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PATENT APPLICATION/TECHNICAL DIGEST PUBLICATION RELEASE REQUEST

FROM: Associate Counsel (Patents) (1008.2)
TO: Associate Counsel (Patents) (1008.2)

Via: (1) Richard Everett (Code 6352)
(2) Division Superintendent (Code 6300)
(3) Head, Classification Management & Control (Code 1221)

SUBJ: Patent Application/Technical Digest entitled: **"METHOD FOR MAKING METAL COATED POWDERS"** Request for release for publication.

REF: (a) NRL Instruction 5510.40C
(b) Chapter 6, ONRINST 5870.1C

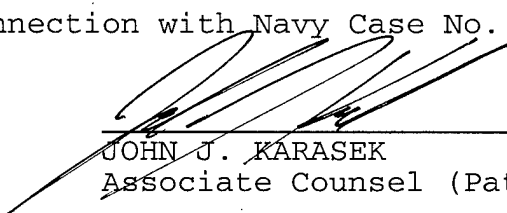
ENCL: (1) Copy of Patent Application/Technical Digest

1. In accordance with the provision of references (a) and (b), it is hereby requested that the subject Patent Application/Technical Digest be released for publication.

2. It is intended to offer this Patent Application/Technical Digest to the National Technical Information Service, for publication.

3. This request is in connection with Navy Case No. 80 242

1/26/01
(date)



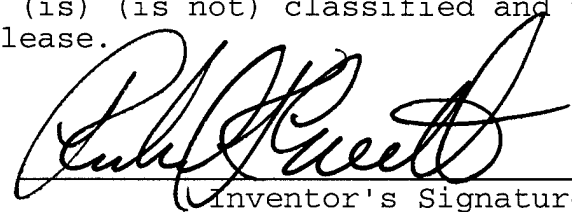
JOHN J. KARASEK
Associate Counsel (Patents)

FIRST ENDORSEMENT

Date: 2/13/01

FROM: Richard Everett (Code 6352)
TO: Division Superintendent (Code 6300)

1. It is the opinion of the Inventor(s) that the subject Patent Application/Technical Digest (is) (is not) classified and there is no objection to public release.



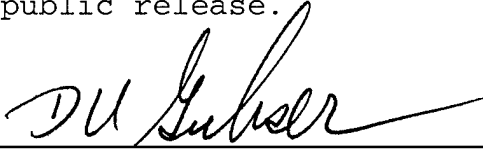
Inventor's Signature

SECOND ENDORSEMENT

Date:

FROM: Division Superintendent (Code 6300)
TO: Classification Management & Control (Code 1221)

1. Release of Patent Application/Technical Digest (is) (is not) approved.
2. To the best knowledge of this Division, the subject matter of this Patent Application/Technical Digest (has) (has not) been classified.
3. This recommendation takes into account military security, sponsor requirements and other administration considerations and there in no objection to public release.



Division Superintendent

THIRD ENDORSEMENT

Date:

FROM: Head, Classification & Control (Code 1221)
TO: Associate Counsel (Patents) (1008.2)

1. This Patent Application/Technical Digest is authorized for public release.



Head, Classification, Management & Control

METHOD FOR MAKING METAL COATED POWDERS

Field of the Invention

The present invention relates to a method for making bulk quantities of metal-coated powders at low temperatures.

Background of the Invention

Metal-coated powders can range in size from nanometers to microns. Metal-coated powder can be used in catalysis, electromagnetic shielding, ferro-fluids, magnetic recording, composite precursors and advanced-engineered materials.

Metal-coated powders can be prepared by physical vapor deposition, mechanical blending and mixing, and chemical routes. Vapor methods are not cost effective and can only be used to make small amounts of material. Mechanical blending often introduces impurities into the final product. Fluidized beds have been used to coat powders with metals, but, as in vapor methods, the initial equipment is expensive, and it is difficult to coat the powders evenly and to handle powders of different sizes.

Others in the art have prepared micron and submicron-size metallic powders of cobalt, copper, nickel, lead and silver using the polyol method. These particles consisted of single elements. Depending upon the type of metallic precursors used in the reaction, additional reducing and nucleating agents were often required.

Maruyama, in U.S. Patent No. 6,033,622, described a method for making metal matrix composites using reinforcing particles coated with a metal matrix produced by chemical vapor deposition or electrochemical deposition. However, this process does not permit deposition of

all types of ferrous and non-ferrous metals and alloys, and the coating thickness and uniformity cannot be closely controlled.

