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ESR study on Welding Fume[†]

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Abstract

ESR study on various welding fumes was performed. Divalent manganese and trivalent iron ions in these fumes produce two electron resonances. These ions are in the forms of MnO or Fe₃O₄ and/or MnFe₂O₄ phases in these fumes, respectively. A broad resonance was observed in the fumes of gas shielded welding (G-series fumes). The broadness is mainly attributable to the dipole-dipole interaction between Fe³⁺ ions.

KEY WORDS: (Welding Fume) (Manganese Oxide) (Electron Spin Resonance)

1. Introduction

Welding fume is aggregate from particles of which size lies between 0.1 μm and 10 μm ¹⁾. These particles are produced from vapors of metals and flux components during welding. As expected from the compositions of substrate metal, wire and flux, various metallic elements such as Fe, Mn, Cr and Si are contained in welding fumes. In most cases, these metallic elements turn into the oxides because metallic vapors are oxidized by air. In some cases, fluorides are detected as the result of binding metallic vapor to fluorine or of the vaporization of flux components.

Most of constituents in welding fumes give harmful influences to human body²⁾. Especially, some of transition metal ions show high toxicity³⁾, so that it is one of the most essential subject to clarify the state of these elements in welding fumes. In this study, states of various welding fumes were investigated by electron spin resonance (ESR) spectroscopy as the continuation of the previous study on manganese in welding fumes⁴⁾.

2. Experimentals

The details on various welding conditions and collecting method of fumes are described in the previous paper⁴⁾. A definite amount of fume was weighed precisely and sealed in an evacuated silica tube for ESR measurement.

ESR spectra were measured using a spectrometer of Varian E-109 type. Modulation frequency and field are 100 kHz and 10 gauss, respectively. Magnetic separation of fume was performed by a permanent magnet which was covered by wrapping papers.

3. Results

Table 1 shows the results of chemical analysis of welding fumes and crystalline phases in these fumes detected by X-ray diffraction analysis⁴⁾. Among these phases, the phases containing transition metal ions are the important ones in ESR measurement. Fumes of G-series consist of metallic iron and its oxides. In the fumes of L-series, manganese ions were detected. Fumes of S-1 and H-1 contain chromium compound as well as manganese and iron ones. Chemical analysis shows that iron content in the fume of G-series are very high and manganese content lies between 8% and 14% as MnO. On the other hand, the iron content in the fume of L-series are fairly low and lies between 9% and 13% as Fe₂O₃. Maximum value of manganese content was obtained in the fume of H-1.

Figs. 1 to 3 show ESR spectra obtained from MnCO₃ and the fumes of G and L series, H-1 and S-1. The line-widths of these resonances, which were estimated by peak-to-peak width, are given in Table 2. ESR spectra

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obtained from the fumes of G-series display very large linewidths which lie in the range of 800 to 1400 gauss before magnetic separation whereas no resonance was observed in all fumes of G-series. Two resonances were observed in all fumes of L-series before magnetic separation. After magnetic separation, only a sharp resonance

was observed in each fume of L-series. Fumes of H-1 and S-1 show a fairly sharp resonances. After magnetic separation, a similar resonance was obtained from the S-1 fume whereas no resonance was observed in the H-1 fume.

