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A new phenomenon involving the formation of liquid mobile metal–carbon particles in the low-temperature catalytic graphitisation of amorphous carbon by metallic Fe, Co and Ni

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The reaction of Fe, Co and Ni with amorphous carbon and its catalytic graphitisation at relatively low temperatures (600–700 °C) *in vacuo* is accompanied by the formation of liquid mobile metal–carbon (M–C) particles; the mechanism by which these particles are formed and maintained in the liquid state is suggested.

The transition of amorphous carbon into graphite occurs at 2500–3 500 °C.[1,2] Graphitisation accelerates and occurs at substantially lower temperatures in contact with graphitisation catalysts such as Fe, Co and Ni.[1–6] Depending on the state of these catalysts, graphitisation mechanisms are classified as solid-phase[3–5] and liquid-phase ones (at temperatures above 1500 °C).[1,2]

In the present work, we discovered and studied for the first time the formation of liquid mobile M–C particles at relatively low temperatures (600–670 °C) in the reaction of Fe, Co and Ni with amorphous carbon[†] accompanied by catalytic graphitisation of the latter. The experiments were carried out *in situ* in the column of a JEM-100CX electron microscope equipped with a video system. The residual pressure of the gases was 10^{-4}–10^{-5} Torr.

The chemical and phase transformations of catalyst precursors and the formation of liquid intermediate M–C compounds and graphite is described by Schemes (1)–(3) for the Fe–C, Ni–C and Co–C individual systems:

$$\text{-FeO(OH), Co(OH)}_2\text{, Ni(OH)}_2\text{/C}_{\text{am}} \xrightarrow{250\text{–}400\ ^\circ\text{C}} \text{-Fe}_2\text{O}_3\text{, CoO, NiO/C}_{\text{am}} \qquad (1)$$

$$\text{-Fe}_2\text{O}_3\text{, CoO, NiO/C}_{\text{am}} \xrightarrow{400\text{–}550\ ^\circ\text{C}} \text{Fe}_3\text{O}_4\text{, CoO}_{1-\delta_1}\text{, NiO}_{1-\delta_2}\text{/C}_{\text{am}} \qquad (2)$$

$$\text{Fe}_3\text{O}_4\text{, CoO}_{1-\delta_1}\text{, NiO}_{1-\delta_2}\text{/C}_{\text{am}} \xrightarrow{600\text{–}670\ ^\circ\text{C}} \text{Fe}_\text{s}\text{, Co}_\text{s}\text{, Ni}_\text{s}\text{/C}_{\text{am}} \xrightarrow{T_{\text{cr}}\ \text{(rapid transition)}} \{\text{(Fe–C)}_{\text{liq}}\text{, (Co–C)}_{\text{liq}}\text{, (Ni–C)}_{\text{liq}} + \text{graphite}\}\text{/C}_{\text{am}} \qquad (3)$$

(where δ_1 and δ_2 indicate possible changes in the oxide stoichiometry).

Figure 1 shows a typical electron microscopic picture of Fe–C particles and graphite tracks formed on movement of liquid particles through the amorphous carbon film.

Transition mode of the formation of M–C particles in the liquid state. Heating of metal hydroxides in the chamber of the electron microscope results in the processes shown in Schemes (1) and (2). Reaching the T_{cr} temperature and reduction of the oxides to the metals [Scheme (3)] are critical for the transition of catalyst particles to the liquid state. The T_{cr} values are 640, 600 and 670 °C, respectively, for the Fe–C, Ni–C and Co–C systems. A prerequisite for this transition is contact of the oxide particles with the amorphous carbon film. Simultaneously with reduction of the oxides to metals, absorption of carbon by the metals occurs. At the same time, the particles rapidly (unresolvable on the real time scale) sink into the carbon film bulk. The existence of the particles in the liquid state is confirmed by the continuous change in their shapes, the disappearance of point reflexes on micro-electronograms and the absence of a contrast typical of crystals in the TEM images. For example, Figure 2(*a*) shows how strongly the contrast of a particle image decreases at the instant of its transition to the liquid state (0–0.15 s). The state of the M–C particles formed upon interaction of metal oxides with amorphous carbon depends on their size, *i.e.* either totally liquid particles or those containing both crystalline and liquid parts are formed.

Sizes 100–500 Å. The formation of the liquid state over the total bulk of Fe–C, Ni–C and Co–C particles is characteristic of these sizes. Liquid M–C particles of these sizes are formed almost simultaneously. Flow of the particles through the carbon film starts [Figures 1 and 2(*a*)].

