

Part III. Brazing Fumes and Gases

Introduction

As part of the American Welding Society research program "Improving the Welding Environment," Battelle-Columbus examined the fumes generated during brazing. The broad objective of this task was to show experimentally the relationship of the fumes given off to the brazing filler metal used.

Early in the program a literature search was conducted to learn the extent and usefulness of the bibliographic data available. The major conclusions drawn were:

(1) The cadmium oxide fume hazard has received by far the most attention, but even this takes the form of "case histories" without significant attention to the basic causes of the problem. Only a few investigators have chosen to examine the effects of process and procedure variables on the magnitude of the hazard.

(2) The possibility of harmful fluoride concentration in the brazing environment is covered briefly in the literature. As in the case of cadmium, there is a dearth of useful information that would permit adequate definition of the hazard under varying conditions of use.

(3) Almost no information exists that can be used to define the brazing environment and the safe practices to be followed.

Based on these conclusions and the experiences of members of the AWS Research Committee, an experimental research program on brazing fumes was agreed upon. The experimental approach was developed without benefit or knowledge of any published prior experience by other investigators. Its magnitude and scope were restrained by the availability of funds assignable for brazing fume studies.

Scope

The research plan was designed to minimize the variables caused by changes in flame shape, character, and position that occur during torch brazing. Thus, procedures similar to those used during welding fume studies were suggested. Total fume samples collected in the AWS-Battelle welding fume collection chamber would be used to find the influence of brazing variables on the fume generation rates and quantities. Also the fume sample would be analyzed by atomic absorption methods to determine how brazing variables affect fume compositions. Unfortunately, it increasingly became evident as the program progressed that the procedures chosen did not provide the precision required for accurate measurement of filler metal fumes.

The filler metals chosen were: Ag-15Cu-16Zn-24Cd (BAg-1) and Ag-22Cu-20Zn-7Cd-1Sn. These filler metals have similar melting characteristics and are used extensively in industry for torch brazing.

Limitations

The investigation was limited to the BAg-class filler metals and was directed toward determining the fume generation characteristics of two filler metals having widely different cadmium contents.

As the data presented in this report show, the quantity of fume developed during brazing with filler metals containing cadmium and zinc is quite small. They also show that when a flux is used, it is the major contributor to the fume produced. In addition, the results clearly indi-

cate the need for the prior development and validation of precision procedures for use during any experimental study of the fumes produced by brazing filler metals and fluxes.

Program

The experimental program covered the following tests, conducted in random order:

(1) BAg-1 filler metal and Type 3A flux, heated to 1200° F (649° C), to 1250° F (677° C) and to 1350° F (732° C); five tests at each temperature.

(2) BAg-1 filler metal under CO₂ shielding, heated to 1200° F, to 1350° F, and to 1500° F (816° C); five tests at each temperature plus three extra tests at 1500° F.

(3) Low cadmium filler metal and Type 3A flux, heated to 1250° F, to 1350° F, and to 1500° F; four tests at each temperature plus two extra tests at 1500° F.

(4) Low cadmium filler metal under CO₂ protection, heated to 1250° F, to 1350° F, and to 1500° F; four tests at each temperature plus one extra at 1250° F (of questionable accuracy and therefore discarded).

Equipment, Materials, Procedure

Crucibles (boats)

All brazing filler metal melting was carried out in shallow pure alumina boats having these nominal internal dimensions: 1.75 x 1.13 x 0.38 in. (44 x 29 x 9.7 mm, approximately). The internal dimensions varied because the wall thickness was not uniform from boat to boat.

The possible surface area variable was neglected and not recorded during the study because not enough boats were available to permit sorting for uniformity.

During analysis of the results, the surface area variation was found to range between -4 and +12 percent from the nominal area; thus it was considered a significant possible source of error in the data collected.

Filters

Initial experiments were run using two types of filters: glass fiber absolute filters (MSA, Cat. No. 75428) when weight determinations were desired and cellulose membrane filters (Millipore Type RA, 1.2µm pore size) for samples to be analyzed.

It was found, however, that the absolute filters gave excessive variation in results. A satisfactory explanation of these variations was not found; therefore, all fume data used for study of the results were taken from samples collected on membrane filters.

The active filter area was 33 square in. (21 290 mm²) in all tests. No prefilter was used. Each filter was dried for 1 hour at 220° F (105° C) immediately prior to weighing and use.

Melting Furnace and Fume Collection Chamber

A resistance furnace capable of heating the brazing filler metal to melting temperature in less than 10 minutes and to 1500° F (816° C) in less than 15 minutes was built for the program. The melting furnace was enclosed in the AWS-Battelle fume collection chamber when in use. It is shown in position in Fig. 3.1. Closeup views of the furnace prepared for melting under a flux and under a CO₂ gas blanket are shown in Figs. 3.2 and 3.3 respectively. The CO₂ gas outlet was a flare fitting with an opening measuring 0.050 x 1.813 in. (1.27 x 46 mm).

A standard temperature control system utilizing a chromel-alumel thermocouple was used. For tests under CO₂, the gas flow was regulated through a flow meter at 8 ft³ per hour (3.8 liters per minute, approximately).

Filler Metals

The composition of the filler metals chosen for study was given above.

The standard BAg-1 filler metal was furnished in 1.50 x 1.25 x 0.38 in. (approx. 38 x 32 x 9.7 mm) blocks. These were cut to 1.5 x 1.00 x 0.38 in. (approx. 38 x 25 x 9.7 mm) in order to fit the crucible (boat). The excess pieces were used in check tests near the end of the study. The weight of the cut-down blocks varied between 84.7 and 82.6 grams. Melts made with the excess pieces varied between 74.7 to 76.6 grams. Atomic absorption analyses of these blocks made at Battelle gave these results: 25.4 percent Cd and 16.5 percent Zn. The liquidus 1145° F (618° C) was taken as that given in the literature.

The low cadmium filler metal was furnished as 1.50 x 1.00 x 0.13-in. (approx. 38 x 25 x 3.2 mm) blocks. Three blocks were used for each melt, the weight of which varied between 85.0 and 85.8 grams. Battelle atomic absorption analysis of these blocks gave these results: 7.02 percent Cd, 19.6 percent Zn. The liquidus of this filler metal was determined at Battelle and found to be 1210° F (654° C).

