Supplementary material

Welding fume nanoparticles from solid- and flux-cored wires: solubility, toxicity and role of fluorides

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Content: Figures A1-A6; Tables A1-A7

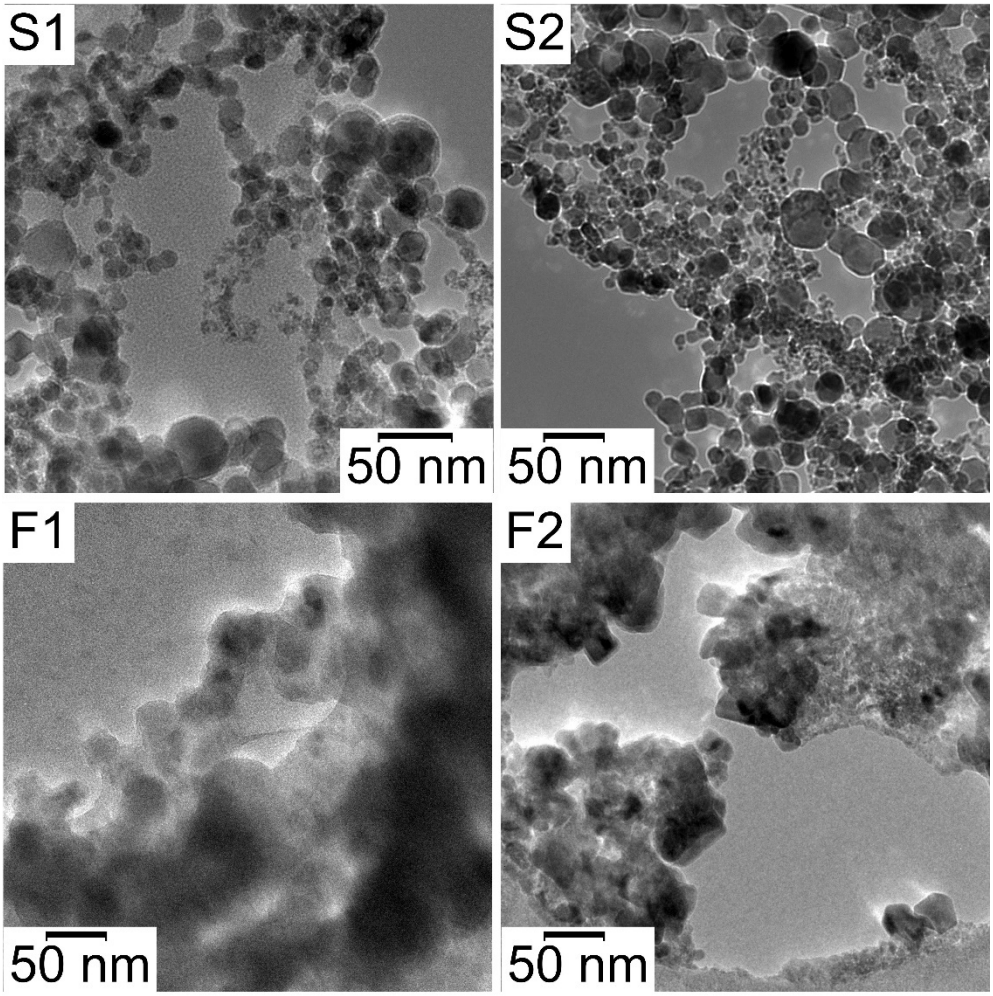

Figure A1. *Overview TEM images of the welding fume samples S1-S2 and F1-F2 (Solid wire: S1, S2 and flux core wire: F1 and F2).*

