

[54] METHOD FOR PREPARING MAGNETIC
ALLOY POWDER BY SURFACE NITRIDING

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148/126; 75/205

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[58] Field of Search..... 75/.5 BA, .5 B, .5 R, 204,
75/205, .5 AA; 148/105, 16.6, 31.55, 126

[56] References Cited

UNITED STATES PATENTS

2,497,268 2/1950 Neel..... 75/.5 AA

2,660,522 11/1953 Marquaire 75/.5 BA
2,666,724 1/1954 Beller..... 148/16.6
2,686,714 8/1954 Schlecht et al. 75/.5 AA
2,812,276 11/1957 West et al..... 148/31.55
3,337,327 8/1967 Jordan et al. 75/.5 AA
3,348,982 10/1967 Dunton 148/105
3,399,085 8/1968 Knechtel et al..... 148/16.6

OTHER PUBLICATIONS

Bozorth, R.; *Ferromagnetism*, New York, 1951, pp.
239-240, (QC753B69).

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[57] ABSTRACT

In the course of the reduction of metal salts powder
such as a ternary oxalate of Fe, Co and Ni by heating
in a reducing atmosphere, a nitrogen-containing com-
pound gas such as NH₃ is introduced into the reaction
system atmosphere in order to form a layer of metal
nitride on the surface of the powder. The nitride layer
protects the resulting alloy powder against air-
oxidation and deterioration in the magnetic proper-
ties.

