ENGINEERING RESEARCH INSTITUTE
UNIVERSITY OF MICHIGAN
ANN ARBOR

PROGRESS REPORT

APPLICATION OF THE POLAROGRAPH TO ANALYSIS OF TITANIUM-BASE ALLOYS

By

PHILIP J. ELVING

CHARLES L. RULFS

ROBERT W. PARRY

GRAHAM A. STONER

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SUMMARY

The present report covers the period from April 7, 1953, to June 7, 1953. During this period, further results were obtained for the determination of chromium, but a large part of the work was confined to a study of the ferricyanide system in 0.8 M potassium hydroxide solution. This study was considered necessary because the heights of the ferricyanide waves were often very inconsistent. Useful results have been obtained for the amperometric determination of vanadium.

SUMMARY OF RESULTS

A. Simultaneous Determination of Chromium and Iron

Further work was done on the simultaneous determination of iron and chromium in the titanium-base alloy described in the last Progress Report (April, 1953). The iron and chromium contents had been determined by emission spectrographic, spectrophotometric, and titrimetric methods for a probable 2.14% chromium and 1.06% iron. Samples for polarographic analysis were prepared and examined by the procedure described in the April Progress Report. The following results were obtained for chromium on four separate samples: 2.06%, 2.03%, 2.19%, 2.19% (probable Cr content: 2.14%).

The disproportionately large iron waves which were previously obtained have been eliminated. These appear to have been due to one or more of the following difficulties:

(a) Employment at one stage of unnecessarily large amounts of potassium fluoride and of potassium cyanide, both of which apparently were of dubious purity.

(b) Failure to recognize the greater stability with reference to resistance to boiling of titanium peroxydisulfate as compared to persulfate ion.

Excess of the latter is usually readily removed by boiling the solution.

(c) The appreciable instability of ferricyanide ion in alkaline media. The first two difficulties were recognized early and were eliminated before the iron determinations (concordant with the above chromium runs) were made.

The iron waves were compared with those obtained from a standard ferricyanide solution; the results obtained were found to be more inconsistent than could reasonably be ascribed to any heterogeneity of sample or other causes. The following results were obtained for the four samples: 1.58%, 1.59%, 1.19%, and 0.83% (probable Fe content: 1.06%). It was also observed that the height of the polarographic iron wave decreased with time. This observation led to a study of the stability of pure potassium ferricyanide in 0.8 M potassium hydroxide solution. A visual change was apparent in that the yellow ferricyanide solution turned colorless upon standing a few hours; this change was not detectable, of course, in the samples which contained chromate. Spectrophotometric curves indicated that the ferricyanide ion had all been converted into ferrocyanide within an interval of four hours.

Since aqueous solutions of ferricyanide ion are fairly stable for reasonable periods of time, the rapid disappearance of ferricyanide might be attributed to its basic environment. More specifically, we may assume that in the alkaline medium the ferricyanide ion oxidizes hydroxyl ions to oxygen and is itself reduced. Such a supposition can be examined on the basis of the standard electrode potentials of the redox half-cells concerned. The values for the latter, based on Latimer, Oxidation States of the Elements (Prentice-Hall, 1952) are:

$$\underset{1\,\underline{M}}{4\,OH^-} = O_2 + 2H_2O + 4\,\underline{e} \qquad E^\circ = -0.40 \text{ volt}$$

$$Fe(CN)_6^{-4} = Fe(CN)_6^{-3} + \underline{e} \qquad E^\circ = -0.36 \text{ volt}$$

When ferricyanide ion is in equilibrium with ferrocyanide ion in basic solution, ΔF for the redox reaction involving the two half-cell systems cited must be equal to zero.

Accordingly, we may write the following expression at room temperature:

$$-0.36 - \frac{0.059}{1} \log \frac{[Fe(CN)_6^{-3}]}{[Fe(CN)_6^{-4}]} = -0.40 - \frac{0.059}{4} \log \frac{1}{[OH^-]^4}$$

The pH at which the concentration of ferricyanide ion at equilibrium is a hundred times greater than that of the ferrocyanide ion can be calculated:

$$-0.36 - 0.059 \log 100 = -0.40 + 0.059 \log [OH^-]$$

$$-0.08 = 0.059 \log [OH^-]$$

$$\log [OH^-] = -1.3$$

$$\therefore \ pOH = 1.3 \text{ and } pH = 12.7$$

This indicates that at pH 12.7 we should have one hundred times as much ferricyanide present as ferrocyanide, providing the theory formulated and the data available are correct. We have been working with solutions having a pH of about 13.3 to 13.5, where a calculation based on the theory indicates comparable concentrations of ferricyanide and ferrocyanide. Accordingly, it would seem worthwhile to study the ferricyanide system at a pH value of about 10.5, where ferrocyanide formation should be minimized. It is not possible to work at pH values much below 10, since the chromate reduction wave shifts to more positive potentials as the pH decreases and is also more poorly defined, which then makes it increasingly difficult to differentiate it from the iron wave.

B. Determination of Vanadium

The experimental difficulties which had handicapped the first work with an amperometric titration of vanadium have been largely eliminated. At the present time, results accurate to within 2% of the vanadium content over a limited (fivefold) concentration range in the presence of titanium and excess urea, and without the necessity for oxygen-removal, have been validated. With further work, we anticipate that this technique should prove to be applicable over a wide range of concentration with a precision and accuracy of 0.5 to 1.0%, in the presence of most or all expected foreign ions; moreover, it should be possible to proceed from a single-sample attack, i.e., to remove an aliquot for analysis in the course of the iron-chromium procedure described in detail in the last bimonthly report (April, 1953).

FUTURE WORK

A quantitative study of the stability of ferricyanide ion over the pH range of about 9 to 13 is under way. The series of test titanium alloys which we have recently obtained from Wright Field will be analyzed for their iron and chromium content by the simultaneous polarographic procedure.

The vanadium procedure will be examined relative to its precision, accuracy and range of applicability.

We propose to reduce the iron, chromium, and vanadium methods to a workable laboratory procedure which will be applicable for any one, two or three of these constituents in a single sample of a titanium-base alloy. The procedure will include a full definition of accuracy, ranges, and any interferences.

Starting June 8, three graduate students will be working three-quarter time on the project as compared to the one or two men working three-quarter time or less during the previous life of the project. Work is to be begun on the polarographic determination of manganese as requested by Wright Air Development Center in its letter of April 15, 1953.

Analytical data will be obtained on the standard samples furnished by Wright Air Development Center.

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