

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 463 180 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art.
158(3) EPC

(21) Application number: **91902751.6**(51) Int. Cl.⁵: **H05B 6/64**(22) Date of filing: **16.01.91**(86) International application number:
PCT/JP91/00035(87) International publication number:
WO 91/11083 (25.07.91 91/17)(30) Priority: **19.01.90 JP 11492/90**
09.07.90 JP 182334/90(43) Date of publication of application:
02.01.92 Bulletin 92/01(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE(71) Applicant: **KABUSHIKI KAISHA KOURANSHA**
1664, Arita-cho Nishimatsuura-gun
Saga-ken 844(JP)

(72) Inventor: **MATSUKI, Masaharu Kabushiki**
Kaisha Kouransha
1664, Arita-cho Nishimatsuura-gun
Saga-ken 844(JP)
Inventor: **YOSHIHARA, Toshiaki Kabushiki**
Kaisha Kouransha
1664, Arita-cho
Nishimatsuura-gun Saga-ken 844(JP)
Inventor: **IKEDA, Miki Kabushiki Kaisha**
Kouransha
1664, Arita-cho
Nishimatsuura-gun Saga-ken 844(JP)
Inventor: **KURITA, Sumihiko**
91-26, Oaza-Miyano Yamauchi-cho
Kishima-gun Saga-ken 849-23(JP)

(74) Representative: **Silverman, Warren et al**
HASELTINE LAKE & CO. Hazlitt House 28
Southampton Buildings Chancery Lane
London WC2A 1AT(GB)

(54) **MATERIAL GENERATING HEAT BY ABSORBING MICROWAVES.**

(57) This invention relates to a material which heats and cooks foods from outside by absorbing microwaves of an electronic range and by generating heat. A conductive substance or a nonconductive compound containing transition metals of atomic number 21-29 is mixed in a base material having an Fe group oxide as a principal component. Since the material has a rapid heat generating speed, the temperature in heat-generation is high, and further the material is cheap; it is effective as a material generating heat by absorbing microwaves.

EP 0 463 180 A1

TECHNICAL FIELD:

The present invention relates to a microwave-absorptive heat-generating material, which generates heat as a result of absorption of microwave energy and has especially excellent heat-generating characteristics in an electronic oven.

BACKGROUND ART:

An electronic oven is such device that irradiating microwaves would give frictional vibrations to molecules of water and the like contained in an article to be cooked and cooking is effected by temperature rise caused by the frictional heat, and it has a merit that cooking can be done in a short time because it can heat foods from their inside.

However, since it cannot cook foods from their surfaces by conduction heat or radiation heat as is the case with a gas cooker and a resistance heater, it cannot give schorch or crispness (crispy nature) to the food surface. Therefore, it was not suitable for cooking foods to be accompanied by schorch or crispness such as scorched fishes, roasted meats, a pizza pie and the like.

As a countermeasure for this shortcoming, a method of heating foods from their surfaces with a heat-generating body making use of a material which absorbs microwaves and generates heat, in an existing electronic oven and thereby schorch or crispness is given to the foods, has been known.

However, a heat-generating speed of the heat-generating material in the prior art is slow, and it cannot be said to be sufficiently useful as a heat-generating material in an electronic oven which necessitates quick cooking.

The present invention has been worked out in view of the above-mentioned problems in the prior art, and one object of the invention is to provide a novel microwave-absorptive heat-generating material, which can heat up in a shorter period of time and attain to a higher temperature.

DISCLOSURE OF INVENTION:

According to the present invention, the above-mentioned object is achieved by the following microwave-absorptive heat-generating material. That is:

(1) A microwave-absorptive heat-generating material characterized in that the material is formed by mixing an electrically conductive substance in a base material principally consisting of Fe group oxides.

(2) A microwave-absorptive heat-generating material as described in numbered paragraph (1) above, wherein the aforementioned electrically conductive substance is metal, alloy or compound of metal.