10 Claims, 5 Drawing Figures

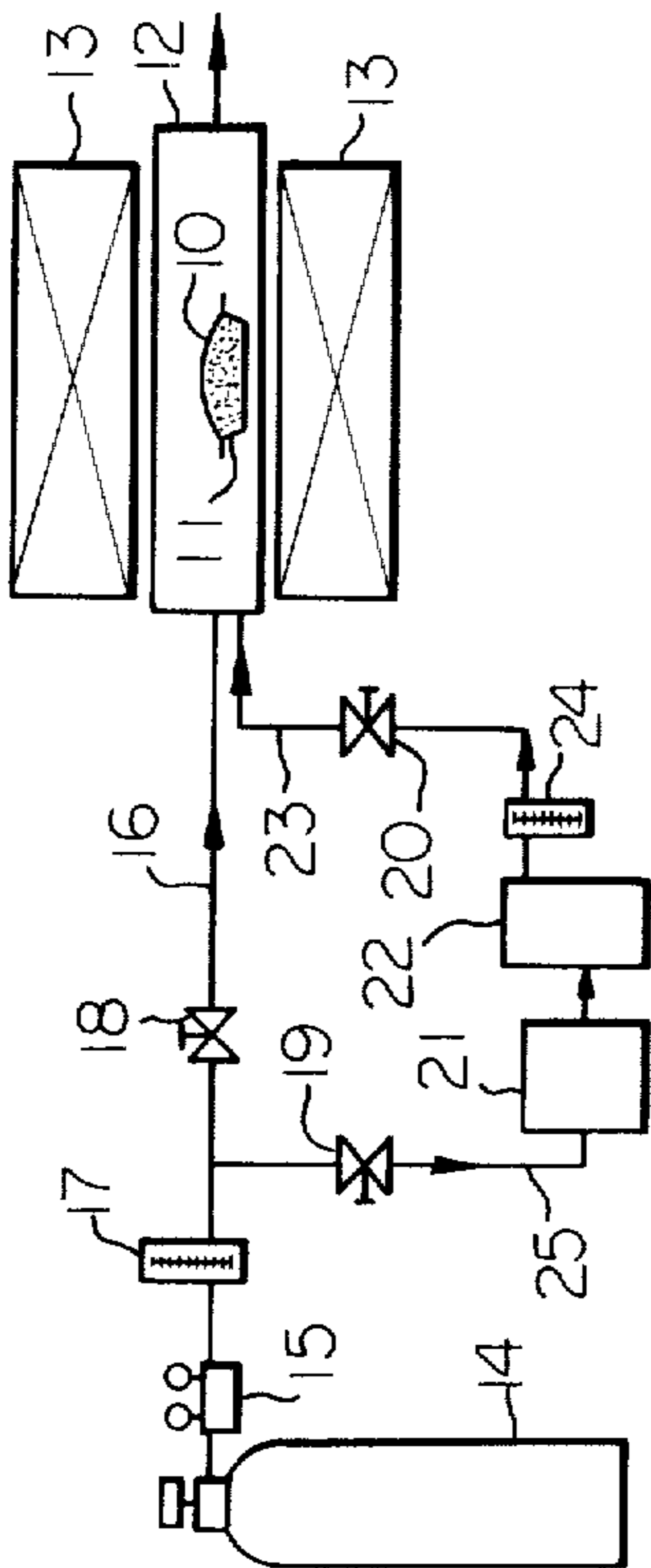


Fig. 1

