No Nickel Carbonyl Detected when Welding Stainless Steels or Nickel Alloys

Fume and gas analyses are presented for 36 combinations of welding processes, stainless steels, nickel alloys and shielding gases

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ABSTRACT. This comprehensive study was undertaken primarily to test the hypothesis that nickel carbonyl, $Ni(CO)_4$, is formed during welding. Thirty-six combinations of welding and cutting processes, base metals, and electrodes were tested under typical industrial conditions, emphasizing those combinations with the best chance of producing $Ni(CO)_4$. No significant concentration was found (0.2 parts per billion or less) despite the confirmed presence of carbon monoxide (CO) in the gas and nickel in the fume. Adsorption and possible decomposition prior to the gas analysis were investigated, but the results did not weaken the conclusion that no carbonyl was formed. Fume quantities and analyses are presented for the full range of processes, including various chromium species in selected cases.

Introduction

The suspected or alleged formation of $Ni(CO)_4$ during the welding of steels and alloys containing nickel has been reported in the literature. For example, $Ni(CO)_4$ was reported as the suspected toxic agent in an incident involving illness resulting in the death of one person and hospitalization of 24 others, following exposure to welding fumes in confined spaces (Refs. 1, 2). Subsequent unpublished investigation, including autopsy of the deceased, showed that the death was not related to occupational exposure. Reference 3 stated, "The welding of high-nickel-content metal provides an opportunity for the formation of nickel carbonyl." Reference 4 said that ". . . a significant exposure to nickel carbonyl is likely" when welding nickel alloys without adequate ventilation or respiratory protection. Reference 5 unequivocally stated that nickel carbonyl is produced by the welding of nickel alloys. Measurements to confirm the suspected or alleged formation of $Ni(CO)_4$ have seldom been attempted, largely because of the scarcity of analytical techniques that are sufficiently sensitive and readily available.

A Swedish study by Hallne and Hallberg (Ref. 6) investigated welding of cast iron with nickel electrodes. The reported carbonyl concentrations were at or below their detection limit of 20 ppb, even though they confirmed the presence of 60 to 100 ppm of CO, believed to have been generated from oil on the workpiece. Unpublished data from the INCO Ltd. carbonyl refinery in Wales showed no measurable $Ni(CO)_4$ (<0.05 ppb) via infrared spectrometry and gas/liquid chromatography. The materials welded by INCO varied from mild steel to Monel®[1] alloy, but details of these materials and the welding process were not recorded. Other authors (Refs. 7–10) have reported measurement of significant concentrations of $Ni(CO)_4$ generated from thermal cutting of stainless steels. However, a recent paper (Ref. 11) provides evidence that the response of the analytical procedures used for these measurements was almost entirely due to nickel in fine particles that penetrated the prefilters.

The present study was undertaken at INCO's Copper Cliff Nickel (carbonyl) Refinery by the refinery's technical group, because of its familiarity with $Ni(CO)_4$ and the availability of a continuous chemiluminescence analyzer capable of detecting 0.1 ppb of $Ni(CO)_4$ in air. This instrument is similar to the analyzers that are used to monitor the work atmosphere in the refinery.

[1]*Monel® is a trademark of the INCO family of companies.*

KEY WORDS

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Fume Generation Rates
Fume Desorption
Chromium (VI)
Health Hazard

Test Apparatus and Procedures

Fume-Collection Chamber and Sampling of Fume and Gas

The fume-collection chamber was fashioned after those described in earlier studies by AWS and Battelle Columbus Laboratories (Refs. 12, 13). Fumes were exhausted by a fan attached to the exit side of the filter holder. A glass fiber "absolute" filter (MSA CT75428) was used to collect fumes. Reference 11 presents evidence that filters are seldom, if ever, absolute. Two glove ports were provided to facilitate welding with and without filler metal.

Gas sampling for CO and $Ni(CO)_4$ analysis was normally done downstream of the filter. Additional gas samples within 15–25 cm (6–10 in.) of the arc were also taken.