(3) A microwave-absorptive heat-generating material as described in numbered paragraph (2) above, wherein the aforementioned electrically conductive material is Fe, Al, Cu, Cr, Ni, Ti, C, Si, TiN, MoSi₂, TiB₂ or SiC, or alloy or compound containing at least one kind among these.

(4) A microwave-absorptive heat-generating material characterized in that an electrically non-conductive compound among compounds of transition metal having an atomic number 21~29 is mixed in a base material principally consisting of Fe group oxides.

(5) A microwave-absorptive heat-generating material as described in numbered paragraph (4) above, wherein the aforementioned electrically non-conductive compound is oxide.

The microwave-absorptive heat-generating material according to the present invention is such material that an electrically conductive substance or electrically non-conductive compound of transition metal having an atomic number 21~29 is mixed and solidified in a base material principally consisting of Fe group oxides.

"Fe group oxide" means oxide of Fe alone such as FeO, Fe₂O₃, Fe₃O₄ and the like or complex oxide in which a part of Fe is substituted by another metallic element.

"Electrically conductive substance" means inorganic or metallic electrically conductive substance, for instance, it is most metal and alloys such as Fe, Ni, Co, Cr, Mo, W, Al, Si, Cu, Ag, Au, Zn, Ti, Zr, etc. or an inorganic substance such as C, SiC, TiC, TiN, TiB₂, ZrB₂, MoSi₂, etc. and they can be used appropriately either singly or in mixture. Among these, especially Fe, Al, Cu, Cr, Ni, Ti, C, Si, TiN, MoSi₂, TiB₂, SiC, etc. are practically useful. While the proportion of addition of the electrically conductive substance is, strictly speaking, varied in various ways depending upon the nature of the substance, as a tentative measure, about 1~50 vol.% of the base material of Fe group oxide can be substituted. The electrically conductive substance is mixed in the form of powder or fibers, and a grain diameter of the powder is suitably about 100~400 meshes. In the case of fibers, a minor axis diameter of 10~100 μm and a major axis diameter of 100μm~10mm are suitable.

"Electrically non-conductive compound of transition metal having an atomic number 21~29" means electrically non-conductive one among compounds of these metals and O, N, C, B, etc. Above all, compounds of these and O are most preferable. The amount of addition of these is preferably in the range of 0~0.5 mol for 1 mol of iron (Fe) in the base material.

In other words, according to the present invention, it is proved that as described above regardless of whether it is an inorganic substance or metal, electrically conductive ones are all effective, but even if it is electrically non-conductive one, compounds of transition metals having an atomic number 21~29 are effective.

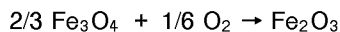
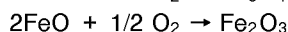
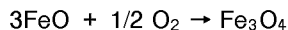
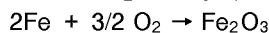
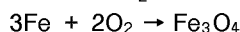
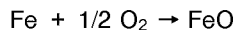
Solidification of the Fe group oxide of the base material mixed with these electrically conductive or electrically non-conductive substances is achieved by sintering after having been shaped into a desired configuration, or if necessary, it is achieved by making use of a cold-setting type adhesive. In the case of solidifying by sintering, the sintering temperature is sufficient at about 800~1200 °C.

As a microwave-absorptive heat-generating mechanism according to the present invention, the following three mechanism are conceived. That is, they are heat generations by magnetic loss, dielectric loss and ohmic loss.

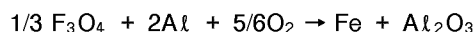
Ferrite which is microwave-absorptive heat-generating material in the prior art, generates heat by magnetic loss among these, as a result of absorption of microwaves. However, in this method, the energy of microwaves cannot be converted efficiently into thermal energy, and hence a sufficient heat-generating speed and a sufficient temperature cannot be obtained.