Sizes 500–1500 Å. Initially, only the outer parts of the particles in contact with the amorphous carbon pass into the liquid state. The particle cores are immobile and remain in the solid crystalline state. The thin liquid M–C layer that has formed flows away from the particle core. The following possibilities may result:

1) The thin liquid M–C layer is drawn back into the parent particle, leaving an empty space in the film due to the absorption of carbon. Consequently, the absorbed carbon is distributed throughout the particle bulk. As a result of repeated acts of carbon absorption, the concentration of carbon in the particle becomes sufficient for the transition of the whole bulk to the liquid state. Subsequently, liquid M–C particles start moving through the carbon film [Figure 2(*b*), 0.90–1.05 s].

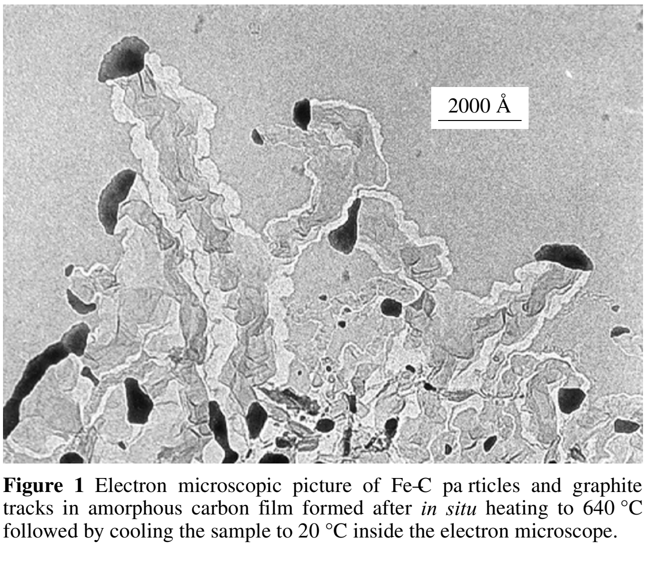

Figure 1 Electron microscopic picture of Fe–C particles and graphite tracks in amorphous carbon film formed after *in situ* heating to 640 °C followed by cooling the sample to 20 °C inside the electron microscope.

[†] Amorphous carbon films were 200–300 Å thick and were obtained by thermal atomisation of spectrally-pure carbon rods *in vacuo* (10^{-4} Torr). One-phase crystalline hydroxides, namely, -FeO(OH), $Co(OH)_2$ and $Ni(OH)_2$, with specific surface areas of 82, 19 and 75 $m^2\,g^{-1}$, respectively, were used as catalyst precursors. The -FeO(OH) sample consisted of needle-shaped crystals with characteristic sizes $l \times h = 2500 \times 200$ Å; $Co(OH)_2$ consisted of thin plane crystals 0.2–1.0 m wide and 300–500 Å thick, and $Ni(OH)_2$ consisted of hexagonal thin crystals (50–200 Å). The carbon films were coated with the hydroxides from suspensions in ethanol by means of ultrasonic treatment and then dried. The carbon films were attached to molybdenum meshes and placed in the heating block of an electron microscope.

