on the Fe–Cr alloys. Further, it is also an important problem as to what composition the newly

* Metals Research Institute, Faculty of Engineering.

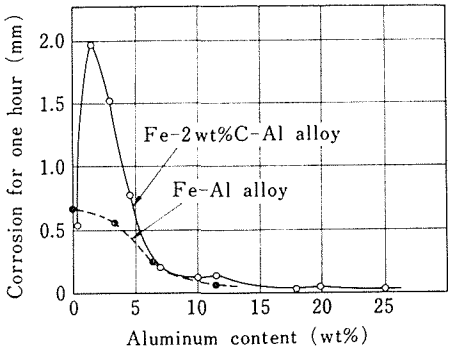

Fig. 1 Change in corrosion behavior of Fe-2%C alloys with aluminum content as well as Fe-Al alloys. The alloys were exposed to an atmospheric pressure of sulfur vapor at 900°C for one hour

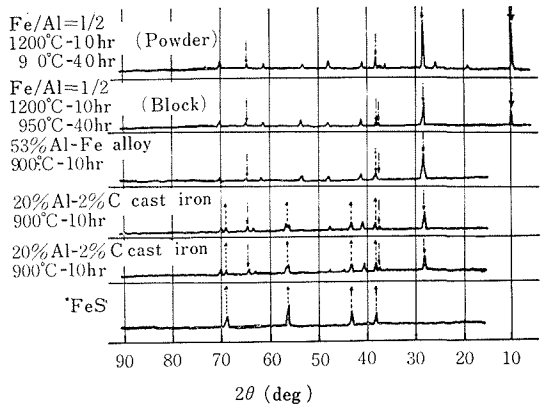

Fig. 2 Comparison of x-ray diffraction patterns from composite sulfides with sulfide scales grown on Fe-Al alloys in sulfur vapor (Fe kα)
Arrow ↓ shows main peaks of composite sulfide

formed compound has and whether its lattice parameter is variable or not with Fe/Al ratio of the compound formed. Especially, the determination of many physical and chemical properties of the sulfide will be an essential background to elucidate the corrosion mechanism of these Fe-Al alloys against sulfidation.

In our laboratory spinel-type double sulfides showing cubic crystals were already found in the scale formed on Fe-Cr[13] and Al-Cr[14] alloys in the atmospheres of pure sulfur vapor and of H_2S gas, (see **Fig. 3**). However it is doubtful to make an assumption directly from the formation of $FeCr_2S_4$[7,12] with the metal powder having a ratio of Fe : Cr = 1 : 2 to the effect that the compound formed with the composition of Fe : Al = 1 : 2 should be a spinel-type cubic crystal, because many peaks do not correspond to these of a cubic crystal as seen in Fig. 2.

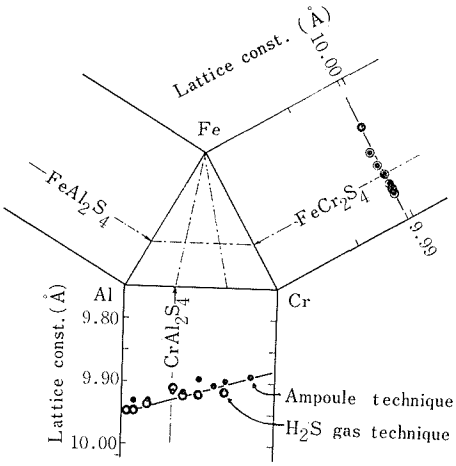

Fig. 3 Lattice parameters of Fe-Cr and Al-Cr sulfides

From this point of view the present paper is presented to report on the course of identification of the special sulfide compound synthesized with numerous kinds of powdered samples with various ratios of Fe/Al.

2. Experimental Procedure

At first, as a synthesizing technique the mixed powder of Fe and Al metals were sulfurized in a quartz ampoule under a constant sulfur vapor (=1 atm). But since the resistance of quartz against temperature is limited to about 1200°C, we used also another technique in order to shorten the synthesizing time at higher temperatures in a siliconit furnace, that is, pure H_2S gas passed over powdered

mixed metals in a high-quality aluminum boat. The following describes the details of these techniques.

