

PYROPHORIC IRON NANOPARTICLES FORMED
BY SELECTIVE EXTRACTION FROM Fe–Al ALLOYS:
A MÖSSBAUER STUDY

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Abstract

Pyrophoric iron nanoparticles were unexpectedly formed during the preparation of Fe–Al alloys for resonance Mössbauer detectors. Selective dissolution of aluminium in dilute NaOH produced aggregates of ultrafine α -Fe particles that self-heated and ignited in air. The precursor, fresh pyrophoric product and aged oxidation product were characterised by ^{57}Fe Mössbauer spectroscopy, scanning electron microscopy and energy-dispersive X-ray analysis. The fresh material contains crystalline α -Fe grains, a broadened disordered surface/intercrystalline component and a minor superparamagnetic or residual Fe–Al fraction. A model-based particle diameter of 7–8 nm was obtained. Paraffin-coated samples stored for more than 20 years retained substantial metallic iron, while slow oxidation produced magnetite. The results relate nanoscale disorder to pyrophoricity and highlight a persistent industrial hazard.

Key words: pyrophoric iron, nanoparticles, self-ignition, explosion hazard, Mössbauer spectroscopy

Introduction. Finely divided iron can self-heat and ignite spontaneously in air. This behaviour was first reported by MAGNUS in 1825 [1] and was subsequently studied for reduced iron powders and their controlled passivation [2].

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Pyrophoric iron and related iron compounds also represent ignition sources in oil and gas storage systems, pipelines and chemical equipment, where exposure of dry deposits to air may cause fires or explosions [3–6].

Pyrophoricity is governed by surface reactivity, particle size, structural disorder and oxidation kinetics. The microscopic relation between these factors remains insufficiently documented for metallic iron nanoparticles. Here we report the unexpected formation of strongly pyrophoric iron during the selective removal of aluminium from Fe–Al alloys originally prepared as converter materials for resonance Mössbauer detectors. The precursor alloy, fresh product and material aged under paraffin were compared by Mössbauer spectroscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDAX).

Experimental method. Fe–Al samples containing up to 50 at.% Al were prepared by sintering fine Fe powder of natural isotopic abundance with Al powder in hydrogen. The Fe–Al system and the alkaline preparation of porous Raney-type iron have been described previously [7, 8]. The original aim was to obtain a ^{57}Fe –Al converter with a narrow Mössbauer line for a resonance detector [9]. Alloys that did not show the required spectrum were treated with dilute NaOH to extract aluminium selectively.