Figlarz et al., in U.S. Patent No. 4,539,041, discloses producing metallic powders by reducing a solid oxide, hydroxide, or salt of a metal in a liquid phase. The solid compound is suspended in a polyol and the formed metallic precipitate is isolated. Ong et al., in U.S. Patent No. 5,698,483, discloses a method of preparing nano sized powders comprising mixing an aqueous continuous phase comprising at least one metal cation salt with a hydrophilic organic polymeric disperse phase, thereby forming a metal cation salt/polymer gel and heat treating the gel at a temperature sufficient to drive off water and organics within the gel, leaving as residue a nanometer particle-size powder.

Hidaka et al., 5,250,101, discloses a process for producing a fine powder with a primary particle diameter of not more than 0.5 microns by heating an organic acid metal salt in the presence of palladium, which lowers the thermal decomposition temperature of the salt, and thermally decomposing the organic acid metal salt in the presence of the palladium.

Viau et al., in U.S. Patent No. 5,925,166, discloses a process for obtaining iron or iron-based powders by organic liquid phase precipitation. Metal precursors are introduced into a basic polyol or, optionally, into a simple alcohol solution, heating the reaction medium to obtain a metal precipitate, and recovering and treating the precipitate to obtain the desired powder.

Klapdor et al., in U.S. Patent No. 5,951,739, discloses a process for preparing nanocrystalline metal powders by reacting halides of metals with alkali metal hydrides or alkaline earth metal hydrides in an organic solvent with continual milling.

Chow et al., in U.S. Patent No. 5,759,230, describes producing nanostructured metal powders and films using an alcoholic solvent. A mixture of a metal precursor is heated in an alcoholic solvent to reduce the metal precursor to a metal precipitate, which can then be isolated, *e.g.*, by filtration.

Unfortunately, the presence of the additional nucleating and reducing agents during the reaction may result in undesirable and trapped impurities, particularly non-metallic impurities, and there has not been yet devised a method for producing powders which are evenly coated with metals in any size desired.

Summary of the Invention

It is an object of the present invention to overcome the aforesaid deficiencies in the prior art.

It is another object of the present invention to form nanostructured metal coated powders.

It is a further object of the present invention to produce nanostructured metal coated powders and to produce metal alloy coatings and precursors for metal/ceramic composites.

It is a further object of the present invention to produce nanostructured metal coated powders and films of metals, metal alloys, and metal/ceramic composites.

It is another object of the present invention to provide a method for making metal coated powders in bulk ranging in size from nanometers to microns.

According to the present invention, metal coated powders are produced at a relatively low temperatures by suspending a precursor metal salt and the powder to be coated in a glycol. As

the mixture is heated, the metal is reduced and precipitates as a coating onto the powders. Suspension of the powder may be accomplished by proper choice of glycol, powder size, combined with ultrasonification, mechanical agitation, or stirring, or using conventional foam bubbling. The mixture, when heated to reflux and reduction and precipitation or growth of the metal films, occurs in solution. The metal-coated powders are removed from the solution, generally by filtration.

The concentration of the metal precursor salt, time, and temperature of reflux can be used to control the coating thickness.

The process of the present invention makes it possible to deposit more types of ferrous and non-ferrous metals and alloys than as previously been possible, with more control over coating thickness and coating uniformity. This improved control could make possible several advantageous improvements to a composite material's microstructure larger mean nearest neighbor distance (and reduced nearest neighbor distance standard deviation), and thus improved mechanical properties (higher proportional limit and yield stresses, and larger strains to failure). These generic improvements to the composite, which are independent of the matrix and particle composition, allow more widespread usage of composites in critical applications.

Of the metal powders that can be used in the present invention are any metal powder that is not soluble in the glycol used at any temperature. This includes metal oxides, borides, carbides, nitrides, silicides, and the like.

Any glycol or diol can be used, either alone or in combination with another alcohol.

The time for formation of the metal powder depends upon the coating thickness desired,

and can range from a few minutes to a few hours.

Brief Description of the Drawings

The figure shows a La Mer diagram for formation of monodisperse particles.

Detailed Description of the Invention

To make metal coated powders according to the present invention, a metal precursor is mixed with a powder to be coated and a glycol. Among the glycols that can be used are aliphatic glycols or corresponding glycol polyesters which are liquid at the reaction temperatures. The aliphatic glycols can be alkylene glycols having up to 6 carbon atoms in the main chain, or a ethanediol, a propanediol, a butanediol, a pentanediol, or a hexanediol, as well as polyalkylene glycols derived from these alkylene glycols. Other glycols include ethyleneglycol, diethylene glycol, tri-ethylene glycol, dipropylene glycol, and polyetheylene glycols liquid at the reaction temperatures, or glycerol.