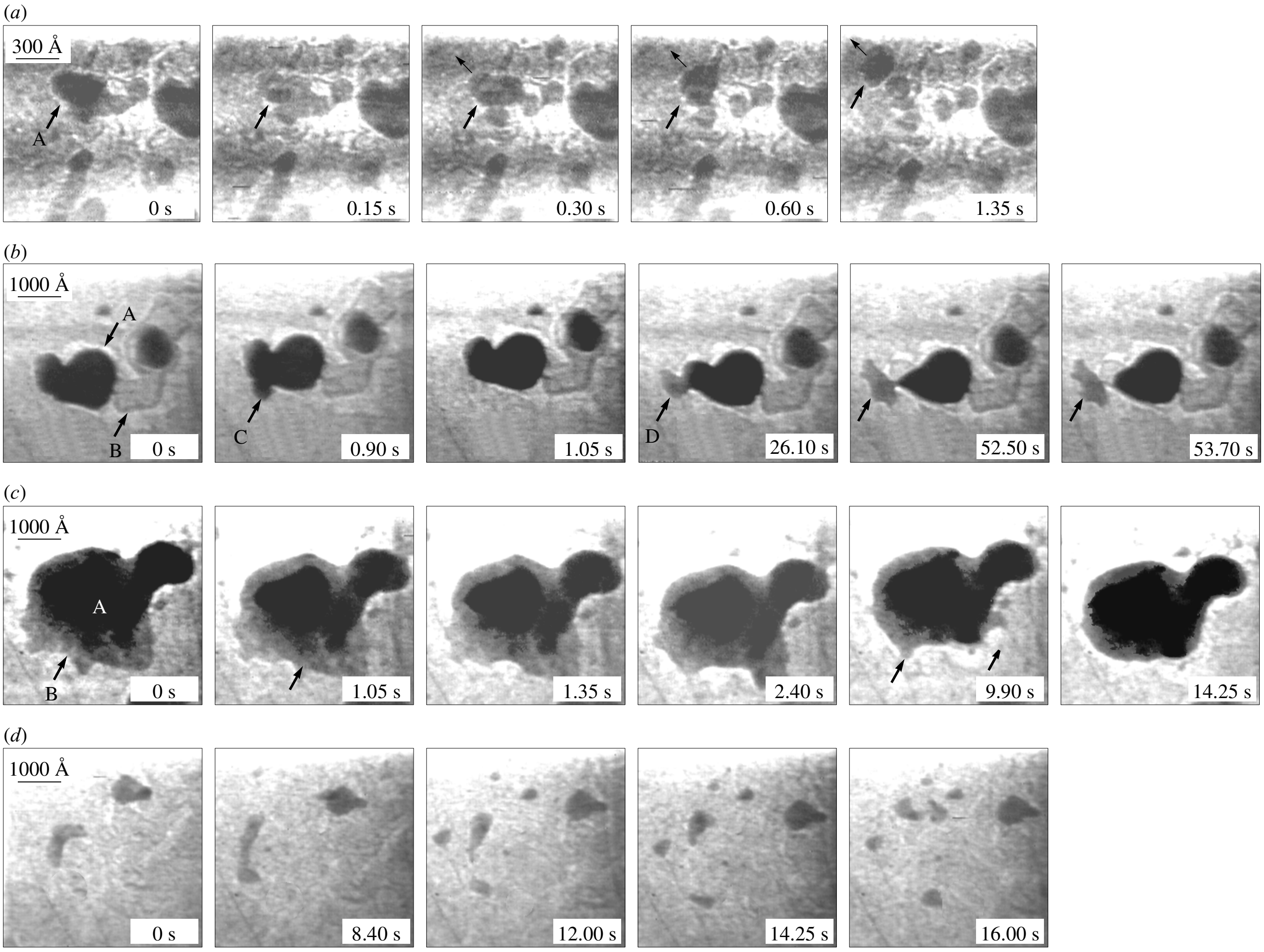

Figure 2 Fragments of the video record. The arrows indicate the particles and the directions of their movements: (*a*) formation of a liquid Fe–C particle: 0 s, solid Fe_3O_4 particle (A); 0.15 s, liquid Fe–C particle immediately after formation; 0.30–1.35 s, flowing of the liquid particle in the carbon film; (*b*) evolution of a Ni–C particle of *ca.* 1500 Å size: 0 s, slowly moving Ni–C particle (A) and a graphite track (B) behind it; 0.90–1.05 s, formation of a thin liquid layer (C) and rapid drawing it back into the parent particle; 26.10–53.70 s, formation and separation of a thin liquid layer (D) with formation of a separate liquid Ni–C particle; (*c*) evolution of a Co–C particle of *ca.* 5000 Å size: 0 s, immobile Co–C particle containing a crystalline core (A) and liquefied thin layers (B) on the edges; 1.05–14.25 s, drawing fragments of the thin liquid layer into the parent particle; (*d*) repeated division of a Co–C liquid particle: 0–12.00 s, initial division of a horseshoe-shaped particle; 14.25–16.00 s, subsequent division of the fragments that formed.

2) The thin liquid layer separates from the parent particle to form a liquid M–C particle 100–500 Å in size, which then moves independently [Figure 2(*b*), 26.10–53.70 s].

Sizes 1500–5000 Å Such large particles are most typical of cobalt- and nickel-containing samples. Only the outer parts of the particles, which are in contact with amorphous carbon, pass into the liquid M–C state due to their interaction with carbon. The particle cores remain solid and immobile [Figure 2(*c*)]. According to micro-diffraction data obtained *in situ*, the structure of the metal particles corresponds to the metal.