1. Ampoule technique

One part of a transparent quartz ampoule (I. D. = 20 mmϕ) containing molten sulfur kept at boiling point, and the other supported metals powder to be sulfurized as shown schematically in **Fig. 4**. This technique is called a two-step furnace technique. At first the ampoule containing sulfur and powdered metals was evacuated up to an order of 10^{-6} mmHg and sealed, and then it was annealed for specified time intervals in an electric furnace kept at desired temperatures. Referring to the case of synthesis[13] of the $FeCr_2S_4$ compound, the total holding time was limited to 50 hr, that is, 10 hr at 1200°C and 40 hr at 950°C. This process is based on the fact that the melting point of Al_2S_3 compound is nearly 1100°C[15] and that FeS_{1+x} compound has a maximum melting point at about 1193°C[16], hence at higher temperatures, the faster the process will proceed. Further, maintaining at 950°C for an extreme length of time is based on the fact that the heat treatment at such temperatures for a considerable length of time required for producing a perfect crystal has already been recognized.

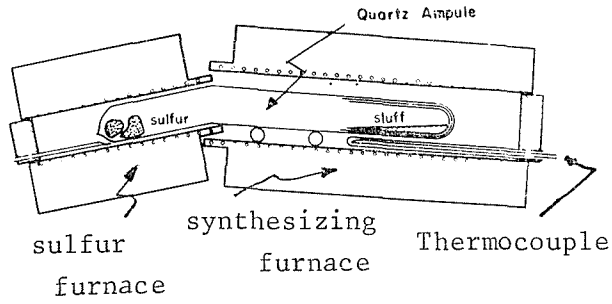

Fig. 4 Schematical presentation of synthesizing apparatus (ampoule technique)

Because of the reaction between the product and quartz ampoule while maintaining at 1200°C for a corsiderable length of time, in this case, the holding time interval at that temperature was limited to a relatively shorter time. Contact of the product with quartz resulted frequently in fracturing of an ampoule because of the change in temperature, thus duplicated quartz tubes were used in which the sample powder was inserted as shown in the figure. Metal materials used were electrolytic iron powder with 99.9 wt% and aluminum powder was filed from a 99.99 wt%Al ingot. Sulfur was from a commercial guaranteed grade.

2. H_2S gas technique

It was uncertain at first whether the double sulfide compound would be synthesized or not under the sulfur partial pressure formed by the dissociation of H_2S gas (about 0.17 atm) at this temperature range (for example, at 1200°C). However, by a preliminary experiment it was found that the synthesis of the double sulfide was possible at 1,300°C (Ps_2 = 0,2 atm) and 1,500°C (Ps = 0.25 atm). Under these conditions samples were maintained at each peak temperature for one hour and then they are cooled in the furnace, under a constant flow of H_2S gas. The apparatus used here is schematically shown in **Fig. 5**. The furnace heating time was about 2–2.5 hr to raise the temperature to 1,300–1,500°C.

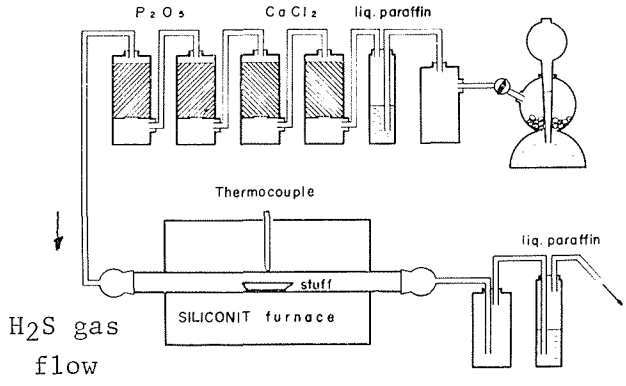

Fig. 5 Schematical presentation of synthesizing apparatus (H_2S gas technique)

3. Preqaration of samples

In the preliminary experiment the sample used was only one kind of Fe/Al = 1/2, and then the original metal ratio was varied as seen in **Table 1** under constant heating conditions, that is, the ratio of Fe and Al (Fe/Al) was varied from 1/0.5 to 1/9 and the initial total weight of powdered metal sample was 2 gr. The amount of sulfur involved in the ampoule was in excess of that required from calculation.