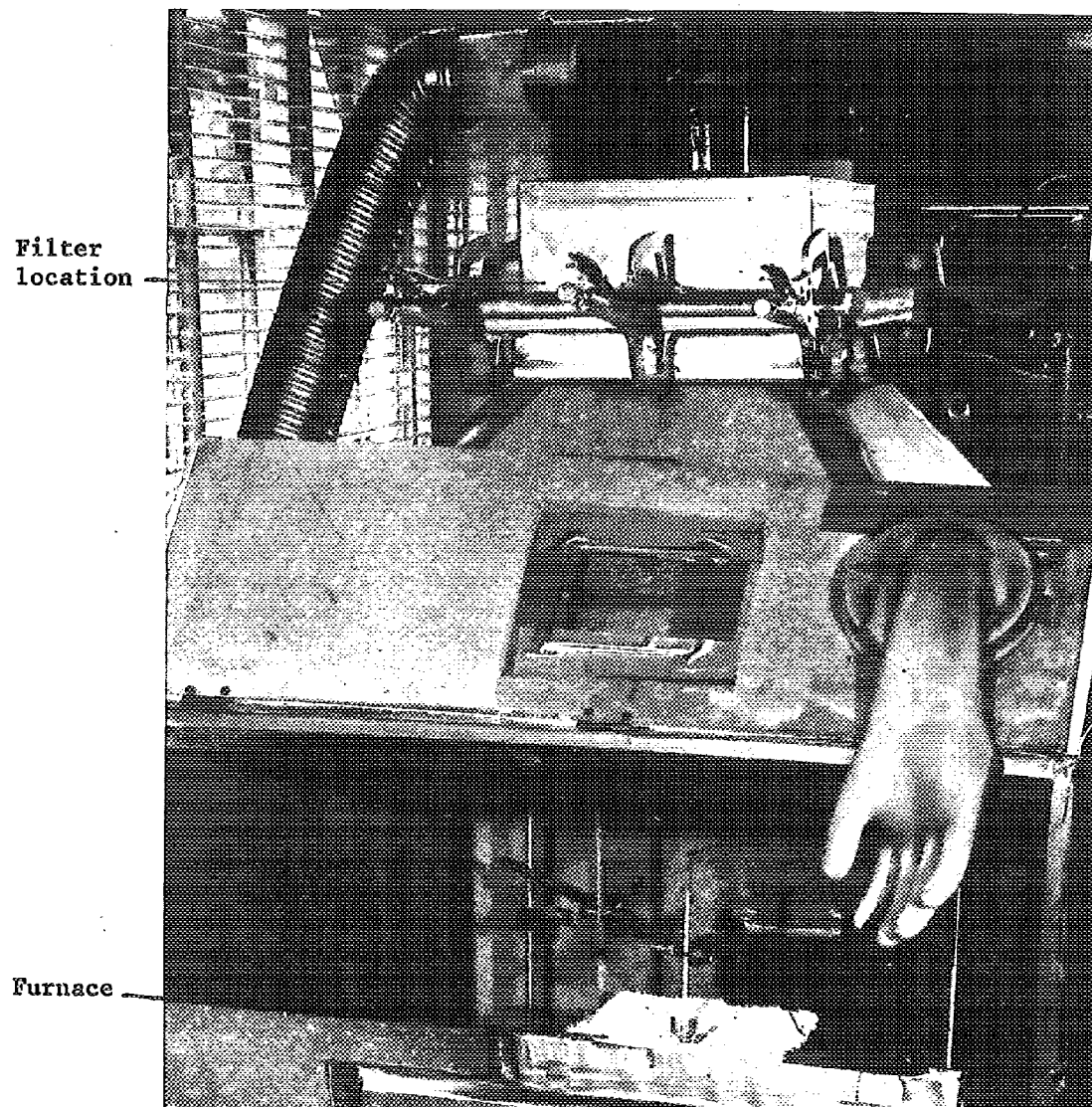
Other Materials

The flux used was commercial AWS Type 3A and was weighed to give 3 to 4 grams for each melt. Standard welding grade CO₂ gas having a -50° F (-46° C) specified dew point was used. The actual dew point was not checked.

Test Procedure

The standard procedure used for brazing filler metal melting and fume collection was as follows:

- (1) Weigh ingot
- (2) Add 3 to 4 g flux, or start CO₂ gas flow, as required
- (3) Place in cool furnace in fume collection chamber



**Fig. 3.1—Brazing filler metal melting furnace
in AWS-Battelle welding fume
collection chamber**

118/FUMES AND GASES

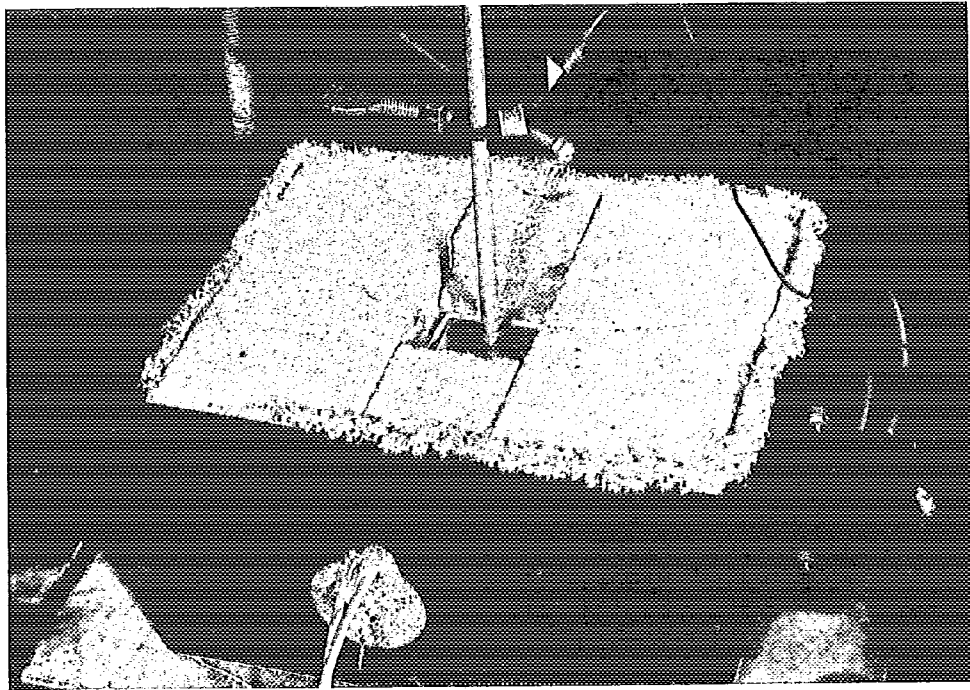


Fig. 3.2—Brazing filler metal melting furnace with ingot, boat, and thermocouple in place

