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Standard Practice for
Electrolytic Extraction of Phases from Ni and Ni-Fe Base Superalloys Using a Hydrochloric-Methanol Electrolyte[1]

This standard is issued under the fixed designation E963; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers a procedure for the isolation of carbides, borides, TCP (topologically close-packed), and GCP (geometrically close-packed) phases (Note 1) in nickel and nickel-iron base gamma prime strengthened alloys. Contamination of the extracted residue by coarse matrix (gamma) or gamma prime particles, or both, reflects the condition of the alloy rather than the techniques mentioned in this procedure.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* (See 3.3.2.1 and 4.1.1.)

NOTE 1—Ni_3 Ti (eta phase) has been found to be soluble in the electrolyte for some alloys.

2. Terminology

2.1 *Definitions:*

2.1.1 extraction cell—laboratory apparatus consisting of a beaker to contain the electrolyte, a dc power supply, a noble metal sheet or screen cathode and a noble metal wire basket or wire to affix to the sample (anode).

2.1.2 geometrically close-packed (GCP) phases—precipitated phases found in nickel-base alloys that have the form A_3 B, where B is a smaller atom than A. In superalloys, these are the common FCC Ni_3 (Al, Ti) or occasionally found HCP Ni_3 Ti.

2.1.3 *topologically close-packed (TCP) phases*— precipitated phases in nickel-base alloys, characterized as composed of close-packed layers of atoms forming in basket weave nets aligned with the octahedral planes of the FCC γ matrix. These generally detrimental phases appear as thin plates, often nucleating on grain-boundary carbides. TCP phases commonly found in nickel alloys are σ, μ , and Laves.

3. Significance and Use

3.1 This practice can be used to extract carbides, borides, TCP and GCP phases, which can then be qualitatively or quantitatively analyzed by X-ray diffraction or microanalysis.[2]

3.2 Careful control of parameters is necessary for reproducible quantitative results. Within a given laboratory, such results can be obtained routinely; however, caution must be exercised when comparing quantitative results from different laboratories.[3]

3.3 Comparable qualitative results can be obtained routinely among different laboratories using this procedure.[3]

4. Apparatus

4.1 *Cell or Container for Electrolyte*— A glass vessel of about 400-mL capacity is recommended. For the sample size and current density recommended later in this procedure, electrolysis can proceed up to about 4 h, and up to about 4 g of alloy can be dissolved in 250 mL of electrolyte without exceeding a metallic ion concentration of 16 g/L. Above this concentration, cathode plating has been observed to be more likely to occur. A mechanism for cooling the electrolyte is recommended. For example, an ice water bath or water-jacketed cell may be used to keep the electrolyte between 0° and 30°C.

4.2 *Cathode*—Material must be inert during electrolysis. Tantalum and platinum sheet or mesh are known to meet this requirement. Use of a single wire is to be avoided, since cathode surface area should be larger than that of sample. Distance between sample and cathode should be as great as possible, within the size of cell chosen. For example, a sample with a surface area of 15 cm^2 should have no side closer than 1.2 cm to the cathode. If the cell is cylindrical, as for the case of a beaker or the upper part of a separatory funnel, the cathode could be curved to fit the inner cell wall to facilitate correct sample-cathode distance. The sample would then be centered

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[1] This practice is under the jurisdiction of ASTM Committee E04 on Metallography and is the direct responsibility of Subcommittee E04.11 on X-Ray and Electron Metallography.

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[2] Donachie, M. J. Jr., and Kriege, O. H., "Phase Extraction and Analysis in Superalloys—Summary of Investigations by ASTM Committee E-4 Task Group I," *Journal of Materials* , Vol 7, 1972, pp. 269–278.

[3] Donachie, M. J. Jr., "Phase Extraction and Analysis in Superalloys—Second Summary of Investigations by ASTM Subcommittee E04.91," *Journal of Testing and Evaluation*, Vol 6, No. 3, 1978, pp. 189–195.