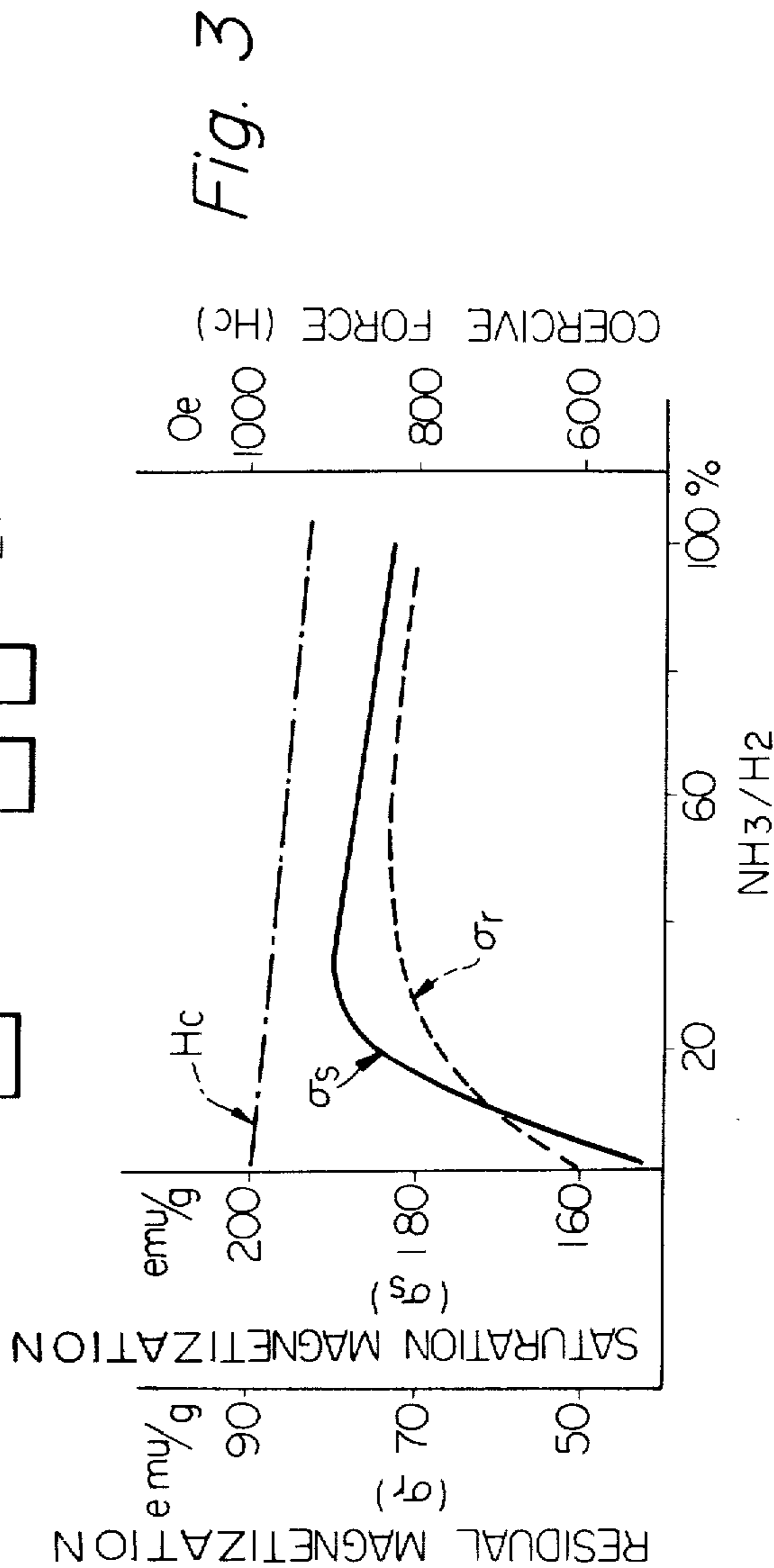


Fig. 3

Fig. 2

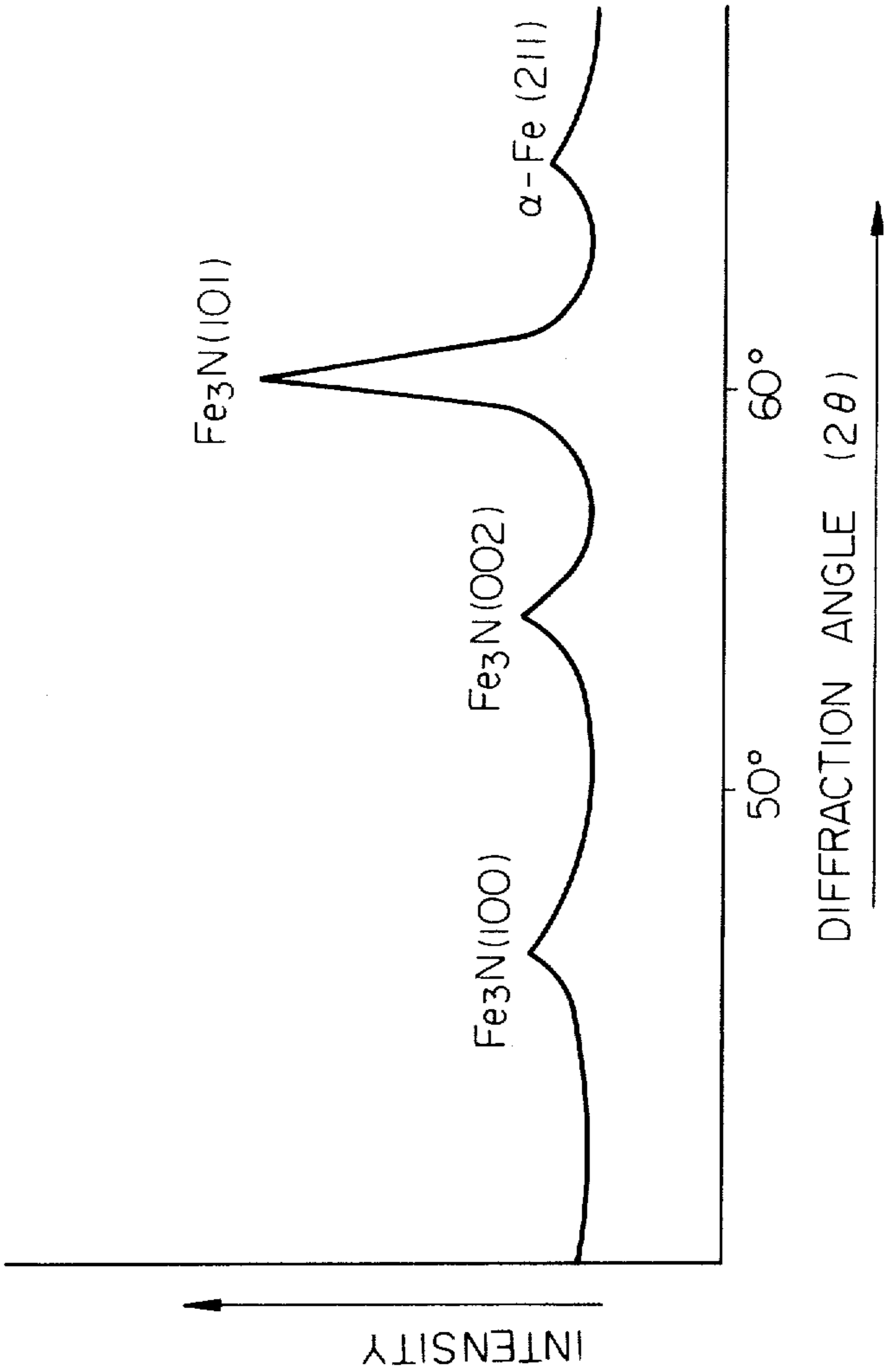


