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**Abstracts & Titles, No. 158~162**  
**BULLETIN**  
**OF THE**  
**FACULTY OF ENGINEERING**  
**HOKKAIDO UNIVERSITY**

**No. 158**  
 January 1992

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## Comparison of Structural Analysis Methods of Incomplete Composite Girder Bridges

Koichi SATO  
(Received October 30, 1991)

### Abstract

This paper presents a practical structural analysis of composite girders with incomplete interaction by two stiffness matrix methods. One is the stiffness matrix method derived from the general solutions of difference equations, and the other is based on differential equations. Both matrices can be obtained by using Anfang Parameter Method. These stiffness matrix methods are applicable to an analysis of composite girders considering deformations and variable spacings of headed stud connectors and can be extended to an analysis of continuous composite girders with variable cross sections. The validity of the stiffness matrix methods presented herein is examined and checked by numerical calculations.

## Buckling Loads of Incomplete Composite Plates Consisting of Two Isotropic Layered Plates

Koichi SATO  
(Received October 30, 1991)

### Abstract

This paper offers a set of partial differential equations designed to accomplish elastic buckling analysis of incomplete composite plates consisting of two layers of isotropic materials. The paper also analyzes the relationship of critical loads among complete composite plates, incomplete composite plates, and individual plates that do not interact with simply supported rectangular composite plates.  $\beta=0$  signifies complete composite plates.  $0<\beta<1$  signifies incomplete composite plates.  $\beta=1$  signifies individual plates that do not interact. The paper also submits a diagram that represents the essential features of the critical load characteristics of simply supported rectangular incomplete composite plates suitable for most design purposes. Critical loads can be derived by the use of the diagram without too much difficulty.

## **Visualization of Eddy Structure and its Characteristics in a Turbulent Jet Diffusion Flame**

Takemi CHIKAHISA, Kazusige KIKUTA, Hiromu UMEDA,  
Mitsuru KONNO and Tadashi MURAYAMA  
(Received October 31, 1991)

### **Abstract**

This paper explains the visualization method of eddy structure in a turbulent jet flame by using a pulse laser and an image intensifier. For understanding turbulent diffusion combustion, it is very important to know the characteristics of the mixing process and eddy structure. As it is rather difficult to visualize the eddy structure due to the luminous flame, the structure is usually estimated from local fluctuations in temperature or in velocity.

The study compares pictures of the eddy structure and measured eddy scales by conventional methods. The paper also shows the diffusion characteristics and instantaneous flame shape, which is quite different from the regular shape.

## **Numerical Investigation on Combustion Similarity in Diesel Engines Using 3-D Simulation Program, KIVA**

Kazushige KIKUTA, Koudai YOSHIKAWA,  
Takemi CHIKAHISA, and Tadashi MURAYAMA  
(Received October 31, 1991)

### **Abstract**

The paper examines the possibility of a combustion similarity in diesel engines by computer simulation. In a previous work the authors analyzed fundamental equations which govern combustion phenomena in diesel engines, and predicted the possibility of combustion similarity in different sized diesel engines. The numerical analysis was conducted with a 3-D simulation program, KIVA; with some modifications. Comparison was made for engines with bore sizes from 125 to 400 mm under a variety of conditions in combustion chamber configuration, injection speed, swirl speed, and engine revolution. The results showed good agreement with the theoretical prediction. Development of temperature and fuel concentration distributions were very similar when theoretically predicted conditions necessary for the similarity were established.

## Nonlinear Time Series Analysis

### 1. A New Method of Analysis and The Theoretical Background

Norio OHTOMO\*, Saburou TERACHI\*\* and Yukio TANAKA\*\*\*

(Received October 29, 1991)

#### Abstract

There are still many unsolved problems in the procedures of nonlinear analysis of time series. Chaotic analysis, the currently remarkable one, is a marked breakthrough in this field. The aim of this paper is to present a newly-devised theoretical procedure of nonlinear analysis which is generally applicable to nonstationary time series data.