Table 1-(a) Chemical compositions of Welding fumes

Welding method	Specimen	Shield gas	Chemical composition (%)												
			Fe ₂ O ₃	SiO ₂	MnO	sol.MnO	TiO ₂	CaO	MgO	BaO	Cr ₂ O ₃	Na ₂ O	K ₂ O	F	
Gas shielded arc welding	G-1	Ar	94.91	3.40	8.72	0.04	—	—	—	—	—	—	—	—	
	G-2	80Ar-20CO ₂	84.17	7.50	11.87	0.21	—	—	—	—	—	—	—	—	
	G-3	50Ar-50CO ₂	84.44	7.60	12.11	0.19	—	—	—	—	—	—	—	—	
	G-4	CO ₂	79.10	10.70	14.16	0.20	—	—	—	—	—	—	—	—	
	G-5	98Ar-2O ₂	86.05	6.90	11.52	0.12	—	—	—	—	—	—	—	—	
Arc welding with covered electrode	L-1	—	19.13	7.50	7.06	0.01	0.03	14.71	0.79	4.09	—	8.43	17.77	15.70	
	L-2	—	14.74	5.90	14.12	0.01	0.03	13.47	0.73	3.77	—	8.63	17.64	15.52	
	L-3	—	16.36	6.80	16.10	0.06	0.03	14.05	0.68	4.19	—	18.73	5.58	14.77	
	S-1	—	9.38	6.30	15.15	0.24	6.36	3.41	0.10	—	6.47	0.51	32.68	14.04	
	H-1	—	12.95	3.80	38.86	0.09	0.04	7.54	0.08	—	4.38	7.16	11.00	11.50	

Table 1-(b) Crystalline phases in typical welding fumes by x-ray diffraction analysis

Specimen	crystalline phases
G-1	metallic Iron, Fe ₃ O ₄
G-4	metallic Iron, FeO, Fe ₃ O ₄
L-2	Fe ₃ O ₄ , MnFe ₂ O ₄ , MnO, KMnO ₂ (K ₂ Mn ₄ O ₈), NaF, CaF ₂ , KCaF ₃ , BaCO ₃
L-3	Fe ₃ O ₄ , MnFe ₂ O ₄ , MnO, NaF, CaF ₂ , K ₂ MnO ₂ (K ₂ Mn ₄ O ₈)
S-1	Fe ₃ O ₄ , MnFe ₂ O ₄ , α-K ₂ CrO ₄ (K ₂ FeO ₄)
H-1	Fe ₃ O ₄ , MnFe ₂ O ₄ , NaF, CaF ₂ , KCaF ₃ , γ-Mn ₂ O ₃ , KMnO ₂ (K ₂ Mn ₄ O ₈), α-K ₂ CrO ₄ (K ₂ FeO ₄)

Table 2 Linewidths of electron spin resonances in welding fumes

Specimen	Before magnetic separation	After magnetic separation
G-1	820 gauss (asymmetry)	No resonance
G-2	820 (asymmetry)	"
G-3	1040 (symmetry)	"
G-4	1440 (symmetry)	"
G-5	1080 (asymmetry)	"
L-1	Two resonances	186 gauss
L-2	Two resonances	192
L-3	Two resonances	174
S-1	304 gauss	no resonance
H-1	207 gauss	208 gauss
MnCO ₃	232 gauss	—