Particularly interesting polyols for use in the process of the present invention include ethylene glycol, diethylene glycol, tri-ethylene glycol, tetra-ethylene glycol, 1, 2-propanediol, dipropylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, and 2,3-butanediol. These glycols are advantageous because of their significant reducing power, their boiling temperatures are between about 185° and 328°C, the proper thermal stability, and their low price. Furthermore, these glycols raise fewer potential toxicity problems.

To produce coated metal powders according to the present invention, the metal precursor or precursors are mixed with the powder to be coated and a glycol solvent. At the time of mixing, the glycol solvent may be either heated or unheated. Then, the resulting mixture is

reacted at temperatures sufficiently high to dissolve, or to allow the reaction of the metal precursor or precursors, and to liberate the free metal as a precipitate on the powder. Generally, the mixture is reacted at about 80-360°C, depending upon the reflux temperature of the glycol. The preferred temperature depends on the reaction system used. After the metal precipitates onto the powder, the reaction mixture is cooled naturally in air or quenched. Because quenching provides greater control over the reaction time, it is generally preferred to perform natural ambient air cooling. For quenching to be useful in coating a powder, the powder substrate must be able to withstand rapid thermal changes. If the powder cannot withstand these rapid temperature changes, then air cooling should be used.

The method of the present invention may be used to form particles coated with various metal and alloys or composites thereof. For example, powders coated with vanadium, chromium, magnesium, iron, cobalt, nickel, copper, niobium, molybdenum, ruthenium, rhenium, palladium, silver, indium, tin, tantalum, tungsten, osmium, iridium, platinum, gold or alloys thereof, or metastable alloys containing these metals as primary constituents. The precursor form of the metal depends upon the metal itself. Generally, the precursor may be any metal-containing compound that, under the reaction conditions, can be reduced to the elemental metal. Typical precursors include metal acetates and hydrates thereof, metal chloride and hydrates thereof, metal nitrates, metal oxides, metal oxalates, metal hydroxides, and acids, including the desired metal as part of an oxyanion (*e.g.*, tungstic acid) and salts of such acids (*e.g.*, sodium tungstate and potassium hexachloroplatinate). The best precursors to use for the formation of metal-coated powders will depend upon the metal selected. For best results, the metal precursors used in the present

invention should be substantially soluble in the reaction mixture.

Typical metal precursors include metal acetates and hydrates thereof, metal acetylacetonates, metal chlorides and hydrates thereof, metal nitrates, metal oxides, metal oxalates, metal hydroxides, and acids, including the desired metal as part of an oxyanion (*e.g.*, tungstic acid) and salts of such acids (*e.g.*, sodium tungstate and potassium hexachloroplatinate). The best precursors to use for producing nanostructured metal.; coated powders depend upon the particular metal selected. Typically, to provide nanostructured materials, the precursors used in the present invention should be substantially soluble in the reaction mixture.

The powders that can be coated by the process of the present invention include metals and ceramic oxides, borides, nitrides, and carbides. The particle size of the powders to be coated ranges from about 0.1 to about 1000 microns.

Example 1: Co Films

Cobalt coated powders can be used for magnetic, structural, electronic, and catalytic applications. This polyol process can achieve nanostructured cobalt films formed on boron carbide.

Two grams of B_4C was added to a solution of ethylene glycol and 6.0 grams cobalt acetate. The solution was brought to reflux, about $185^\circ C$, for two hours and allowed to cool to room temperature.

This reaction was repeated using 1,2-propane diol as the solvent rather than ethylene glycol

Example 2: Cu Films

Copper-coated alumina powders formed by this method.

Two grams of alpha-form alumina, -325 mesh, as added to a stirred solution of ethylene glycol and 6.99 grams copper acetate. The solution was refluxed for two hours at 185°C, cooled to room temperature, and filtered.

Example 3: Co-coated Powders in the Presence of a Magnetic Field

Example 2 was repeated except that two magnets were placed around the flask.

The choice of powder or film can be controlled by the selection of the proper synthesis conditions to favor either nucleation or growth, respectively.

Figure 1 is a LaMer diagram showing formation of monodispersed particles. At phase I, prenucleation, nuclei form. At phase II, nucleation, particles form. At phase III, growth, films form. Growth is a function of concentration of atoms in solution, time, and temperature.

The crystallinity and phase of the prepared materials was confirmed by X-ray diffraction. Analysis of as-prepared materials by SEM and TEM demonstrated that the particle sizes were in the nanometer range.

