Investigations on Chemical Composition of Welding Fumes

Fume composition is governed as follows: with non-lime type coverings—by vaporization from molten electrode tip; with lime type coverings—by vaporization from molten slag surface

BY M. KOBAYASHI, S. MAKI, Y. HASHIMOTO, AND T. SUGA

ABSTRACT. Variations in the contents of elements in the fumes have been studied as functions of respective contents in the covering, using different commercial covered electrodes and some test electrodes. Together with observation of welding arc by means of a high speed camera, fume generating phenomena and mechanisms have been studied.

In general, the content of elements in fumes increases linearly with the increasing content of elements in the covering. The higher the vapor pressure, the larger the regression coefficient. In the cases of iron oxide and alkaline metals, correlation between the content in the fumes and in the covering differs according to the type of covering, i.e., lime or non-lime. The peculiar behavior of alkaline content in lime type is caused by an abundance of Ca, especially CaF_2.

The arc of non-lime electrodes is generated from the molten metal at the tip of the electrode, while the arc from lime electrodes comes through the molten slag that covers the hanging droplet at the tip. Therefore, the former fume composition is regulated by the molten metal composition and the latter by the molten slag. Thus, the mechanism of the difference between lime and non-lime can be explained.

Introduction

In arc welding processes, the generation of welding fumes is inevitable, and welders cannot avoid inhaling fumes to some extent since they are obliged to stay very close to the source of the fumes. As for their harmfulness, the fumes produced from lime type electrodes, which might cause welders acute symptoms such as headache or fever, have been the chief subject of studies.

In recent years, all types of fumes have been comprehensively studied since the inhalation of fumes can lead to pneumoconiosis if it lasts for a long period. To prevent a health problem for welders due to fumes, steps have been taken as a matter of course to improve the working environment in welding; these steps include a provision for the total ventilation system as well as local air exhaust devices and protectors for breathing. It is also necessary, however, to carry out research on welding materials, including research on how to suppress the amount of fumes generated (Ref. 1-3, 9, 10) or on how the fumes can be transformed into less harmful ones (Ref. 4, 5). Some results of this prior research have already been incorporated in the commercial products.

In researching the quantity or quality of fumes, it is important to study the essential characteristics of fumes, especially their formation mechanism. From this point of view, the author et al. (Ref. 6) have observed fume generation by a high speed camera; they have also investigated fume supply sources by a so-called tracer method. The results are as follows: The fumes mainly originate as vapor which emanates from the molten liquid at the tip of a welding electrode. In other words, the high temperature vapor is blown off by air blow from the lower part of the arc column into the air. This vapor is oxidized and condensed rapidly into solid particles to form welding fumes—Fig. 1.

It seems that many of the characteristics of fumes can be explained by reference to this mechanism. However, the fume composition in shielded metal arc welding is complicated, and the relation between the composition of the covering and that of the fumes has not yet been explored in full detail. Thus, in this paper, variations in the contents of elements in the fumes have been studied as functions of respective contents in the covering.

The experiments discussed here were conducted by using 44 different commercial covered electrodes. In addition, an investigation of the fume generating phenomena of alkaline metals and iron oxide, both of which exhibit peculiar behavior, was carried out by using test electrodes and a high speed camera. The results and discussion are presented under appropriate headings.

Experimental Procedure

Sampling and Analysis of Fumes

The fumes were sampled and analyzed in accordance with the methods prescribed in Japan Welding Engineering Society Standard WES 9005 "Methods for chemical analysis of welding fumes generated by covered electrode"—that is, the bead-on-plate welding was carried out at 170 amperes (A) using AC current in a fume collecting chamber having a volume of about 700 mm^3 (0.043 $in.^3$). Next, the total amount of fumes generated was collected on the filter paper of a high-volume air sampler installed at the top of the chamber. Finally, the fume sample for analysis was obtained by

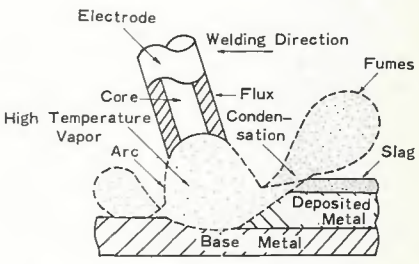

Fig. 1—Schematic diagram of the fume generation mechanism

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Table 1—Tested Commercial Covered Electrodes

Type of covering	JIS specification	Number of brands
Lime	D4316 or D5016	19
Ilmenite	D4301	10
Titania	D4313	2
Iron powder iron oxide	D4327	2
Lime-titania	D4303	4
Others	—	7

sweeping off the fumes from the filter paper with a soft brush. Specimens obtained in this manner are then subjected to analysis.