The x-ray diffractometer used for the identification of the sample was of an ADX-1083 type and three kinds of the x-ray tubes with Cu, Fe and Cr targets were used when required, where they were all calibrated by using pure NaCl powder of a guaranteed grade. The intensity of each peak was obtained from the area above the noise level.

Table 1 Composition of initial mixed powder

Fe/Al	1/0.5	1/1	1/1.5	1/2	1/2.5	1/4	1/9
at % Al	33.3	50	60	66.7	71.4	80	90

Metal sample: 99.9 wt% electrolytic iron powder
99.99 wt% aluminum ingot (filed powder)

3. Experimental results

1. Observation of the surface of the synthsized compound

The surface structure of the compound obtained was indicated in **Photo. 1** which is from that of Fe/Al = 1/2. The geometrical pattern was not shown clearly and it contains at times numerous conical protuberances.

Further as seen in **Photo. 2** which are the scales on an Fe-Al alloy (Fe/Al = 1/2; 49 wt%Al) and a 20 wt%Al cast iron, high Al-Fe alloys show characteristic features of the scale with fiberous texture.

The surface observation of the compounds formed under the varied synthesizing conditions with the ampoule method are summarized in **Table 2.** From the above it can be divided into two groups, namely, the properties common to those with all ratios and those different from each one.

Especially, the common characteristic feature is that all compounds taken up from the ampoule after heat-treatment produce a strong H_2S gas like smell and

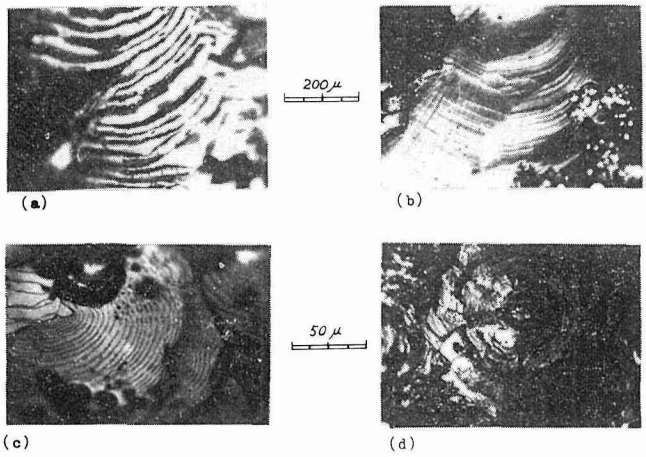

Photo. 1 Composite sulfide prepared from Fe–Al mixed powder (Fe/Al) 1/2) by keeping in sulfur (1 atm) at 1200°C for 10 hr and at 950°C for 40 hr

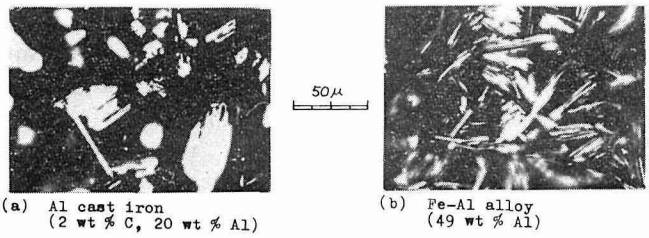

Photo. 2 Sulfide scale growth on the alloys by keeping in sulfur vapor (1 atm) at 900°C for 10 hr

Table 2 Appearance of composite sulfide

a) Properties common to every sample:
   1. Glassy black surface
   2. Many voids in the sulfide
   3. Easy to powderize; not so sticky
   4. Storong H_2S smell, but fades in time
   5. Strong adhesion to silica ampoule (especially, stronger with Al content)

b) Properties distinct by composite ratios:
   1. Fe/Al=1/1.5~1/2.5: Black crystals
   2. Fe/Al=1/4~1/9: Strong reaction with silica ampoule (surface is black, but inside is brown)

their diffracted patterns vary gradually with time, hence all products must be examined immediately by x-ray diffraction.