Nickel Carbonyl Analysis

Analysis of minute traces of $Ni(CO)_4$ in air via its chemiluminescence with ozone in the presence of pure CO is described in Refs. 14 and 15. Development of this technique was undertaken at the University of Michigan with support from INCO Ltd. The technology was used by Thermo Electron (TECO®) to build commercial atmosphere-monitoring instruments for INCO Ltd., based on the TECO 12A NO/NOx analyzer. The original model, capable of detecting 0.1 ppb by volume of $Ni(CO)_4$ in air, was used in the present study for continuous analysis of gases extracted from the fume column. Calibration of the analyzer at 1.0 ppb was

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undertaken before and after each test series by diluting a gas standard of 1 ppm $Ni(CO)_4$ in CO, with air using rotameters. The gas standards are prepared by injecting liquid carbonyl with a microsyringe into a gas cylinder and pressurizing with CO to achieve the desired concentration. The mixture is checked by wet chemical analysis of a bromine/alcohol solution used to collect Ni from a measured volume of the gas.

CO Analysis

Continuous CO analysis of gases extracted from the fume column was performed using a Gastec® Model M1050 analyzer, capable of measuring CO in air in ranges from 0–100 and 0–500 ppm, with a quoted accuracy of ±5% of scale. The principle of the analysis is the electrochemical oxidation of CO and measurement of the electrolytic current. Calibration with a standard gas mixture (50 ppm CO in air) was performed prior to each test series.

Metals Analysis

Fume collected on the glass fiber filter was analyzed by dissolving the entire filter and analyzing the solution by inductively coupled plasma atomic emission spectrometry. Each sample represented 4 min of welding plus about 6 min of fume collection to clear the hood.

CO in Shielding Gas

A level of 4% CO in shielding gases for welding of high-nickel materials was included in the test procedures. This ensured the presence of CO at the arc, since it was not possible to predict how frequently and to what extent CO would be produced from oil on the base metal (Ref. 6), carbon in the weld materials, CO_2 in shielding gas, or CO_2 generated from flux.

Desorption of Nickel Carbonyl from Weld Fume

Since there was some concern that $Ni(CO)_4$ could adsorb on fume particles, perhaps to the extent that none would reach the carbonyl analyzer in filtered gases, desorption tests were performed. The collected fume and filter were immediately placed in a flask and heated in a nitrogen atmosphere. Any desorbed carbonyl would have been detected in a continuous sample of the nitrogen conveyed to the carbonyl analyzer. Filters and fume samples, collected a few hours (up to a day) previously, were deliberately exposed to known carbonyl concentrations in air in a flask, followed by similar desorption tests.

Chromium (VI) Analysis

Fume analyses initially included only total nickel, iron, cobalt and chromium. Since hexavalent chromium is generally considered to be the most toxic form of chromium, selected welding tests were repeated to determine the proportions of various species of chromium in the fume. Most of the fume for this analysis was collected in the same manner as previously described, while two small samples were simultaneously collected inside the hood using 37-mm Gelman DM Metricell® copolymer membrane filters. Soluble Cr(VI) in these samples was analyzed by leaching with sodium carbonate solution at room temperature, and insoluble Cr(VI) by leaching with hot 3% sodium carbonate/2% sodium hydroxide solution. (These analytical procedures are described in Ref. 16, and an important modification to stabilize Cr(III) is described in Ref. 17.)

Table 1—Approximate Metal Contents of Base Metals and Electrodes

	Metal Content (%)			
	Ni[a]	Fe	Cr	Cu
Base Metals				
Ni 200	99.5	2	–	0.13
INCONEL® Alloy 600	76	8	15.5	0.25
MONEL® Alloy 400	66.5	1.25	–	31.5
INCOLOY® Alloy 800	32.5	46	21	0.38
316 Stainless	10–14	~ 68	16–18	–
304 Stainless	8–12	~ 70	18–20	–
Electrodes				
Nickel 61	93	1	–	0.25
INCO-WELD® Welding Composition A	65–73	6–12	13–17	–
INCONEL® Alloy 182	63–72	6–10	13–17	0.5
INCONEL® Alloy 82	67	3	18–22	0.5
MONEL® Alloy 60N	62–69	–	–	29–36
MONEL® Alloy 190	62–68	–	–	27–33
NI-ROD® Weld rod 55	53	45	0	–
NI-ROD® Weld rod 44	44	45	–	–
ER 316	11.5	~ 67	19.5	
ER 308	9.5	~ 70	20	

(a) Some CO included in some cases.
Note: All trademarks indicated in the Tables are the property of the INCO family of companies; except as noted.