Fig. 4

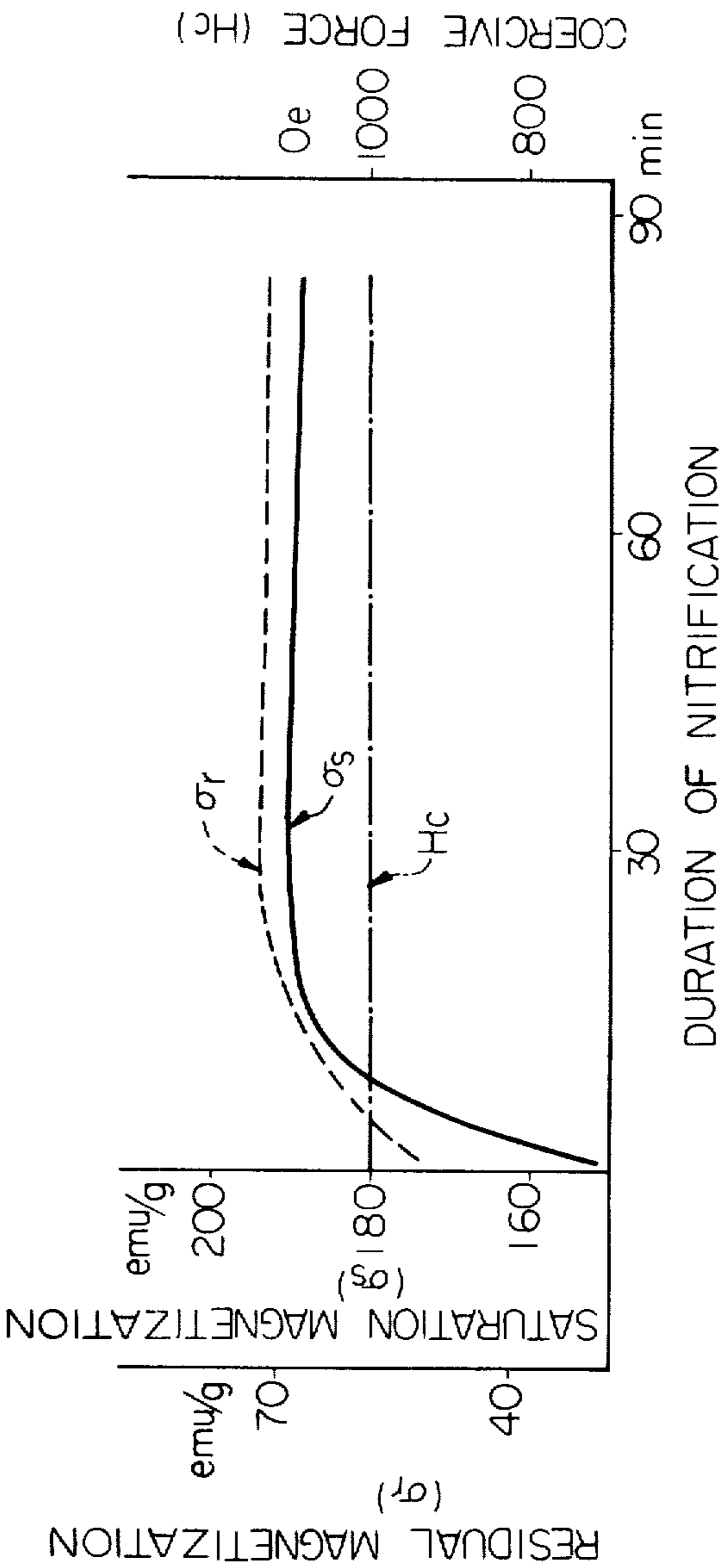
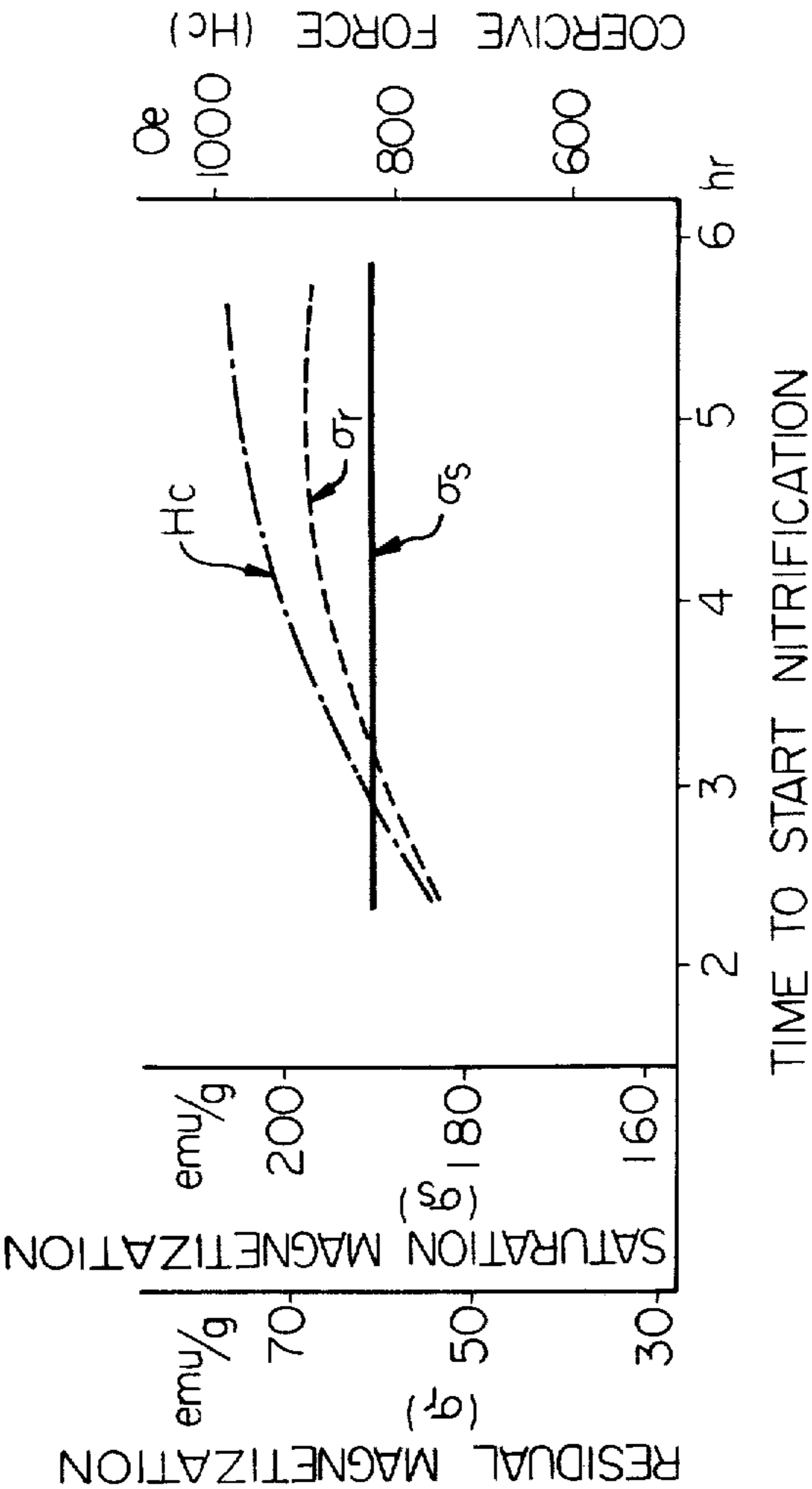