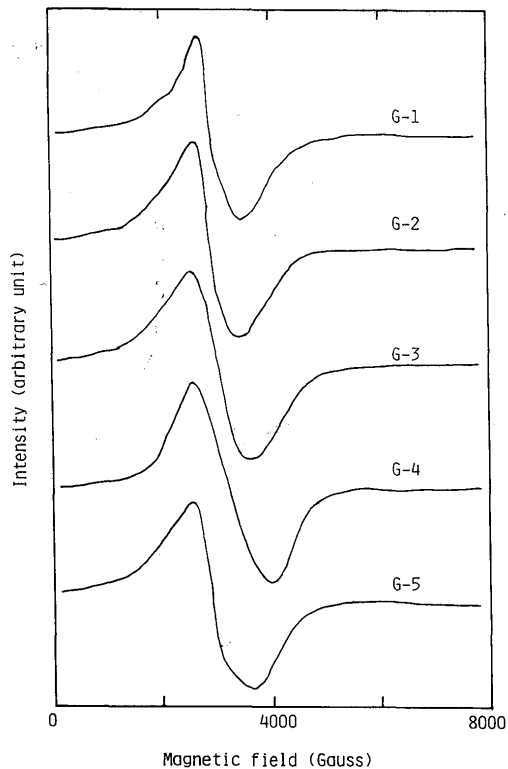


Fig. 1 ESR spectra of the welding fumes of G-series

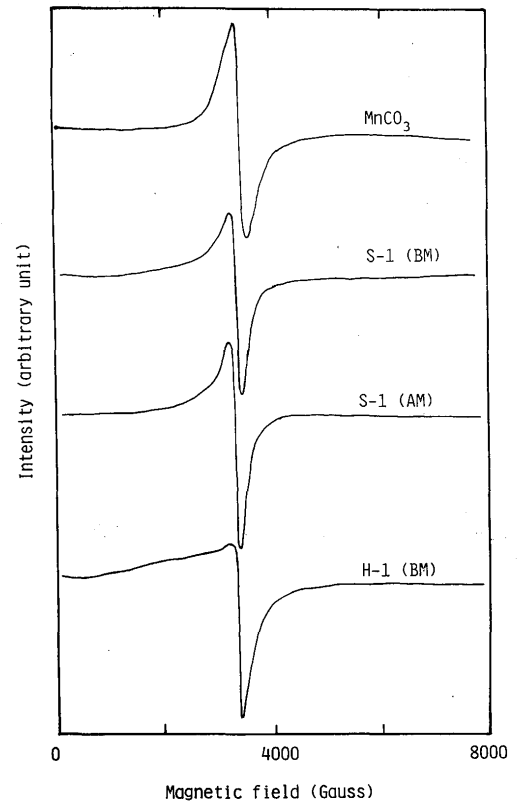


Fig. 3 ESR spectra of MnCO_3 , S-1 and H-1 fumes.

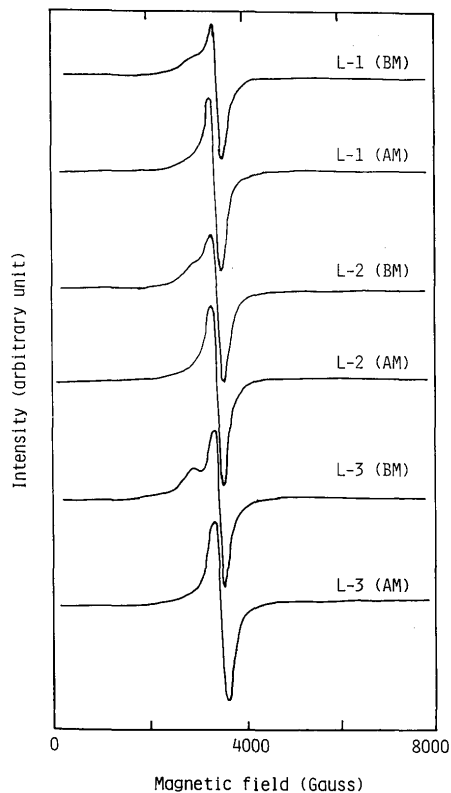


Fig. 2 ESR spectra of the welding fumes of L-series (BM: before magnetic separation, AM: after magnetic separation)

4. Discussion

Most important elements in welding fumes are the transition metal ions such as manganese and chromium ions from the standpoint of toxicity³). Most of transition metal ions are paramagnetic ones and electron spin resonances related to these ions are observable. From the results by X-ray diffraction analysis⁴), states of iron, chromium and manganese are in question in the fumes studied. These transition metal ions show various ESR spectra, relating to their valencies and the difference of crystal field.

Excellent reviews have been reported by some investigators^{5,6}). In the case of iron ions, ferric ions in crystalline oxides give a resonance near 3400 gauss. Ferric ions in oxide glasses show a characteristic resonance which is sharply observed in a glass containing a small content of ferric ions and observed in a broad shape near 3400 gauss in a glass containing fairly large amount of ferric ions⁷). On the other hand, no resonance of ferrous ions is observable at liquid N_2 temperature. At liquid He temperature, a resonance due to ferrous ions has been detected in some oxides⁵).