2. Analytical results of the synthesized product

One part of these synthesized product was analyzed based on JIS standard in order to recognize its chemical constituents.

The result was summarized in **Table 3** from which it may be noted that there are relatively high amounts of SiO_2 in the product. However, it is not always probable that the product contains some amount of SiO_2, and then even if it contains Si, it is not certain whether it is soluble in the sulfide or not. Here,

Table 3 Chemical analysis of composite sulfides

Fe/Al	Process	Condition	Amount for analysis	Chemical composition, wt%				Fe : Al : S by analytical result
				Fe	Al	S	SiO_2	
1/2	Silica ampoule	1200°C-10 hr 900°C-40 hr	0.2 gr 〃	20.28 20.26	15.47 15.70	39.86 39.88	24.10 24.10	1 : 1.6 : 3.4
1/4	〃	〃	〃	19.56 19.58	20.34 20.30	40.08 40.12	19.91 19.85	1 : 2.2 : 3.6
1/9	〃	〃	〃	10.16 10.16	30.88 30.88	28.93 28.93	30.20 30.20	1 : 6.3 : 5.0
1/2	H_2S process Al_2O_3 boat	1300°C-1 hr Furnace cool	0.2 gr 0.1 gr	23.75 23.73	20.83 20.86	46.95 46.84	8.41 8.44	1 : 1 8 : 3.4

on the assumption that the element is contained in the product as a foreign phase, the composition (mole) ratios were calculated from data of Fe, Al, alone, with S excluding the other elements. The result shows that all data contains less Al than that of the original ratio and, especially, higher Al-containing sample shows such a stronger deviation.

Further, it was found that the ampoule method showed a higher consumption of Al in the product than that obtained by other methods. But even the H_2S gas method showed a consumption of Al since the alumina boat used in the latter case contained 20–25% of SiO_2. In these experiments by judging from coloring of some parts of the quartz vessel, it seems that a certain amount of Al dissolved in the quartz vessel producing at times Al_2O_3 in it because it was well known the quartz vessel is colored reddish brown when Al was doped on quartz.

In both methods a negative effect on the synthesis of the present compound was that the synthesized product invariably came in contact with the quartz vessel, hence other heating techniques such as using a graphite crucible are necessary.

3. X-ray diffraction patterns from the Fe–Al–S compounds

All diffraction patterns by Fe, Cr, and Cu targets were obtained for every synthesized product, but it was found that that obtained by a Cu target was the sharpest and the most convenient for a successful processing. These results are summarized in **Fig. 6** in which it is observed that diffracted peaks from an FeS_{1+x} type compound were mixed in the case of a low Al-content such as 1/0.5, and 1/1.0. All diffraction angles (2θ) of these peaks were shown in **Table 4** and all diffraction peaks were numbered successively from that of low angle toward that of high angle. Among these 25 peaks, it was identified that those from an FeS_{1+x} type correcsponded to the numbers of 7, 10, 14, and 19, but those of 9, 13, and 18 corresponded to an αAl_2S_3 compound. In the other peaks the numbers of 3, 1, 6, 11 and 2 showed high peaks. Further, all in the latter group were found to be almost equal diffraction angles for the case of Fe/Al=0.5–1/4 within the limit of error and also were found to coincide with those found in the sulfide scale formed on the previous Fe–Al alloys[4,5], hence all these peaks appear to be from the newly synthesized product. Those from the Fe/Al=1/9 sample, however, are different somewhat from the others. Thus further calculation was based on the data obtained from the diffraction patterns from the Fe/Al=1/4 sample, where the diffraction intensities were relatively high.

