The Bulk Fusion of Platinum

EARLY EXPERIMENTS BY LAVOISIER AND SEGUIN

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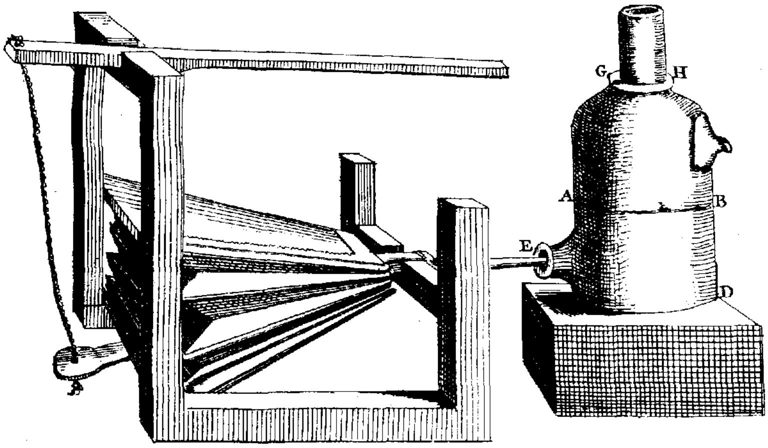
In 1789 the French Academy of Sciences initiated action which was to result in the drawing up of plans for the establishment of a uniform system of weights and measures, a system intended to replace the many local standards then currently in existence throughout the French kingdom. Soon afterwards it was suggested that examples of the new measures of length and of weight, when determined, should be executed in platinum and deposited as standards at the Hôtel de Ville, in Paris, while other copies might be sent to foreign countries who, it was hoped, would also adopt the new system of standards.

At that time chemists were only too well aware of the difficulty of working large quantities of platinum to a high degree of purity. Soon after samples of native platinum had been brought to Europe from America in the late 1740s, it became clear to chemists that ordinary methods of heating were inadequate to bring the metal into a state of fusion, and it was not until 1758 that Macquer and Baumé gained partial success, using a large burning mirror to concentrate the sun's rays on a small quantity of the crude metal (1). In 1775 Joseph Priestley suggested that intense heats might be obtained by blowing a fire with oxygen, a gas which he had succeeded in preparing only the previous year (2). The same idea was put forward by Antoine Laurent Lavoisier, probably independently, in 1782 (3).

From about 1786 the Parisian Master Goldsmith, Marc-Étienne Janety, had been able to produce malleable platinum using arsenic to help bring about the fusion of the metal, and he had a secret process for removing the arsenic afterwards, a process that was not always entirely satisfactory judging from a contemporary account (4). It is not surprising, therefore, to find that some chemists should have been attempting to improve the design and operation of their furnaces so that platinum could be brought into fusion without the addition of fluxes. Efforts made by

A. L. Lavoisier
1743–1794

Lavoisier took an active part in efforts to establish a new system of weights and measures in France. He had particular responsibility, with Haüy, for determining the new standard of weight, to be derived experimentally from the weight of a known volume of distilled water at the ice point



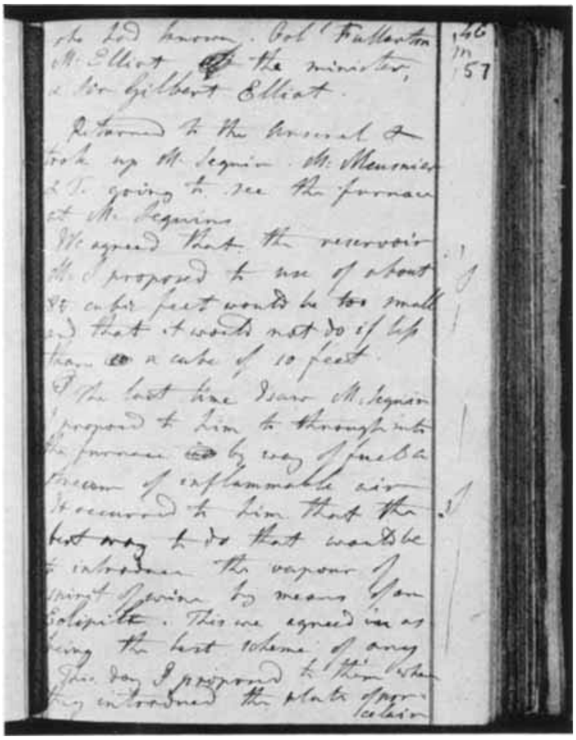
The type of furnace probably used by Lavoisier and Seguin in their attempts to melt platinum. The illustration is taken from Lavoisier's Traité Élémentaire de Chimie *of 1789. The engraving was made by Lavoisier's wife*

Lavoisier, Meusnier and Seguin, working together to this end have recently become known following an examination of the diary kept by the Scottish geochemist, Sir James Hall, who paid a short visit to Paris in 1791 (5).