Results and Discussion

Fume Samples

Base metal and electrode compositions are given in Table 1. Table 2 lists the 36 tested combinations of welding processes, base metals, electrodes and shielding gases. Table 3 gives the weights of fume and metals and the peak concentrations of carbon monoxide and nickel carbonyl.

Agreement among the repeat tests is generally not very good, either in total fume weights or in metal content. Some of the factors contributing to this variability are: analytical accuracy for both total fume and components, particularly when fume generation is minimal; welding technique variability; and condition of electrode, particularly the tungsten electrode. Welding current, shielding gas flow, etc., were held as constant as possible for each combination of welding conditions, but the welding gun was hand held in all cases, undoubtedly contributing some variability, such as would normally occur in the workplace.

Total fume generation rates for the various welding processes, in ascending order, are: submerged arc (SAW), gas tungsten arc (GTAW), gas metal arc (GMAW), shielded metal arc (SMAW), air carbon arc cutting (AAC), plasma arc cutting (PAC), and flux cored arc (FCAW). Since the last three processes were tested, respectively, only for three, two and one sets of conditions, the relative fume generation rates shown should not be assumed to apply over a wider range of conditions. SMAW, FCAW and GMAW rates fit well within the ranges found for similar processes and materials in Refs. 13, 18, 19(a) and 19(b).

Others have published results showing relatively low fume generation for GTAW (Ref. 20) and high values for plasma arc cutting and welding (Ref. 21), consistent with this work. However, these particular references quote measurements of breathing-zone fume concentrations rather than generation rates so that no direct comparisons can be made.

Compositions of fumes for SMAW, GMAW and FCAW processes were compared with Refs. 13, 19(a) and 19(b) and found to be similar. It is interesting to

Table 2—Summary of Test Materials and Conditions

Case Number	Welding Process	Base Metal	Electrode or Filler Metal	Electrode Diameter (in.)	Current (A)	Shielding Gas
1	GTAW	Nickel 200	None	NA	130	He
2	GTAW	Nickel 200	None	NA	130	4.2% CO in He
3	GTAW	Nickel 200	Nickel 61	0.062	130	Ar
4	GTAW	Nickel 200	Nickel 61	0.062	120	4.2% CO_2 in Ar
5	GTAW	Nickel 200	Nickel 61	0.062	110	3.9% CO in Ar
6	GMAW	Nickel 200	Nickel 61	0.062	200	Ar
7	GMAW	Nickel 200	Nickel 61	0.062	210	4.2% CO_2 in Ar
8	GMAW	Nickel 200	Nickel 61	0.062	200	3.9% CO in Ar
9	GMAW	Cast Iron	NI-ROD®44	0.045	85	4.2% CO_2 in Ar
10	Arc Air Cutting	Nickel 200	AC Cu Coated Carbon	0.25	275	–
11	Plasma Arc Cutting	Nickel 200	NA	NA	100	N_2/CO_2
12	GTAW	INCONEL® 600	INCONEL®82	0.062	100	Ar
13	GMAW	INCONEL®600	INCONEL®82	0.062	200	Ar
14	SMAW	INCONEL®600	INCONEL®182	0.125	160	–
15	SAW	INCONEL®600	INCONEL®82	0.062	180	INCO FLUX®4
16	GTAW	INCOLOY®800	INCONEL®82	0.062	70	Ar
17	GMAW	INCOLOY®800	INCONEL®82	0.062	120	Ar
18	SMAW	INCOLOY® 800	INCO-WELD®A	0.125	160	–
19	GTAW	304 SS	ER 308	0.045	100	Ar
20	GMAW	304 SS	ER 308	0.045	100	Ar
21	SAW	304 SS	ER 308	0.045	100	U4S®(Union Carbide)
22	SMAW	304 SS	ER 308-16	0.125	140	–
23	GTAW	316 SS	ER 316-16	0.062	70	Ar
24	GMAW	316 S5	ER 316	0.062	200	Ar
25	SAW	316 SS	ER 316	0.062	170	U4S®
26	SMAW	316 SS	ER 316-16	0.156	160	–
27	Arc Air Cutting	316 SS	DC Cu Coated Carbon	0.156	230	–
28	Plasma Arc Cutting	316 SS	NA	NA	105	N_2/CO_2
29	GTAW	MONEL®400	MONEL®60N	0.062	100	Ar
30	GMAW	MONEL®400	MONELT 60N	0.062	200	Ar
31	SMAW	MONEL®400	MONEL®190	0.0937	100	–
32	Arc Air Cutting	MONEL®400	DC Cu Coated Carbon	0.156	230	–
33	SMAW	9% Ni Steel	INCO-WELD®A	0.125	160	–
34	SAW	9% Ni Steel	INCONEL®82	0.062	170	INCO-FLUX®4
35	FCAW	Cast Iron	NI-ROD®FC55	0.09	200	–
36	SMAW	Cast Iron	NI-ROD®55	0.125	160	–