Experimental Materials

Commercial Covered Electrodes. Six types, consisting of the 44 brands of covered electrodes shown in Table 1, were selected from commercial electrodes with known covering composition of 4 mm (0.16 in.) in core diameter, and the relations between their covering compositions and fume compositions were investigated. The composition of each covering was determined by using percentages of the elements.

Mixing of Lime and Ilmenite Type Coverings. In order to investigate the behavior of alkaline elements which are influenced significantly by covering types, the following three kinds of experiments were carried out, using the test electrodes of 4 mm (0.16 in.) in core diameter. The core wire was of mild steel, and drying was carried out at 130°C (266°F) for 1 hour (h).

First, the test electrodes whose covering compositions are numbered 1 to 20 in Table 2 were prepared. In the case of these electrodes, K_2CO_3 or Na_2CO_3 was added as an alkaline element to the various-ratio mixed coverings of lime and ilmenite types (the coverings of both types did not contain any raw materials with alkaline elements). Colloidal silica which contains almost no alkaline elements was used as a binder. In Table 2, the values in the silica column include SiO_2 contained in colloidal silica; K_2CO_3 and Na_2CO_3 are added in such a manner that the contents of K_2O and Na_2O reach 2 and 4%, respectively.

Table 2—Covering Constituents of the Experimental Electrodes Nos. 1–37, %

No.	Mix ratio of lime type	Calcite	Fluorite	Rutile	Mn-oxide	Silica	Ilmenite + Fe oxide	Fe-Mn	Fe-Si	Organic matter	K_2CO_3	Na_2CO_3	AlF_3
1											2.9	0	
2	100	50	18	6	0	6	0	2	12	1	5.9	0	0
3											0	3.4	
4											0	7.0	
5											2.9	0	
6											5.9	0	
7	75	40	13.5	6.5	1	10.5	6.5	5.5	9	2.5	0	3.4	0
8											0	7.0	
9											2.9	0	
10	50	30	9	7	2	15	13	9	6	4	5.9	0	0
11											0	3.4	
12											0	7.0	
13											2.9	0	
14	25	20	4.5	7.5	3	19.5	19.5	12.5	3	5.5	5.9	0	0
15											0	3.4	
16											0	7.0	
17											2.9	0	
18	0	10	0	8	4	24	26	16	0	7	5.9	0	0
19											0	3.4	
20											0	7.0	
21			0								5.1	6.0	
22	—	50	2.5	6	0	6	0	2	12	0.5	5.3	6.2	0
23			5								5.5	6.4	
24			10								5.8	6.8	
25			0								6.4	7.4	
26			2.5								6.5	7.6	
27	—	10	5	8	4	24	26	16	0	6.5	6.7	7.8	0
28			10								7.0	8.2	
29		0											
30	—	5	0	8	4	18	26	16	0	6.5	0	0	0
31		10											
32		16											
33		23											
34			5										0
35	—	10	10	8	4	18	26	16	0	6.5	0	0	0
36			0										5
37			0										10

