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Monitoring of chromium and nickel in biological fluids of stainless steel welders using the flux-cored-wire (FCW) welding method

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Abstract Objective: This study was undertaken to investigate the exposure to chromium (Cr) and nickel (Ni) in flux-cored wire (FCW) welders welding on stainless steel (SS). **Method/design:** Seven FCW welders were monitored for 3 days to 1 workweek, measuring Cr and Ni in air, blood, and urine. The welders were questioned about exposure to Cr and Ni during their whole working careers, with emphasis on the week of monitoring, about the use of personal protective equipment and their smoking habits. **Results:** The air concentrations were mean $200 \mu\text{g}/\text{m}^3$ (range 2.4–2,744) for total Cr, $11.3 \mu\text{g}/\text{m}^3$ (<0.2–151.3) for Cr^{VI} , and $50.4 \mu\text{g}/\text{m}^3$ (<2.0–416.7) for Ni during the workdays for the five welders who were monitored with air measurements. The levels of Cr and Ni in biological fluids varied between different workplaces. For Cr in whole blood, plasma, and erythrocytes, the mean levels after work were 1.25 (<0.4–8.3) and 1.68 (<0.2–8.0) and 0.9 (<0.4–7.2) $\mu\text{g}/\text{l}$, respectively. For Ni most of the measurements in whole blood and plasma were below the detection limits, the mean levels after work being 0.84 (<0.8–3.3) and 0.57 $\mu\text{g}/\text{l}$ (<0.4–1.7), respectively. Mean levels for Cr and Ni in the urine after work were 3.96 (0.34–40.7) and 2.50 (0.56–5.0) $\mu\text{g}/\text{g}$ creatinine, respectively. **Conclusion:** Correlations between the Cr^{VI} levels measured in air and the levels of total Cr in the measured biological fluids were found. The results seem to

support the view that monitoring of Cr in the urine may be versatile for indirect monitoring of the Cr^{VI} air level in FCW welders. The results seem to suggest that external and internal exposure to Cr and Ni in FCW welders welding SS is low in general.

Keywords Hexavalent chromium · Chromium · Nickel · Blood · Urine · Work atmosphere · Welding · Flux-cored wire (FCW) · Flux-cored arc welding (FCAW) · Biological monitoring

Introduction

The flux-cored-wire welding method (FCW) (in the USA, flux-cored arc welding [FCAW]) has been applied on a larger scale for 10–15 years. The present study was performed as part of a study on biological monitoring of welders welding on stainless steel (SS). The FCW method is quite similar to the metal inert gas (MIG) and metal active gas (MAG) welding methods except that welding is carried out by the use of a continuous metal wire electrode. Self-shielded tubular electrodes often contain barium carbonate or barium fluoride. They do not need a shield gas, but for flux-cored wires not containing gas-forming compounds, a shield gas must be used. Both carbon dioxide (CO_2) and argon-rich gas mixtures are used (Antonini 2003). To our knowledge, no published investigations on biological monitoring of welders using this method have appeared. However, Zober et al. (1985) did a corresponding study without examining FCW welders.

The aim of the present study was to investigate the possible relationships between nickel (Ni) and chromium (Cr) (Torgrimsen 1982) concentrations in the work atmosphere generated by welders welding SS and those of the biological fluids of these welders when using the FCW welding method.

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Material and methods

The male subjects examined in this study were selected among welders who welded on SS and used the FCW method. The participants were chosen among those welders who used this method only during the week of monitoring. Whenever possible, each participant in this study was followed for 1 entire week of work, from Monday through Friday. During this week, air samples were collected from the individual welder's breathing zone and from the work atmosphere in the workshop during the whole workday. The air samples were analyzed for total dust, iron, manganese, Ni, and total Cr, as well as Cr^{VI} (Karlsen et al. 1994, 1996).

Seven FCW welders were included in the study, of whom five were followed with whole-day air measurements. Four of these seven FCW welders wore air-stream helmets, and three used no personal airway protection. Three had access to local suction at their workplace and used it 50–100% of the welding time.

Six FCW welders were current smokers and had smoked for 15–42 (mean 26) years, smoking between 10 and 25 cigarettes a day. One had stopped smoking 9 years ago. Their mean age was 43 years (range 30–62). They had started welding 4–28 years ago (mean 19 years) and had welded SS for 0–19 years (mean 7 years).

One welder monitored for 2 days welded inside an SS tank, 4 m diameter and 7 m high, 1 m from the ceiling, inside a factory. The only ventilation inside the tank was outside air blown into the tank. Six welders welded in three different shipyards. In all these shipyards, other welders welded with other methods in the same room. These six FCW welders welded in workshops in which concurrent MIG/MAG welding was performed. One participant also welded in a room in which another welder performed manual metal arc (MMA) welding.