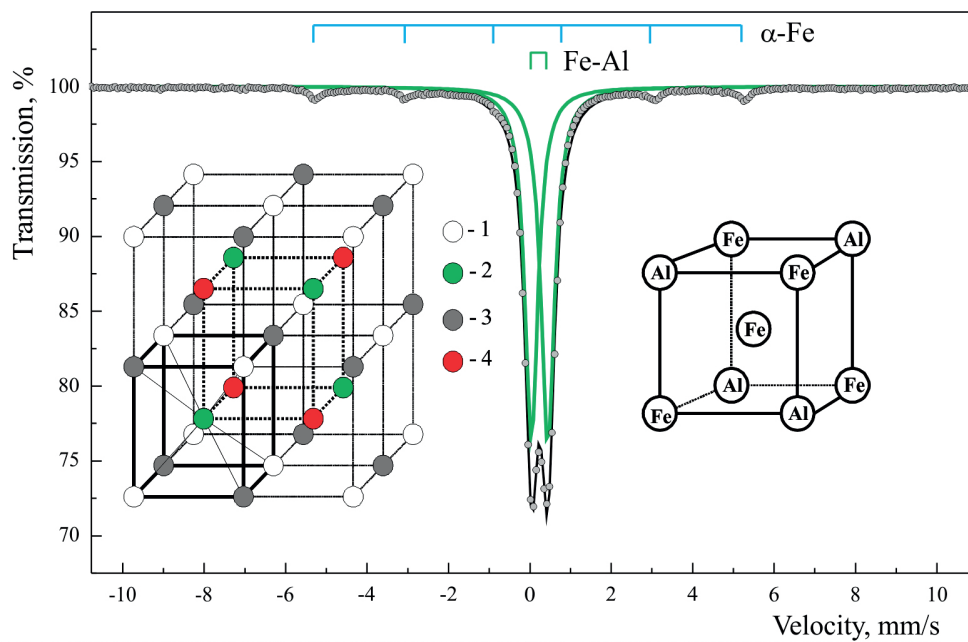
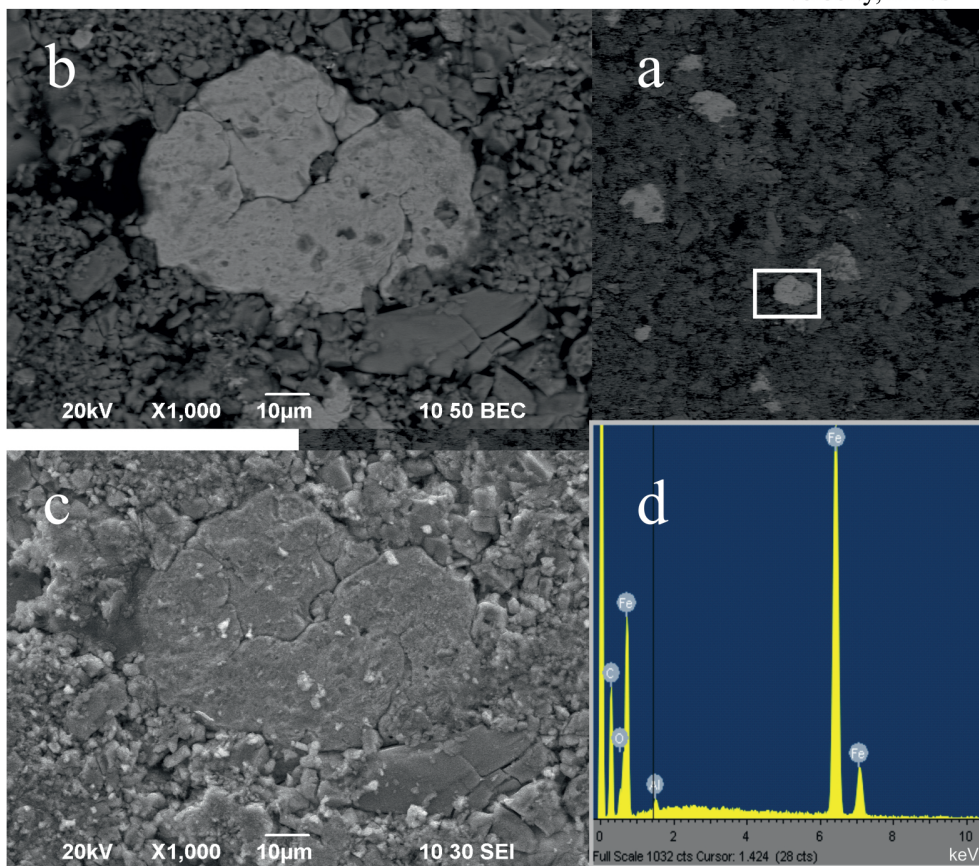
The chemical treatment, acetone washing and solution decantation were carried out under a thin layer of liquid paraffin at approximately 70 °C. After the final decantation, the ultradisperse iron particles remained coated with solid paraffin at room temperature. Unprotected material self-heated and ignited with sparks within seconds after exposure to air.

Mössbauer spectra were recorded in transmission geometry at 293, 77 and 4.2 K using thin paraffin-embedded absorbers and ^{57}Co sources in Pd or Rh matrices with activities of 20–30 mCi. The velocity scale and isomer shifts were calibrated against α -Fe at room temperature. SEM images and EDAX spectra of the precursor were obtained with a JSM-6390 microscope. Direct SEM examination of the final product was avoided because of its extreme pyrophoricity.

Results and discussion. The investigated $\text{Fe}_{1.1}\text{Al}_{0.9}$ alloy exhibits a quadrupole doublet with a minor α -Fe sextet (Fig. 1, top). Its spectrum is consistent with the compositional and ordering effects known in Fe–Al alloys [7, 8]. Before aluminium extraction, SEM reveals a micrometre-scale granular composite (Fig. 1a–c); EDAX confirms that the bright inclusion is predominantly α -Fe (Fig. 1d).

After aluminium extraction, the residual powder consists of nanoparticle aggregates and shows pronounced pyrophoricity. Its room-temperature spectrum

Fig. 1. (Top) Mössbauer spectrum of rapidly quenched $\text{Fe}_{1.1}\text{Al}_{0.9}$ and structural models of the bcc Fe–Al lattice and ordered Fe_3Al . (a) Low-magnification SEM image ($\times 100$); (b,c) backscattered- and secondary-electron images of the marked region ($\times 1000$); (d) corresponding EDAX spectrum