note the low proportion of total SMAW and FCAW fumes accounted for as nickel, iron and chromium because of the large contribution of flux components. Surprisingly high chromium contents, in proportion to nickel and iron, were observed for some SMAW cases, especially 22 and 26, an important observation in view of the analyses for Cr(VI) reported below.

Gas Concentrations

The carbonyl detection limit for the analyzer used in this study is about 0.1 ppb, due to zero drift. However, results in Tables 3 and 4 include readings between 0 and 0.1, which were recorded anytime that the recorder chart pattern suggested something more than the usual random drift. The recorded number is an upper limit; no attempt was made to average the readings over the welding period. Note that in Table 3, of 32 nonzero readings, only four were above 0.1, and 12 were 0.1.

The maximum reading of 0.2 ppb (Case 28) is well below OSHA's PEL of 1 ppb and of little concern if compared to the American Conference of Governmental Industrial Hygienists TLV of 50 ppb. Attempts were made to confirm legitimacy of the positive readings. In some cases, a fourth test was run at a later date (triplicate tests were often run on the same day). Despite ostensibly identical conditions, positive readings were not repeated in Cases 26 and 31, but only in Case 18 (Table 3). A previously reported series of tests (Ref. 19(c)) was performed with the same facilities except that the ventilation rate through the hood was lower by a factor of about 13. The collected fume quantities were generally lower, presumably due to greater losses to the interior hood surfaces, and measured CO concentrations were at least five times higher. If $Ni(CO)_4$ had actually been present in the earlier tests, its concentration would have been similarly increased, but this was not the case.

Table 4 compares $Ni(CO)_4$ and CO concentrations measured in the hood exhaust with other samples taken inside the hood, within 15–25 cm of the arc. A small glass fiber absolute filter was placed over the analyzer sample probe to minimize interference or fouling due to particulate being drawn into the analyzers. Table 4 shows the trend in CO concentrations in the exhaust and near the arc with and without a filter in place at the hood outlet. Except for Case 6, for which no CO was detected under any conditions, the readings inside the hood were higher than those in the exhaust, regardless of whether or not the filter was in place. Also, the presence of the filter, which reduces the ventilation rate from approximately 5.7 to 3.8 m^3/min (clean filter), causes an increase in the CO concentration in the hood, due to the reduced dilution. No such trend is shown for $Ni(CO)_4$, again failing to confirm its presence.

As the flow rate through the hood dropped due to fouling of the filter (typically to 10% of the initial value within 2 min if fume generation was high), the expected trend of the gas concentrations would be a continuous increase during the welding period and a continuous decrease as the hood was subsequently cleared. This type of pattern was generally observed for CO, but carbonyl readings did not show any consistent pattern. Again, the absence of any trend with

decreasing dilution casts doubt on the presence of $Ni(CO)_4$.

In Table 3, the nonzero $Ni(CO)_4$ readings are often accompanied by significant CO readings, but not always. There are many cases with significant CO concentrations with no indication of $Ni(CO)_4$. Obviously, the presence of significant concentrations of the CO is necessary to produce $Ni(CO)_4$ and the lack of consistent correspondence between the CO and $Ni(CO)_4$ readings tends to suggest that the carbonyl readings are not legitimate.