Chromium ions also give the resonances related to their valencies and crystal fields. For example, Cr^{3+} ions show a resonance near 3400 gauss in crystalline oxides containing small amount of Cr^{3+} ions. In some oxide glasses, a

broad resonance is observable near 1200 gauss⁸⁾. No resonance is arised from Cr^{4+} ions at room temperature though the ions show a resonance at liquid He temperature in ruby⁹⁾. Cr^{5+} ions often show a sharp resonance near 3400 gauss. The existence of no-paramagnetic Cr^{6+} ions offer produces Cr^{5+} ions in oxide glasses⁸⁾ because Cr^{5+} ions correspond to electron trapped Cr^{6+} ions. The resonance attributed to Cr^{2+} ions has not been observed at room and liquid N_2 temperatures.

Electron spin resonance due to manganese ions in oxides is observable near 3400 gauss when the oxides contain divalent or tetravalent manganese ion⁵⁾. When the content of divalent manganese ion is small, six-line hyperfine structure is observed.

Clear difference before and after magnetic separation is observed in the fumes of L-series. The shoulder peaks are attributed to magnetic phases. According to X-ray diffraction analysis⁴⁾, the phases are Fe_3O_4 and/or MnFe_2O_4 . Therefore, the shoulder peaks arise from Fe^{3+} ions and their broadness is produced by dipole-dipole interaction between Fe^{3+} ions. The resonances with narrow linewidth which is observed before and after magnetic separation are assigned to Mn^{2+} ions in MnO phase from the X-ray diffraction results.

Very broad resonances were observed in the fume of G-series and their linewidths depend on the atmosphere during welding. These broad resonances are mainly attributed to Fe_3O_4 phase because the fumes of G-series consist of metallic iron, FeO and Fe_3O_4 phases and the broadness originates from dipole-dipole interaction between Fe^{3+} ions. However, it is shown from chemical analysis that fairly large amount of manganese ion is contained in the fumes of G-series. Therefore, it is expected that the linewidth is partly connected with the concentration of manganese ion. As shown in Table 1 and 2, the linewidth of the resonance in the fumes of G-series seems to increase with increasing MnO content. No X-ray diffraction peaks was observed in the fumes of G-series irrespective of existence of about 10% MnO, so that it is considered that manganese ions dissolve into Fe_3O_4 phase. From the simple X-ray diffraction analysis and ESR study, it can not be clarified whether manganese ions can dissolve into Fe_3O_4 phase in the form of Mn^{2+} or Mn^{3+} ion. However, one can easily imagine the phase such as $[\text{Fe}_{1-x}\text{Mn}_x^{2+}][\text{Fe}_{1-y}\text{Mn}_y^{3+}]_2\text{O}_4$ because Mn^{2+} and Mn^{3+} ions can easily replace Fe^{2+} and Fe^{3+} ions,

respectively. Conclusively, it is suggested that the position of peaks in delivative curve of the resonance depends on the dipole-dipole interaction between Fe^{3+} ions and the position of the minimum is partly affected by divalent manganese concentration in Fe_3O_4 phase.

The resonances obtained from S-1 and H-1 fumes are fairly sharp irrespective of the existence of Fe_3O_4 and MnFe_2O_4 phases. No resonance was observed in H-1 fume after magnetic separation. This indicates that any resonance is not obtained from $\gamma\text{-Mn}_2\text{O}_3$, KMnO_2 and $\alpha\text{-K}_2\text{CrO}_4$ phases. The result in S-1 fume is inconsistent with that in H-1 fume because a resonance was observed after magnetic separation. The inconsistency may due to incomplete magnetic separation.

5. Summary

State analysis of various welding fumes was performed by ESR spectroscopy. Electron spin resonances arised from these welding fumes are originated from Mn^{2+} ions in MnO and Fe^{3+} ions in Fe_3O_4 and MnFe_2O_4 . The broadness of linewidth in the fumes of G-series is attributable to the dipole-dipole interaction between Fe^{3+} ions in Fe_3O_4 phase and/or MnFe_2O_4 phases and the contribution of the resonance due to Mn^{2+} ions.

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