Each participant completed a comprehensive questionnaire on individual welding history and on welding methods applied during the study week, the previous month, and the previous year. They were also asked about their first year of welding and their first year of welding on SS, as well as the duration of SS welding in their career. They were also asked in detail about their duration and intensity of smoking. The individual use of personal protective equipment and the use of consumable welding material were recorded throughout all days of monitoring.

Referent subjects were selected from fellow workers, matched to age, gender, and smoking habits. Only subjects who had never welded or grinded SS were accepted as referents. Most referent subjects were white-collar workers, some working in the same company and some in other trades. The referent subjects were asked the same questions as the welders regarding smoking habits and work history.

To minimize the inconvenience of blood sampling, blood was sampled before and after work on Monday,

Wednesday, and Friday of the monitoring week. From the referent subjects, blood samples were taken only once or twice (Stridsklev et al. 1993, 1994).

Each day during the monitoring week a sample of the first morning urine was collected, a second sample was collected just before changing to working clothes, and a third sample was taken immediately after finishing work, always after personal washing and changing to private clothing. Chromium and Ni content was analyzed in whole blood and plasma. As Cr^{VI} is known to penetrate into cells (Langård et al. 1978), the Cr content was also analyzed in erythrocytes.

Chromium and Ni in these biological samples were analyzed by heated graphite furnace atomic absorption spectrophotometry (AAS) with Zeeman compensation according to methods reported previously (Angerer et al. 1985; Emmerling et al. 1990; Schaller and Zober 1982).

Urine samples were also analyzed for Cr and Ni by using the same analytical technique (Angerer et al. 1985). To correct for differences in fluid intake, the urinary values were related to the respective creatinine values (Araki and Aono 1989). To permit an analysis of the data, we chose to use "dummy" figures for nondetectable levels of Cr and Ni. For levels below the detection limits, the numbers were chosen at 50% of the respective level of detection. The detection limits during this study for Cr have varied between 0.3 and 0.5 µg/l in whole blood, between 0.1 and 0.4 µg/l in plasma, between 0.3 and 0.4 µg/l for erythrocytes, and between 0.1 and 0.3 for urine.

The detection limits for Ni were between 0.48 and 1.5 µg/l in whole blood, between 0.3 and 0.9 µg/l in plasma, and 0.3 for urine.

Statistical methods

The mean levels and ranges were calculated for total Cr and Ni in the urine, whole blood, and plasma, and for total Cr in the erythrocytes, for all subjects before and after work each day of the monitoring week. The levels of total Cr in the different body fluids were also tested for internal associations. The levels of total Cr in biological fluids were tested for correlation with the Cr^{VI} and with the levels of total Cr in air. The corresponding associations for the Ni levels in air and in biological fluids were also tested. The above associations were tested for the individual data whenever both air levels and biological levels were measured, as well as whenever twin sets of results from two or more biological fluids were present.

Results

All but one welder, who was followed for 3 days, were followed for 1 whole working week. The welders had been welding for 14–21 days the previous month and for 60–250 days the previous year. All but one subject, who

had used the MIG method, had mostly welded FCW the previous year.

For the five FCW welders who were monitored by air measurements, the levels of total Cr in the air were mean $200 \mu\text{g}/\text{m}^3$ (range 2.4–2,744). The Cr^{VI} levels were mean $11.3 \mu\text{g}/\text{m}^3$ (range <0.2–151.3). The Ni levels were $50.4 \mu\text{g}/\text{m}^3$ (range <0.2–416.7). The welder welding inside the tank of SS had the highest levels for all parameters.

Compared with the levels of Cr and Ni among the referent subjects, the levels for the FCW welders were somewhat higher. The mean concentrations of whole blood Cr in the referent subjects were $0.37 \mu\text{g}/\text{l}$ (range <0.3–1.5), $0.30 \mu\text{g}/\text{l}$ (range <0.1–2.2), and $0.33 \mu\text{g}/\text{l}$ (range <0.3–1.4) in whole blood, plasma, and erythrocytes, respectively. For Ni, the mean levels for the referent subjects were $0.66 \mu\text{g}/\text{l}$ (range <0.48–1.4) and $0.55 \mu\text{g}/\text{l}$ (range <0.2–2.2) in whole blood and plasma, respectively.