The reason why the heat-generating speed of the microwave-absorptive heat-generating material according to the present invention is extremely high, is surmised that it is because as a result of the addition of the above-described electrically conductive or electrically non-conductive substance, heat-generation caused by ohmic loss or heat-generation caused by dielectric loss is induced in addition to the magnetic loss. In addition, according to results of X-ray analysis after heat-generation of the microwave-absorptive heat-generating material according to the present invention, formation of oxides is recognized, and it is considered that the reaction heat caused by these oxidation or thermit reactions also contributes to the heat-generating characteristic.

As this oxidation reaction, when the ferrite is Fe_3O_4 and the metal is Fe, the following reactions are conceived:



Also, as the thermit reaction, when the ferrite is Fe_3O_4 and the metal is Al, the following reactions are conceived:



Furthermore, on the basis of the reduced Fe, the above-described oxidation reactions are conceived.

In addition, it can be considered that on the basis of secondary and tertiary products produced through these reactions, even after release of the reaction heat, further microwave absorption occurs and it contributes to heat-generation.

BRIEF DESCRIPTION OF DRAWINGS:

FIG. 1 is a curve showing a heat-generating characteristic when Fe powder was added to Fe_3O_4 powder; Fig.2 is a curve showing a heat-generating characteristic when Al powder was added to Fe_3O_4 powder; Fig.3 is a curve showing relations between an added amount of various kinds of elements to 1 mol. of Fe versus a temperature obtained by heat-generation; and Fig.4 is a curve showing relations between a thickness of a sample plate versus a temperature obtained by heat-generation.

BEST MODE FOR CARRYING OUT THE INVENTION:

(1) After Fe powders of 0, 5, 10, 15, and 12 wt% were respectively added to Fe_3O_4 powder, 10g of the mixtures were respectively packed in a crucible which is excellent in a thermal shock proofness, and they were used as test samples. Subsequently, these samples were heated by microwaves in an

electronic oven of 2,450 MHz in frequency and 750 W in output power, and a surface temperature was measured by means of a radiation thermometer. The results of measurement are shown in Fig.1.

As will be seen from Fig.1, by adding Fe powder a heat generating speed rises, and in contrast to the fact that it takes five minutes for a temperature of a sample consisting of Fe_3O_4 alone to reach 500°C, it took about 2 minutes in every case for a sample added with Fe powder. In addition, with regard to the highest temperature also, rise of about 100°C was observed.

(2) After powders of Fe, Cu, Cr, Ni, Ti, C, Si, TiN, MoSi_2 , TiB_2 and SiC of 5wt% were respectively added and mixed to Fe_3O_4 powder, the mixtures were packed in the above-described crucibles, respectively, and heated by microwaves in an electronic oven used in the preferred embodiment (1) above, and surface temperatures were measured by means of a radiation thermometer. The temperatures after 2 minutes and after 7 minutes are shown in Table-1 together with the data in the case of a sample consisting of F_3O_4 alone.

For every sample added with powder, remarkable heat-generating characteristics were obtained as compared to the sample consisting of F_3O_4 alone. In addition, among these added powder materials, powder materials whose existence was recognized by X-ray analysis even after heat-generation were only MoSi_2 , SiC and C, and with regard to the other powder materials, it is surmised that heat of formation by oxidation as well as heat generated by secondary and tertiary products also contributed to the heat-generating characteristics.

Table-1

Added Substances	Temperature (°C)	
	2 Minutes	7 Minutes
Fe	449	618
Cu	415	537
Cr	438	620
Ni	340	530
Ti	492	634
C	561	610
Si	583	598
TiN	479	658
MoSi_2	530	684
TiB_2	634	723
SiC	498	597
—	325	539

(3) After Al powders of 0, 5, 7 and 10wt% were respectively added and mixed to Fe_3O_4 powder, the mixtures were respectively packed in the above-described crucibles and heated by microwaves in an electronic oven used in the preferred embodiment (1) above, and surface temperatures were measured by means of a radiation thermometer. The results of measurement are shown in Fig.2.