The time series  $x(t)$  is assumed to be given by  $x(t)$ =systematic part+fluctuating part. The systematic part is extracted from the time series data and the nonlinear fluctuating part is also analyzed by the present procedure. The procedure of analysis proposed by the present authors acts as a bridge between the conventional time series analysis and the chaotic analysis. Examples of the application of the present procedure to several kinds of time series data in physical, medical or engineering branches are reported.

## Bound - State Solutions for One - Dimensional Periodic Potential with Multiple Barriers per Period

Yutaka ABE

(Received November 1, 1991)

Laboratory of Quantum Instrumentation,  
Faculty of Engineering, Hokkaido University,  
Sapporo, 060, JAPAN

#### Abstract

The energy bands of electrons in a one-dimensional periodic potential consisting of multiple rectangular barriers and wells per period are calculated using transfer matrix method. It is shown that the energy bands can be derived from the reflection and transmission amplitudes of the individual rectangular barriers and can be easily extended to the cases of complex configurations of barriers and wells in the unit cell. The numerical results suggest the possibility of new type of superlattice devices composed by two different quantum-wells inside the unit cell.

**Surface Characterization and Gas Desorption Measurements ( I )**  
**— Effects of Surface Treatment for the Gas Desorption**  
**from Type 6063 Aluminium Alloy —**

Yuko HIROHATA, Masao HASHIBA,  
Tomoaki HINO and Toshiro YAMASHINA  
(Received October 28, 1991)

**Abstract**

The surface characterization and gas desorption of a type 6063 aluminum alloy were performed from a view point of vacuum engineering. Two different samples treated with extrusion (sample A) and with milling by a diamond lath (sample B) were examined in terms of their surface morphology and surface roughness. The surface roughness factor of these sample A, B, were obtained 12.6, 4.9, respectively. The thickness of oxide layer of sample B obtained by AES measurement was 10 nm, about three times smaller than that of sample A. The species of gases desorbed from samples were mainly H<sub>2</sub>, H<sub>2</sub>O and CO. The amount of all of desorbed gases from sample A was larger than that of sample B and was larger than the amount of gases calculated from surface roughness. Gas desorption behavior from samples were influenced not only by the surface roughness but also by the thickness of oxide layer and the amount of impurity.

**Test Acceleration of Hokudai 45MeV Linear Accelerator**  
**for Nano-Second Pulsed Electron Beam Generation**

A. HOMMA, S. SAWAMURA\*, T. AKIMOTO\*\*, H. TANIDA\*,  
K. SATO\*, T. AOKI, T. SAWAMURA, and H. YAMAZAKI  
(Received October 31, 1991)

**Abstract**

The short-pulse response of the electron gun which has been used for the Hokudai 45 MeV Linac was studied in order to generate a nano-second pulsed electron beam.

A harmful reflection of the grid drive pulses, caused by the discontinuities of impedance at the input-terminal and at the grid-cathod assembly, was found.

The insertion of a matching resistor across the gun input-terminal and the driving by a high voltage nano-second pulser (~3 kV output peak voltage, 3 ns pulse width) with a large grid bias voltage was adopted to overcome these reflected signals.

The characteristics of the accelerated beam were obtained ; the dose measured by the pulse radiolysis method was about 30-45 Gray, and the pulse width was about 3.5 ns determined by the time-distribution of bremsstrahlung photons obtained by bombardment to a tungsten target with the electrons.

## Study On Characteristics of Lubrication by Sliding Surface Structure

Ikuya NISHIMURA, Toshio YUHTA, and Tuyoshi SAITOH  
(Received October 31, 1991)

### Abstract

This paper presents an improvement on the characteristics of lubrication by surface structure. There is certainly friction if the bodies are in contact with each other, the force of friction was certainly brought about by the motion of bodies. It is very important for the mechanical design to decrease the force of friction and to prevent the wear.

In this study, in order to decrease the force of friction, we coated the soft material (Au) with as the solid lubricant on the hard material (Titanium nitride, TiN). TiN was coated as shown in the pattern. Load was supported with the projection of the pattern, and the solid lubricant was constantly supplied from the hollow of the pattern.