Hall first became acquainted with the chemist Lavoisier in 1786, during the course of a visit to Paris, undertaken as part of a Grand Tour of Europe. Five years later, when Hall was again in the French capital, he immediately renewed his acquaintanceship with Lavoisier and subsequently dined with him at almost weekly intervals during the ensuing three months. Hall's diary records that after one such dinner, early in June 1791, Lavoisier, Meusnier and Seguin discussed a furnace for melting platinum, the fire of the furnace to be made more intense by feeding it with a stream of oxygen. Shortly afterwards work began on the project; the furnace was built in Seguin's house, and Hall spent a good deal of his time with Seguin who appears to have been largely responsible for the constructional work.

Details regarding the design of the furnace are not given in Hall's diary. We know from the account of a visit which Arthur Young made to Lavoisier's laboratory in 1787 that the furnaces there did not seem to be so well calculated for the higher degrees of heat as some he had seen elsewhere (6). In 1789 Lavoisier described a form of furnace that he proposed to build, which would produce an intensity of heat very much higher than any previously known. It could well be that this proposal was acted upon in 1791 (7).

From Lavoisier's account of 1789 we learn that the furnace would have two openings, one adapted to take the nozzle from a pair of bellows and the other fitted to receive a pipe leading from a gasholder. Lavoisier intended to heat the furnace to as high a temperature as possible using a fire of glowing charcoals blown by a draught of air from a pair of bellows. When the furnace had attained its highest temperature by this method of firing, the draught from the bellows would be shut off and oxygen from the gasholder would be admitted under a pressure said to be of four or five pounds. By drawing from a number of gasholders in turn Lavoisier hoped to maintain the oxygen supply so that eight or nine cubic feet of gas would be available for blowing the furnace.



The page from the diary of Sir James Hall for July 4th, 1791, which records ideas for firing the furnace in order to attain the high temperature necessary for melting large quantities of platinum

It seems that by 1791 Lavoisier's ideas had developed to the point where he envisaged a gasholder of some 85 cubic feet capacity for storing oxygen under pressure. It was soon realised that even this quantity would be insufficient for the purpose in hand, and Hall, Seguin and Meusnier agreed that the total capacity would need to be increased to 1,000 cubic feet. Hall suggested that a stream of alcohol vapour might be used as fuel for the furnace, and Seguin thought that this could best be injected into the furnace by means of an eolipile. Hall and Seguin discussed a scheme for mixing streams of alcohol vapour and of air from a number of small jets to serve as fuel for the furnace, and Seguin proposed that a similar result might be obtained by forcing a stream of air through spirit of wine from which it would take up sufficient spirit to ensure complete combustion.

It is unfortunate that political events in Paris in mid-July 1791 were such that Hall deemed it wise to return forthwith to England, for with his departure the eye-witness account of experiments with the furnace comes to an abrupt end. We know that Hall was present on one of the early occasions when the furnace was lighted, but that attempts to set a pot of spirit of wine within the furnace as fuel did not achieve the desired end.

On his way home and when passing through London, Hall delivered a letter from Lavoisier addressed to Josiah Wedgwood, the English potter. In this letter Lavoisier appears to have asked for a clay that could be used in the manufacture of vessels capable of resisting the intense fire that he and Seguin proposed to employ for the fusion of platinum. Wedgwood experimented with various clay mixtures and finally wrote to Lavoisier recommending one of burnt earth of alum with a gelatinous precipitate of alum made by alkali, and specimens of this composition were despatched to Lavoisier for trial (8). Seguin later wrote to Wedgwood seeking information about fuels found by English workers to produce the most intense heat; he also enquired whether the greatest heat was in the middle of the burning fuel or at the extremity of the flame, and whether large bellows for blowing or a very high chimney to the furnace would produce the greatest effect (9). Wedgwood consulted Priestley on these points but the latter was unable to give any advice save that he considered magnesia to be the most likely substance to stand up to such intense heats (10).