The mean blood concentrations of total Cr in the FCW welders after work were $1.25 \mu\text{g}/\text{l}$ (range <0.4–8.3), $1.68 \mu\text{g}/\text{l}$ (range <0.2–8.0), and $0.9 \mu\text{g}/\text{l}$ (range <0.4–7.2) in whole blood, plasma, and red cells, respectively. Two-thirds of the concentrations of Cr in the erythrocytes were below the detection limit. The corresponding Ni levels were mean $0.84 \mu\text{g}/\text{l}$ (range <0.8–3.3) and $0.57 \mu\text{g}/\text{l}$ (range <0.4–1.7) in whole blood and plasma, respectively.

Twenty-two out of 38 of the Ni concentrations in whole blood and 25/36 of those in the plasma were below the level of detection. The results suggested a slight increase in the blood Ni levels during the workweek (Table 1). Table 1 presents the mean Cr and Ni levels in blood over the whole exposure time for the FCW welders.

The urinary Cr concentrations for these seven welders measured during 1 week are shown in Table 2. The

mean levels of Cr in urine were 3.8 (range 0.48–18.0), 3.2 (range <0.24–30.1), and $3.96 \mu\text{g}/\text{g}$ creatinine (range 0.34–40.7) for first void, just before work, and just after work, respectively. The corresponding mean levels of and ranges of Ni from the first void, just before and after work, were $1.9 \mu\text{g}/\text{g}$ (1.05–5.59), 2.7 (1.11–4.37), and $2.5 \mu\text{g}/\text{g}$ creatinine (0.56–5.0).

Associations were observed between the concentrations of air Cr^{VI} and the levels of total Cr in the urine after work, as well as between the Cr levels after work and the first void in the morning ($P < 0.001$). Associations were also found between the Cr^{VI} levels in air the previous day and the levels of total Cr in urine measured in the first void in the morning as well as in the void just before the start of work. An association was also noted between the levels of total Cr in plasma after work and Cr^{VI} in air the same day ($P = 0.002$), as well as between the levels of total Cr in the plasma before work and Cr^{VI} in air the day before ($P = 0.02$).

There were also associations for the chromium levels before and after work between the different blood compartments as well as between plasma and urine. The association between whole blood and urine after work was <0.001; the same was found for the levels of red cells and urine before work. The associations between the increase in Cr levels during the day were generally not convincing (Table 3). No associations were found between the Ni levels in air and in the biological fluids. There were, however, statistically significant associations between the Ni levels in whole blood and plasma before and after work.

Discussion

The levels for Cr and Ni measured in the present small study among FCW welders were generally low. The re-

Table 1 Mean levels ($\mu\text{g}/\text{l}$) of chromium and nickel in whole blood, plasma, and erythrocytes in seven flux-cored-wire welders over the week of exposure

	Monday				Wednesday				Friday			
	Mean	Range	N	*	Mean	Range	N	*	Mean	Range	N	*
Chromium												
Whole blood												
Before work	1.54	<0.4–3.8	6	2	1.24	<0.4–3.9	7	2	1.33	<0.4–2.3	6	3
After work	0.56	<0.4–0.9	5	1	1.00	<0.4–2.7	7	3	2.00	<0.4–8.3	7	1
Plasma												
Before work	1.41	0.2–1.2	6		0.98	0.3–2.6	6		1.18	0.2–3.0	6	
After work	0.66	<0.2–1.1	5	1	1.70	0.2–6.0	7		2.41	0.3–8.0	7	
Red cells												
Before work	0.62	<0.4–3.2	6	4	0.30	<0.4–0.5	5	3	0.78	<0.4–1.6	5	3
After work	0.26	<0.4–0.6	5	4	0.28	<0.4–0.6	5	4	1.80	<0.4–7.2	7	4
Nickel												
Whole blood												
Before work	1.71	<0.8–5.9	6	3	0.78	<0.8–1.6	7	4	0.70	<0.8–2.0	6	4
After work	0.50	<0.8–1.3	5	5	0.81	<0.8–1.6	7	3	1.12	<0.8–3.3	7	3
Plasma												
Before work	1.36	<0.4–6.8	6	5	0.53	<0.4–1.3	6	4	0.42	<0.4–1.1	5	4
After work	0.50	<0.4–1.0	5	3	0.56	<0.4–1.7	7	5	0.64	<0.4–1.4	7	4

N number of measurements, * number of measurements below detection limit

Table 2 Mean levels of chromium and nickel and ranges in µg/g creatinine in urine in seven flux-cored-wire welders