As will be seen from Fig.2, if Al powder is added, heat-generating speed rises abruptly in about one

minute due to a thermit reaction. In the case of the samples of 7 and 10wt% addition, thereafter a temperature falls abruptly and reaches a constant value in the proximity of 500 °C. Also, in the case of the sample of 5 and 7 wt% addition, rise of the highest temperature was observed as compared to the sample consisting of Fe₃O₄ alone.

(4) A powder mixture prepared by adding Fe, Al or TiN powder of 5wt% to Fe₃O₄ powder and powder consisting of Fe₃O₄ alone were respectively applied by making use of an inorganic binder onto a ceramic sheet of 10cm x 10cm up to a film thickness of 200μm, and it was used as a heat-generating body. This was placed on a refrigerated gratin sold on the market as shown in Fig.3, then a cooking test was conducted in an electronic oven used in the preferred embodiment (1) above, and schorch on the surface as well as a cooked condition inside of the foods were observed. The results are shown in Table-2.

Table-2

Added Substances	180sec.		210sec.		240sec.		270sec.	
	surface	inside	surface	inside	surface	inside	surface	inside
Fe	△	△	○	△	○	○	×	○
Al	△	△	○	○	×	○	×	×
TiN	△	△	○	△	○	○	×	○
—	△	△	△	△	△	△	○	○

○: well cooked

△: insufficiently cooked

×: excessively cooked

The heat-generating body added with Fe, Al or TiN necessitates a short cooking time as compared to that consisting of Fe₃O₄ alone, and a cooking time could be shortened by 30 seconds in the case of a heat-generating body added with Fe or TiN, and by 60 seconds in the case of a heat-generating body added with Al.

(5) Oxide powders of Ti, Cr, Mn, Co, Ni, Cu, Sr and Ba were respectively added to Fe₃O₄ powder at an element ratio of 0~0.7 mol to 1 mol of Fe. The mixtures were press-shaped and then sintered at 800~1200 °C to prepare samples of 30mm in diameter and 2mm in thickness. Next, microwave-heating was effected for 30 seconds in an electronic oven of 2,450 MHz in frequency and 1500 W in output power by making use of this sample, and the surface temperature was measured by means of a radiation thermometer. The results of measurement were shown in Fig.3.

As will be seen from Fig.1, a tendency that the temperature becomes high as a result of addition of metal oxide, is recognized, but if the ratio of the added amount exceeds 0.7 mol, the temperature is, on the contrary, lowered. Especially, in the case of a material added with oxide of transition metal in the fourth period (atomic number 21~29) such as Ti, Cr, Mn, Co, Ni or Cu, a high temperature characteristic was obtained.

(6) Oxide powders of Ti, Cr, Mn, Co, Cu, Sr and Ba were respectively added to Fe₃O₄ powder at an element ratio of 0.3 mol to 1 mol of Fe. The mixtures were press-shaped and then sintered at 800~1200 °C, and the thus prepared samples of 30mm in diameter and 1~8mm in thickness were heated by microwaves for 30 seconds in an electronic oven used in the preferred embodiment (5) above, and the surface temperatures were measured by means of a radiation thermometer. The results of

measurement is shown in Fig.4.

In the case of a material added with oxide of Sr or Ba, the temperature lowers if the thickness of the heat-generating body becomes thin, but in the case of a material added with transition metal, a high efficiency was obtained even if the sample is thin.

(7) Metal powders of Ti, Mn and Sr were respectively added to Fe_3O_4 powder at an element ratio of 0.3 mol to 1 mol of Fe, a samples prepared by press-shaping the mixtures and thereafter sintering were ground, then the ground powder was coated onto one side surface of a crystallized glass sheet ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ group) having a strong thermal impact proofness and a diameter of $\Phi 150\text{mm}$ up to a thickness of 0.5mm by means of an inorganic binder to form a heat-generating film, and thus a heat-generating body was prepared. This coated sheet was heated by microwaves for 30 seconds in an electronic oven used in the preferred embodiment (5) above, and the surface temperature was measured by means of a radiation thermometer. The results of measurement were shown in Table-3.