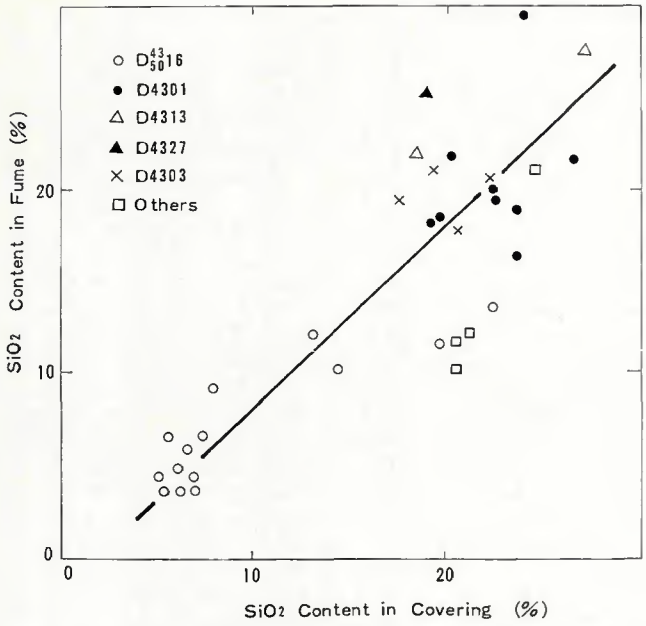

Fig. 2—SiO_2 content in fume as a function of its content in covering

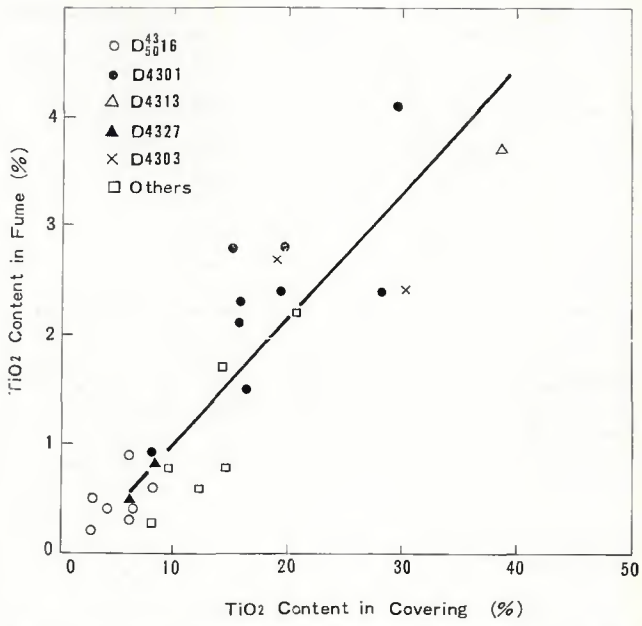

Fig. 3—TiO_2 content in fume as a function of its content in covering

Using the above test electrodes, the variation of alkaline content in the fumes as functions of covering types was studied.

Gradual Addition of Calcium Fluoride to Coverings. Test covered electrodes were made by adding calcium fluoride (CaF_2), gradually to lime or ilmenite type coverings. K_2CO_3 and Na_2CO_3 were added in such a way that the contents of K_2O and Na_2O respectively might reach 4%. As a binder, colloidal silica was used.

By using these electrodes, the variation of alkaline content in the fumes was studied as a function of CaF_2 content in the covering. The covering compositions are given for nos. 21–28 in Table 2.

Separation of Ca and F Influences. The influence of calcium fluoride was considered by studying Ca and F separately.

The variation of alkaline content in the fumes was examined for $CaCO_3$ and AlF_3 in ilmenite type coverings. In this case, potassium water-glass was used as a binder; this was added so that the K_2O content in the covering might reach 4%. The covering compositions are given for nos. 29–37 in Table 2.

Observation by High Speed Camera

In order to inquire into the difference in fume elements between lime type and non-lime type from the viewpoint of arc phenomena, the arc generating phenomena of lime type and non-lime type covered electrodes were observed with a high speed camera. In photographing, the back-light method was adopted using an extra-high voltage mercury lamp as a light source; the film velocity was 2000 pictures per second(s).

Experimental Results and Discussion

Fumes from Commercial Covered Electrodes

Relationships between the contents of elements in fumes and in the coverings are shown in Figs. 2–10 for SiO_2, TiO_2, MgO, CaO, MnO, F, Fe_2O_3, Na_2O, and K_2O, respectively. Here, the data were obtained in an experiment involving various commercial covered electrodes.

Considering the manner of fume formation as shown in Fig. 1, it seems reasonable to conclude that each element in the fumes exists in the form of an oxide (partially, a fluoride). It can be presumed also that the contents of elements in the fumes increase in accordance with the increase of the elemental contents in the covering. Experimental results suggest that this presumption can be regarded as a general fact. Each of the above oxides, as well as the F, are considered below in detail:

1. SiO_2 (Fig. 2). Metallic silicon contained as Fe-Si in the covering is not accounted for when calculating SiO_2 content in the covering. If this is taken into account, the group of lime type shifts to the right and disperses in the graph.

Heile et al. (Ref. 7) have reported that high SiO_2 content in gas metal arc welding fumes was due to the formation of an SiO molecule at high temperature; such a process will naturally occur also in shielded metal arc welding. Furthermore, the reaction process in shielded metal arc welding is more complex by reason of the complicated composition of the covering. Therefore, it is difficult to discuss the vaporization process under silicate's co-existence with metallic silicon. Aside from metallic silicon in the covering, it can be recognized that the SiO_2 content in the covering is proportional to its content in the fumes with the coefficient of about 1.

2. TiO_2 (Fig. 3). A rather straight correlation can be seen between TiO_2 content in the fumes and in the covering. In this case, TiO_2 in the covering exists in the form of TiO_2 or $FeTiO_3$. Since the vapor pressure of TiO_2 is low, the regression coefficient is as low as about 0.1 and the TiO_2 content in the fumes is one-tenth of that in the covering.

3. MgO (Fig. 4). The regression coefficient is about 0.4. The three points which are out of place upwards represent the case where metallic Mg is contained in the covering. Almost all metallic Mg is likely to be transformed into fumes by virtue of its high vapor pressure and high chemical activity.

4. CaO (Fig. 5). The major sources of CaO are $CaCO_3$ and CaF_2, but any significant difference in Ca behavior is not likely to exist between these two raw materials, so far as the diagram indicates. The regression coefficient is about 0.3.