The result of the friction experience, it was shown that the sample that was coated with patterned TiN and Au had a low coefficient of friction and high load durability. Au was found to be the most malleable metal, so leaning contact of frictional surface was corrected and wear of frictional surface was prevented. It was shown that the surface structure what was patterned with TiN and Au is effective for decreasing the force of friction and the extension of the sample life.

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## **A High-speed Generation of Shaded Pictures by Extracting the Visible Boundary Faces from the CSG Model**

Takashi KAWAKAMI, Suguru SAWAI and Yukinori KAKAZU

(Received December 27, 1991)

### **Abstract**

This paper proposes a new approach to high-speed generation of shaded pictures from a given 3-dimensional constructive solid geometry (CSG) model. The proposed approach consists of the following procedures ; Namely, (1) generating the 3- dimensional boundary data which includes a set of edges and surfaces information, (2) making a set of data of 2-dimensional perspective edges which includes only visible lines from the given boundary data and calculating a set of countour lines from given CSG data, (3) translating the data of 2-dimensional data into an undirected graph and partitioning the noted whole 2- dimensional domain to a set of visible faces by the identified set of edges of the graph, and then (4) applying a smooth shading technique to each of the extracted visible faces. Some computer experiments are carried out which show the usefulness of the proposed approach.

## **The Fabrication and Properties of InAs/GaAs Quantum Wells by ALE**

Keiichi HIGUCHI, Shu GOTO, Takashi FUKUI and Hideki HASEGAWA

(Received December 25, 1991)

### **Abstract**

The atomic layer epitaxy (ALE) of GaAs and InAs, and properties of InAs/GaAs quantum wells (QW) are studied. Trimethylgallium, Trimethylindium and AsH<sub>3</sub> were used as source materials in a vertical atmospheric pressure metalorganic vapor phase epitaxial (MOVPE) system. Successful ALE growth conditions for InAs/GaAs QWs are determined. The properties of QWs were characterized by the Hall effect and photoluminescence (PL) measurements.

## Surface Characterization and Gas Desorption Measurements (II)

— Effects of Surface Treatment for Outgassing Behavior of Type 2017 Aluminium Alloy —

Yuko HIROHATA, Masao HASHIBA, Tomoaki HINO and Toshiro YAMASHINA

(Received December 6, 1991)

### Abstract

The surface characterization and outgassing behavior of a type 2017 aluminum alloy were performed to examine their potentials for the use in vacuum devices from a view point of vacuum engineering. Four different samples treated with milling (Sample A), discharging (Sample B), chemical etching (Sample C) and mechanical polishing (Sample D) were examined in terms of their surface morphology by surface profilometry, scanning electron microscopy, and xenon adsorption. The surface roughness factor was obtained as 5.9, 42.8, 9.0 and 4.5 for sample A, B, C and D, respectively. The thickness of oxide layer were measured by the sputter-AES method as 4nm, 8nm, 7nm and 6.5nm for sample A, B, C and D, respectively. Outgassing characteristics of these samples were measured by a thermal desorption method heating up to 300 °C. H<sub>2</sub>O, CO and CO<sub>2</sub> were main outgassing components and maximum desorption temperature was observed in the range between 110 °C and 160 °C. The amount of all of desorbed species was large with increasing surface roughness and with decreasing chemical etching time. But the desorption spectra from the surface after these samples were annealed and exposed to the air can be characterized mainly by the effective surface area obtained from the SRF value and geometrical surface area. The surface roughness factor and thickness of surface oxide layer were found to be important factors for outgassing characteristics.

## Surface Characterization and Gas Desorption Measurements from Aluminium Alloy (III)

— Diffusion Constant of Hydrogen into Aluminium by Thermal Desorption Analysis —

Yuko HIROHATA, Satoshi FUJIMOTO, Tomoaki HINO and Toshiro YAMASHINA

(Received December 5, 1991)

### Abstract

Aluminium alloy has been widely used as an ultra and extreme high vacuum chamber material. In the use of Al-alloy as a vacuum chamber, it is important to investigate on the gas desorption behavior. We have so far studied the gas desorption rate and the amount of hydrogen desorbed from Al metal and Al-alloy based on the thermal desorption

spectroscopy(TDS) technique. The TDS technique has been used mainly to investigate the kinetics of desorption from surface.