Fig. 5



METHOD FOR PREPARING MAGNETIC ALLOY POWDER BY SURFACE NITRIDING

The present invention relates to magnetic alloys and more particularly to a process for preparing magnetic ferroalloy powders by reduction of metal salts.

The magnetic material for a magnetic recording medium such as magnetic tape is required to have high saturation magnetization and residual magnetism values and a large coercive force. With the rise in the high recording density requirement for magnetic recording media in recent years, the demand for magnetic materials of improved magnetic properties has been growing. To meet the demand, magnetic alloy powders such as the Fe-Co series and the Fe-Co-Ni series have been proposed and used as these materials are superior to the common magnetic materials such as γ -hematite.

A typical method of producing such alloy powders is the so-called reduction process, in which suitable salts of the metals are heated for some hours in a reducing atmosphere. Metal salts powders for this process is prepared, for example, as follows: An aqueous solution containing water soluble salts of iron, cobalt and nickel with a proportional composition corresponding to that of the desired Fe-Co-Ni or Fe-Co alloy is mixed with an aqueous solution of an organic acid such as, for example, oxalic acid or formic acid, or an organic acid salt such as ammonium oxalate, to coprecipitate a sparingly water-soluble ternary crystal or co-crystal. Hydrogen is usually used to reduce the thus prepared crystal powder to the alloy powder.

Unfortunately, the magnetic properties of the alloy powders prepared by this process are below the theoretical level, expected from their fundamental composition, due to a certain restriction on the reduction temperature and the air-oxidation of the formed alloy powder. A relatively high temperature is required to produce an alloy powder of a high saturation magnetization value, but heating at a high temperature suitable for developing this property causes the powder particles to be sintered causing a considerable decrease in the coercive force. When, on the other hand, the metals are reduced at a lower temperature to obtain a large coercive force, the particles are easily internally oxidized by an exothermic reaction with the oxygen in air when taken out from the reaction apparatus. The oxidation causes a great decrease in the saturation magnetization value.