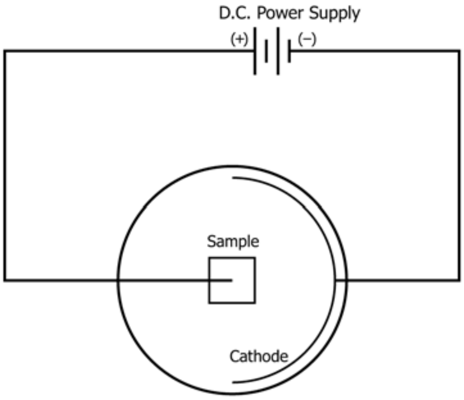

FIG. 1 Schematic Diagram of Extraction Cell

within the cell at the same height as the cathode. The cathode need not make a complete ring around the sample nor be more than 5 cm high.

4.3 *Anode*—The sample must be suspended in the electrolyte by a material that is inert during electrolysis. Anode connection material should be cleaned to prevent any contaminating material from falling into the cell. Good electrical contact should be maintained between the sample wire and the permanent anode wire from the dc power supply. Two methods are found to be successful. Either method is subject to disconnection of the sample due to shrinkage, which puts a limit on the electrolysis time:

4.3.1 Suspend the sample by platinum or platinum-rhodium thermocouple wire (20 gauge) wrapped around it to form a basket. To avoid a shielding problem, the ratio of sample area covered by the wire to the exposed sample area should be small.

4.3.1.1 Mechanically attach or spot weld the platinum or platinum-rhodium thermocouple wire to the sample.

4.3.2 If the weld is not immersed, non-inert wire may be substituted; for example, chromel, nichrome, 300 series stainless steel, etc. Stop-off lacquer should be used below the meniscus to maintain constant electrolyte level. This also eliminates formation of insoluble deposits immediately above the meniscus and prevents arcing.

4.3.2.1 **Warning**—Care must be taken to prevent arcing between anode and cathode which could ignite the methanol.

4.4 *Power Supply*—A variable dc power supply capable of providing 0 to 5 V is needed to obtain currents from 0 to 1.2 A depending on total surface area of the sample. For example, a sample with total surface area of 15 cm^2, electrolyzed at a current density of 0.1 A/cm^2, requires:

$$15\ \mathrm{cm}^2 \times 0.1\ A/\mathrm{cm}^2 = 1.2\ A \tag{1}$$

4.4.1 Current and voltage fluctuation should be no more than ±5 %. A ±5 % current fluctuation represents a current density fluctuation of about ±5 % which, for samples under 15 cm^2 total surface area, is less than or equal to one-half the current density shift due to sample shrinkage over 4 h. Potentiostatic control is not necessary, but may be helpful for determining optimum current density when setting up procedures for a new alloy.

4.5 *Membrane Filter*—Must be solvent and electrolyte resistant, with pore size of 0.4 to 0.8 µm. Filters made of poly(vinyl chloride) (fibrous) or polycarbonate (nonfibrous) meet these requirements and are available commercially, as are suitable filter holder assemblies. Mass loss for these materials in 10 % HCl-methanol is 10 %. The 2.5-cm diameter size is useful for preparing the residue for the X-ray diffractometer, which is commonly used for phase analysis of the residue. Otherwise, filter diameter is not critical. Filters should be handled with blunt tweezers.

4.6 *Centrifuge*—Centrifuging for residue collection can be performed as an alternate to microfiltration.

4.7 *Balance*—If quantitative analysis is desired, a balance sensitive to 0.0001 g is required.

5. Reagents

5.1 *Electrolyte*—Add and mix 1 part of 12 *N* hydrochloric acid (sp gr 1.19) to 9 parts of absolute methyl alcohol by volume to make a 10 % HCl-methanol solution. For alloys containing W, Nb, Ta, or Hf, add one part by weight tartaric or citric acid to 100 parts by volume HCl-methanol to make an approximately 1 % tartaric or citric acid solution. All reagents should be of at least ACS reagent grade quality.