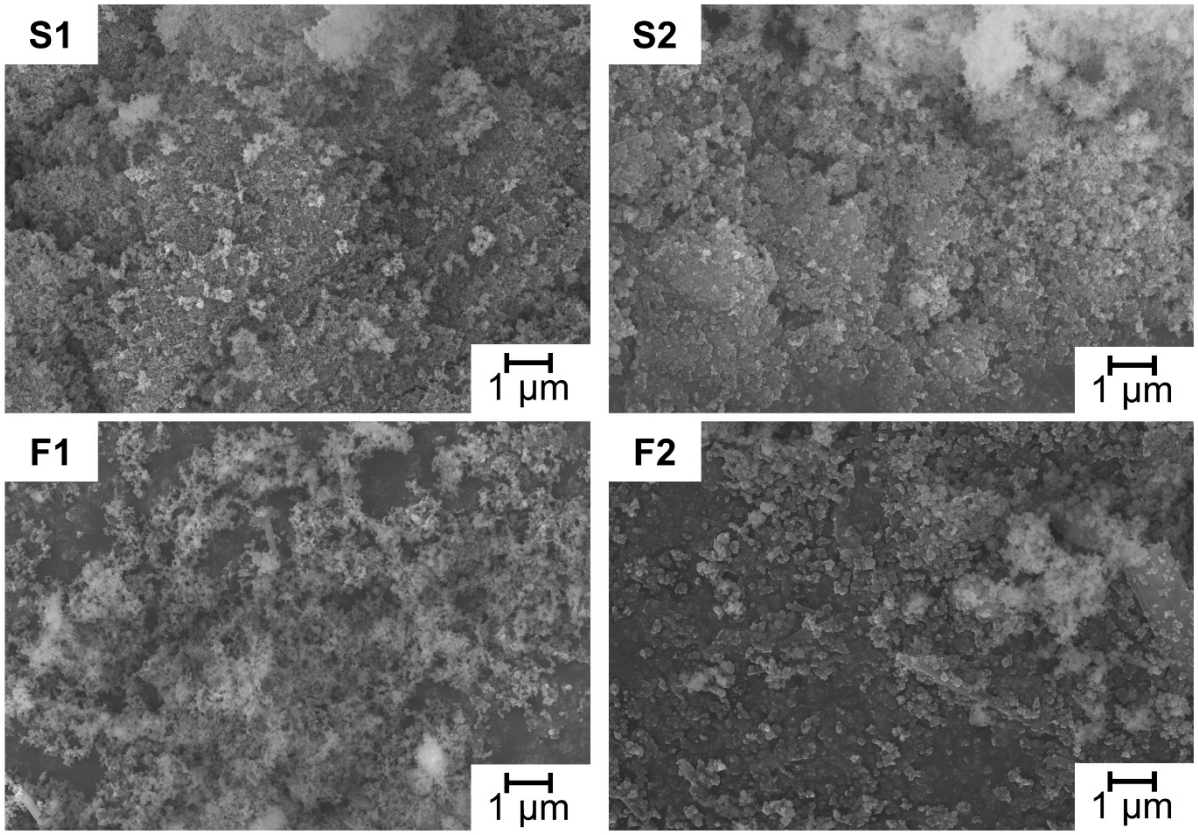

Figure A2. *SEM overview images (SE detection mode) of the welding fume samples (Solid wire: S1, S2 and flux core wire: F1 and F2).*