5. MnO (Fig. 6). The MnO content in the fumes is plotted along the ordinate axis of Fig. 6, and the Mn content in the covering is plotted along the abscissa from the viewpoint that a great portion of MnO source is Fe-Mn. Because metallic Mn is contained also in the core wire, the regression line does not pass the

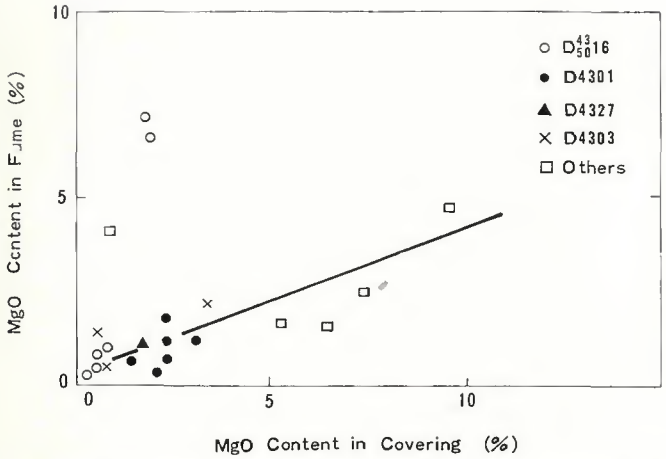

Fig. 4—MgO content in fume as a function of its content in covering

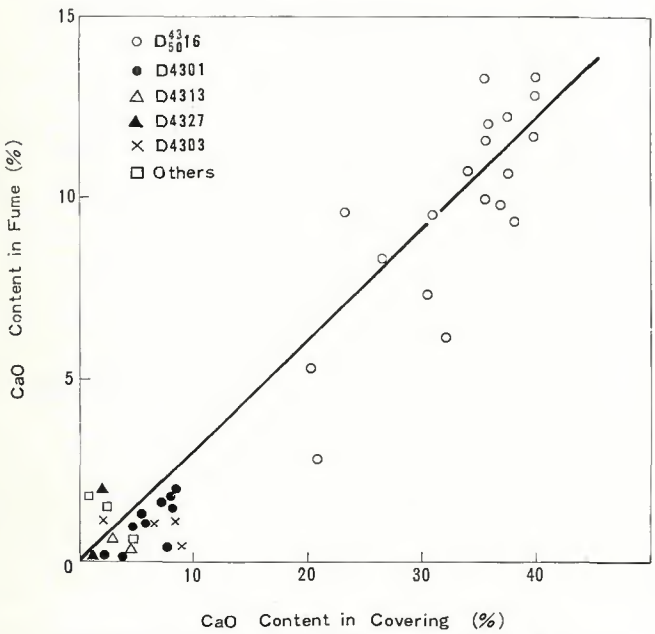

Fig. 5—CaO content in fume as a function of its content in covering

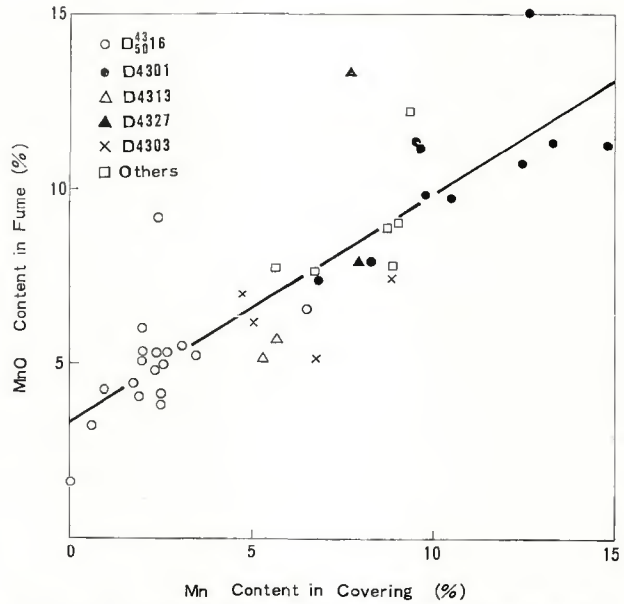

Fig. 6—MnO content in fume as a function of Mn content in covering

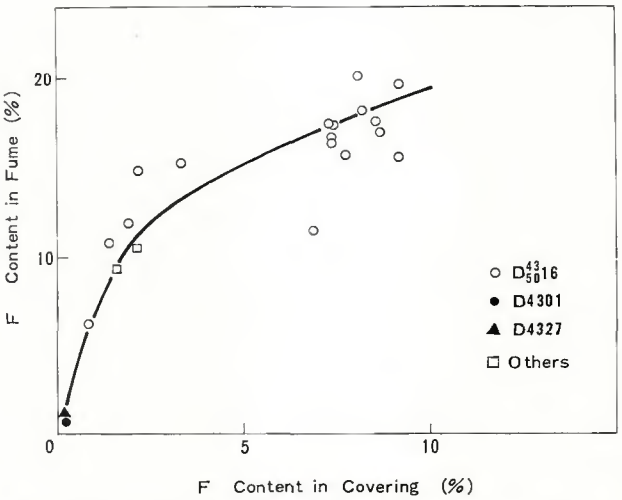

Fig. 7—F content in fume as a function of its content in covering

origin, and the MnO content in the fumes, which is originated by metallic Mn in the core wire, shares about 3.5% in the fumes.

6. F (Fig. 7). Covered electrodes containing F are largely limited to those of the lime type. As indicated in Fig. 7, the ratio expressing the change from the material into fumes ("fume-feasibility") is higher for F than for any of the other elements previously described. Moreover, the correlation between F content in the fumes and in the covering presents a peculiar nature. There are a lot of interesting facts about the behavior of F that will provide a research theme in the future.

7. Fe_2O_3 (Fig. 8). Metallic Fe is not accounted for when calculating Fe_2O_3 content in the covering. As is clear from the diagram, a distinct grouping is made between lime type and non-lime type. The Fe_2O_3 content in the fumes from non-lime type is about 50% regardless of iron oxide content in the covering; the Fe_2O_3 content in the fumes from lime type does not exceed even half the one from non-lime type.

