



Designation: E 963 – 95 (Reapproved 2000)

## Standard Practice for Electrolytic Extraction of Phases from Ni and Ni-Fe Base Superalloys Using a Hydrochloric-Methanol Electrolyte<sup>1</sup>

This standard is issued under the fixed designation E 963; 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 ( $\epsilon$ ) 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<sub>3</sub> 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<sub>3</sub> B, where B is a smaller atom than A. In superalloys, these are the common FCC Ni<sub>3</sub> (Al, Ti) or occasionally found HCP Ni<sub>3</sub> 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  $\gamma$  matrix. These generally detrimental phases appear as thin plates, often nucleating on grain-boundary carbides. TCP phases commonly found in nickel alloys are  $\sigma$ ,  $\mu$ , and Laves.

<sup>1</sup> 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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### 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.<sup>2</sup>

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.<sup>3</sup>

3.3 Comparable qualitative results can be obtained routinely among different laboratories using this procedure.<sup>3</sup>

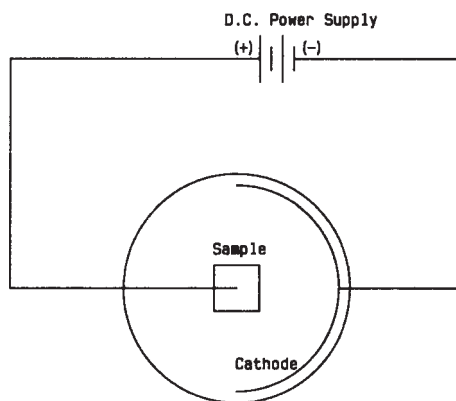
### 4. Apparatus

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<sup>2</sup> 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

<sup>2</sup> 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.

<sup>3</sup> 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**

sample-cathode distance. The sample would then be centered 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<sup>2</sup>, electrolyzed at a current density of 0.1 A/cm<sup>2</sup>, requires:

$$15 \text{ cm}^2 \times 0.1 \text{ A/cm}^2 = 1.2 \text{ A} \quad (1)$$

**4.4.1** Current and voltage fluctuation should be no more than  $\pm 5\%$ . A  $\pm 5\%$  current fluctuation represents a current density fluctuation of about  $\pm 5\%$  which, for samples under 15 cm<sup>2</sup> 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  $\mu\text{m}$ . 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<sup>2</sup>. 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