Powders can be coated with refractory metals and their alloys such as tungsten, molybdenum, rhenium, and tantalum. If the oxides of these metals are chemically stable under the reaction conditions used, they cannot be reduced to form coatings on powders. Therefore, the precursors of these refractory metals should be chosen to avoid the formation of such stable oxides or their stable intermediates. Generally, the precursors of refractory metals should be salts or acids, rather than oxides or hydroxides, including the desired refractory metal or metals. Acids

and salts including the oxyanion of the desired refractory metal or metals, however, may be preferred.

Unlike the process disclosed in Chow et al., U.S. Patent No. 5,759,230, in which there is no nucleating agent, the present invention implicitly contains a nucleating agent, *i.e.*, the powder which is to be coated. The metal which is reduced is coated onto the powder to produce a powder-coated metal. However, as in Chow et al., there is no requirement for a catalyst, so that the resulting coated powders are free or essentially free of impurities that would deleteriously alter their properties.

If desired, surfactants and/or dispersants may be added to the reaction mixture to avoid the agglomeration of nanoparticles. If a highly pure product is desired, these surfactants and dispersants should be essentially free of insoluble materials, or capable of being burnt out of the final product. Where a surfactant is used, the best choice of surfactant depends upon the desired metal. Steric stabilization using a nonionic surfactant (*e.g.*, a high temperature polymeric surfactant) is preferred, since ionic surfactants may undesirably alter the pH of the reaction system during reduction of the metal precursor. If desired, however, a mixture of ionic and nonionic surfactants can be used.

The pH may influence the method of the present invention. For example changing the pH during the reaction may be used to alter the solubility of the reaction product in the reaction mixture. If a constant pH is desired throughout the reaction, the reaction mixture may be modified to include a buffer.

During the reaction, the reaction mixture may, but need not be, stirred, or otherwise

agitated, for example by sonication. The effects of stirring during the reaction depend upon the metal coating to be produced and the energy added during stirring. Stirring during production of magnetically coated materials would most likely increase agglomeration, in which case the use of a surfactant would be beneficial.

The method of the present invention can also be used to produce nanostructure composite metal coatings on powders. As defined herein, a composite metal film includes at a least one metal first component and at least one other component that is intentionally included in amounts that significantly enhance the desirable properties of the film or powder. The other component is usually, but not necessarily, another metal. Where the other component is a metal, the metal may be any metal, not just those metals that could be deposited as a pure coating according to the present invention. Throughout the present specification and claims, the term "alloy" applies to inter-metallic compounds and solid solutions of two or more metals. The term "composite" applies to phase-separated mixtures of a metal with at a least one other component. Where the other component of the coating is a chemically stable ceramic, the present invention provides a powder coated with a metal/ceramic composite. Generally, a metal/ceramic composite includes at least 50 volume percent metal, in the form of a single phase material or an alloy. Throughout the present specification and claims, the term "composite" includes alloys and metal/ceramic composites.

To produce complex coatings on powders according to the present invention, at least one precursor for the at least one metal component and at least one precursor for the other component or components of the coating are combined in the reaction mixture before heating the mixture to

the reaction or re-fluxing temperature. Otherwise, the process proceeds as described above to make single metal coated powders.

In producing composite coatings according to the present invention, the initial molar ratios of the components to each other may not be reflected in the final product. Additionally, the ability of precursors of the components to atomically mix in the reaction solution does not assure that the components will form a composite substance final coating material. For this reason, the correct starting ratios of the precursors of each compound for any composite substance must be determined empirically. The relative reduction potentials of each component can provide some guidance in making this empirical determination.

The process of the present invention makes it possible to produce larger quantities of metal coated powders than conventional techniques, while achieving better chemical homogeneity because of mixing of the constituents at the molecular or atomic level. Additionally, the chemical route used does not require expensive processing equipment, and the production cost is relatively low.

The solvent used in the process is recyclable, and the coating thickness can be controlled by selecting the synthesis conditions to favor either nucleation or growth.

The process of the present invention can be used to deposit magnetic materials as well as non-magnetic materials. Additionally, the process can be used to deposit single elements, alloys, or multi-component elements.

The powder feedstock can be of any size and shape. In particular, powders having a particle size ranging from about 0.01 micron to about 1000 microns can be advantageously

prepared according to the present invention. These coated particles can be used to make particulate-reinforced composites.