In the present study, we applied this method for the hydrogen desorption of Al metal due to diffusion process. The TDS spectrum was calculated for Al sample of a slab shape. It was assumed that the temperature was lineary raised. The calculated TDS spectrum became asymmetric with respect to peak temperature,  $T_p$ . In addition,  $T_p$  was independent of the hydrogen concentration of the sample. From this calculation, it was found that the spectrum due to diffusion reaction limit became similar to that of the surface reaction limit of first order reaction.

By using the modedified equation for desorption rate due to diffusion reaction limit, the activation energy was obtained from a slope of a straight line of plotting  $\ln T_p^2 \beta$  against  $1/T_p$ . The activation energy was independent of the thickness of the slab sample. In addition, the obtained value was well consistent with the assumed diffusion parameter in the model.

For 1001 Al sample, the desorption spectrum of hydrogen was measured. Based on the present analysis, the activation energy and frequency factor were obtained as  $50 \pm 5$  kJ/mol and  $(0.5 \sim 3.5) \times 10^{-3}$  cm<sup>2</sup>/s, respectively.

The desorption spectrum due to diffusion was subtracted from the observed spectrum, and then the spectrum due to surface reaction limit became symmetric with respect to the peak temperature. The activation energy due to the surface reaction limit of second order reaction was obtained as  $21 \pm 2$  kJ/mol. The total outgassing amount of hydrogen was also evaluated as  $(2.8 \pm 0.4) \times 10^{16}$  moleces/cm<sup>3</sup>.

By the present analysis, it was found that the TDS technique was useful also to examine the gas desorption due to diffusion reaction limit.

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## **$^{27}\text{Al}$ MASNMR and XPS study of mechanochemical amorphization reaction of hydrated aluminas**

Takeshi TSUCHIDA

(Received March 23, 1992)

### **Abstract**

Three hydrated aluminas, gibbsite ( $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ), bayerite ( $\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) and boehmite ( $\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), were changed to an amorphous phase after 4 or 8hr grinding in a planetary ball mill.

From the appearance of Al(4) spectra in  $^{27}\text{Al}$  MASNMR and the shift of binding energy of O1s, Al2s and Al2p in XPS spectra of the amorphous phase, it was found that a part of the amorphous phase underwent mechanochemical dehydration to form amorphous alumina, although most parts consisted of amorphous hydrated alumina with the same stoichiometric component as the separate starting hydrated alumina.

On the other hand, diaspore ( $\beta\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) was not entirely in an amorphous phase even after 24hr grinding, and it was difficult to determine whether mechanochemical dehydration underwent or not.

## **Nonlinear Time Series Analysis**

### **2. The Construction of A Data Analysis System "MemCalc"**

Yukio TANAKA\*) Norio OHTOMO\*\*) Saburou TERACHI\*\*\*)

(Received March 27, 1992)

### **Abstract**

The purpose of the present paper is to propose a newly-devised analysis system of time-series data, which is called "MemCalc" which has been worked out on personal computers.

MemCalc system is composed of three procedures: (1) a spectral analysis based on the maximum entropy method for the frequency domain, (2) an optimum fitting by the nonlinear least-squares method for time domain, and (3) a generation of artificial time-series data. Especially, it is noted that the MemCalc successfully overcomes substantial difficulties in the nonlinear least-square fitting.

Thus, this system is available for a wide variety of time-series data in many fields such as natural science, medical science, biology, engineering, economy, and so on. The above-mentioned three parts are described in detail.