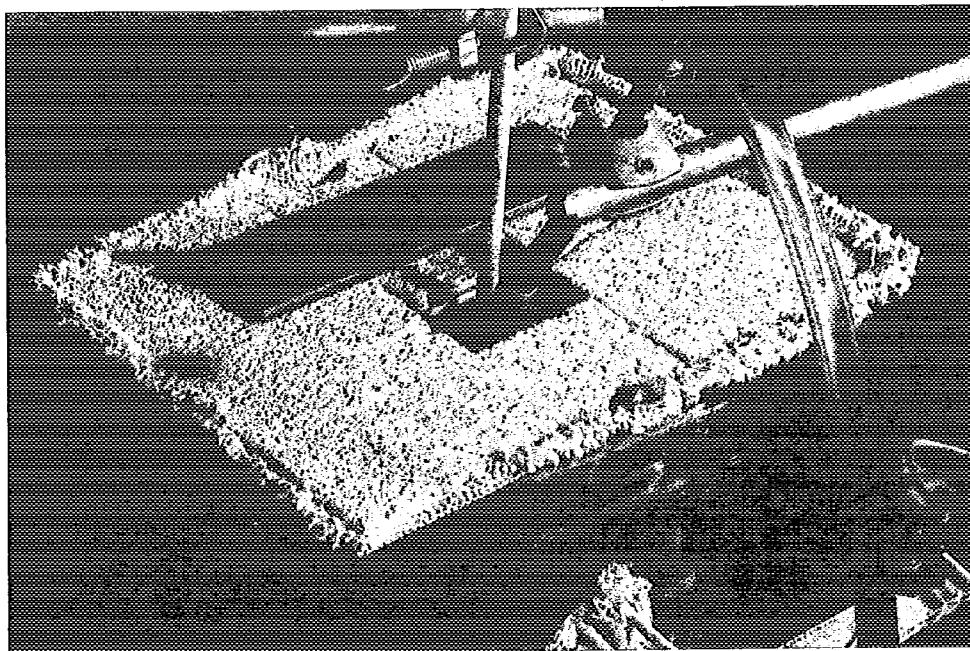


Fig. 3.3—Brazing filler metal melting furnace with CO₂ gas outlet in place

Section IIIA. Total Fume Generation Characteristics/119

- (4) Weigh filter and place in collection chamber
- (5) Start heating and fume collection
- (6) Heat to test temperature and hold 3 minutes
- (7) Turn off heat, continue fume collection for 10 minutes

- (8) Weigh filter

- (9) Weigh ingot before and after cleaning and drying

All weighings were made to ± 0.1 mg. Times were recorded to the even minute. The relative humidity in the laboratory was recorded at least hourly. The minimum relative humidity recorded was 36 percent and the maximum, 54 percent; 16 of the 60 tests conducted were outside the range of 42 to 50 percent. Blank filters run for the length of an average sampling time showed small weight gains of approximately 0.12 percent which might be attributed to moisture pickup. Used filters were sealed in polyethylene bags and stored in a desiccator until transfer for analysis.

All tests were conducted at random with respect to test temperature and flux or gas cover. Each filler metal was evaluated in a separate group of tests. Test temperatures for BAg-1 were 1200, 1350, and 1500° F (649, 732, and 816° C). The low cadmium filler metal was tested at 1250, 1350, and 1500° F (677, 732, and 816° C).

Summaries of the laboratory data collected on the fume generation characteristics of the brazing filler metals tested are found in Appendix C. These data were summarized and are included in the report where their discussion occurs.

Section IIIA. Total Fume Generation Characteristics

The data collected on the amount of fume produced by each of the two filler metals studied at these different temperatures were averaged and are given in Tables 3.1 and 3.2. The data from these tables are shown graphically in Fig. 3.4 and 3.5. The average loss in weight of the ingots is also given along with other desirable data.¹⁰ As mentioned previously, tests made with the glass fiber filters and the BAg-1 filler metals were excluded from consideration. This explains the fewer number of tests for BAg-1 than for the low cadmium filler metal.

10. Ingot weight losses are discussed later in this report.

Table 3.1
Brazing fume generation by filler metals
covered with AWS Type 3A flux

	1200° F (649° C)	1250° F (677° C)
	BAg-1 filler metal, avg.	Low cadmium filler metal, avg.
Number of tests	3	4
Time molten, min	6	7
Sampling time, min	25	27
Ingot loss, g	0.0422	0.0058
Fume weight, g	0.0684	0.0550
1350° F (732° C)		
	BAg-1 filler metal, avg.	Low cadmium filler metal, avg.
Number of tests	3	4
Time molten, min	8	8
Sampling time, min	28	26
Ingot loss, g	0.0527	0.0252
Fume weight, g	0.0770	0.0602
1500° F (816° C)		
	BAg-1 filler metal, avg.	Low cadmium filler metal, avg.
Number of tests	3	6
Time molten, min	12	16
Sampling time, min	30	31
Ingot loss, g	0.1095	0.1896
Fume weight, g	0.1670	0.0933

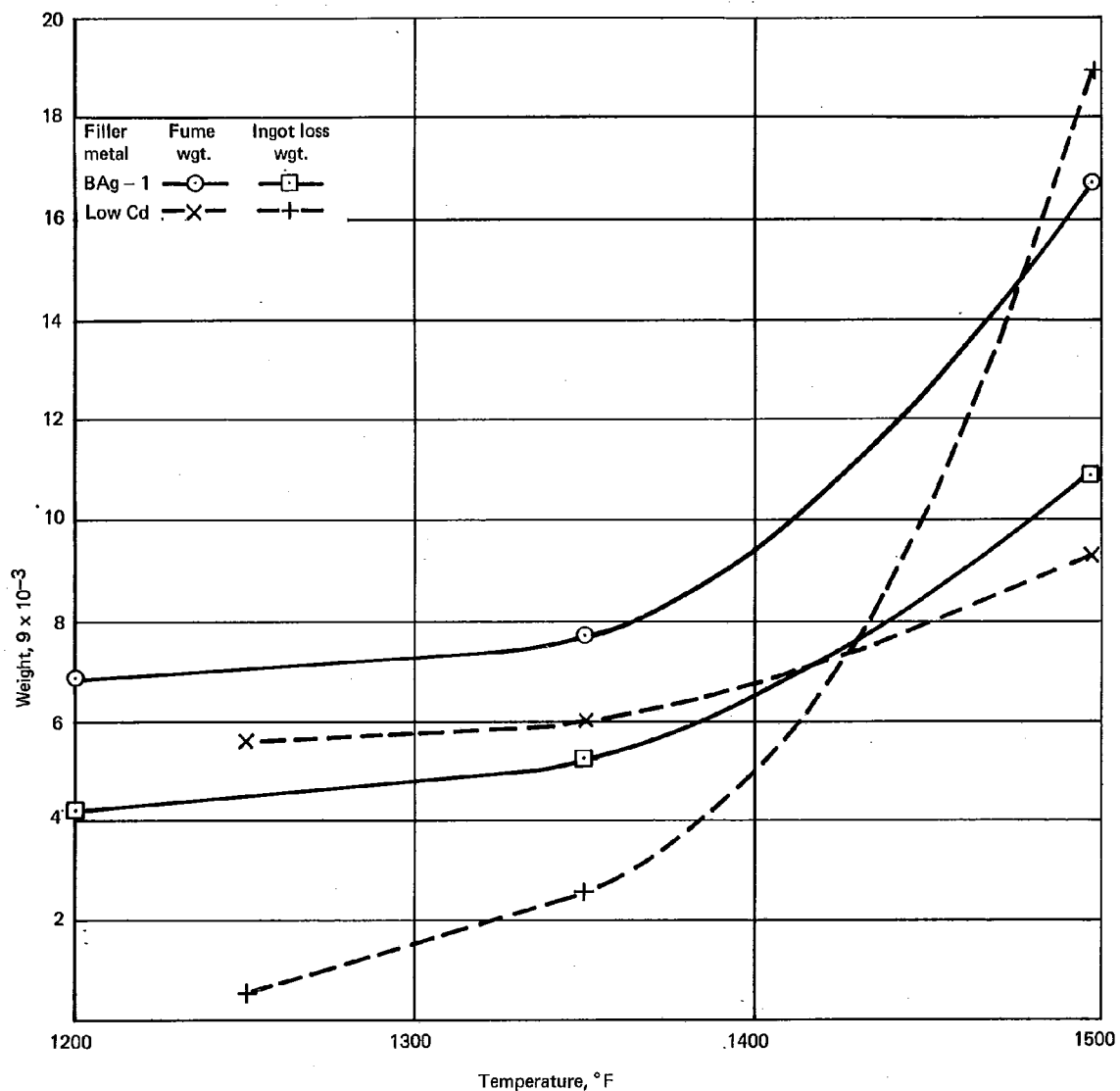


Fig. 3.4—Brazing fume generation and metal losses by flux covered filler metal

Flux Covered Melts

Examination of the fume weight data for both filler metals when melted under a flux (Table 3.1) shows the trend that would be expected: increased temperature results in increased fume weight. The actual weight of fume produced was smaller than expected. This may be attributed to the relationship between the filter location