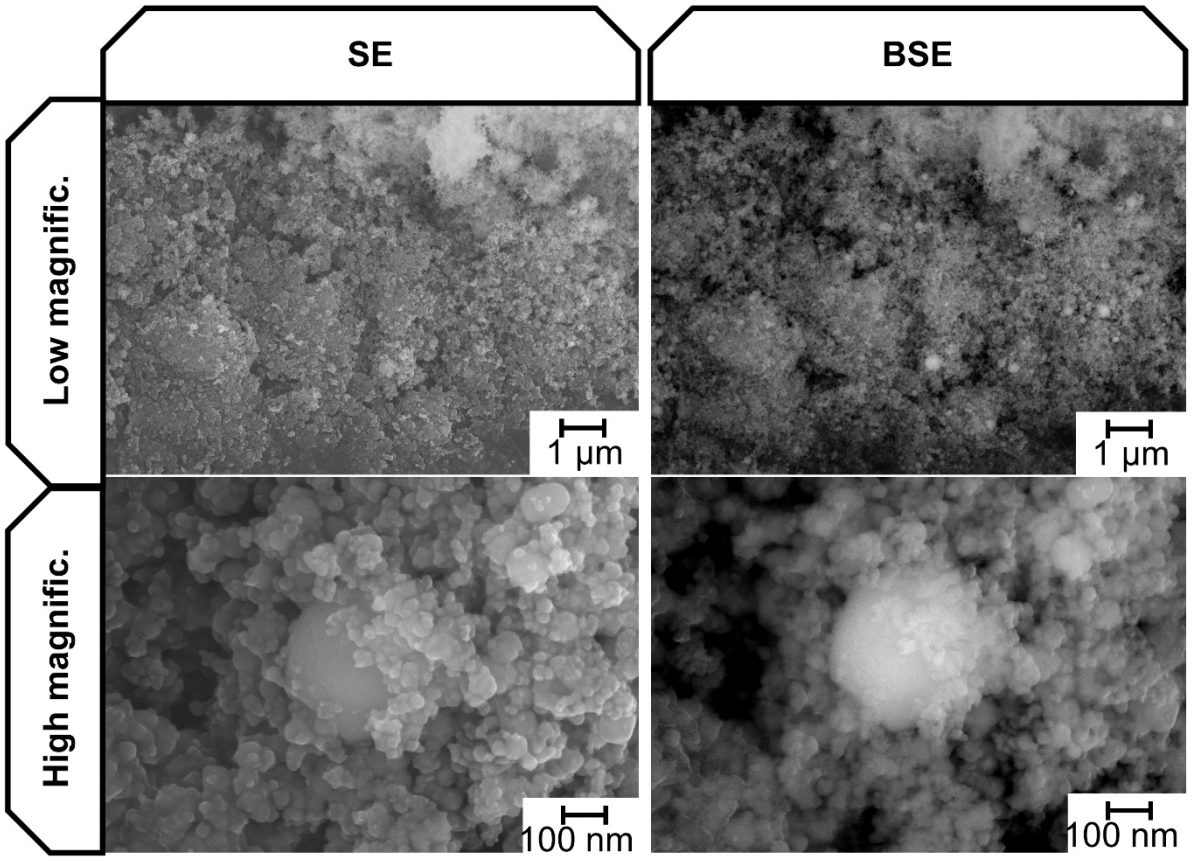

Figure A3. *SEM images (low magnification, top, and high magnification, bottom) of solid wire welding fume sample S2. Left: SE detection mode, which shows the surface topography; Right: BSE detection mode, which shows average atomic contrast. Note that the spherical, bigger particles are metallic, while the smaller nano-sized nanoparticles are oxide particles.*