Testing of plasma arc cutting of 304 stainless steel is reported in Ref. 11. A maximum $Ni(CO)_4$ reading of 0.4 ppb was reported. Evidence of particulate penetration of sample prefilters is also given. Since the analyzer actually measures the chemiluminescence of nickel oxide, it was postulated that the minor carbonyl readings obtained were a response to particulate. However, it is clear that the chemiluminescence method is relatively insensitive to particulate, as compared to methods that involve nickel analysis of impinger solutions or adsorbents. These include, as carbonyl, virtually all the nickel in any particles that have penetrated the prefilters.

The decomposition of $Ni(CO)_4$ in air was carefully studied by Hikade (Ref. 22). His findings were applied to conditions in this work to estimate to what extent $Ni(CO)_4$, if any were formed, could decompose before reaching the analyzer. Average gas residence time in the hood for the initial clean filter condition was about 15 s, and the lag time from the sampling probe to the analyzer detector was less than 10 s. In comparison, for a final $Ni(CO)_4$ concentration of 0.2 ppb, the Hikade data predict a possible range of half-life from about 3 min (30°C/86°F, 10 ppm CO) to 34 min (20°C/68°F 50 ppm CO). For lower ventilation rates due to filter blinding or the preliminary tests of this study (Ref. 19(c)), and for very low CO concentrations, the residence time in the hood could conceivably be greater than the half-life of any $Ni(CO)_4$. However, the sampling from within the hood (Table 4) virtually eliminated the lag time, at the same time confirming the presence of enough CO, in most cases, to stabilize any carbonyl present, even if the delay before analysis was several minutes.

CO concentrations reported in Tables 3 and 4 are, as in the case of $Ni(CO)_4$, not averaged over the welding period, but peak values observed normally around the end of the 4-min welding period, when dilution (ventilation rate) was at a minimum due to blinding of the filter in the hood exhaust. Significant CO concentrations were measured, somewhat unpredictably, but presumably arising from: CO or CO_2 in the shielding gas; covered electrodes that generate CO_2 and hence CO; the carbon electrode in air carbon arc cutting; oil or other contamination of the base metal; and/or carbon in the weld materials. No comprehensive literature search was done on the subject of CO in welding fumes. References 6 and 12 provide some information, the former with regard to oil on the workpiece and the latter with regard to CO generated from CO_2 in shielding gas. Reference 11 reports high CO concentra-