and the molten metal surface, although no fume could be wiped from the collection chamber walls even after several test runs. A different sampling system, such as a smaller, completely closed chamber, would be required to validate or refute the magnitude of the fume weights produced. Also, the influence of the presence of a flux and the composition of the fume must be considered.

The data show a large increase in weight of fume pro-

duced at 1500° F (816° C) for both filler metals when compared to that produced at lower temperatures. This would be expected because cadmium boils at 1409° F (765° C) and zinc has high vapor pressure (approx. 300 mm of Hg) at the same temperature. The rate of fume formation at the two lower temperatures was nearly the same, but this rate increased significantly at 1500° F whether or not the rates are calculated on the basis of time molten or total sampling time. For example, using the fume weights produced by BAg-1 filler metal and the average time molten or sampling time, the calculated rates of fume formation are as follows:

Temperature, °F	°C	Rate for time molten, g/min.	Rate for sampling time, g/min.
1200	649	0.0114	0.0027
1350	732	0.0096	0.0028
1500	816	0.0139	0.0056

The low cadmium filler metal appears to produce about one-third less fume than the BAg-1 filler metal.

Gas Covered Melts

The data in Table 3.2 summarize the fume formation attributes of the two brazing filler metals studied where they are "protected" by a flowing CO₂ gas blanket rather than a flux. The results parallel those obtained where a flux was used. Thus, the same comments on the general trends apply.

A significant difference is noted when the amounts of fume produced by the BAg-1 filler metal are compared to those from the low cadmium filler metal. In all cases more fume was produced by BAg-1 under CO₂ gas than under a flux; the opposite was true for the low cadmium filler metal. There appear to be two possible explanations for such an event: (a) the higher vapor pressure of cadmium at all temperatures and (b) an observed more tenacious and impervious dross that formed on the low cadmium filler metal.

The observations made while making fume collections on melts protected by a flowing CO₂ atmosphere indicate

Table 3.2
Brazing fume generation by CO₂ covered filler metals

	1200° F (649° C)	1250° F (677° C)
	BAg-1 filler metal, avg.	Low cadmium filler metal, avg.
Number of tests	3	4
Time molten, min	6	7
Sampling time, min	27	30
Ingot loss, g	0.0134	0.0079
Fume weight, g	0.1035	0.0435
	1350° F (732° C)	
	BAg-1 filler metal, avg.	Low cadmium filler metal, avg.
Number of tests	3	4
Time molten, min	8	9
Sampling time, min	27	32
Ingot loss, g	0.0446	0.0311
Fume weight, g	0.0924	0.0357
	1500° F (816° C)	
	BAg-1 filler metal, avg.	Low cadmium filler metal, avg.
Number of tests	4	4
Time molten, min	12	15
Sampling time, min	33	35
Ingot loss, g	0.0626	0.1144
Fume weight, g	0.2127	0.0635

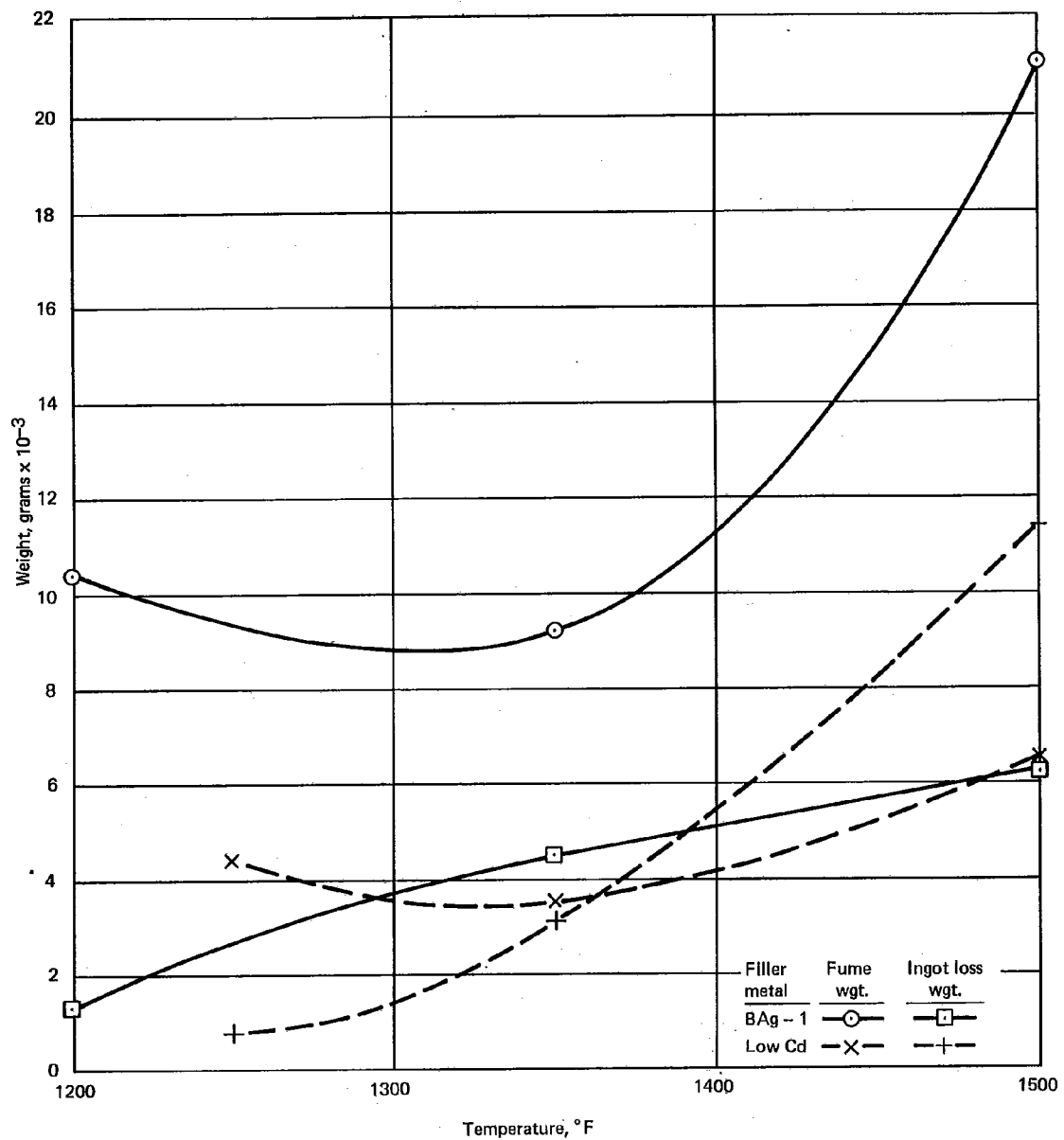


Fig. 3.5—Brazing fume generation and metal losses by CO₂ gas covered filler metal

that an improved technique should be used when making such studies. The use of a completely protective atmosphere, rather than a flowing blanket, is indicated to exclude air.