Since core wire and the iron powder in the covering should be considered as a source of iron oxide, it is futile to discuss the Fe_2O_3 content in the fumes by relating to that in the covering. It is, however, notable that the Fe_2O_3 content in the fumes indicates a constant value, being classified into two large groups—lime type and non-lime type.

8. Na_2O and K_2O (Figs. 9 and 10). Correlation in lime type is clearly different from that in non-lime type, just as in the case of Fe_2O_3. The "fume-feasibility" of lime type indicates a markedly high value, as illustrated by the fact that the regression coefficient is about 10. As alkaline metals have the highest vapor pressure of the elements treated in these experiments, the "fume-feasibility" of alkaline metals can be said to be most remarkable. Meanwhile, the marked difference in the behavior of iron oxide and alkaline metals between lime and non-lime coverings suggests that there must be a distinct difference in the fume generating process.

In order to discuss the "fume-feasibilities" of the elements, respective vapor pressures at high temperature should be considered. Unfortunately, the data of the vapor pressure of inorganic compounds at high temperature is so poor that it is impossible to make a precise discussion on the "fume-feasibilities" of each element. It is also difficult to guess the form of the gaseous state of each element, such as the formation of an SiO molecule. Consequently, only qualitative evaluations have been made in this paper.

Fume Composition of Test Electrodes with Mixed Covering of Lime and Non-Lime Types