	Weekday											
	Monday		Tuesday		Wednesday		Thursday		Friday		Monday	
	Value	<i>N</i>	Value	<i>N</i>	Value	<i>N</i>	Value	<i>N</i>	Value	<i>N</i>	Value	<i>N</i>
Chromium												
First void	2.71	2	1.22	4	3.46	4	4.04	4	7.89	3	0.41	2
Range	0.77–4.65		0.68–2.46		0.78–8.25		0.48–10.1		2.22–18		0.24–0.57	
Before work	0.50	4 ^a	2.74	4	2.44	5	6.99	6	1.51	4		
Range	< 0.24–1.0		1.03–5.89		0.71–6.63		0.41–30.1		0.54–2.46			
After work	1.33	5	3.91	6	4.57	6	7.25	7	1.73	6		
Range	0.34–2.79		0.66–14.5		0.50–11.6		0.37–40.7		0.36–3.83			
Nickel												
First void	1.21	2	2.07	4	2.27	4	2.87	4	3.20	3	5.02	2
Range	1.05–1.35		1.53–3.07		1.6–2.85		2.15–3.58		1.91–5.59		3.27–6.77	
Before work	2.29	4	2.78	4	2.51	5	3.34	6	2.50	4		
Range	1.11–2.92		1.95–3.09		1.61–3.33		2.00–4.37		1.46–3.81			
After work	1.64	5	1.95	6	2.77	6	2.81	7	3.13	6		
Range	0.56–2.78		1.64–2.64		1.77–3.53		1.00–5.00		1.87–4.73			

Days 1–5 are in the sampling week, and day 8 represents the following Monday
N number of measurements, ^aone individual result is below detection limit

sults show that FCW welding may result in exposure to Cr^{VI}, resulting in marked elevations of total Cr in the biological fluids monitored in this study. An association was observed between the Cr^{VI} levels in air and the levels of total Cr in the biological fluids monitored. Correlations were also observed between the Cr levels of the different blood compartments and the urinary levels of total Cr. These results seem to support the view that measuring the urinary levels of total Cr after work may

be useful for monitoring the uptake of Cr in welders, as was concluded in the study by Zober et al. (1985).

Because of the variability observed in the Cr concentrations in the present welders' biological fluids, further studies on the relationships between Cr in the air and the biological fluids of FCW welders are recommended. In this study, hardly any correlations were found between the daily levels of Cr and Ni in the air and the corresponding daily increase in the levels for

Table 3 Levels, regression (*R*), and *P*-values for chromium in biological fluids in flux-cored-wire welders during 1 workweek

	<i>N</i>	Mean chromium levels		<i>R</i>	<i>P</i>
Whole blood/plasma					
Before work	19	Blood (µg/l)	Plasma (µg/l)	0.666	0.002
After work	20	1.17	1.4	0.923	< 0.001
Mean increase	18	1.58	1.9	0.539	0.021
Whole blood/red cells					
Before work	17	Blood (µg/l)	Red cells (µg/l)	0.561	0.019
After work	17	1.06	0.84	0.957	< 0.001
Mean increase	15	1.15	0.90	0.004	0.989
Plasma/red cells					
Before work	17	Plasma (µg/l)	Red cells (µg/l)	0.920	< 0.001
After work	17	0.84	1.24	0.975	< 0.001
Mean increase	15	0.90	1.41	-0.436	0.104
Whole blood/urine					
Before work	16	Blood (µg/l)	Urine (µg/gC)	0.386	0.139
After work	19	1.41	3.3	0.965	< 0.001
Mean increase	15	1.22	4.5	0.569	0.029
Plasma/urine					
Before work	15	Plasma (µg/l)	Urine (µg/gC)	0.670	0.006
After work	19	1.5	3.1	0.807	< 0.001
Mean increase	14	1.6	4.5	0.738	0.003
Red cells/urine					
Before work	14	Red cells (µg/l)	Urine (µg/gC)	0.670	< 0.001
After work	16	0.88	3.1	0.256	0.339
Mean increase	12	0.51	1.9	0.256	0.421
		-0.05	1.07		

µg/gC µg/g creatinine, *N* number of measurements

blood and urine. Because the urinary values were found above the detection limit, it does seem as if urinary measurements are more versatile than all of the blood parameters for Ni in the air as well as for low air levels of Cr.

During the present research project, other welding methods were monitored: manual metal arc welding (MMA) (Stridsklev et al. 1993) and tungsten inert gas welding (TIG) (Stridsklev et al. 1994). As in the study of Zober et al. (Zober et al. 1985), the levels for Cr and Ni in TIG welders were low and comparable to those of unexposed referents.

The levels for Cr in air and in biological levels in MMA welders were higher in both studies, while the Ni levels were also relatively low for MMA welders.

In this study, the levels of Ni in biological fluids were at the same level or slightly higher for the FCW welders than for the MMA welders, and were rather lower for the FCW welders than for the TIG welders, perhaps with a slight exception for the welder inside the tank. The levels of Cr in air and in biological fluids were quite similar for the FCW welders and the MMA welders, except for the highly-exposed welder in the tank.

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