Various means have been tried to protect the alloy particles against the oxidation. A technique is to soak the cooled particles in an organic solvent such as petroleum benzine or toluene containing an aliphatic hydrocarbon such as stearic acid to form a protective film of the hydrocarbon on the surface of the particles. It is, however, very difficult to control the film thickness, and it takes many hours (more than 12 hours) to form an effective film. In addition, the use of large amounts of organic solvent necessitates solvent recovery and post-treatments. Another example of the oxidation protection means is to form a protective oxide layer on the surface of the particles by passing oxygen little by little over the particles maintained in an inert atmosphere. This method requires more than 10 hours of such treatment and difficult layer thickness control problems ensue and, nevertheless, some deterioration in the magnetic properties are inevitable due to the oxidized region. An organic polymer coating on the particle sur-

face by means of the micro-capsule method is proposed as still another technique, but the method seems unpractical because it requires the particles to be dispersed to the extent of complete isolation of every particle from each other.

Consequently, magnetic alloy powders produced by the conventional reduction process are insufficient in some magnetic properties as compared with the inherent properties of the alloy, despite the anti-oxidation treatment.

It is therefore an object of the present invention to provide a method for preventing iron-containing magnetic alloy powders from deterioration in their magnetic properties.

A feature of a method of the invention is to pass a gaseous nitrogen-containing compound such as, for example, ammonia or hydrazine, over the reducible crystal powder for a certain period during which the heated partially reduced crystal powder in order to form a nitride layer on the powder particles. The nitrogen-containing compound gas may be introduced into the reaction system either alone or mixed with the reducing gas, and its introduction is started after an initial reduction period during which the reduction reaction proceeded to some extent. The metal nitride layer formed on the surface region of the particles protects them against oxidation in the atmosphere. Thus, the magnetic properties inherent to each alloy can be maintained, and besides, the other properties can be altered or adjusted to desired values by control of the nitrifying reaction conditions.

Other objects, features and advantages of the invention will be understood from the following detailed description referring to the accompanying drawings, in which:

FIG. 1 is a diagram of an example of an apparatus for performing the method of the invention;

FIG. 2 is a graph showing a result of X-ray diffraction test with an alloy powder prepared by the method of the invention;

FIG. 3 is a graph showing the variation of magnetic properties of the alloy powders with the supplied quantity of ammonia gas;

FIG. 4 is a graph of the similar magnetic properties vs. the duration of the nitrifying reaction; and

FIG. 5 is a graph of the similar magnetic properties vs. the duration of the reducing reaction before the start of the nitrifying reaction.

In the embodiments of the invention, the reduction of the intermediate, or precipitated crystal powder of metal salts such as, for example, oxalates of iron and cobalt; or oxalates of iron, cobalt and nickel is carried out similarly to the conventional method both in apparatus and in procedures. Referring now to FIG. 1, a suitable quantity of the crystal powder 10 is put in boat 11, and the boat 11 is placed in reaction tube 12, which can be heated in an electric furnace 13. Hydrogen gas from a tank 14 provided with a pressure regulator 15 is introduced into the reaction tube 12 through a conduit 16 provided with a flowmeter 17 and a stopcock 18 at a rate of, for example, 0.5 l/min. In this stage, stopcocks 19 and 20 are kept closed so that a nitrogen-containing compound gas from a gas generating apparatus 21 will not flow into the reaction tube 12. The reaction tube 12 is heated to a temperature of above 270°C by the furnace 13 when filled with hydrogen gas, and the heating is continued for 2 to 10 hours with a continued hydrogen gas flow to reduce the crystal powder 10.

After heating for this predetermined period, the stopcock 20 is opened to introduce a nitrogen-containing compound gas, such as, for example, ammonia or hydrazine produced in the apparatus 21 and dried in a drier 22, into the reaction tube 12 through a conduit 23 provided with a flowmeter 24. If the nitrogen-containing compound gas alone is employed, the stopcock 18 is closed at this instant. When a mixed gas supply is desired, hydrogen gas may be passed through the conduit 23 via by-pass conduit 25 instead of the stopcock 18. The nitrogen-containing compound gas is pre-heated, for example, in the drier 22 so that its temperature at the inlet of the reaction tube 12 may be preferably equal to or slightly above the temperature for the reduction reaction. The partly reduced crystal powder 10 in the tube 12 is heated successively in the stream of, for example, ammonia, which is supplied at a rate of 0.05 to 1.0 l/min, for a period of about 15 to 60 minutes. The surface region of the powder 10 is converted into metal nitrides by reacting with the nascent nitrogen produced by the decomposition of ammonia. The use of a nitrogen-containing compound gas, not nitrogen gas, is a requisite of the method of the invention. The source of ammonia or hydrazine is not limited to the gas generating apparatus 21 as shown in FIG. 1, but a commercially available tank of such gas may be used.