Results of the analysis for alkaline con-

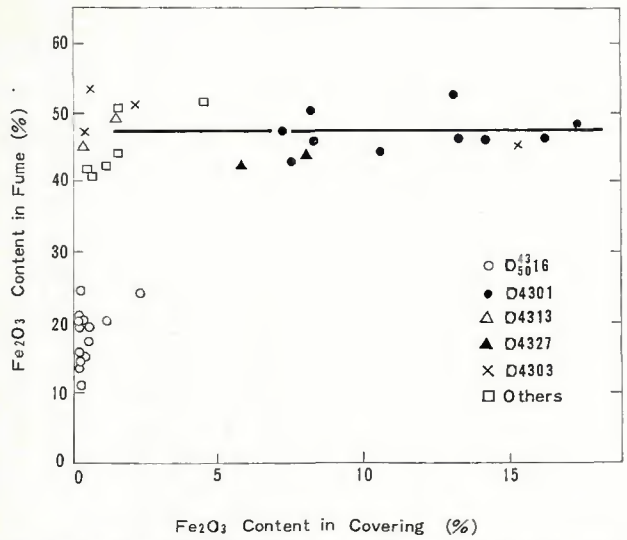

Fig. 8—Fe_2O_3 content in fume as a function of its content in covering

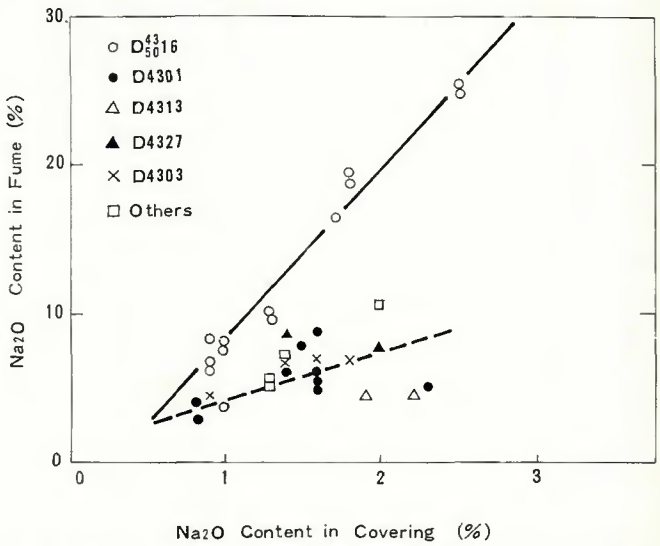

Fig. 9—Na_2O content in fume as a function of its content in covering

tent in the fumes generated from the test electrodes having the intermediate composition between lime and non-lime types are shown in Fig. 11. As the ratio of lime type to ilmenite type increases, the alkaline content in the fumes registers a slow increase. It reaches the same level as obtained in the case of 100% lime type, when the lime type accounts for about 75% of the mixture.

This result points out that the cause of increased alkaline content in the fumes is the lime itself, or a special element in the lime type covering. It was also confirmed that the iron oxide content in the fumes gradually decreases as the proportion of lime type increases from 0 to 75%.

Fumes from Test Electrodes with Calcium Fluoride Gradually Added

The most characteristic difference of lime type from ilmenite type involves CaF_2. The results of experiments where calcium fluoride was gradually added to lime or ilmenite type coverings, are shown in Fig. 12.

When CaF_2 is added to ilmenite type covering, the alkaline content in the fumes increases and, at about 5% CaF_2, reaches the same level as in the case of lime type. On the other hand, as the CaF_2 content in lime type covering is lowered, the alkaline content in the fumes begins to decrease at 5% CaF_2; however, it is considerably different from the alkaline content in ilmenite type even when CaF_2 content reaches zero.

This result tells us that CaF_2 plays a big part in the "fume-feasibility" increase of alkaline elements in the covering. Also, there must be other factors affecting this phenomenon besides the existence of CaF_2.

Fumes from Test Electrodes with Ca and F Added Individually

Results of an analysis for K_2O content in the fumes generated from the electrodes in which Ca and F are added individually to the covering are shown in Fig. 13.

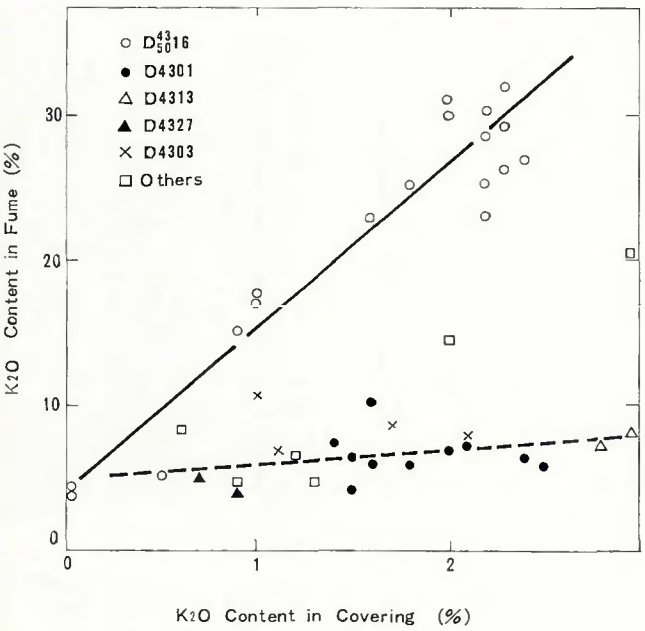

Fig. 10—K_2O content in fume as a function of its content in covering

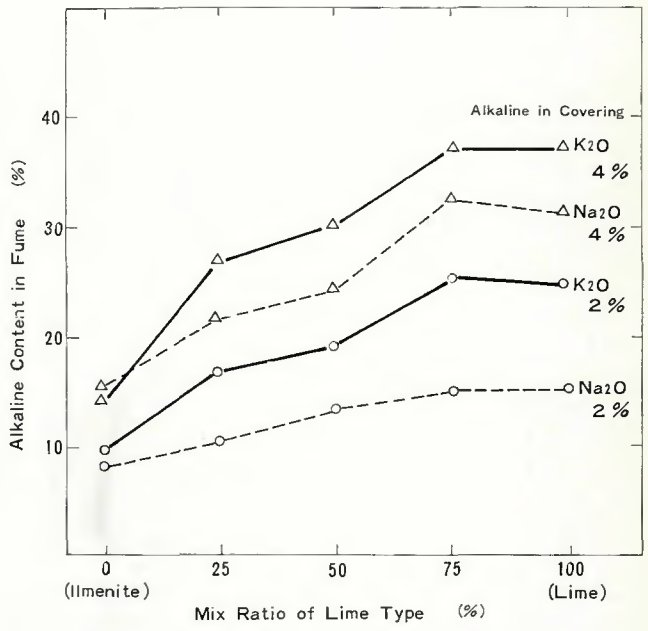

Fig. 11—Variation of alkaline content in fume with mixed covering of lime and ilmenite type