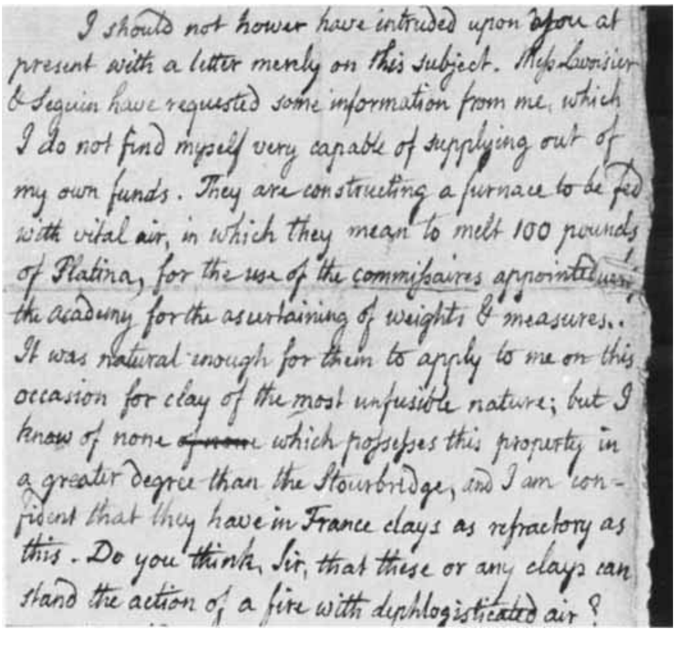
From a letter written by Seguin to Sir Charles Blagden, one of the two Secretaries of the Royal Society, we learn that Lavoisier and Seguin intended to melt 100 French pounds (about 49 kilograms) of platinum which was required by the Commissioners appointed by the Academy of Sciences in order to make the toise, the pendulum and various cylinders that would be needed in the determination of weights and measures (11).

The Registers of the Commission of Weights and Measures provide evidence that Lavoisier, who was appointed Treasurer of the Commission in September 1791, soon became involved in buying any platinum metal that came on the market. It would appear, however, that towards the end of that year the pressure of other work caused Lavoisier to devote less of his time to the practical problems of melting platinum. From then on Seguin appears to have been the main, if not the sole, experimenter.

Very little is known about subsequent operations by Seguin. A draft communication from the Commission of Weights and Measures, undated but addressed to Citizen Seguin, refers to the series of experiments on platinum which he had undertaken, and goes on to state that he possessed all the apparatus necessary for the successful working of the metal. Lavoisier was to be authorised to supply Seguin with crude platinum amounting to two French pounds, and Seguin was advised that all expenses entailed by extending his experiments to larger quantities of the metal than had hitherto been involved would be borne on funds that were at the Commission's disposal.

No record is known which gives details of the experiments that Seguin carried out on behalf of the Commission. It appears that at a meeting of the Commission, possibly in September 1791, Meusnier gave an account of experiments on platinum that had been carried out at Seguin's house. The note of this meeting ends with the tantalising statement that Seguin would give the details of these experiments when they were more complete (12).

Meusnier died in 1793 and Lavoisier met his death at the guillotine in 1794. Seguin lived until 1835 and was active for many years after the turn of the century, continuing to publish the results of his chemical studies. From the absence of any account by Seguin relating to his attempts to melt platinum in bulk, we can perhaps conclude that these efforts were not ultimately crowned with success. This conclusion seems all the more



I should not hower have intruded upon you at present with a letter merely on this subject. Mess Lavoisier & Seguin have requested some information from me, which I do not find myself very capable of supplying out of my own funds. They are constructing a furnace to be fed with vital air, in which they mean to melt 100 pounds of Platina, for the use of the commissaires appointed by the academy for the ascertaining of weights & measures.. It was natural enough for them to apply to me on this occasion for clay of the most unfusible nature; but I know of none ~~of more~~ which possesses this property in a greater degree than the Stourbridge, and I am confident that they have in France clays as refractory as this. Do you think, Sir, that these or any clays can stand the action of a fire with dephlogisticated air?