Table 4 Comparison of diffffraction patterns from each sample (Cu kα)

Numbers of diffraction peaks	Diffraction angles (2θ) (deg.)						
	Samples with different Fe/Al ratios						
	1/0.5	1/1	1/1.5	1/2	1/2.5	1/4	1/9
1	7.27	7.38	7.25	7.30	7.31	7.32	7.38
2	–	14.70	14.65	14.66	14.70	14.68	–
3	20.04	22.10	20.04	22.03	22.10	22.06	22.30
4	–	–	–	–	28.14	–	–
5	–	29.22	29.18	29.17	29.16	–	–
6	–	29.67	29.59	29.57	29.60	29.64	29.71
⑦	29.58	30.04	–	–	–	–	30.08
8	31.94	31.95	31.98	31.94	31.88	31.90	32.44
* 9	–	32.70	32.69	–	–	–	–
⑩	33.90	–	–	–	–	–	–
11	–	37.30	37.23	37.27	37.24	37.30	–
12	–	41.34	41.32	41.32	41.30	41.39	42.06
*13	–	42.55	42.55	–	–	–	–
⑭	43.76	43.75	–	–	–	–	–
15	–	–	–	–	–	45.14	–
16	–	47.37	47.34	47.37	47.33	47.35	–
17	–	49.95	49.91	49.88	49.87	49.93	50.98
*18	–	50.97	50.87	–	–	–	50.97
⑲	53.10	53.12	–	–	–	–	–
20	–	–	–	–	–	53.17	–
21	54.10	54.10	54.00	54.00	54.03	54.05	54.93
22	–	–	–	–	55.08	–	–
23	–	–	–	61.53	61.47	61.50	–
24	–	–	–	–	–	70.27	–
25	–	–	–	–	–	79.46	–

Note: Circles show the patterns from FeS_{1+x} and stars from α Al_2S_3

Next, in order to observe the general behavior of these peaks all peak intensities obtained from the same number of each peak found in the Fe/Al = 1/0.5–1/4 samples are compared with each other as seen in **Figs. 7** and 8 by an Fe kα x-ray. From these figures it is clear that the first group of diffraction peaks indicates that each of d (lattice spacing) bears a relation of integral multiplication with each other, and is quite different from those in the other group. Further, peak 17 was understood to have the other hkl index different from those in Fig. 8. These facts observed above are also recognized in the results obtained from the peak intensity by a Cu kα x-ray. Accordingly, the last group of peaks remaining undetermined were examined by use of various techniques[17] to determine in what manner the crystalline structure of the newly synthesized product was and the results obtained indicated that these peaks were all included in a same crystalline form as seen in the later section. That is, the special sulfide contained in the scale is a hexagonal type and its lattice parameters are as follows:

$$a_0 = = 3.65 \text{ Å}, \text{ and } c_0 = 12.05 \text{ Å}$$

Further the approximate molar ratio was estimated as Fe : Al : S = 1 : 2 : 4 by our previous chemical analysis.

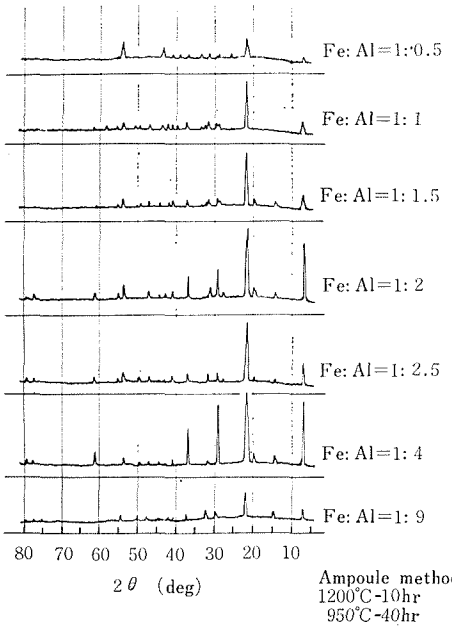

Fig. 6 x-ray diffraction patterns from composite sulffdes prepared with different Fe/Al mixtures (Cu kα)