## Nonlinear Time Series Analysis

### 3. An Analysis of Time-Series Data in Natural Science and Engineering Branches by The Use of "MemCalc"

Norio OHTOMO\*) SaburoU TERACHI\*\*) Hirokatsu IWASA\*) and Yukio TANAKA\*\*\*)

(Received March, 27, 1992)

#### Abstract

Time-series data in natural science and engineering branches, such as variations of temperature in chemical reaction processes, sunspot numbers, river flow, density-fluctuations of turbulent plasma and white noise, are analyzed by the use of MemCalc system, which is a newly-devised realization of nonlinear analysis (see paper 2 in the present series).

PSD's (power spectral densities), autocorrelation functions and the best fitting curves for these time-series data are calculated by MemCalc. Residual time-series, which is the remaining factor obtained by a subtraction of the best fitting curve from the raw data, is also analyzed. An example of forecasts is demonstrated. The lag-dependence of MEM-PSD and the log-transformation are discussed.

## A Study on Reaction between Superoxide and Nitro Blue Tetrazolium by the Pulse Radiolysis Methode

Kenji TAKAHASI, Bai Shyu-Shen, Sadashi SAWAMURA,  
Masatosi KITAICHI and Meiseki KATAYAMA

(Received March 19, 1992)

#### Abstract

Pulse Radiolysis studies of the reaction between Superoxide anion radicals ( $O_2^-$ ) and Nitro Blue Tetrazolium (NBT) were performed by an improved Pulse Radiolysis equipment.

A reaction mechanism between  $O_2^-$  and NBT was proposed based on the experimental results of transient absorption spectra.

The absorption observed immediately after the pulse at 420nm was attributed to the Tetrazolanyl radical, which was produced rapidly by one electron transfer from  $O_2^-$  to NBT.

The Tetrazolanyl radicals were changed to Monofolmazan by one electron reduction.

Finally, Blue Folmazan was produced from NBT.

## No. 161

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## Effects of Carbon Particles in Flowing Air on Hot-Wire Heat Transfer and Anemometry

Noboru MIYAMOTO, Hideyuki OGAWA and Katsunori OHASHI  
(Received June 23, 1992)

### Abstract

An analysis was made on the characteristics of hot-wire heat transfer and anemometry in flowing air containing carbon particles. In the experiment, three types of hot wires with different diameters were independently installed in a wind tunnel where the carbon particle concentration in the air flow was controlled. The velocity of the air flow and the temperature of the hot wires were varied in the tests. The results showed the influence on the carbon particles in the air flow on the hot-wire heat transfer was stronger with higher wire temperature, smaller wire diameter, and higher particle concentration. However, small amounts of carbon particles did not affect the apparent mean flow velocity measured by the hot-wire anemometry, but it was shown that turbulent intensity increased significantly.

## Properties of gears with slits

— Regarding the vibration and noise —

Hiroshi OCHIAI and Takashi KANNO  
(Received June 25, 1992)

### Abstract

The demand to mesh gears without backlash is growing in accompanying the recent development of the mechatronics control.

However, it is dangerous to mesh the gears without backlash because the teeth have profile error interfere with each other.

It is thought that the flexible teeth of the gear would be effective measures to solve this problem.

Thus the authors compared gears with certain slits in the teeth with normal gear without slits by experiments while changing the value of backlash and revolution velocity under no-load conditions.

As a conclusion, it was found, possible to mesh the gears with backlash smaller than the value recommended by JIS.

Also, it is effective to cut the slits in the teeth of the gear when backlash is zero or minus value caused by the eccentricities of the gears and smaller center distance of the gears.

When decreasing the value of the backlash, it is necessary to control the eccentricity and the addendum modification coefficient of the gear as strictly as possible.

## On the Factors of Generating Blowhole Defects in Welding

Takayoshi UKAI, Toshiaki TAKADA and Hiroshi TAKOH

(Received June 29, 1992)

### Abstract

In this study, the authors selected blowhole defects among the numerous defects in the welding process.

The experiments were carried out concerning these three factors ;

1) amount of CO<sub>2</sub> shield gas, 2) the oxide scale in the surface of backing plate, and 3) the clearance between the base metal and the backing plate.