Quasi-steady state mode for the formation and movement of liquid M–C particles. As soon as they have formed, liquid Fe–C, Ni–C and Co–C particles start moving in random directions through the amorphous carbon film, transforming the amorphous carbon into graphite tracks. This unusual liquid state is realised and maintained only under dynamic particle movement conditions. M–C particles do not react with the graphite phase. Therefore, when no amorphous carbon remains, the M–C particles stop and dissolved carbon rapidly settles out as graphite layers covering the surface. The movement of individual M–C particles, 100–1000 Å large and not interacting with each other, through the amorphous carbon film is quasi-periodic and is characterised by accelerations and decelerations. This results in the formation of a track in the form of a graphite pipe separated by walls (Figure 3). The transition to the liquid state requires the absorption of such an amount of carbon that its volume is about the same as that of the metal particle. It follows that the limiting concentration of dissolved carbon in liquid M–C particles at 600–700 °C is close to 50 atom%. Hence, the liquid particles observed constitute an anomalously supersaturated solution of carbon in the metal.

Liquid M–C particles with initial sizes from 100 to 1000 Å gradually change their sizes to 200–400 Å after a series of fusions and break-ups as they flow through the carbon film [Figure 2(*d*)], displaying self-organising properties with respect to their morphology and size. The quasi-steady state graphitisation rates of liquid Fe–C, Ni–C and Co–C particles moving in the film at the rates of 10^{-4}, 10^{-6} and 3×10^{-6} cm s^{-1} are 1.6×10^{-5}, 1.6×10^{-7} and 4.8×10^{-7} mol cm^{-2} s^{-1}, respectively. These rates are 2–4 orders of magnitude higher than the rates of steady-state diffusion through solid Ni or Fe.[7]

Transition mode of formation of solid particles from liquid M–C particles. Decreasing the temperature to 30–40 °C below the critical value results in the transition of liquid M–C particles to the solid state. After short stops (tens of seconds) followed by returning the temperature above the critical value, the solid particles pass into the liquid mobile state once more. After longer stops (1–30 min), metal carbides (FeC, Co_3C) and face-centred cubic Ni are formed. It is known that carbides of metals of the iron group are stable up to 400–550 °C.[8–10] At higher temperatures, the carbides decompose to give eventually the metal and graphite. The stability of carbides decreases in the order $Fe_3C > Co_3C > Ni_3C$, which explains our results on the phase composition of solid particles.

The key question is the reason for this considerable decrease in the melting points of solid particles (by 500–900 °C) in

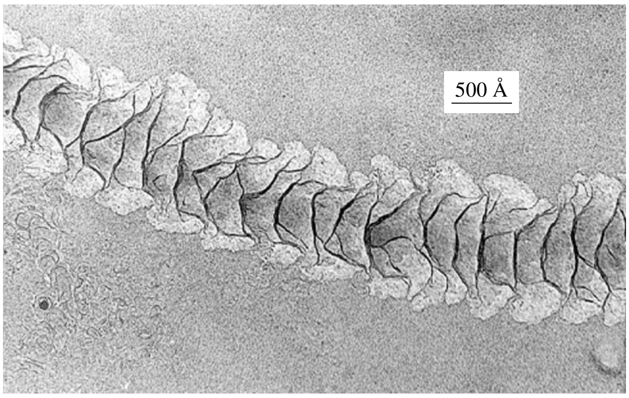

Figure 3 Graphite track formed after flowing a liquid Fe–C particle through an amorphous carbon film. Quasi-periodic graphite walls are observed about every 200–300 Å.

comparison with those of the usual metals or their eutectics with carbon, which remain in the solid state up to 1100 °C.[3] At 700 °C, the solubility of carbon in these metals is 0.2–0.4 atom%.[2,7] Hence, the formation of unusual liquid M–C particles, anomalously supersaturated with carbon, at relatively low temperatures (600–700 °C) cannot be explained in terms of metal–carbon interaction in equilibrium systems. In addition, this phenomenon cannot be a consequence of the dimensional effect of melting point decrease, which is observed only for metal and M–C particles smaller than 100 Å.

Thus, on heating of ‘metal particle–amorphous carbon’ systems *in vacuo* to 600–700 °C, an efficient interaction mechanism is realised, which involves the activation of the C–C bond, abstraction of carbon atoms and dissolution of atomic carbon in the metal with formation of a liquid M–C state. When a limiting concentration (up to 50 atom%) of dissolved carbon is reached, the structure of solid metal particles becomes unstable.

The ‘amorphous carbon–mobile liquid metal–carbon particles–graphite’ systems studied by us are open and substantially non-equilibrium physicochemical systems with self-organisation. The liquid M–C particles are catalytic intermediates of low-temperature graphitisation of amorphous carbon.

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