Table-3

Added Elements	Average Temperature (° C)
Ti	511
Mn	402
Sr	314

In addition, a refrigerated pizza Pie sold on the marcket of 150 mm in diameter was placed on the above-described heat-generating body and cooked in an electronic oven, and cooked conditions of the ingredients topping the surface of the pizza pie as well as a pizza craft on the back surface were observed. The results of observation are shown in Table-4.

Table-4

Added Elements	Cooking Time					
	80 sec.		60 sec.		90 sec.	
	inside	outside	inside	outside	inside	outside
Ti	△	△	○	○	×	×
Mn	△	△	○	○	×	×
Sr	○	△	×	△	×	○

○: well cooked

△: insufficiently cooked

×: excessively cooked

A heat-generating body added with Ti or Mn has a high temperature, hence upon cooking of a pizza pie crispness could be given to a pizza craft, also the entire foods could be cooked uniformly, and had good

taste.

As described in detail above, the heat-generating material according to the present invention is effective in melting of refrigerated foods and shortening of a cooking time because it has a remarkably fast heat-generating speed as compared to the heat-generating material in the prior art. In addition, owing to the attainable high temperature, with a smaller amount of the material than the heat-generating material in the prior art, cooking is possible, and so, it is economical.

INDUSTRIAL APPLICABILITY:

The material according to the present invention can be utilized effectively in an electronic oven as a material for heating and cooking foods from the outside by absorbing microwaves of an electronic oven and generating heat at the time of cooking with an electronic oven.

Claims

1. A microwave-absorptive heat-generating material, characterized in that an electrically conductive substance is mixed in a base material principally consisting of Fe group oxides.
2. A microwave-absorptive heat-generating material as claimed in claim 1, wherein said electrically conductive substance is metal, alloy or compound of metal.
3. A microwave-absorptive heat-generating material as claimed in claim 2, wherein said electrically conductive substance is Fe, Al, Cu, Cr, Ni, Ti, C, Si, TiN, MoSi₂, TiB₂ or SiC or alloy or compound containing at least one kind among these.
4. A microwave-absorptive heat-generating material, characterized in that an electrically non-conductive compound among compounds of transition metal having an atomic number 21~29 is mixed in a base material principally consisting of Fe group oxides.
5. A microwave-absorptive heat-generating material as claimed in claim 4, wherein said electrically non-conductive compound is oxide.