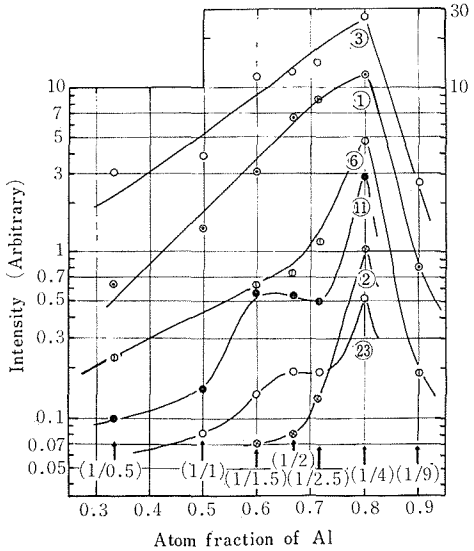

Fig. 7 Comparison of intensities of diffraction patte-ns of each sample (Fe kα)-I, where the number in a circle corresponds to that of difiraction pattern

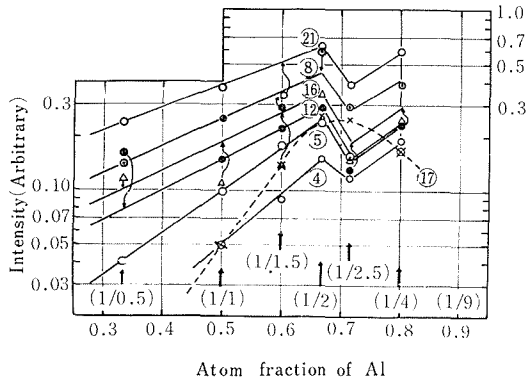

Fig. 8 Comparison of intensities of difiraction patterns of each sample (Fe kα)-II, where the number of a circle corresponds to that of diffraction pattern

4. Consideration

However, the study on these double sulfides has already been done by Flahaut[18] in France, who prepared the double sulfide by heating Al sulfide and metal (Fe) sulfide mixed or FeS, Al metal, with excess sulfur in a graphite

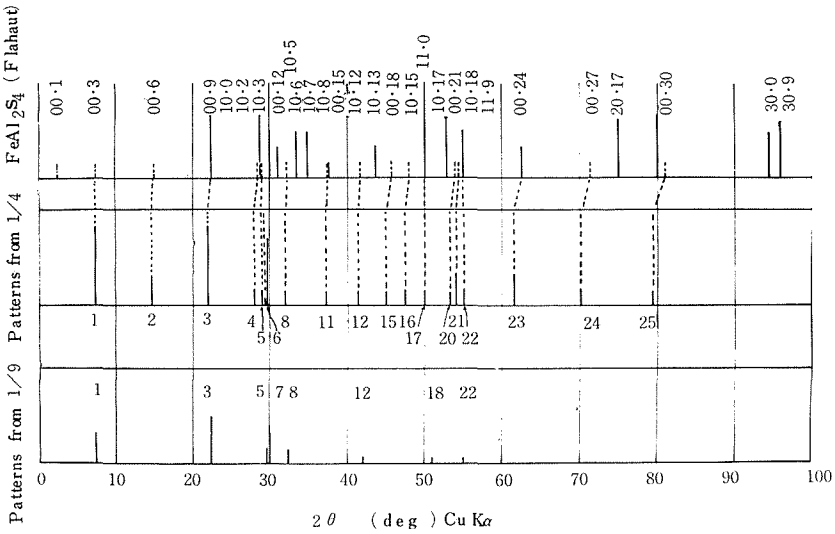

Fig. 9 Comparison of x-ray diffraction patterns from Fe-Al composite sulfide with Flahaut's data

crucible at 1100°C with special care taken to avoid moisture entering. The sulfide product obtained was then identified by x-ray diffraction with a Cukα ray. The upper part of **Fig. 9** indicates data with diffraction indices referring to numerical values of Flahaut. Peaks obtained in the present study were also plotted in the middle part of the figure, all of which were also in similar positions of angle to those of the upper part, although their intensities were somewhat different from the former.