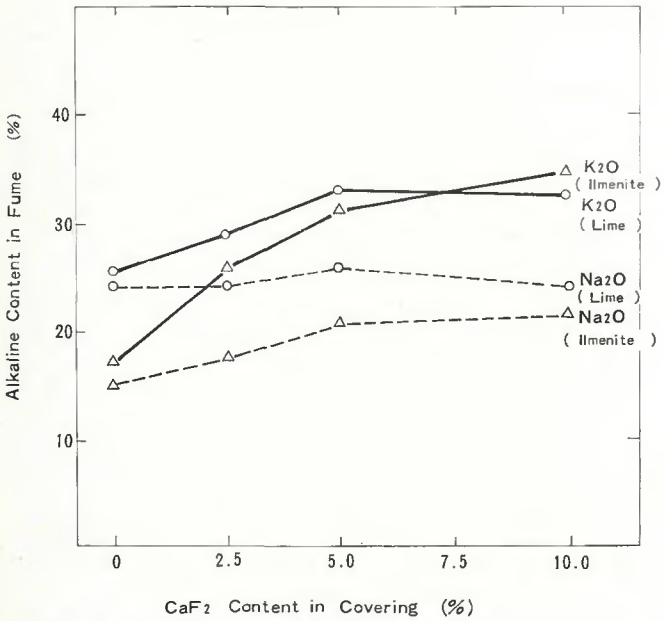

Fig. 12—Variation of alkaline content in fume with CaF_2 content in covering

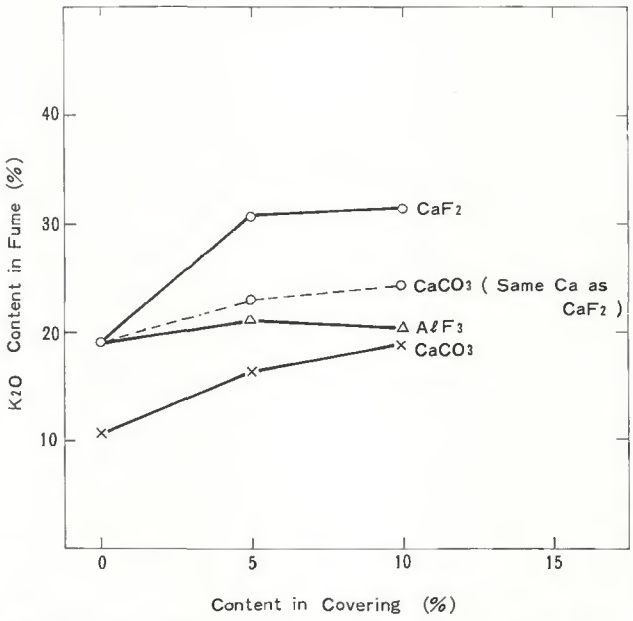

Fig. 13—Variation of K_2O content in fume with addition of CaF_2, AlF_3, or $CaCO_3$ in ilmenite type covering

When $CaCO_3$ forms 10% of the covering, the alkaline content in the fumes obviously increases as the CaF_2 content in the covering is raised, but there is no essential change even if AlF_3 is added. The alkaline content in the fumes also increases when $CaCO_3$ is added to the covering in an amount corresponding to the Ca content in CaF_2; however, the degree of this increase is smaller than that with the CaF_2 addition.

This result points out that the increase of alkali in the fumes is based on the effect of Ca in the covering and that this effect is most noticeable when the source of Ca is CaF_2.

Observation by High Speed Camera

Figure 14 shows typical examples of arc generating situations with both ilmenite and lime type coverings. In ilmenite type, the arc generates from the inside of the flux-sheath in almost all cases. On the other hand, the arc of lime type comes from the tip of a hanging droplet.

The mechanism shown in Fig. 1 indicates that the fume generation is regulated by vaporization from the molten liquid at the tip of the electrode. The arc generating surface at the tip of the electrode is the most remarkable vaporization surface, since its surface is most hotly heated by the arc. Then, if the arc generating area is mostly composed of molten metal, the main constituent of fumes becomes iron oxide.