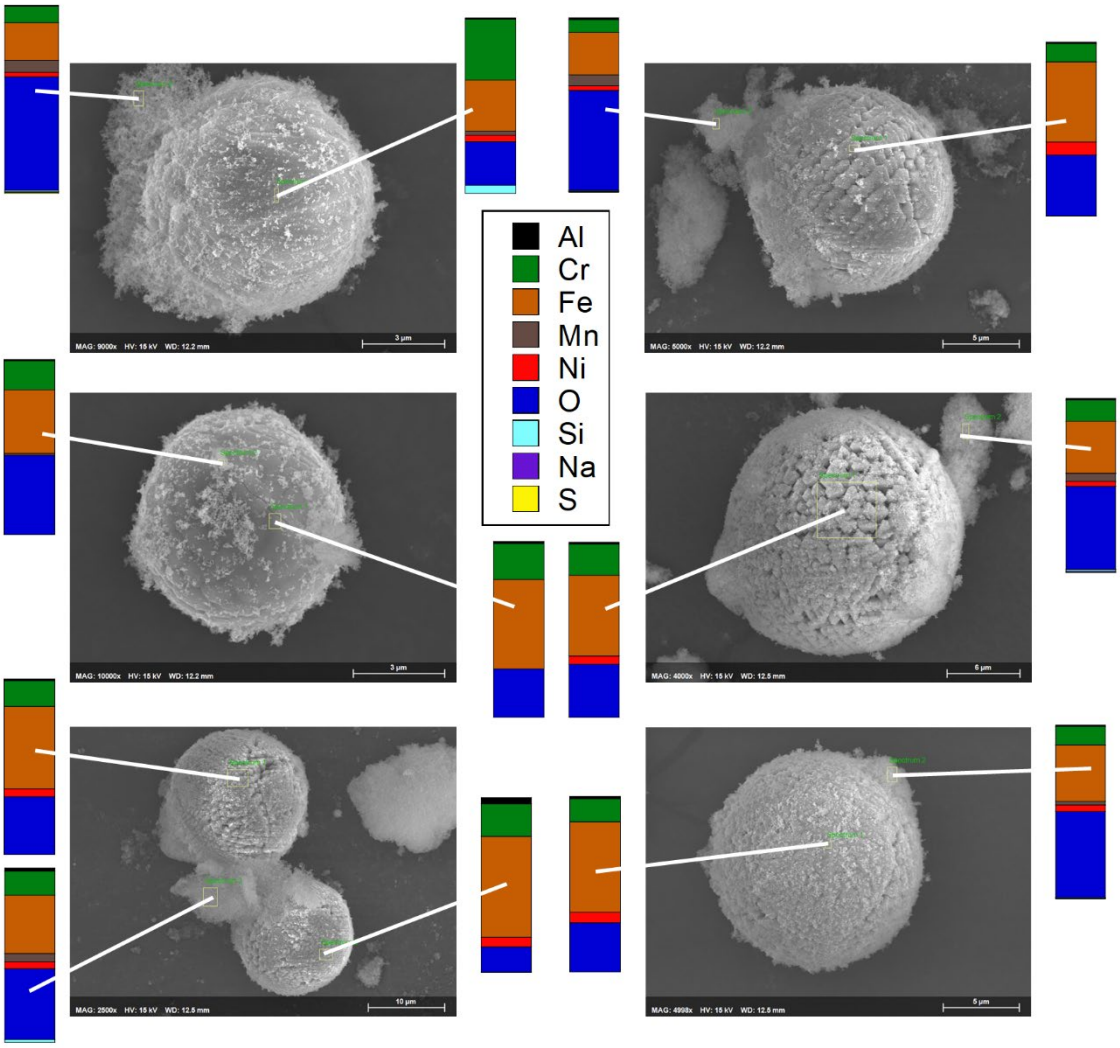

Figure A4. *SEM images of welding fume samples S1 (top row and middle row to the left) and S2 (bottom row and middle row to the right) with corresponding spot EDS results of Al, Cr, Fe, Mn, Ni, O, Si, Na, and S (C excluded due to carbon tape background) – relative composition in weight-%. Note that all micrometer-sized spherical particles also were covered by nanometer-sized particles.*