Table 3—Experimental Gas Concentrations, Fume Weights and Contained Metals

Case Number	Collected Fume[a] (mg)				Gases[b]	
	Ni	Fe	Cr	Total	CO (ppm)	$Ni(CO)_4$ (ppb)
1	10.1, 7.3, 6.2	1.4, 1.1, 1.1	<0.1, <0.1, <0.1	26, 26, 23	50, 30, 30, 0	0, 0, 0
2	229, 59, 475	1.5, 1.4, 1.3	<0.1, <0.1, <0.1	305, 91, 624	25, 0, 50	0, 0, 0
3	12.6, 15.2, 5.4	1.5, 1.6, 1.5	<0.1, <0.1, <0.1	26, 36, 27	13, 13, 13, 0	0, 0, 0
4	34, 27, 33	1.4, 1.2, 1.4	<0.1, <0.1, <0.1	80, 80, 76	13, 13, 25	0.14, 0.08, 0.07
5	4.9, 14.2, 9.7	1.2, 1.4, 1.4	<0.1, <0.1, <0.1	5.4, 18, 17	25, 38, 0	0, 0.05, 0.05
6	306, 276, 236	4.2, 3.6, 5.1	0.61, 0.25, 3.0	402, 374, 310	0, 0, 0	0, 0, 0
7	310, 320, 304	2.2, 1.6, 1.6	0.28, 0.10, 0.10	388, 408, 383	0, 0, 0	0, 0, 0
8	256, 274, 258	7.2, 1.7, 1.6	1.7, 0.21, 0.20	327, 351, 333	25, 13, 25	0, 0, 0
9	84, 108, 98	132, 156, 147	0.55, 0.36, 0.39	592, 655, 639	13, 0, 0	0, 0.02, 0
10	720, 1090, 790	62, 87, 23	11, 23, 4.5	1317, 1933, 1259	60, 100, 60	0, 0.1, 0.1
11	587, 1954, 2911	2.5, 221, 6.3	0.25, 0.73, 0.19	868, 3149, 3785	40, 0, 10	0.08, 0.06, 0.08
12	2.6, 0.73, 0.96	1.6, 1.1, 1.1	0.10, 0.10, 0.13	16, 12, 19	38, 63, 13, 0	0, 0, 0
13	136, −, 106	6.6, −, 5.6	57, −, 46	334, 319, 262	5, 0, 0	0, 0, 0
14	71, 77, 81	17, 20, 18	39, 37, 50	1238, 1268, 1468	13, 0, 5	0.1, 0.05, 0.05
15	1.0	1.4	0.3	9.3	0	0
16	0.46, 0.46, 1.34	1.3, 1.5, 1.7	0.13, 0.19, 0.32	9.2, 12.9, 14.5	0, 25, 25	0, 0, 0
17	81, 126, 117	4.3, 6.5, 5.8	21, 39, 36	236, 325, 338	0, 0, 0	0, 0, 0
18	112, 157, 162	18, 28, 28	56, 93, 84	673, 1370, 1294	0, 0, 5	0.1, 0.1, 0.15, 0.09
19	0.82, 0.58, 1.1	2.4, 2.1, 3.8	0.31, 0.32, 0.60	27, 15, 20	0, 0, 0	0, 0, 0
20	52, 61, 52	288, 352, 297	79, 95, 80	663, 749, 665	13, 13, 13	0, 0, 0
21	0.6, 0.4, 0.3	4.8, 2.2, 1.8	1.5, 0.1, 0.2	31, 7, 6	0, 0, 0	0, 0, 0
22	8.6, 8.0, 6.8	76, 74, 66	81, 66, 62	923, 779, 782	0, 0, 0	0, 0, 0.05
23	0.55, 0.86, 0.44, 1.7	1.6, 1.4, 1.3, 1.6	0.13, 0.11, <0.1, 0.16	7.2, 11.8, 7.0, 18.5	13, 25, 13, 35, 0	0, 0, 0, 0
24	107, 36, 60	580, 197, 306	209, 91, 110	1416, 490, 668	0, 0, 13	0.05, 0, 0
25	1.0, 1.2, 0.7	6.7, 6.5, 4.9	2.3, 1.9, 1.5	60, 53, 47	0, 0, 0	0, 0, 0
26	11.5, 10.4, 10.5	109, 102, 86	89, 85, 65	1496, 1486, 1446	25, 25, 13, 0	0.1, 0.1, 0.1, 0
27	167, 282, 210	220, 213, 251	68, 57, 67	815, 980, 923	0, 0, 0	0, 0, 0
28	95, 160, 118	554, 840, 796	174, 257, 253	1720, 2405, 2343	0, 40, 40	0, 0.2, 0.2
29	2.5, 1.7, 0.5	4.1, 3.1, 3.2	0.53, 0.22, 0.24	6.2, 1.9, 2.9	0, 0, 0	0.1, 0, 0
30	105, 86, 76	3.9, 4.2, 5.0	0.33, 0.51, 0.29	347, 222, 235	0, 0, 0	0, 0, 0
31	27, 38, 41, 50	1.9, 2.6, 2.7, 2.8	0.1, 0.1, <0.1, 0.1	496, 765, 852, 992	0, 0, 13, 13	0.05, 0.05, 0.03, 0
32	333, 267, 485	62, 30, 76	15, 5.9, 16	1161, 928, 1411	0, 0, 0	0, 0, 0
33	133, 197, 128	40, 72, 51	50, 71, 47	1293, 1715, 1106	3, 3, 0	0, 0, 0.1
34	0.4, 0.4, 0.5	1.2, 1.5, 1.4	<0.1, <0.1, <0.1	0.5, 1.1, 2.5	0, 0, 0	0, 0, 0
35	158, 169, 201	144, 172, 190	0.3, 0.4, 0.4	3361, 2808, 2864	0, 0, 0	0.1, 0.1, 0
36	59, 19.5, 27	131, 52, 71	0.70, 0.36, 0.54	1169, 506, 1000	6, 6, 6	0, 0, 0

(a) Collected in 4 min of arc time and six additional minutes for clearing the hood.
(b) Peak values observed.