The results are summarized as follows ;

(1) Numerous blowholes like "wormholes" appeared by less than 3 l/min CO<sub>2</sub> shield gas, and a limited number of small blowholes by more than 5 l/min.

(2) As for the effect of oxide scale on the surface, it caused many blowholes to generate as compared with polished backing plates, because of FeO is a composition of oxide scale.

(3) Less than 0.4 mm clearance between the base metal and backing induced a large number of blowholes. It appears to be because of the movement and escapement of CO gas in melted metal was prevented by minimal clearance.

## A Test for Redundancy of Some Sets of Variables

Hideyuki IMAI and Tsutomu DA-TE

(Received June 30, 1992)

### Abstract

In canonical correlation analysis, Siotani(1957) and Fujikoshi(1982) obtained the likelihood ratio statistic and its asymptotic expansion under null hypothesis for redundancy of variables.

Horst(1961) extended ordinary canonical correlation analysis to those of two or more sets of variables.

In this paper, we obtain the likelihood ratio statistic and its asymptotic expansion under the null hypothesis for redundancy of several sets of variables.

## Nonlinear Time Series Analysis

### — 4. An Analysis of Time-Series Data in Economic Branches by The Use of "MemClac" —

Norio OHTOMO, Saburou TERACHI and Yukio TANAKA  
(Received June 30, 1992)

#### Abstract

Time-series data in economic branches, such as variations of the Dow-Jones average price by Nippon-Keizai-Shinbunsha, international airline passengers, house constructions, automobile accidents resulting in injury or death, and sales of a goods in drug-stores, are analyzed by the use of MemCalc system (see paper 2 in the present series). Power spectral densities (PSD's), autocorrelation functions and the best fitting curves for these time-series data are calculated by MemCalc. Examples of forecasts are also demonstrated.

### An Exact Numerical Method for Calculating Fermi Energy and Carrier Concentrations in Secoductors

—An example of transcendental equation solver—

Yutaka ABE  
(Recieved June 30, 1992)

#### Abstract

An efficient numerical method is described for calculating the Fermi energy, free electron and free hole concentrations, and the ionized impurity concentrations in semiconductor materials. Several detailed calculations for the temperature dependence of free electrons in uncompensated, and partially compensated Silicon single crystals are reported.

The Fermi energy for highly doped specimens are discussed in terms of broadening of the impurity level and band-edge tail due to random impurity potentials.

## Nitrization of Aluminium by Using ECR Nitrogen Plasma

Tomoaki HINO, Ichiro FUJITA and Toshiro YAMASHINA

(Received June 4, 1992)

### Abstract

Numerous nitrization experiments for Al were carried out using ECR nitrogen plasma. Since the aluminium surface is covered by a stable oxide, the surface was etched by Ar plasma bombardment before the nitrization. By this pretreatment, the nitrogen content on the surface was largely increased. Since it was observed from the emission spectroscopy analysis that the nitrogen ion,  $N_2^+$ , was effective for the nitrization, the nitrogen ion flux was enhanced by applying a negative bias to the substrate. The nitrogen content was increased several times by negative voltage, compared with the case of free voltage. It was also found by the XPS analysis that the aluminium nitride, AlN, was formed by the present plasma nitrization.

### A primary study of the antithrombogenesis of deposited Alumina film by reactive sputtering

— Effect of oxygen partial pressure in sputtering —

Yukiaki KIKUTA, Masayuki NAKAGANE, Ikuya NISHIMURA,  
Ayumi MITOH, Shun MURABAYASHI and Toshio YUHTA

(Received June 30, 1992)

### Abstract

In this paper the antithrombogenesis of Alumina film by reactive sputtering in vitro test was described. It has long been known that artificial surfaces activate components of the blood, both cellular and plasmatic.

We have focused our attention on the biocompatibility of Aluminas to be applied on artificial heart valve. Then we suggested that the Alumina ceramics had the same blood compatibility as silicon rubber. However, it is not easy to produce heart valves of Alumina ceramics because they are very hard materials. If an endurable material can be coated with an Alumina film, it may have a good blood compatibility. Therefore we studied about the interaction of Alumina films.