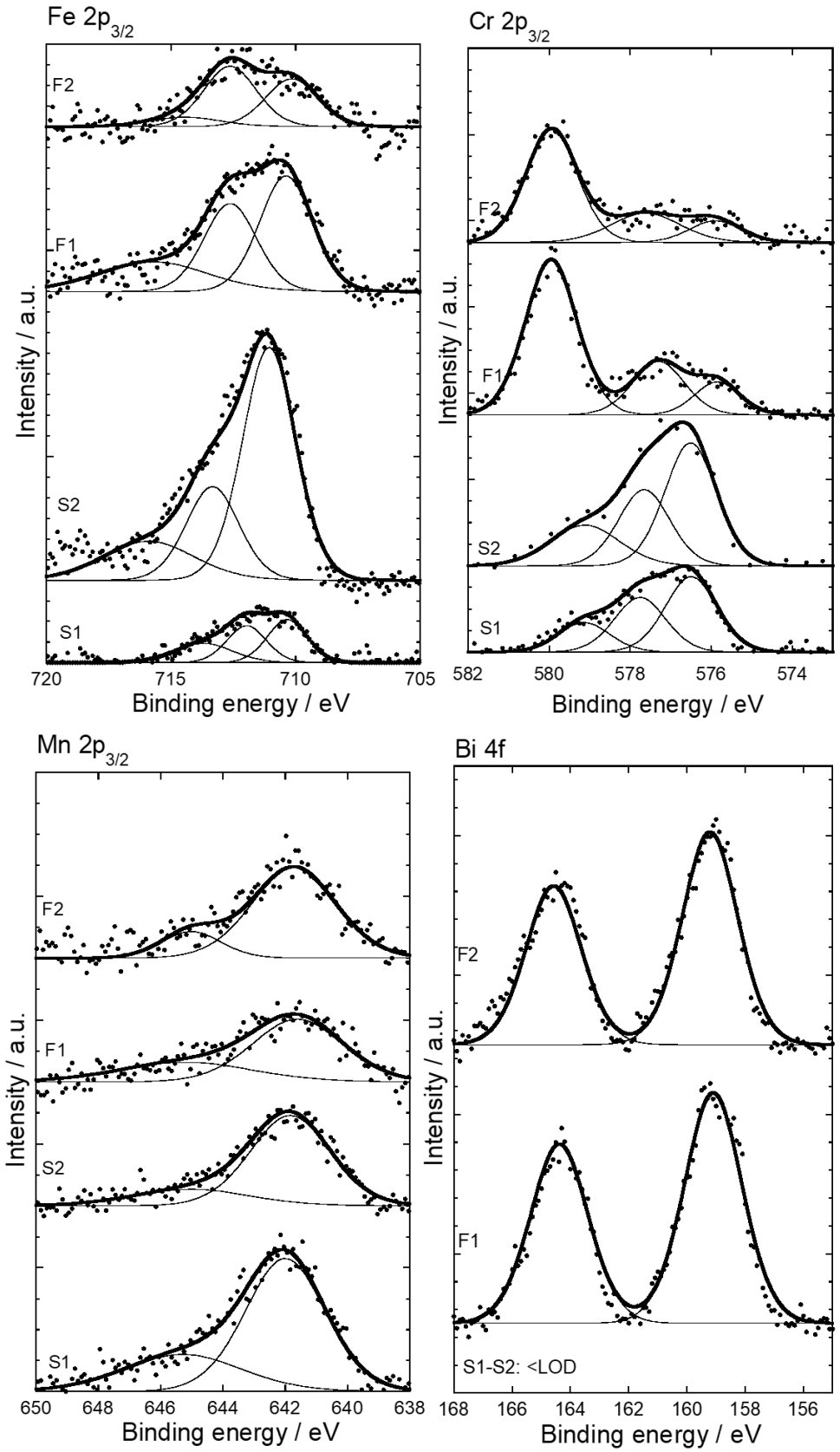

Figure A5. *XPS spectra for Fe 2p3/2, Cr 2p3/2, Mn 2p3/2, and Bi 4f for the four different welding fume particles. <LOD – below limit of detection. The dots show the raw data and the curves the fitted curves for quantification, which do not necessarily correspond to specific species or multiplet split peaks.*