Table 4—Gas Analyses 15–25 cm from the Arc

Case Number	Welding Process	Base Metal	Electrode	Shielding Gas	Sample Location	Filter[a] at Hood Outlet	CO (ppm)	$Ni(CO)_4$ (ppb)
6	GMAW	Nickel 200	Nickel 61	Ar	Hood exhaust	Yes	0	0
6A	GMAW	Nickel 200	Nickel 61	Ar	Near arc	No	0	0
7	GMAW	Nickel 200	Nickel 61	4.2% CO_2 in Ar	Hood exhaust	Yes	0	0
7A	GMAW	Nickel 200	Nickel 61	4.2% CO_2 in Ar	Near arc	No	5	0
7B	GMAW	Nickel 200	Nickel 61	4.2% CO_2 in Ar	Near arc	Yes	21	0
8	GMAW	Nickel 200	Nickel 61	3.9% CO in Ar	Hood exhaust	Yes	21	0
8A	GMAW	Nickel 200	Nickel 61	3.9% CO in Ar	Near arc	No	35–70	0
14	SMAW	INCONEL®600	INCONEL®182	—	Hood exhaust	Yes	6	0.07
14A	SMAW	INCONEL®600	INCONEL®182	—	Near arc	No	10	0
14B	SMAW	INCONEL®600	INCONEL®182	—	Near arc	Yes	54	0.06
31	SMAW	MONEL®400	MONEL®190	—	Hood exhaust	Yes	6	0.03
31A	SMAW	MONEL®400	MONEL®190	—	Near arc	No	13	0

(a) Filter causes reduced ventilation rate. See text.

Table 5—Desorption Tests

Test No.	Process Generating Fume on Filter	$Ni(CO)_4$ Concentration Used to Treat Fume Sample	Maximum Desorption Gas Temperature (°C)
1	GMAW, Ni 200, Ni 61, 4.2% CO_2 in Ar	None	83
2	GMAW, Ni 200, Ni 61, 4.2% CO_2 in Ar	50 ppb	78
3	GMAW, INCOLOY® Alloy 800, INCONEL® Weld Rod 82, Ar	20 ppb	38
4	GTAW, INCOLOY® Alloy 800, INCONEL® Weld Rod 82, Ar	20 ppb	50
5	GMAW, Ni 200, Ni 61, 4.2% CO_2 in Ar	1500 ppb	37

tions from 250 to >500 ppm from the plasma arc cutting of 304 stainless steel with CO_2 shielding gas.

Fume Desorption Tests

All the desorption tests outlined in Table 5 resulted in no indication of desorbed $Ni(CO)_4$ (<0.1 ppb), even when the fume sample was treated with gas containing 1500 ppb $Ni(CO)_4$. These results may be attributed to any of the following assumptions:

1) Carbonyl does not adsorb on welding fumes or the glass filter.

2) It is destroyed (oxidized) simultaneously as adsorbed (in air) on the active surface.

3) It is destroyed (decomposed) as it is desorbed in nitrogen.

4) Conditions were not severe enough to desorb it.

Assumption 1 is considered unlikely because of the large surface area available, and the known strong adsorption of carbonyl on other surfaces.

Assumption 2 is plausible, since the rapid homogeneous oxidation of $Ni(CO)_4$ in air has been carefully studied (Ref. 22), and more rapid heterogeneous oxidation on any active surface in the presence of oxygen would be expected.

Assumptions 3 and 4 are not consistent with carbonyl refinery experience, which shows that carbonyl adsorbed, in a CO atmosphere, onto carbonylation residue or alumina adsorbent can be readily desorbed with heat and detected even in air, and at temperatures lower than those used on the welding fumes.