Extract from draft of Wedgwood's letter of September 2nd, 1791, to Priestley, in which he refers to Lavoisier and Seguin's efforts to melt platinum likely in view of the fact that when in 1792 Janety revealed the secret of his process for producing malleable platinum, it was to Janety and not to Seguin that the Academy of Sciences turned for the supply of platinum required for use in connection with the work of the various Commissions of Weights and Measures (13).

The problem of melting platinum in quantity was not quickly solved. It was not until 1859 that Deville and Debray announced their method for melting between 12 and 15 kilograms of platinum, and it is interesting to compare their method with that of the early French workers. For fuel they used a mixture of oxygen and coal gas, and their furnace was lined with lime, a material which they chose on two counts, namely, that it was the worst conductor of heat known and that it was a most effective radiator of heat and light (14).

References

1 Macquer, *Mém. Acad. r. Sci. Paris*, 1758, 119–133
2 J. Priestley, "Experiments and Observations on Different Kinds of Air" (London, 1775), **II**, 100–101
3 Lavoisier, *Mém. Acad. r. Sci. Paris*, 1782, 457–465
4 Nat. Lib. of Scotland MS. 6332, folios 49–50
5 *Ibid.*, MSS. 6329–6332
6 A. Young, "Travels during the Years 1787, 1788, and 1789 Undertaken more particularly with a View of ascertaining the Cultivation, Wealth, Resources, and National Prosperity of the Kingdom of France" (Bury St Edmunds, 1792), 64
7 A. L. Lavoisier, "Traité Élémentaire de Chimie" (Paris, 1789) **II**, 557–558
8 Archives de France MS. F^{17} A 1326, dossier 18, item 368
9 Keele Univ. Library Wedgwood MS. 4091–5
10 Royal Society Misc. MSS., **V**, letter no. 30
11 Br. Mus. Add. MS. 33272, folio 95 verso
12 Lavoisier, "Oeuvres" (Paris, 1893), **VI**, 680
13 Berthollet and Pelletier, *Ann. Chim.*, 1792 **14**, 20–33
14 H. S-C. Deville and H. Debray, *Ann. Chim. Phys.*, 1859, 3rd series, **14**, 385–496

The Microstructure of Cobalt-Platinum

The equiatomic cobalt-platinum alloy exhibits extremely high values of coercivity when in the partially ordered condition. Since optical and electron micrographs of the partially ordered material yield comparatively little information, the mechanism of ordering has been investigated mainly by X-ray diffraction techniques (1). During ordering the diffraction lines become diffuse, and this has been interpreted in terms of coherency strains between regions of ordered and disordered material. Specifically in the optimum magnetic condition the microstructure has been regarded as consisting of a very fine dispersion of ordered domains within a disordered matrix. Craik recently reviewed current theories of the mechanism of high coercivity in such a microstructure (2).

Recently, Southworth of the Department of Metallurgy, Cambridge, has been studying the mechanism of ordering in this alloy using the technique of field-ion microscopy. As a result rather a different picture of the ordering process is proposed (3). It is suggested that a potent source of the diffraction line broadening is the existence of a certain range over which the degree of long range order within the ordered regions varies. Both homogeneous and heterogeneous ordering are thought to occur, their relative importance depending on the transformation temperature.

The optimum magnetic properties appear after ordering for about 40 minutes at 660°C, and here it was found that the microstructure could not be described as two-phase. There *was* a fine dispersion of ordered domains, but they were only partially ordered, and this was *also* true of the matrix in which they lay. There was in addition a considerable variation in the degree of this partial order over the specimen. The partially ordered domains were not aligned; instead their tetragonal *c* axes were distributed in approximately mutually perpendicular directions.

It is apparent from this work that the existing theories for the mechanism of the high coercivity require modification. However, a material which is single-phase from a structural point of view may still have the magnetic properties of a two-phase system when the magnetocrystalline anisotropy encourages abrupt changes in the direction of magnetization across the microstructure.

H. N. S.

1 J. B. Newkirk, *et al.*, *J. Metals*, 1950, **188**, 1249; *J. Appl. Phys.*, 1951, **22**, 290; *Acta Cryst.*, 1951, **4**, 507
2 D. J. Craik, *Platinum Metals Rev.*, 1969, **13**, 95
3 H. N. Southworth, *Scripta Metall.*, 1968, **2**, 551; H. N. Southworth and B. Ralph, (Institute of Metals Monograph No. 33, 1969)