If molten slag exists in the arc generating area or in its vicinity, a large quantity of the slag element will turn to fumes. In the case of ilmenite type, the arc always generates from the inside of the flux-sheath and does not come from the hanging droplet at the tip. It is assumed, therefore, that the arc generates from the molten metal at the tip of the core wire, and that the hanging droplet consists mostly of the molten slag. In other words, it is low in molten slag and rich in molten metal at the area of arc generation.

As for lime type coverings, since no individual transfer of slag is discerned, the surface of a hanging droplet is presumably covered with slag. The arc generates, in this case, mostly from the tip of this hanging droplet; consequently, a large quantity of molten slag is always likely to exist around the arc generating area.

In light of the above, in ilmenite type or generally in non-lime type, fume generation from the molten metal surface will be dominant, while fume generation from the molten slag surface on the hanging droplet will be dominant in lime type. Therefore, in non-lime type, iron oxide shares half the fume composition regardless of covering compositions.

In lime type coverings, the amount of iron oxide decreases considerably, and fumes composed mainly of covering elements are generated. The notable difference in alkaline elements must be due to the fact that alkaline elements have a very high vapor pressure compared to the other elements. Transition of the fume generating mode is made, as shown in Fig. 11, continuously from non-lime type to lime type. Abrupt transition at a certain covering composition has not been discerned.

It is reported that the electrical conductivity of molten slag generally rises with the increase of basicity, and that the rise of the electrical conductivity due to the addition of fluoride is larger in acid melts than in basic ones (Ref. 8). High electrical conductivity in molten slag yields a possibility that welding current flows through the molten slag layer (that is, the arc generates from the slag surface on a hanging droplet).

Experimental results in Fig. 11 indicate that slag elements occupy the major part in the fumes as the slag basicity increases. The results in Fig. 12 show that the effect of calcium fluoride addition is larger in ilmenite type (acid) than in lime type (basic) coverings. These results seem to indicate that the increase in the electrical conductivity of molten slag is the main cause of the lime type mode of fume

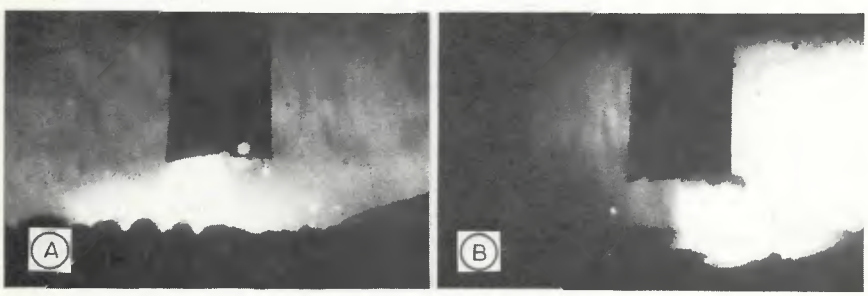

Fig. 14 (left)—High-speed photographs of arc generation on ilmenite and lime type coverings (2,000 frames per second): A—ilmenite type; B—lime type

generation. Further investigation of this subject is anticipated.

Conclusions

The relation between the covering and fume compositions involving various elements was studied by analyzing the fumes from various commercial covered electrodes. Results were then studied together with observations of welding arc by means of a high speed camera, and a consideration of fume generating phenomena and mechanisms, leading to the following conclusions:

1. In general, the content of elements in the fumes increases linearly with the increasing content of elements in the covering. The lower the vapor pressure is, the smaller the regression coefficient becomes.

2. In the case of iron oxide and alkaline metals, the regression characteristics are very different according to the type of covering—i.e., lime or non-lime type. Iron oxide shares almost 50% in the fumes from non-lime covering regardless of covering compositions, while it is always lower than 25% in the fumes from lime covering. Alkaline content is much higher in lime fumes than non-lime fumes even if the content in the covering is almost the same.

3. Behaviors of iron oxide and alkaline metals become intermediate if the composition of covering lies in the middle of the lime and non-lime type.

4. The increase of alkaline metals in the fumes is caused by the influence of Ca in the covering; this influence is more effective when CaF_2 is contained as a source of Ca.

5. The fume composition with non-lime type coverings is regulated by the vaporization from the molten metal surface at the tip of the electrode; that of lime type is regulated by the vaporization from the molten slag surface. This fact can be explained by the difference in arc generating phenomena; it seems to be a reason why fume composition in lime type seems to be of a peculiar nature.

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If you plan to present a paper at the AWS 65th Annual Meeting April 9–13, 1984, be sure to get your abstract with the Author Application Form (opposite page 146-s May issue) into the mail no later than August 15, 1983.

For papers to be presented at the 15th International AWS-WRC Brazing and Soldering Conference, April 10–12, 1984, the Author Application Form (opposite page 58-s, February) and abstract must also be mailed no later than August 15, 1983.