Ingot Weight Losses

The decrease in weight of the brazing filler metal melt (attributable to metal losses to fume) was considered a possible means of evaluating a particular filler metal's fume generation characteristics. Consequently, these losses were recorded during the study and are summarized in Tables 3.1 and 3.2.

In the case of flux covered melting, the losses recorded follow the expected trend: i.e., the greater losses occur at the higher temperatures. There is not a direct relationship between the ingot weight loss and the weight of fumes produced. In no case do the ingot metal losses calculated to oxides equal the fume weight. This should be true because no measure of the contribution made by the flux is evident. It is not reasonable to draw further conclusions from the weight loss data collected especially from that obtained from the higher temperature exposures. This is because of difficulties encountered in removing the fused flux from the ingot without also removing metal. The low cadmium filler metal was especially bad in this respect; it froze with a significant surface roughness which retained the flux residue.

The ingot weight loss data for tests made under a CO₂ blanket follow the proper trend as discussed for other situations. The magnitude of the losses recorded is debatable because of the adherent dross formed.

Because of the flux and dross removal difficulties, it is believed that a fume measurement procedure is a better way than metal weight losses to evaluate brazing filler metals for fume generation characteristics.

Section IIIB. Fume Composition

The composition of the fume produced by the brazing filler metals tested was appraised by analyzing the filter by the atomic absorption method. Analyses were made for cadmium, copper, zinc, and fluorine. The filters were chosen randomly from the tests made. Separate filters were used for the metal and for the fluorine analyses. The composition of the fume when the filler metals were melted under flux is given in Table 3.3. Table 3.4 contains the analysis of fume obtained when flowing CO₂ gas covered the melt. The data in Tables 3.3 and 3.4 are also shown graphically in Figs. 3.6 and 3.7.

Flux Covered Melts

Examination of the data in Table 3.3 shows that as the test temperature increases, the concentration of the more volatile constituents of the system increases. This was expected. In all cases the flux contributes most to the

fume composition. Beyond these two facts that can be derived from the data, much concern must be shown for the tabulated results. A major concern is the low total composition shown by analysis. The highest total obtained on the low cadmium material at 1500° F (816° C) is 34.51 percent when the metals are calculated as oxides. Three possible explanations were immediately apparent: moisture pickup, the use of separate filters for metals and for fluorine, and the possibility that the flux constituent of the fume contains material in addition to fluorine.

A study of moisture pickup was made by running blank tests (all test conditions duplicated without brazing filler metal or flux) to determine if the filter weight increased. It was found that a weight gain attributable to moisture did occur. For seven blank tests made at 45 to 48 percent relative humidity, the average weight gain was 0.0070 grams or about 0.12 percent. The application of a correction factor for moisture based on the blank runs was not sufficient to overcome the fume weight deficit in the analysis. For the example given, 34.51 percent would become 38.06 percent.

The addition of data from two samples to get a single analysis for the fume produced can lead to errors in absolute values. It is believed that fume produced under like conditions should have essentially the same composition and, therefore, can be used to show relative values of composition. The error introduced by this technique cannot account for the loss recorded.

The use of a more thorough analysis for other fume constituents and the form they take in the fume should eliminate an important portion on the losses recorded. An indication of the possibility of other important fume constituents was obtained and is covered later in this section of the report.

Gas Covered Melts

The data recorded in Table 3.4 for the atomic absorption analysis of fume from brazing filler metals protected by a blanket of flowing CO₂ are questionable. The trends noted in the total fume and the flux covered melt analytic data are not evident in Table 3.4. The low cadmium filler metal appears to produce a higher cadmium fume than BAg-1. This is the opposite of other results. Also, the data show the greatest cadmium concentration in the fume from the filler metals tested at 1350° F (732° C). These observations and the very low recovery for the BAg-1, 1500° F (816° C) tests lead to a concern for the validity of all the data.

Discussion of Analytical Data

The experiences gained from the work covered by this report permit a number of suggestions to be made to those who may initiate future brazing fume studies, particularly studies whose objective is to compare characteristics of different filler metals.

124/FUMES AND GASES

Table 3.3
Composition of fumes from flux covered filler metals covered with AWS Type 3A flux

Element	1200° F (649° C)			1250° F (677° C)		
	BAg-1 filler metal			Low cadmium filler metal		
	Fume wgt., g	Element wgt., g	% as element	Fume wgt., g	Element wgt., g	% as element
Cadmium	0.0821	0.000320	0.39	0.1035	0.000110	0.11
Copper	0.0821	0.000008	0.01	0.1035	0.000010	0.01
Zinc	0.0821	0.000023	0.03	0.1035	0.000020	0.02
Fluorine-total	0.0453	0.000420	0.93	0.0198	0.000870	4.39
Fluorine-soluble	0.0453	0.000120	0.26	0.0198	0.000150	0.76
1350° F (732° C)						
Cadmium	0.0802	0.000390	0.49	0.0332	0.000240	0.72
Copper	0.0802	0.000008	0.01	0.0332	0.000010	0.03
Zinc	0.0802	0.000019	0.02	0.0332	0.000050	0.15
Fluorine-total	0.0645	---	---	0.0365	0.001800	4.93
Fluorine-soluble	0.0645	0.000330	0.51	0.0365	0.000250	0.69
1500° F (816° C)						
Cadmium	0.2809	0.007500	2.67	0.1269	0.002100	1.65
Copper	0.2809	0.000011	0.01	0.1269	0.000010	0.01
Zinc	0.2809	0.005450	1.94	0.1269	0.005200	4.10
Fluorine-total	0.0831	0.006400	7.70	0.0687	0.012100	17.61
Fluorine-soluble	0.0831	0.003200	3.85	0.0687	0.006800	9.90

*Sample destroyed during analysis procedure.

Notes:

1. Copper in blank filter shows 0.000007 g equivalent to 0.01 percent in the table. Thus, copper must be at a very low level in the fume.
2. Cadmium and zinc are found in the blank filter at a slightly lower level than copper.