The nitride layer thus formed on the alloy particle surface protects the alloy powder from oxidation and resulting deterioration in the magnetic properties. It is possible to predetermine the extent of the nitrification or the thickness of the nitride layer by the control of the reaction conditions and to obtain alloy powders of various magnetic properties by the selection of the reaction conditions.

The invention will be more readily understood with reference to the following non-limitative examples.

EXAMPLE 1

A ternary oxalate of iron, cobalt and nickel prepared by a conventional co-precipitation method with the composition of 50, 48 and 2% by molar ratio, respectively, was used as a starting material. Fifty mg of the this oxalate powder was put into a boat and placed in a reaction tube, and heated at 300°C for 5 hr in a 0.5 l/min stream of hydrogen. Then ammonia gas was introduced into the tube mixed with the hydrogen stream in an amount of about 10% of hydrogen, continuing the 300°C heating for another 1 hr.

The obtained ternary alloy powder had the saturation magnetization value of 211 emu/g and coercive force of 650 Oe.

EXAMPLE 1A (Prior Art)

The procedures of Example 1 were repeated except that the heating was carried out in the stream of hydrogen gas alone throughout the total period of 6 hr.

EXAMPLE 2

Example 1 was repeated except that the heating temperature was 290°C.

EXAMPLE 2A (Prior Art)

Example 1A was repeated except that the heating temperature was 290°C.

The saturation magnetization and coercive force of the alloy powders prepared in the above Examples are tabulated below.

	Temp. (°C)	Heating time (hr)		Saturation magnetization (emu/g)	Coer- cive force (Oe)
		in H ₂	in NH ₃		
Ex. 1	300	5	1	211	650
Ex. 1A	300	6	0	199	640
Ex. 2	290	5	1	202	630
Ex. 2A	290	6	0	160	640

The effect of the nitrification according to the invention on the saturation magnetization will be apparent from Table 1. The coercive force was substantially constant and satisfactory in these examples because of moderate reaction temperatures. As mentioned before, if a higher temperature is employed to raise the saturation magnetization value above the result of Example 1A according to the prior art, a decrease in the coercive force is inevitable.

In thus formed nitride layer, iron nitride takes the most important part, and it can exist as various kinds of structure ranging from Fe₈N to Fe₃N. The magnetic properties of iron nitride do vary depending on the structure; for example, Fe₈N are ferromagnetic. It is, therefore, possible to obtain various properties of alloy powders, ranging from non-magnetic to ferromagnetic ones, from the same starting material by the control of the extent of the nitrification.

The nitrification in the method of this invention is affected by the reaction temperature, the duration of the reducing heating before introduction of the nitrogen-containing compound gas, the flow rate of that gas and the duration of the nitrifying heating. The heating temperature should be between about 250° and 400°C and preferably above 300°C. Both the reduction and nitrification are difficult to proceed at below 250°C, but excessive nitrification and/or sintering of the powder may result at above 400°C. To achieve the initial reduction of the metal salts, at least a part of the heating in a reducing atmosphere should be carried out prior to the start of, for example, the ammonia gas supply. Hence, it is preferable to commence the nitrifying heating after 2 to 6 hours of the reducing heating. When the initial reducing heating time exceeds 6 hours, the almost completely reduced particles cannot be easily nitrified, and sintering of the particles may be accompanied. From this view point, the nitrogen-containing compound gas is preferably mixed with the reducing gas rather than used alone after completion of the initial reduction. The mixing ratio of the nitrogen-containing compound gas to the reducing gas should be at least 10% by volume and preferably from 20 to 80%. The minimum heating time for the nitrification is considered about 15 minutes.

More examples will be presented to show the effects of these reaction conditions.

EXAMPLE 3

The ternary oxalate powder of Example 1, weighing 80 mg, was put in a platinum boat and placed in a quartz tube. The powder was heated at 300°C in a 0.5 l/min stream of hydrogen gas for 2 hr. After that, ammonia gas was passed in place of hydrogen at a flow rate of 1.0 l/min for 4 hr continuing the 300°C heating. Observation of the resulting powder by an X-ray diffractometer showed peak values corresponding to Fe₃N

as shown in FIG. 2, and the powder was found to be paramagnetic.

EXAMPLE 4 (Prior Art)

In this example and throughout the following Examples 5 to 8, the starting material was 80 mg of a quaternary oxalate powder containing iron, cobalt, nickel and aluminum in the molar ratio of 48.0, 46.1, 1.9 and 4.0%, respectively.