The foregoing description of the specific embodiments will so fully reveal the general nature of the invention that others can, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without undue experimentation and without departing from the generic concept. Therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. The means and materials for carrying out various disclosed functions may take a variety of alternative forms without departing from the invention. Thus, the expressions "means to..." and "means for..." as may be found in the specification above and/or in the claims below, followed by a functional statement, are intended to define and cover whatever structural, physical, chemical, or electrical element or structures which may now or in the future exist for carrying out the recited function, whether or not precisely equivalent to the embodiment or embodiments disclosed in the specification above; and it is intended that such expressions be given their broadest interpretation.

Navy Case No. 80,242
Inventors: Kurihara, et al.

PATENT APPLICATION

ABSTRACT OF THE DISCLOSURE

Metal coated powders are produced by suspending a precursor metal salt and the powder to be coated in a glycol. This mixture is heated, and the metal salt is reduced and the metal precipitates as a coating onto the powder.

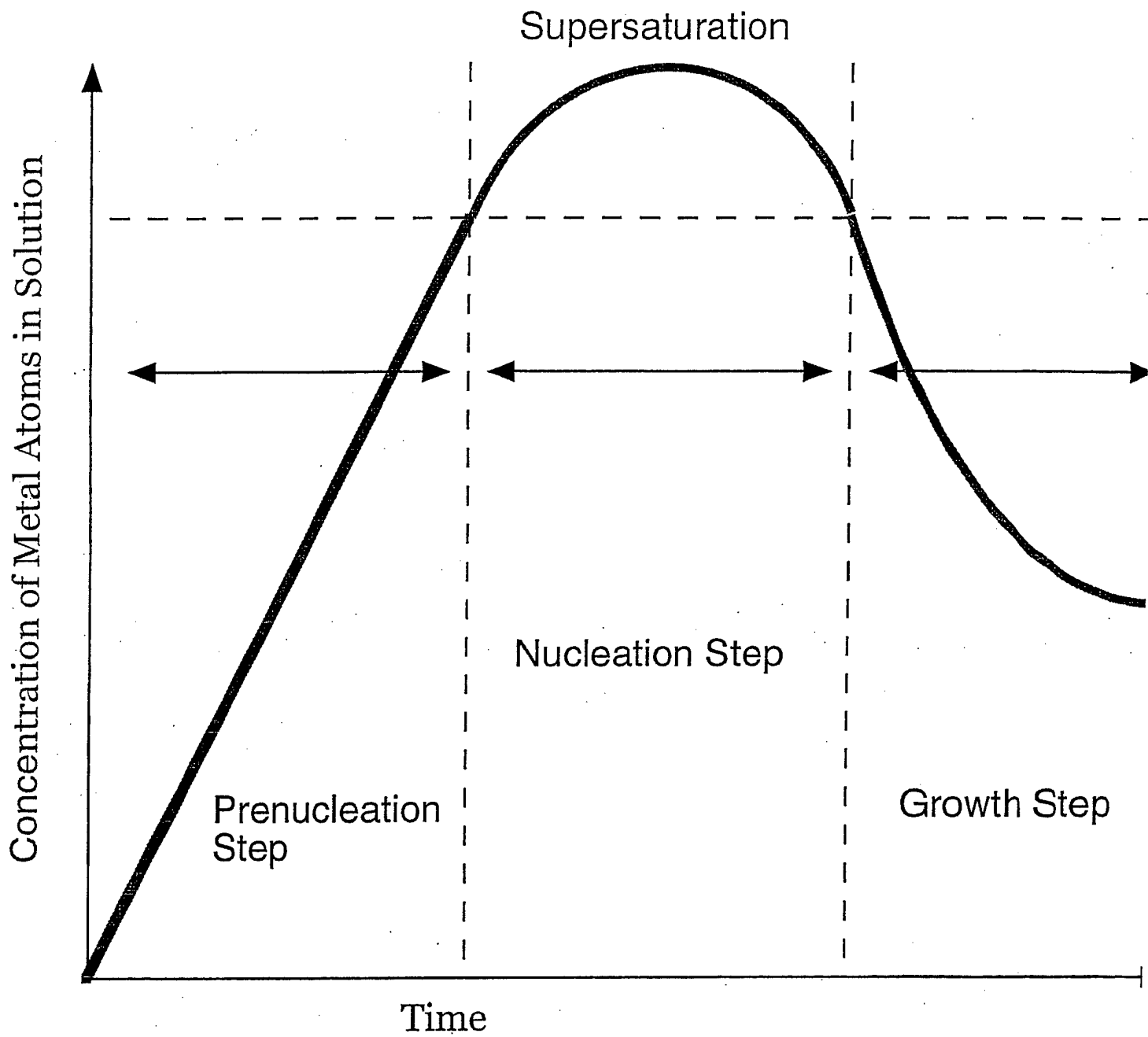


Figure 1