(1) The small quantities of fume produced and its apparent extremely small particle size present problems in filter choice, chamber design, sample weight-analysis balance, and sampling environments. To minimize these problems, it is advisable to use a fume collection chamber with the least volume possible which can be made part of a closed system. The chamber should contain an inert or readily controllable atmosphere. Filters or fume collection media must be capable of collecting very fine particles ($<1\mu\text{m}$) and should be small enough to avoid masking of actual fume weights by large blank filter weights. Continuous sampling through an atomic absorption type of analytical system appears worthy of consideration instead of filter sampling systems.

(2) Attention to the details of actual filler metal melting and fluxing practices are also required. Melt sizes, quantities of flux used, exposed melt surface areas, and heating and cooling rates need attention. Melt size, particularly with respect to exposed areas, may alter

fume generation rate because of flux cover variation. Crucibles should be a metal which is wet by the filler metal to avoid flux collection around the melt. This implies combined weight determination that includes the crucible. Weighing exercises should include checks of flux losses in addition to filler metal losses. Ideally, all tests should begin in a cool chamber and heating furnace to minimize differences in heating and cooling rates. The closed chamber already suggested should eliminate any influence of humidity in the test area.

(3) Analytical procedures for fume analysis should be validated for the tests being conducted. An early phase of any analytical work should be directed toward determining the chemical character of the fume (metal, oxides, soluble, insoluble, etc.). Early analytical work should include complete analyses. Subsequent analysis requirements may be relaxed when all the data are collected.

Application of these suggestions and others that may

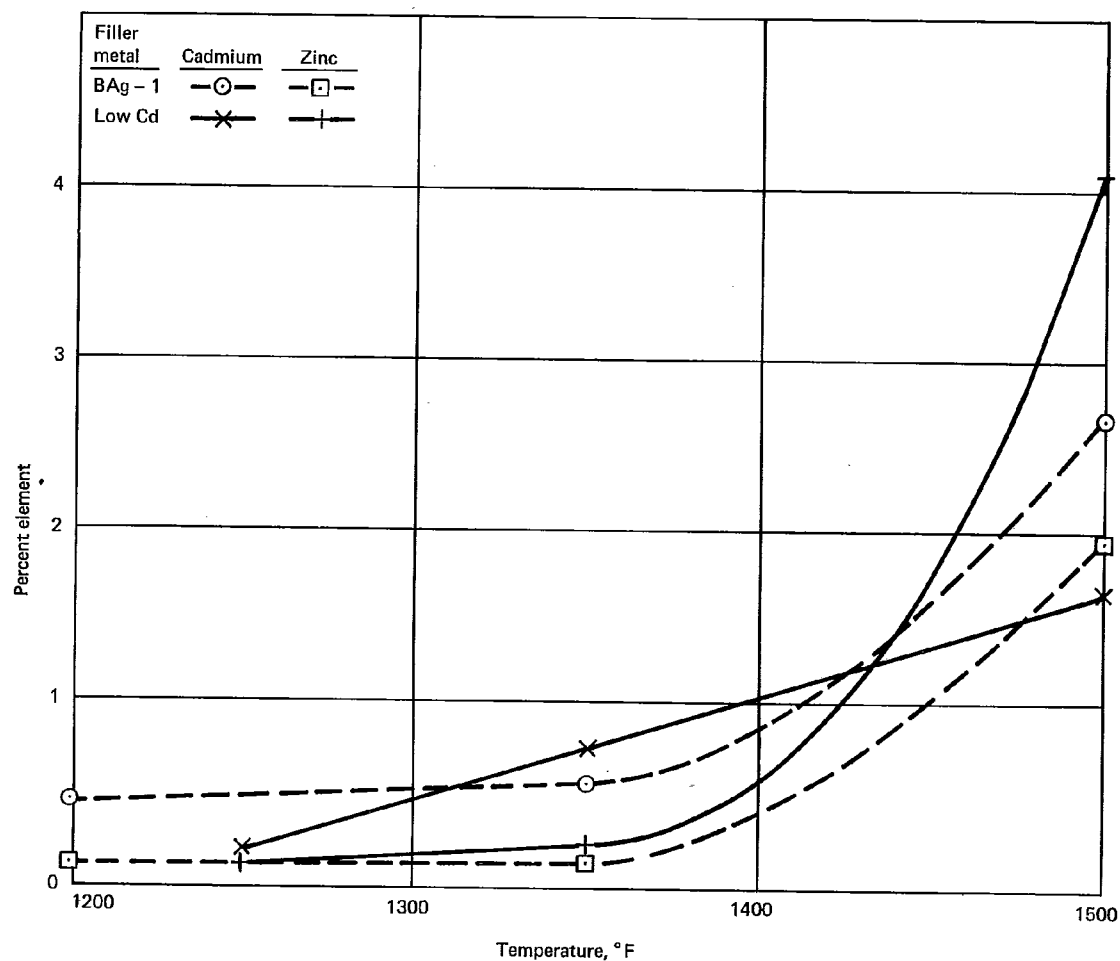


Fig. 3.6—Composition of fumes from flux covered brazing filler metals

occur to the researcher may produce more convincing data on the fumes produced by brazing filler metal usage than were obtained in this study.

Possible sources of error in the analytical data, moisture, and test result combining were discussed previously. In addition, it was not feasible in the present program to identify the form taken by fluorine or the other elements in the flux when they became fume. Such information, if available, could add significantly to the recovery picture. No explanation of the poor recovery recorded on analyses of the fume from gas protected melts is apparent, except for the possibility that brazing fume particle size was too small to be collected on the membrane filter. No data were collected or are known on the particle sizes found in brazing fumes.

An effort was made to find possible causes of low analytical recovery by analyzing selected filters spectrographically. In this way a complete elemental identification and a semiquantitative composition were found for fume generated at 1350°F (732°C) by each filler metal when melted with or without a flux cover. The results are shown in Table 3.5. The compositions are given in milligrams which constitute a quasi-quantitative (± 50 percent or better) analysis of the fume and the filter. The data show the same discrepancy noted in the atomic absorption analyses. When the filter blank composition is subtracted, the remaining components fail to account for all fume that was measured gravimetrically.

A further analytical check was made for ammonium salts not detectable by atomic absorption or emission

Table 3.4
Composition of fumes from CO₂ covered brazing filler metal

Element	1200° F (649° C)			1250° F (677° C)		
	BAG-1 filler metal			Low cadmium filler metal		
	Fume wgt., g	Element wgt., g	% as element	Fume wgt., g	Element wgt., g	% as element
Cadmium	0.0639	0.000090	0.14	0.0483	0.000260	0.54
Copper	0.0639	0.000008	---	0.0483	0.000020	0.04
Zinc	0.0639	0.000013	0.02	0.0483	0.000020	0.04
1350° F (732° C)						
Cadmium	0.0805	0.000230	0.29	0.0177	0.000840	4.75
Copper	0.0805	0.000009	0.01	0.0177	0.000010	0.06
Zinc	0.0805	0.000330	0.41	0.0177	0.000070	0.11
1500° F (816° C)						
Cadmium	0.5127	0.000150	0.03	0.1154	0.002900	2.51
Copper	0.5127	0.000007	---	0.1154	0.000020	0.02
Zinc	0.5127	0.000020	---	0.1154	0.005200	4.50

spectroscopy. Filters were leached and analyzed for NH₃, Cl, SO₄, and NO₃. Although the results were not "finely tuned," they showed that such salts were not part of the fume.