It is worthwhile especially to note that the diffraction peaks with the lowest angle obtained in the present experiment corresponded to the index of 00•3 and not to that of 00•1. Accordingly, referring to the new indices, the revised ones were obtained by multiplying old ones by three and then it was noted that the lattice parameters were different from the previous ones. The calibrated new calculations indicated that similar values to parameters of Flahaut were obtained, but the present data are slightly larger than his values. Both data are listed in the following:

The present results:

$$\left.\begin{aligned} a_0 &= 3.659 \pm 0.004\ \text{Å} \quad \text{(mean value of 2 data)} \\ c_0 &= 36.16 \pm 0.03\ \text{Å} \quad \text{(mean value of 10 data)} \end{aligned}\right\} \tag{1}$$

Flahaut's data:

$$\left.\begin{aligned} a_0 &= 3.639 \pm 0.003\ \text{Å} \quad \text{(mean value of 2 data)} \\ c_0 &= 35.70 \pm 0.11\ \text{Å} \quad \text{(mean value of 4 data)} \end{aligned}\right\} \tag{2}$$

From the data of Fe/Al=1/9 sample the parameters were also calculated and the values obtaind were found to be somewhat smaller than the provious values as follows: $a_0 = 3.587$ Å; $c_0 = 35.91$ Å.

Considering the above results (1) and (2), the differences between two data are $\Delta_0 a/a_0 = 0.55\%$ and $\Delta c_0/c_0 = 1.29\%$, and the reason of the difference is not certain at present. However, even if there is such a difference between them, the synthesized products obtained by both researchers can be concluded to be the same. Furthermore, it is also very clear that all double sufides found in the

various contents of Fe-Al metal powder containing 33.3-80 wt%Al have almost the same lattice parameters. Therefore, the fact that the compound in the sulfide scale formed on the Fe-Al alloys with an Al content of 6 wt%Al and over and Al-cast iron with a higher Al content had the same lattice parameters as the presen product as stated in the previous section means that the new compound is stable under the corrosion conditions and also will have a close relation to these alloys which are highly resistant to sulfurization.

Another fact that such a compound may be converted readily into a spinel type cubic crystal with 2-3 wt% of Cr[19] is also a very important and interesting one from theoretical and practical points of view, because the Fe-Al alloys with about 3 wt%Cr are modified to have a two fold resistance against sulfurization[1].

According to Flahaut the density of the double sulfide crystal is 2.88 gr/cm^3, and then it is calculated that the number of atoms in a hexagonal unit cell is $(FeAl_2S_4)\times 3=21$. On the other hand, this crystal contains $(FeAl_2S_4)\times 1=7$, considering that the crystal is of a rhombohedral type. Hence, it will be necessary to determine the position of each atom in the compound by comparing the relative intensities of diffraction peaks from each x-ray tube.

5. Conclusion

In order to determine the unknown compound obtained in the scale formed on the Fe-Al alloys in sulfurization, Fe and Al powdered metals of various ratios were heated in an atmosphere of sulfur or H_2S gas and the synthesized products obtained were examined by x-ray diffraction. The result showed that numerous peaks of diffraction were present. From these peaks those of Fes_{1+x} and αAl_2S_3 were subtracted and those remaining were analysed with various calculations, and the following results were obtained:

(1) The new compound is hexagonal and its composition ratio is suggested as Fe : Al : S = 1 : 2 : 4.

(2) The lattice parameters of the new compound were at first found to be $a_o=3.65$ A and $c_o=12.05$ A.

(3) From the comparison of the present data with data after Flahaut's experimental result it was found that the present compound showed almost the same positions of diffraction angles as those by Flahaut and also three fold of the present I values corresponded to those of Flahaut's values. Accordingly, the result obtained by recalculation was as follows:

$$a_o=3.695\pm0.004\ \text{Å}$$
$$c_o=36.16\pm0.03\ \text{Å}$$

Acknowledgments

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