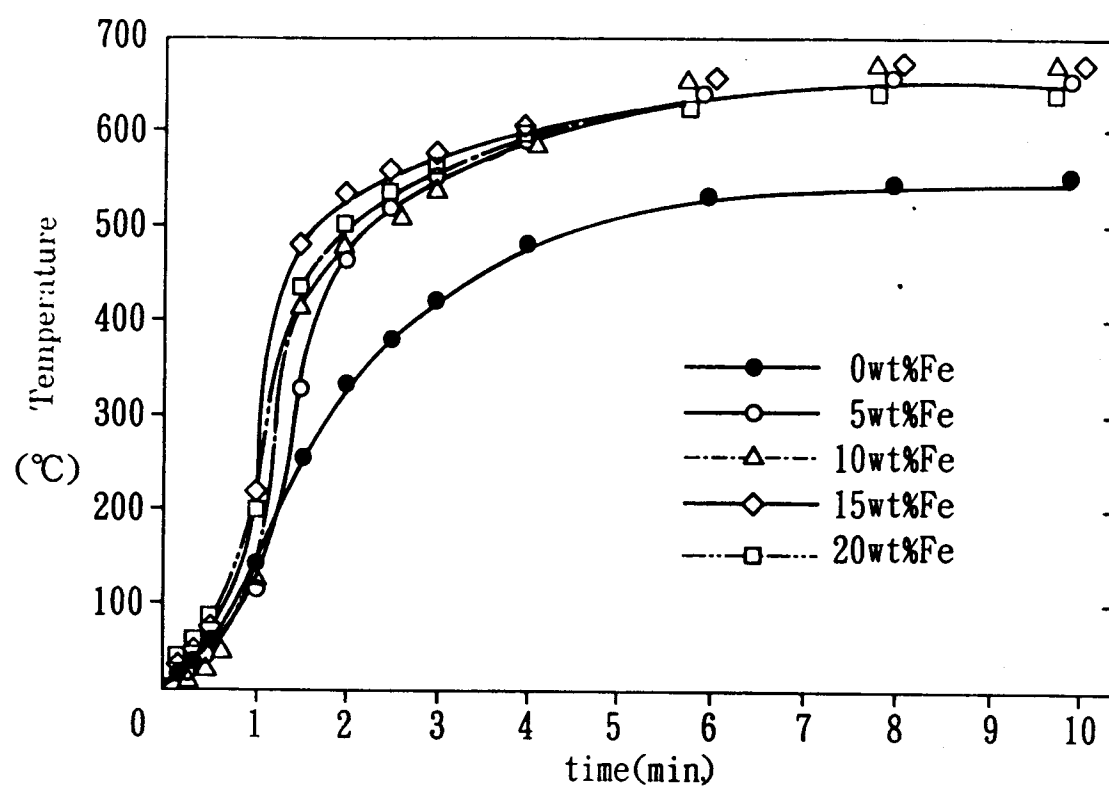


FIG. 1

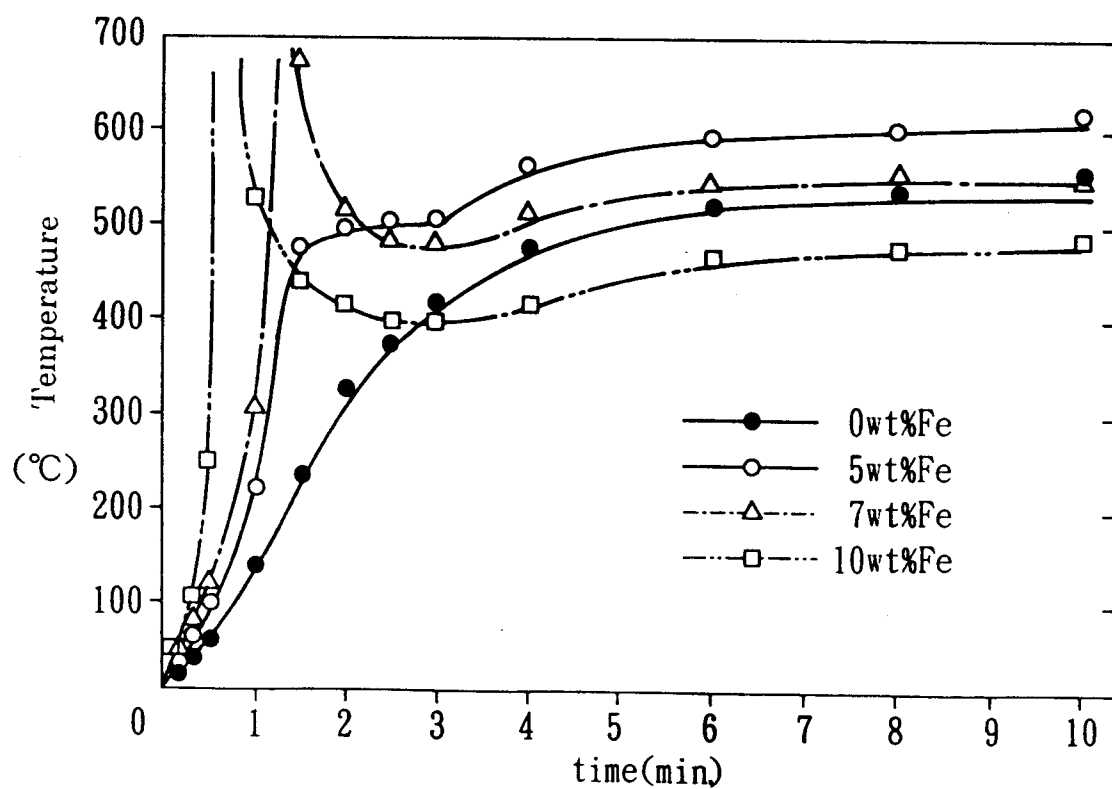


FIG. 2

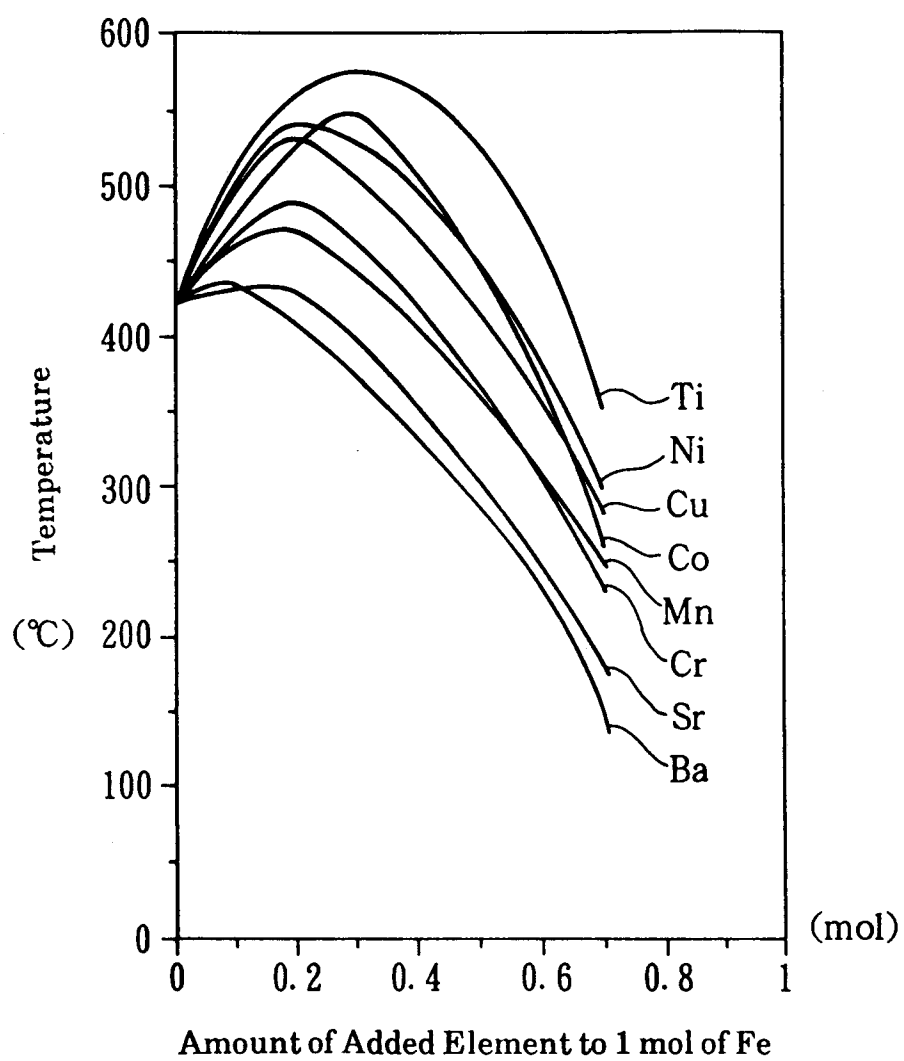


FIG. 3

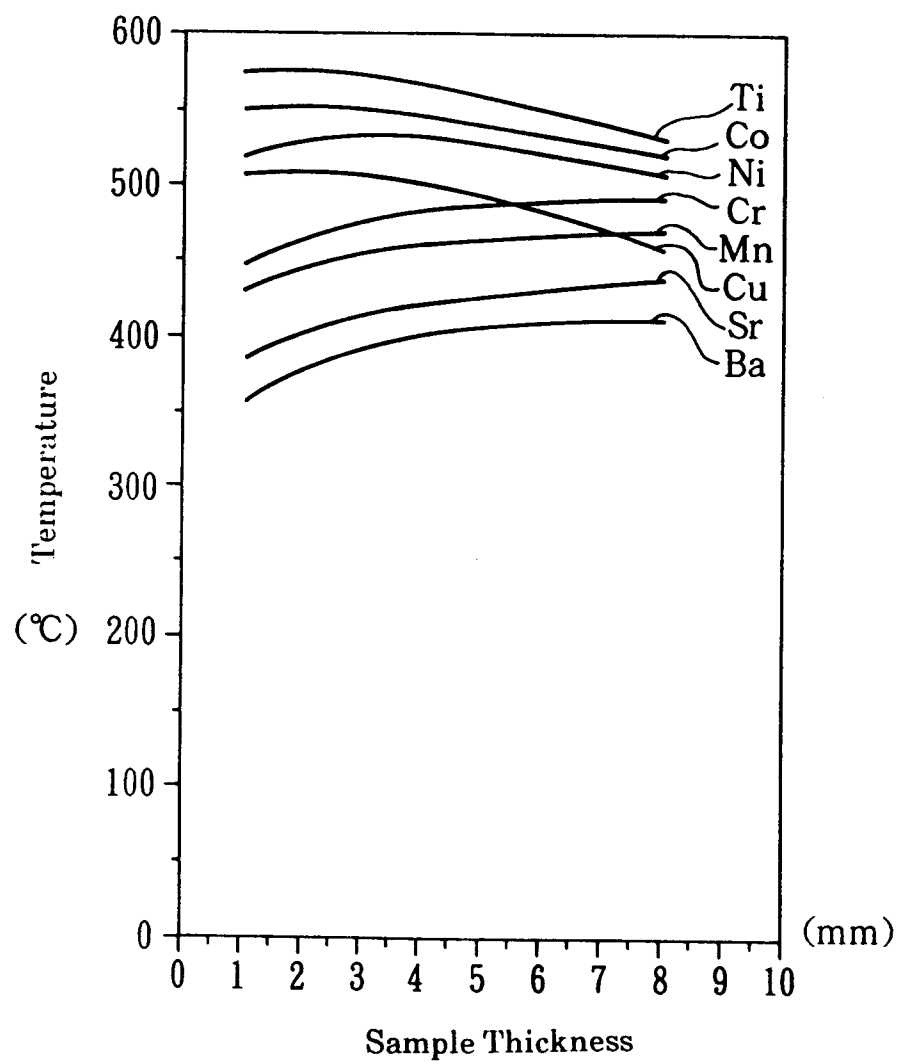


FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP91/00035

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. ⁵ H05B6/64		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC	H05B6/64, 6/74, A47J36/04	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
Jitsuyo Shinan Koho		1926 - 1991
Kokai Jitsuyo Shinan Koho		1971 - 1991
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	JP, A, 49-32232 (Asahi Chemical Industry Co., Ltd.), March 23, 1974 (23. 03. 74), (Family: none)	1-5
A	JP, A, 63-108122 (Yukio Sahara), May 13, 1988 (13. 05. 88), (Family: none)	1-5
* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
April 2, 1991 (02. 04. 91)		April 22, 1991 (22. 04. 91)
International Searching Authority		Signature of Authorized Officer
Japanese Patent Office		