The oxalate powder was placed in a reaction tube similarly to the previous examples and heated at 310°C for 6 hr in a stream of hydrogen gas flowing at 0.75 l/min.

EXAMPLE 5

Example 4 was repeated except that 23% by volume of ammonia gas was admixed with hydrogen gas during the last 1 hr of the 6 hr heating.

EXAMPLE 6

Example 5 was repeated except that ammonia gas was admixed only for the last 15 min.

EXAMPLE 7

Example 5 was repeated except that the amount of ammonia gas was 53% by volume of hydrogen.

EXAMPLE 8

Example 5 was repeated except that the amount of ammonia gas was reduced to 13%.

The magnetic properties of the alloy powders obtained in Examples 4 to 8 are tabulated below.

TABLE 2

	Nitrification Time (min)	NH ₃ /N ₂ (%)	Saturation Magnetization (emu/g)	Coercive Force (Oe)	Residual Magnetism (emu/g)
Ex. 4	0	—	150	1000	60
Ex. 5	60	23	190	1000	70
Ex. 6	15	23	190	900	70
Ex. 7	60	53	187	930	73
Ex. 8	60	13	167	980	65

Although the effects of the reaction conditions can be seen from the results in Tables 1 and 2, graphical representation in FIGS. 3, 4 and 5 will be more helpful to comprehend the relationships.

The graphs of these Figures are based upon the results of Examples 5 to 8 and additional ones essentially similar to the former except for particulars mentioned below. The temperature and total duration of the heating were kept constant, namely, at 310°C and for 6 hr. FIG. 3 shows the effect of variation in the amount of ammonia gas admixed with hydrogen gas. FIG. 4 shows the effect of the duration of the nitrifying heating at the last stage of the 6 hr heating when the ammonia-to-hydrogen ratio was 20%. In FIG. 5 is shown the effect of the time to carry out a 15 min nitrifying heating during the total 6 hr of the reducing heating. The ammonia-to-hydrogen ratio was 20%, and the abscissa represents the time from the start of the reducing heating to the start of the addition of ammonia gas.

As seen from the graphs, the magnetic properties can be varied in wide ranges, and the best result from the viewpoint of the magnetic properties is obtained when the nitrifying heating is carried out in hydrogen atmosphere admixed with about 20 to 30% of ammonia for a period of about 20 minutes after 5 to 6 hours of the reducing heating.

Thus, the object of preventing an iron-containing magnetic alloy powder from deterioration by air-oxidation is attained by forming a nitride layer on the surface region of the powder particles in accordance with the above described method. In addition to the improvement in the magnetic properties of the product and possibility of controlling those properties, the method of the invention is advantageous in that its industrial application is accomplished with few problems from both technical and economical viewpoints because conventional apparatus and procedures for the reduction method can be employed with only slight modification.

What is claimed is:

1. A process for preparing a magnetic alloy powder essentially consisting of iron and at least one of cobalt and nickel, the process comprising the steps of:
 - a. heating a crystalline powder material comprising reducible salts of iron and said cobalt and/or nickel, said reducible salts being selected from the group consisting of oxalates and formates, in a reducing atmosphere at a temperature of about 300°C for a period of 2 to 6 hours to incompletely reduce said salts to the corresponding metals;
 - b. continuing heating the incompletely reduced powder material in a gas stream containing a nitrogen-containing compound gas at a temperature of 250° to 400°C for a period of 15 to 60 minutes to nitrify the surface region of said powder material
 - c. completing the reduction.
2. The method as claimed in claim 1, wherein said nitrogen-containing compound gas is gaseous ammonia

3. The process as claimed in claim 1, in which said reducing atmosphere essentially consists of hydrogen gas.
4. The process as claimed in claim 2 wherein said nitrogen-containing compound is ammonia.
5. The process as claimed in claim 2, wherein said nitrogen-containing compound is hydrazine.
6. A process as claimed in claim 3, in which said gas stream includes hydrogen gas.
7. A method as claimed in claim 6, in which the amount of said nitrogen-containing compound gas is at least 10% by volume of said reducing gas.
8. A process as claimed in claim 6, in which the amount of said ammonia gas is from 20 to 80% by volume of said hydrogen gas.
9. A process as claimed in claim 1, wherein said crystalline powder material is a ternary oxalate of substantially 50 mole % of iron, 48 mole % of cobalt and 2 mole % of nickel.
10. A process as claimed in claim 1, wherein said crystalline powder material is a quaternary oxalate of substantially 48 Mole % of iron, 46 % of cobalt, 2 mole % of nickel and 4 mole % of aluminum.

* * * * *