A very small ratio of adsorbed $Ni(CO)_4$ to fume weight would be of interest, one part per thousand on 2 g of fume being equivalent to about 40 ppb in the fume column, if an average ventilation rate of half the initial value of 3.8 m^3/min is assumed (*i.e.*, 2 mg of $Ni(CO)_4$ in 7.6 m^3 of fume column gases). Note, however, that greater than 99.7% adsorption would have to occur in a few seconds in order for the carbonyl vapor not to be detectable (<0.1 ppb) even when gas samples are extracted prior to the exhaust filter. Deliberate attempts to saturate fume samples (desorption tests 2 to 5) should have produced higher loadings than postulated above, perhaps approaching those experienced in the refinery operations, the only differences being the nature of the adsorbents and the fact the welding fume was exposed to carbonyl in air, not in CO.

Conclusive answers to the adsorption question would require more sophisticated measurements such as gravimetric measurements of adsorbate on to or off the absorbent, or desorption into a solution which would not dissolve other nickel species. However, it is not likely that there is enough adsorbed carbonyl to contribute a significant health hazard to the welding fumes.

Chromium (VI) in Fume Samples

Special chromium test results are given in Table 6. Total fume and chromium contents for the samples collected on the

Table 6—Chromium (VI) in Fume

Case Number	Welding Process	Base Metal	Electrode	Shielding Gas or Flux	Total Fume (mg)	% Total Chromium in Fume	% Chromium (VI) in Fume Soluble	Insoluble	Total
20	GMAW	304	ER 308	Ar	613	11.1	—	—	0.14, 0.46
21	SAW	304	ER 308	U4S®	6.4	12.2	—	—	<0.1
22	SMAW	304	ER 308-16	—	1159	4.8	2.8, 3.3	0.011, 0.013	2.9, 3.3
24	GMAW	316	ER 316	Ar	433	11.1	—	—	0.16, 0.39
26	SMAW	316	316L-16	—	930	5.9	2.0, 4.2	0.15, 0.002	2.1, 4.2

hood exhaust filter were similar to the corresponding results reported in Table 3. Small samples, collected for Cr (VI) analysis in parallel with each of the main samples, were analyzed separately, and the individual results are shown in the table. As expected, a high proportion (more than half) of the Cr in the SMAW fumes was in the hexavalent form. Most of it was soluble because of the presence of alkali metals in the electrode coating. The percentage of hexavalent Cr in the GMAW fumes was an order of magnitude less, although total Cr was greater. No Cr (VI) was detected in the SAW fumes but the sample was extremely small. Precision in these tests, as indicated by comparing the two samples for each case, was not good due to the difficulty of weighing and analyzing the small samples of fume. However, the accuracy is sufficient to clearly show this important difference between the GMAW and SMAW processes.

Moreton, *et al.* (Ref. 19(b)), quote 4% Cr (VI) in SMAW fumes from welding of Type 316 stainless steel, and 5% total Cr. The same reference also reports negligible (0.2%) Cr (VI) in 316 stainless GMAW fume, which contained a total of 13.4% Cr. These results are very similar to those in Table 6. Malmqvist, *et al.* (Ref. 19(a)), report 50% of the 3.4% total Cr in SMAW stainless steel fumes to be soluble Cr (VI). Coenen, *et al.* (Ref. 20), report that workplace measurements for SMAW fumes averaged 40% of Cr as chromate, with 10% of the samples showing all Cr as chromate. The proportion of Cr as Cr (VI) for GTAW and GMAW processes was much lower but more variable.

Conclusions

1) No significant concentration of nickel carbonyl occurred in fume column gases for the entire range of conditions studied, the greatest reading being 0.2 ppb.

2) Desorption tests provided strong evidence that any nickel carbonyl present would, if in contact with fume particles, be destroyed by air oxidation rather than be stabilized by adsorption.

3) In ascending order, the fume generation rates of the various welding processes are as follows: SAW, GTAW, GMAW, SMAW, arc air cutting, plasma arc cutting, and FCAW, with some overlapping of the ranges.

4) The metallic fractions of the fumes from SMAW and FCAW are much lower than for the other processes because of the large contribution of flux components.

5) Soluble chromium (VI) in SMAW fumes from stainless steel was much higher than in GMAW fume.

6) Significant concentrations of carbon monoxide can occur under a variety of welding and cutting conditions.

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