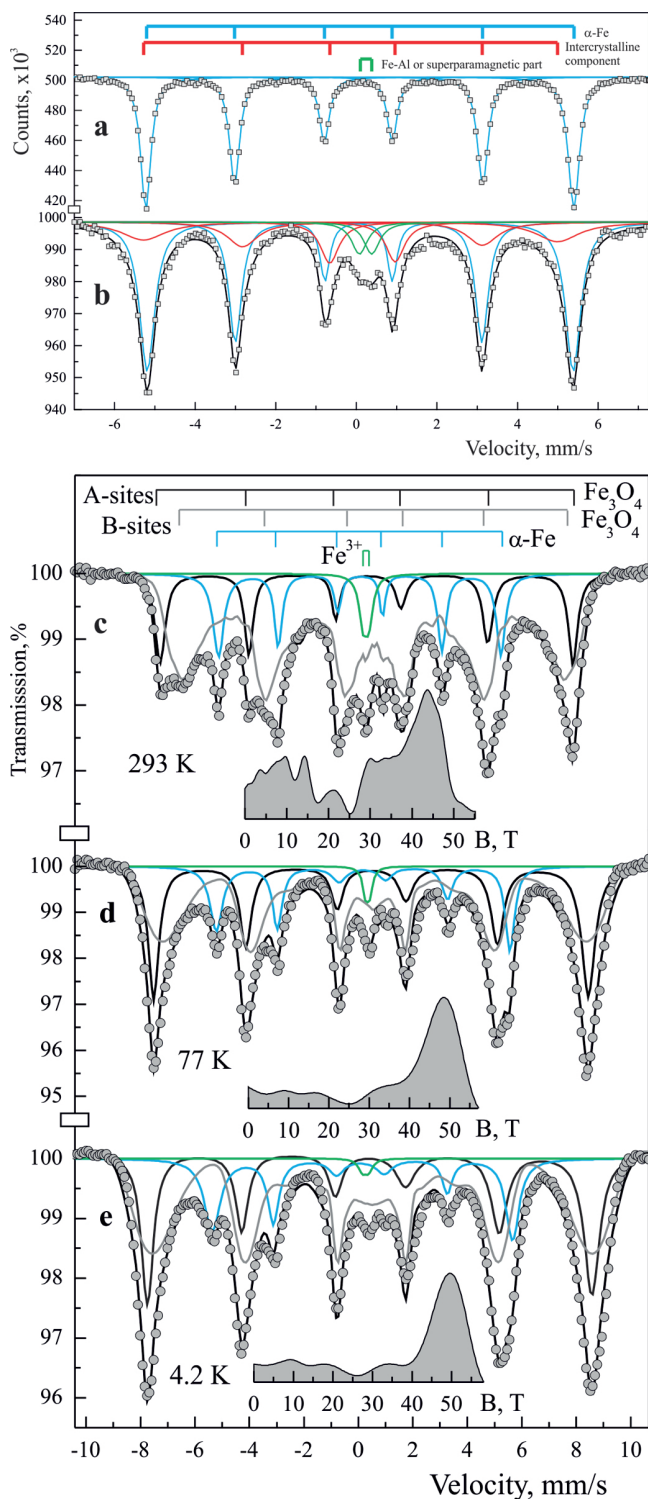


Fig. 2. (a) α -Fe calibration foil and (b) fresh paraffin-coated pyrophoric iron at room temperature. Mössbauer spectra of a paraffin-coated sample stored in dry air for more than 20 years measured at (c) 293 K, (d) 77 K, and (e) 4.2 K. The insets show the magnetic hyperfine-field distributions used for the broadened B-site component of magnetite

T a b l e 1

Mössbauer parameters of the fresh pyrophoric iron.
The uncertainty of the last decimal digit is given in parentheses

Parameter → Subspectra ↓	IS* mm/s	ΔE_Q mm/s	B_{hf} T	Γ_{exp} mm/s	I_{rel} %
Grains interior, α -Fe	0.07(1)	0.04(1)	32.4(1)	0.26–0.30(1)	60.3(5)
Disordered grain surface/ intercrystalline fraction	0.08(1)	–0.11(1)	31.9(1)	0.50–1.74(1)	31.1(5)
Superparamagnetic part or residual Fe-Al alloy	0.22(1)	0.37(1)	–	0.60(1)	8.6(5)
*Isomer shift is related to the standard α -Fe at room temperature.					

(Fig. 2a,b; Table 1) is resolved into an α -Fe component with normal linewidths (60.3%), a strongly broadened disordered surface/intercrystalline component (31.1%), and a minor doublet assigned to a superparamagnetic fraction or residual Fe-Al alloy (8.6%). Similar broadened sextets are characteristic of nanocrystalline iron [10–13].