5.1.1 **Warning**—Add hydrochloric acid to absolute methyl alcohol slowly and with constant stirring; otherwise sufficient heat is generated to cause a hazardous condition. Mixing must be done in an exhaust hood, because the fumes are toxic.

5.2 *Sample and Residue Rinse*—Absolute methyl alcohol is to be used.

6. Procedure

6.1 *Sample Size and Geometry*—A cube, cylinder, or rectangular prism is preferred. Ideally, constant density should be maintained during electrolysis. Flattened samples, especially thin sheet, will experience considerable shrinkage due to edge effects and current density increase as the electrolysis proceeds. A cube approximately 1.6 cm on a side will have a total surface area of approximately 15 cm^2. Smaller samples have larger increases in current density during constant current electrolysis due to shrinkage. Larger samples may require more than 250 mL of electrolyte and a power supply capable of delivering more than 1.2 A. Samples requiring higher total current may cause a cathode plating problem due to the higher voltage required, and may make a cooling mechanism absolutely necessary.

6.2 *Sample Preparation*—The sample must be free of all surface contamination that could be mistakenly identified as included material extracted from the bulk alloy. Two methods known to be useful are as follows: (*1*) Grind all surfaces to 120 grit. This method is not recommended for porous samples which may become imbedded with grit material. An advantage of the method is the removal of surface cracks and irregularities; or (*2*) Perform a light etch cleaning which does not substantially alter the surface. A short electroetch with the same electrolyte and current density as used for the actual extraction is suitable.

6.2.1 Corners, if sharp, may become areas of localized high-current density and therefore must be smoothed. After surface preparation, the sample may be ultrasonically cleaned to remove any adhering particles. A final rinse is done with methanol. Air drying is sufficient.

6.3 *Determine Current Density to be Applied*—Measure the dimensions of each face of the sample and calculate the total surface area in square centimetres (correct for any surface not submerged). Current density is in the range from 0.05 to 0.1 A/cm^2 for most nickel and nickel-iron base alloys. The specific current density required for optimum electrolytic dissolution is a function of both alloy composition and heat treatment. The optimum current density is the highest current density at which no matrix contamination occurs. This can be monitored potentiostatically if such equipment is available.[4] Multiply the chosen current density by total surface area to obtain the required total current.

6.4 *Attach Anode Wire*—Methods are described in Section 4. A length of wire at least 2 in. should project from the sample. This is needed for clamping to or looping to the permanent anode wire.

6.5 *Weigh Sample*—Only if quantitative analysis is performed, weigh the sample (with wire, if welded) then the filter pad or centrifuge tube to the nearest 0.0001 g. Note that for samples over 10 g, a weighing error of ±0.001 g may be considered negligible relative to an error of ±0.0001 g in the mass of the residue.

6.6 *Anode Connection*—Suspend the sample by its wire in the cell. Center the sample with respect to the cathode.

6.7 *Add Electrolyte*—If the anode is prepared as in 4.3.1 or 4.3.1.1 completely cover the sample and cathode with about 250 mL of electrolyte. If the anode is prepared as in 4.3.2, then the weld must remain above the liquid, and the depth of sample immersion must agree with that used in the surface area calculation. At this point the cooling mechanism, if used, should be started.

6.8 *Electrolyze*—Set power supply to the predetermined current. Allow electrolysis to proceed, usually for a period of 4 h. If the power supply will not automatically maintain constant current, monitor the current at 15-min intervals, correcting for any current drift. Record the voltage for future reference. Add fresh electrolyte as required to maintain original volume. This is extremely important for non-totally immersed specimens. Depleted hydrogen ion is replaced by adding 3 mL of concentrated HCl/A-h of electrolysis.

6.9 *Remove Sample*—When power is turned off, suppress the cooling mechanism. Raise the sample above the liquid level and rinse with methanol. Disconnect the anode wire from the power source and remove sample and its attached wire from the cell. If the sample has detached from the wire and fallen into the cell, retrieve it with stainless steel tweezers and rinse with methanol into the cell.