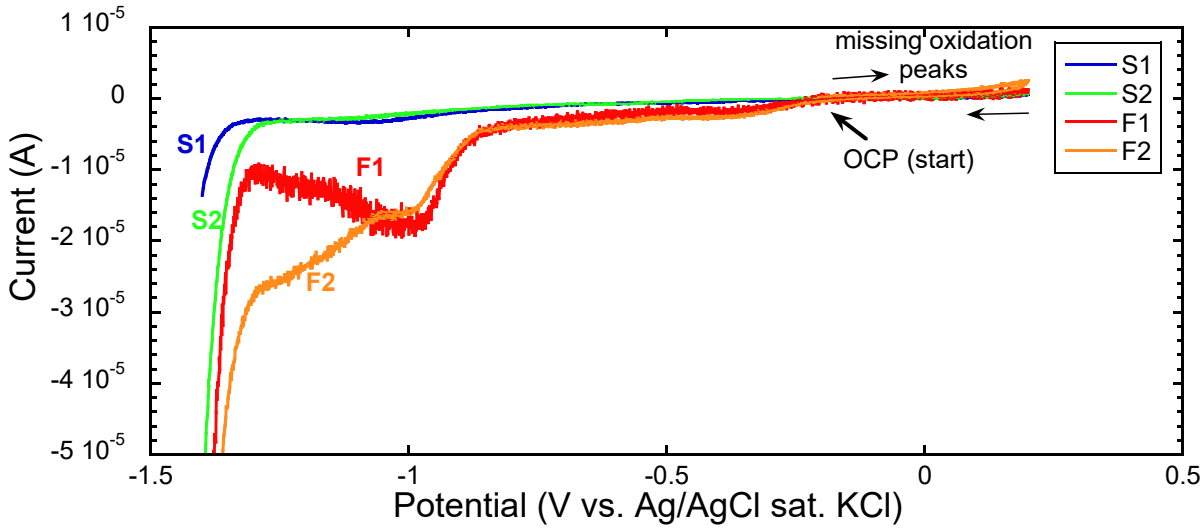

Figure A6. *Cyclic voltammograms (oxidation from open circuit potential, OCP, followed by reduction) at pH 13 of the four welding fume particles. The arrows mark the start potential (OCP), which was about -0.2 V in all cases, and the scanning direction.*

***Table A1**. Nominal composition (wt%) of the base metals, based on supplier information.*

	C	Fe	Cr	Ni	Mn	Si	P	S	Mo	Cu	N	Co	Nb
304L	0.018	72	18.3	8.1	1.1	0.31	0.032	0.001	NA	0.35	0.064	0.14	0.006
2101	0.027	70	21.6	1.6	4.9	0.76	0.020	0.001	0.26	0.35	0.23	NA	NA

***Table A2.** Particle size distribution (mean, standard deviation – SD, minimum and maximum size) based on TEM and SEM images.*

Based on image evaluation from	**Parameter**	**Sample**			
		S1	**S2**	**F1**	**F2**
TEM	**Mean, nm**	12	11	29	15
	SD, nm	4.9	5.5	13	5.7
	Min, nm	4.1	3.0	7.4	5.8
	Max, nm	43	42	99	39
SEM	**Mean, nm**	19	27	34	47
	SD, nm	8.4	14	16	28
	Min, nm	4.4	8.0	9.8	8.8
	Max, nm	50	100	84	180

***Table A3**. EDS compositional analysis of nanoparticle aggregates, in weight-% with carbon excluded. Mean and standard deviation values of 2-3 different areas are shown. Note that only the composition of the aggregates, not the micrometer-sized spherical particles from the melt, is included. <LOD – below limit of detection*