Ingot Composition and Weight Changes

A record of ingot weight losses and the composition of the residual ingot was developed to evaluate the possibilities of rating brazing filler metal fuming characteristics without resorting to the more complex fume collection and analysis procedure. The ingot weight loss expressed in percent and the final composition of the ingots analyzed are given in Tables 3.6 and 3.7.

The ingot weight losses are quite small and appear nearly independent of the type of melt cover at either 1200, 1250, or 1350° F (649, 677, or 732° C). At 1500° F (816° C), the CO₂ cover seems more protective than the brazing flux. This is probably a manifestation of the formation of a protective dross, as mentioned in a previous section of this report. The ingot loss trends are the same as recorded for fume generation characteristics.

On the basis of the results recorded, the measurement of ingot metal loss would be a dubious procedure. Although the data show less metal loss for the low cadmium filler metal, the difference is not great enough for such an estimation except at 1500° F (816° C).

Comparative atomic absorption analysis for filler metal composition before and after melting is not feasible as a procedure for measuring metal in the fume. All the

analytical data in Tables 3.6 and 3.7 are too close to the initial composition and within the limits of experimental error.

Discussion

A study was made to develop information on the fuming characteristics of two widely different silver-base brazing filler metals when used properly and improperly. The methods used were based on the best judgment of a committee of brazing experts, the experience of Battelle in similar fusion welding studies, and the availability of equipment used in welding studies.

The results of the study verify the trends that might have been derived intuitively from the materials and test conditions used:

(1) Increasing the temperature increases the amount of fume.

(2) Metal analysis of the fume depends upon the filler metal composition.

(3) Fluxes, when they are used, are a major contributor to the fume produced (see Table 3.3).

Beyond demonstrating trends, the data collected are of questionable value due to their erratic nature. More thorough analysis of the fume would be expected to provide some additional conclusions, especially in the case of tests made with fluxes.

In the following paragraphs, the procedures and meth-

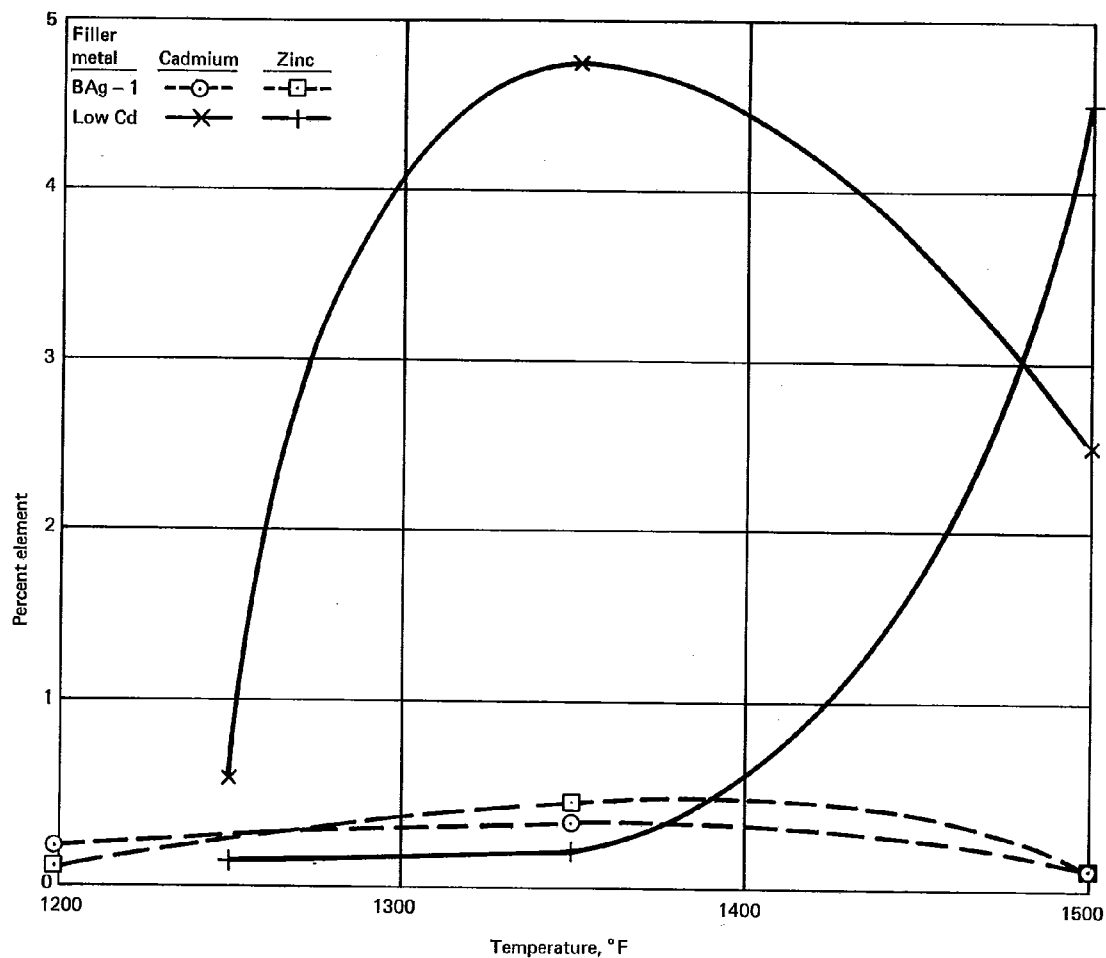


Fig. 3.7—Composition of fumes from CO₂ covered brazing filler metals

ods used in the study are discussed to indicate how they would be changed in any future work. The results would undoubtedly provide much more convincing information than is now on hand.

Filler Metal Handling and Surface Protection

The boats used were pure alumina and were not uniform in inside dimensions. This caused a variation in surface area which, it is believed, contributed to another problem. A controlled weight of flux was used. Because of the variable surface area and the fact that the filler metal did not wet the boat, this permitted the flux to almost completely envelop the melt. It was observed that the envelope was seldom complete, and a window of bare filler metal surface occurred on most melts. Its size varied considerably, permitting easy vaporization of

some of the melt components in some tests and not in others. In addition, the surface area of flux was not constant, a condition that could lead to differing amounts of flux vapors in the fume.

Future studies should use metal boats of uniform size. The boat material should be wet by the filler metal, preventing inconstant envelopment by the flux of the filler metal melt. The flux quantity should be controlled so that a constant depth or a bare melt window of constant area is maintained.