6.9.1 If a heavy coating is adhering to the sample, place the sample in a 100-mL beaker, cover with methanol, and place beaker in ultrasonic cleaner for about 10 s. Remove sample with tweezers and rinse with methanol, collecting the rinsings in the 100-mL beaker. Set the sample aside to air dry. Cover the beaker. If the sample does not require ultrasonic cleaning, set it aside to dry after removal from the cell.

6.10 *Sample Weighing*—Only if quantitative analysis is to be performed, weigh the sample with or without wire as done in 5.5 and calculate the loss in mass of the sample.

6.11 *Residue Collection*—Follow method in 6.11.1 or 6.11.2.

6.11.1 *Microfiltration*—If the cell is not a beaker, transfer the electrolyte to a beaker, rinsing the cell and cathode with methanol and collecting the rinsings into the electrolyte. Normally a 400-mL beaker is of sufficient size. Pour the electrolyte through the tared-membrane filter. Rinse the beaker, pouring the rinsings through the filter.

6.11.1.1 If residue was collected in a 100-mL beaker from ultrasonic cleaning, filter the beaker contents with the same filter used for the electrolyte. Rinse the 100-mL beaker with methanol, pouring the rinsings through the filter.

6.11.1.2 Normally a 500-mL filter flask is sufficient to contain the original electrolyte plus the methanol used for ultrasonic cleaning, plus all rinsings. A water aspirator or filter pump should be used to speed the filtration process.

6.11.1.3 Wash the residue three times with methanol. Remove the filter with residue from the filter support. Place it on a clean surface to dry in air where it is protected from airborne contamination and any other disturbance.

6.11.1.4 If quantitative analysis is being performed, blank one filter pad from the same lot of filter pads, using 100 mL of 10 % HCl-methanol. Remove the blank filter and weigh to the nearest 0.1 mg. Calculate the mass lost to the acid by the blank filter. Weigh the filter with the residue to the nearest 0.1 mg. Calculate the mass of residue collected. Add to this the correction for the mass loss of the blank filter to obtain the corrected mass of residue. Calculate the mass % residue, R, as follows:

$$R = \left[M_r / (M_i - M_f) \right] \times 100 \qquad (2)$$

where:

M_r = mass of residue,

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[4] Hughes, H., "Potentiostatic Techniques in Constitutional Examination of Alloy Steels," *Journal Iron and Steel Institute* , Vol 204, 1966, pp. 804–810.

M_i = initial mass of sample,
M_f = final mass of sample after extraction and cleaning, and
R = residue, mass %.

6.11.2 *Centrifuging*—The residue can be collected using a centrifuge. If a residue trap is not used, the entire volume of electrolyte must be subject to centrifuging. The cell is carefully rinsed with methanol and the rinsings poured into centrifuge tubes.

6.11.2.1 The specimen is removed from the electrolyte and suspended in a centrifuge tube containing methanol. The tube is placed in an ultrasonic cleaner and the adherent residue is removed by the ultrasonic cleaning action.

6.11.2.2 The residue can be driven to the bottom of the tube in 2 to 3 min by the centrifuging action at 18 000 to 20 000 rpm. The solution in the tubes is decanted and the residue (in the tube) is rewashed with methanol (residue must be stirred up) and centrifuged. This rewashing should be done at least three times.

6.11.2.3 For quantitative analysis, the centrifuge tube must be carefully cleaned, dried, and weighed. After residue collection, the outside surface of the centrifuge tube must be carefully cleaned before the tube is weighed. The residue is then removed and the tube recleaned and reweighed. The original tube weight and the final tube weight should be approximately the same.

6.12 If the filtrate or decantate is to be retained for analysis, transfer to an Erlenmeyer flask. Close with a methanol resistant rubber stopper.

6.13 Extracted residue and in-situ particles should be examined microscopically for comparison of morphologies. This allows investigator to assess which in-situ particles have been extracted.

7. Keywords

7.1 borides; carbides; electrolytic extraction; Gamma prime; GCP phases; superalloys; TCP phases