	O	**Fe**	**Cr**	**Ni**	**Mn**	**Si**	**Na**	**K**	**F**	**Ti**	**Others**
S1	29 ± 4.6	37 ± 2.4	15 ± 0.63	3.5 ± 0.31	13 ± 1.5	0.72 ± 0.18	0.17 ± 0.30	<LOD			Al 1.2
S2	27 ± 1.0	40 ± 0.04	19 ± 0.67	3.7 ± 0.20	7.6 ± 0.67	1.5 ± 0.25	<LOD				Al 1.6
F1	32 ± 1.4	15 ± 0.19	7.3 ± 0.53	1.6 ± 0.15	6.1 ± 0.57	3.7 ± 0.88	10 ± 2.0	6.3 ± 0.47	8.8 ± 1.4	1.0 ± 0.13	Al 6.0, Bi 1.9
F2	23 ± 5.4	4.7 ± 1.3	3.5 ± 1.1	<LOD	7.7 ± 2.0	3.2 ± 0.46	27 ± 2.2	1.3 ± 0.74	19 ± 4.3	5.0 ± 1.5	Al 2.4, Bi 1.6, Mo 1.1

***Table A4**. Estimated relative amounts of crystalline phases (wt.%) present in the fume determined from Rietveld analysis. – below limit of detection.*

Sample	**$(Fe,Mn,Cr,Ni)_3O_4$ Magnetite type phase**	**NaF**
S1	100	-
S2	100	-
F1	78	22
F2	33	67

Table A5. *Total metal content of Fe, Cr, Ni, and Mn (µg/mg) in the welding fume samples as determined after digestion. Mean and standard deviations of triplicate samples are shown.*

	Fe (µg/mg)	**Cr (µg/mg)**	**Mn (µg/mg)**	**Ni (µg/mg)**	**Total (wt-%)**
S1	236 ± 38	79 ± 0.69	112 ± 0.88	35 ± 0.19	46 ± 0.15
S2	198 ± 35	64 ± 12	51 ± 0.34	32 ± 0.20	35 ± 3.2
F1	127 ± 5.2	67 ± 3.8	54 ± 2.8	15 ± 0.83	26 ± 1.3
F2	42 ± 0.12	39 ± 0.37	61 ± 0.29	3.0 ± 0.028	15 ± 0.074

Table A6. *Soluble Fe, Cr(III), Cr(VI), Ni, and Mn (µg/mg) after exposure to PBS (pH 7.3, 37 °C, 24 h) released from the welding fume samples. Mean and standard deviations of triplicate samples are shown. < LOD – below limit of detection*

	Fe (µg/mg)	**Cr(III) (µg/mg)**	**Cr(VI) (µg/mg)**	**Mn (µg/mg)**	**Ni (µg/mg)**
S1	0.50 ± 0.43	0.18 ± 0.20	1.8 ± 0.18	0.14 ± 0.18	0.83 ± 0.28
S2	0.16 ± 0.13	< LOD	1.9 ± 0.063	0.82 ± 0.12	0.57 ± 0.41
F1	0.62 ± 0.082	3.5 ± 1.1	25 ± 0.30	3.1 ± 3.1	0.43 ± 0.24
F2	0.28 ± 0.092	0.21 ± 0.37	23 ± 0.55	0.35 ± 0.070	0.036 ± 0.039

Table A7. *Soluble Fe, Cr(III), Cr(VI), Ni, and Mn after exposure to PBS (pH 7.3, 37 °C, 24 h) released from the welding fume samples as percentage of total corresponding metal content. Mean and standard deviations of triplicate samples are shown. <LOD – below limit of detection*

	Fe (wt-%)	**Cr(III) (wt-%)**	**Cr(VI) (wt-%)**	**Mn (wt-%)**	**Ni (wt-%)**
S1	0.21 ± 0.18	0.23 ± 0.26	2.3 ± 0.25	0.13 ± 0.16	2.4 ± 0.80
S2	0.089 ± 0.078	<LOD	3.0 ± 0.61	1.6 ± 0.24	1.8 ± 1.3
F1	0.49 ± 0.081	5.2 ± 1.6	37 ± 2.6	2.8 ± 0.49	2.8 ± 1.5
F2	0.67 ± 0.22	0.55 ± 0.95	58 ± 0.88	0.56 ± 0.12	1.2 ± 1.3