A flowing "protective" gas blanket over the molten brazing filler metal surface does not provide adequate protection for quantitative measurement of fuming characteristics. The surface of the molten metal became covered with an "oxide" skin during the tests, which inconsistently inhibited the vaporization of melt constituents, producing inaccurate fume quantity measurements. If in new studies it is desirable to evaluate fuming

Table 3.5
Results of spectrographic analyses of fume samples collected at 1350° F (732° C)

Test no.	Filler metal	Melt cover	Fume weight, mg	All elements detected and calculated weight in the filter, mg																				
				Ca	Na	K	Al	Si	Mg	Fe	B	Ba	Zn	Cd	Ag	Cu	P	Mn	Pb	Cr	Sn	Ti	Ni	Sr
34	LC*	Flux	1057	400	80	200	40	40	20	12	40	2	4	40	1	10	4	2	1	4	2	2	1	1
28	BAG-1	Flux	865	400	80	600	15	40	20	12	40	2	12	80	1	10	4	2	1	4	2	2	1	1
29	BAG-1	CO ₂	923	400	40	80	20	40	20	12	8	2	80	250	0.4	10	4	2	1	4	1	2	1	1
55	LC	CO ₂	416	400	40	40	15	40	20	12	8	2	4	80	4	10	4	2	1	15	2	2	1	1
	Blank filter			400	20	20	8	40	20	12	2	2	2	<1	<0.1	10	4	2	0.4	4	0.5	1	1	1

*Low cadmium filler metal.

Table 3.6
Composition and weight changes due to melting under a flux

Blank analysis	BAG-1 filler metal	Low cadmium filler metal
	25.4 Cd, 16.5 Zn	7.02 Cd, 19.6 Zn
	1200° F (649° C)	1250° F (677° C)
Test number	7	48
Ingot weight loss, g	0.0495	0.0004
Percent weight loss	0.06	<0.01
Final cadmium content, %	25.9	6.93
Final zinc content, %	17.0	19.7
	1350° F (732° C)	
Test number	11	40
Ingot weight loss, g	0.0487	0.0413
Percent weight loss	0.06	0.05
Final cadmium content, %	25.6	6.94
Final zinc content, %	17.0	19.7
	1500° F (816° C)	
Test number	5	35
Ingot weight loss, g	0.1125	0.2275
Percent weight loss	0.13	0.28
Final cadmium content, %	25.2	6.95
Final zinc content, %	17.1	19.5

Table 3.7
Composition and weight changes due to melting under CO₂ cover

Initial blank analysis (atomic absorption)	BAG-1 filler metal	Low cadmium filler metal
	25.4 Cd, 16.5 Zn	7.02 Cd, 19.6 Zn
	1200° F (649° C)	1250° F (677° C)
Test number	10	50
Ingot weight loss, g	0.0301	0.0119
Percent weight loss	0.04	0.01
Final cadmium content, %	25.7	7.03
Final zinc content, %	17.0	19.4
	1350° F (732° C)	
Test number	6	45
Ingot weight loss, g	0.0495	0.0243
Percent weight loss	0.06	0.03
Final cadmium content, %	25.6	7.00
Final zinc content, %	16.9	19.6
	1500° F (816° C)	
Test number	2	37
Ingot weight loss, g	0.0795	0.1083
Percent weight loss	0.09	0.13
Final cadmium content, %	25.6	6.94
Final zinc content, %	16.7	19.5

130/FUMES AND GASES

characteristics from the free surface of a brazing filler metal, a closed, inert atmosphere system should be used.

Filter System

In the program reported here, filters with a relatively large (33 in.² or 21 290 mm²) surface area and weight (5.9 to 6.4 grams) were used because they fit the available fume collection system. Also, the quantity of fume to be expected from the filler metals at 1500°F (816°C) was not known initially. In practice, the fume quantities were small at 1500°F (816°C) and even smaller at lower temperatures. Thus, the accuracy of the weights measured was minimized because the ratio of the filter weight to the fume weight was high (generally between 60 to 1 and 120 to 1). In addition, the influence of moisture and outside dust pickup during the test was maximized by lack of large fume quantities.

Since brazing filler metals and fluxes of the type studied produce small quantities of fume, especially when used properly, the clean filter weight should be small. This should also be used in small chambers to minimize the air-gas flow required to trap all the fume.

In this study the filter pore size was 1.2 μ m; a smaller pore size filter would be more appropriate for collecting the amounts of fume evolved when brazing. Smaller pore sizes would assure greater confidence for collection of all the fume without concern for clogging the filter.

Test Chamber

The test chamber used for the brazing fume collection was large in comparison to the size of furnace and filler metal melt utilized. This is shown in Fig. 3.1. It was quite satisfactory for welding fume studies where large volumes of gases and fume are produced that require high flow rates through the filter.

A fume collection chamber for brazing fumes should be as small as permitted by the melting furnace used. The filter area and pumping rate should be commensurate with the chamber size.

Analytical Procedures

The atomic absorption procedures used in the work reported are accepted by industry and government alike for welding and brazing fume study. The previously discussed improvements in testing and sampling procedures should eliminate the analytical problems that were encountered. A broader analysis of the fume from tests made with fluxes would be required in any new study.

Summary of Part III

The data collected on the amount of fume produced by each of the two brazing filler metals studied at three dif-

ferent temperatures were averaged and are given in Tables 3.1 and 3.2. The data from these tables are shown graphically in Figs. 3.4 and 3.5. The average loss in weight of the ingots is also given along with other desirable data.

The major conclusions drawn from a study of the measurement information in the literature were:

(1) The cadmium oxide fume hazard has received much attention without significant study of the basic causes of the problem.

(2) The possibility of harmful fluoride concentrations is mentioned briefly. As in the case of cadmium, there is a dearth of useful information.

(3) Almost no information exists which can be used to define the brazing environment or the safe practices to be followed.

In this study the actual weight of fume produced was smaller than expected.

The data show a large increase in weight of fume produced at 1500°F (816°C) for both filler metals when compared to that produced at lower temperatures. This would be expected because cadmium boils at 1409°F (765°C) and zinc has high vapor pressure (approx. 300 mm of Hg) at the same temperature. The rate of fume formation at the two lower temperatures was nearly the same, but this rate increased significantly at 1500°F. The low cadmium filler metal appears to produce about one-third less fume than the BAg-1 filler metal.

The data in Table 3.2 summarize the fume formation attributes of the two brazing filler metals studied where they are "protected" by a flowing CO₂ gas blanket rather than a flux. The results parallel those obtained where a flux was used.

A significant difference is noted when the amounts of fume produced by the BAg-1 filler metal are compared to those from the low cadmium filler metal. In all cases, more fume was produced by BAg-1 under CO₂ gas than under a flux; the opposite was true for the low cadmium filler metal.

The ingot weight loss measurements follow the expected trend: that is, the greater losses occur at the higher temperatures. There is no direct relationship between the ingot weight loss and the weight of fumes produced.

The fume produced by the brazing filler metals tested was analyzed for cadmium, copper, zinc, and fluorine. The composition of the fume when the filler metals were melted under flux is given in Table 3.3. Table 3.4 contains the analysis of fume obtained when flowing CO₂ gas covered the melt. The data in Tables 3.3 and 3.4 are also shown graphically in Figs. 3.6 and 3.7.

The results of the study indicate these trends:

(1) Increasing the temperature increases the amount of fume.

(2) Metal analysis of the fume depends on the filler metal composition.

(3) Fluxes, when used, are a major contributor to the fume produced (see Table 3.3).