The α -Fe and broadened components have isomer shifts slightly above those of bulk α -Fe. The negative quadrupole shift of the broadened component (–0.11 mm/s) is consistent with broken translational symmetry at the particle surface; in α -Fe this effect is largest in the outermost monolayer and is rapidly screened [10]. The reduced hyperfine field and linewidths up to approximately 1.7 mm/s further indicate surface disorder. Within the structural model used for nanocrystalline iron [14–16], the measured spectral areas correspond to a disordered layer of about 4–5 monolayers and an approximate particle diameter of 7–8 nm. This is a model-based estimate rather than a direct microscopic size measurement.

The high surface-to-volume ratio and the large fraction of disordered atoms provide a consistent explanation for rapid oxygen adsorption, self-heating and ignition. The spectrum therefore links the macroscopic pyrophoric response to the nanoscale surface and intercrystalline structure.

After more than 20 years under paraffin, substantial α -Fe remains, whereas slow surface oxidation produces magnetite (Fig. 2c–e; Table 2). The magnetite A-site component has comparatively narrow lines, while the broadened B-site contribution was fitted with a magnetic hyperfine-field distribution. Cooling to 77 and 4.2 K markedly changes this distribution. The low-temperature behaviour is compatible with the Verwey transition, whose visibility and temperature depend strongly on magnetite stoichiometry and particle size [17, 18].

The persistence of metallic iron after prolonged storage demonstrates that an organic coating can greatly retard passivation. Such deposits may therefore remain hazardous and ignite when the protective liquid or organic phase is removed and air is admitted [3–6].

T a b l e 2

Mössbauer parameters of the spectral components
in the aged paraffin-coated sample

Parameter → Subspectra ↓	IS* mm/s	ΔE _Q mm/s	B _{hf} T	Γ _{exp} mm/s	I _{rel} %
Temperature 293 K					
Fe ₃ O ₄ A-sites	0.27(1)	0.06(2)	47.2(1)	0.46(1)**	36.9(1)
Fe ₃ O ₄ B-sites hyperfine magnetic field distribution	0.53(2)	0.02(2)	Distribution	Distribution	24.8(1)
α-Fe	0.01(2)	0.02(2)	32.3(1)	0.48(1)**	31.8(1)
Doublet Fe-Al Singlet/ Superparamagnetic com- ponent	0.21(2)	0.23(1)	–	0.35(2)	6.6(2)
Temperature 77 K					
Fe ₃ O ₄ A-sites	0.42(1)	0.02(2)	49.7(1)	0.48(1)**	54.7(1)
Fe ₃ O ₄ B-sites hyperfine magnetic field distribution	0.50(1)	0.07(1)	Distribution	Distribution	16.5(1)
α-Fe	0.10 (2)	0.03(3)	33.6(1)	0.55(1)**	26.3(1)
Doublet Fe-Al Singlet/ Superparamagnetic com- ponent	0.28(2)	0.16(2)	–	0.25(2)	2.6(2)
Temperature 4.2 K					
Fe ₃ O ₄ A-sites	0.43(1)	0.03(2)	50.1(1)	0.54(1)**	54.0(1)
Fe ₃ O ₄ B-sites hyperfine magnetic field distribution	0.50(1)	0.02(2)	Distribution	Distribution	17.4(1)
α-Fe	0.11(2)	0.08(2)	33.8(1)	0.60(1)**	27.2(1)
Doublet Fe-Al Singlet/ Superparamagnetic com- ponent	0.26(2)	0.24(2)	–	0.34(2)	1.3(2)
*All isomer shifts are related to the standard α-Fe at room temperature.					
**Linewidth of the sextet first line.					

Conclusions. Pyrophoric iron nanoparticles were unexpectedly formed by selective extraction of aluminium from Fe–Al alloys. The Mössbauer spectrum of the resulting material reveals a heterogeneous nanostructure comprising crystalline α-Fe grain interiors, a structurally disordered surface fraction, and an intercrystalline or residual non-magnetic component. The pronounced pyrophoric behaviour is attributed to the high surface reactivity and structural disorder of the ultrafine iron particles.

Samples protected by a paraffin coating and stored for more than 20 years retain a substantial fraction of metallic α -Fe. Under these conditions, oxidation proceeds extremely slowly and leads predominantly to magnetite formation. With progressive oxidation and passivation, the dispersed particles are expected to gradually lose their pyrophoric properties, in agreement with previous studies. Nevertheless, the results demonstrate that pyrophoric iron nanoparticles may remain for prolonged periods in a metastable and highly reactive state. This finding is directly relevant to the safety of storage tanks, pipelines, and reaction systems, where drying of such materials and sudden exposure to air may cause spontaneous ignition or explosion.

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