To observe effects of oxygen partial pressures, several Alumina films were deposited on glass substrates by reactive sputtering and examined the interaction with blood in vitro tests. Activation of the intrinsic coagulation system was estimated based on Kallikrein activity. The platelet reactivity was estimated by using scanning electron microscopic examinations. The results showed it had no effect on the intrinsic coagulation system and 10% oxygen partial pressure was reasonable in the platelet reactivity.

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IN COMMEMORATION OF THE FIFTY ANNIVERSARY OF  
DEPARTMENT OF METALLURGICAL ENGINEERING

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# In situ Infrared Reflection Absorption Spectroscopy at an Electrode-Electrolyte Interface in the Fingerprint Wave-Number Region

Takeshi SASAKI and Tatsuo ISHIKAWA

(Received September 18, 1992)

## Abstract

In order to extend the wave number to the fingerprint region in *in situ* infrared spectroscopy for an electrode system, new techniques were developed. First, a new test cell equipped with a micrometer attached to the test electrode and an O-ring for setting an optical window was made of Kel-F. The cell prepared a thin electrolyte layer imposed between the window and the test electrode, as a stable state during experiments. Next, a new manipulation system for treating the piston attached to the test electrode was devised. This made it possible to manipulate the piston without any interference with the purging effect of N<sub>2</sub> gas. With these new techniques we succeeded in the acquisition of significant signals of monolayer-adsorbed aromatic thiols in the fingerprint region.

The spectra showed that both 2,5-dihydroxythiophenol (DTH) and p-mercaptophenol (MP) adsorbed on the surface of gold with the molecular plane nearly perpendicular to the electrode surface and that the oxidation states changed with the potential changes.

# Hydroaromatic Ring Structure of Coal Hydrogenation Oil by Means of Dehydrogenation and HPLC-GC-LV MS

Susumu YOKOYAMA, Masahito KANEKO,

Masaaki SATOU and Yuzo SANADA

(Received September 18, 1992)

## Abstract

Coal hydrogenation liquid consists of various aromatic ring and naphthenic ring structure condensed to their aromatic ring (hydroaromatic ring) designated as compound type. The chemical structures of these compound types were investigated by HPLC-GC-LV MS to estimate the number of aromatic and naphthenic ring and a representation method for their structural results was proposed. However, the absolute chemical structure of hydroar-

omatic species can not be elucidated because mass analysis is difficult to distinguish among isomers which have identical molecular weight but different ring structures.

In this study, dehydrogenation reaction were performed on various compound classes separated by amine column HPLC for SRC-II oil and the hydroaromatic compounds were converted to the corresponding polyaromatic compounds which were analysed by means of GC-LV MS. Species of hydroaromatic ring types consisting of five and six member naphthene ring were clarified.

### **In-situ FT-IR Spectroscopic Studies of Coal Drying**

Haruo KUMAGAI<sup>1)</sup>, Bruce A. Grigor<sup>2)</sup> and Russell F. Howe<sup>2)</sup>

(Received September 18, 1992)

#### **Abstract**

The low temperature drying of lignite and bituminous coal was investigated using in-situ diffuse reflectance FT-IR spectroscopy. Vacuum drying was found to be more effective than flowing nitrogen. FT-IR spectra of coal showed the existence of two types of adsorbed water i. e. weakly bound water which may be hydrogen bonded to hydrocarbon species in the coal and strongly bound water which may be adsorbed through hydrogen bonding to hydroxyl groups in the coal. Hysteresis effects were observed for the both types of adsorbed water, and this effect became more pronounced at higher temperature, and more pronounced for lower rank coal than higher rank coal.

# Evaluation Methods of Coking Coal for Coke Manufacturing

—Hydrogen and Electron Transfer Abilities of Coal—

Y. SANADA, M. SASAKI and K. NAKAMURA\*

(Received September 18, 1992)

## Abstract

Evaluation method for coking coal has been proposed for coke manufacturing. The distribution of optical textures in coke was evaluated by an automatic image analysis system. Hydrogen donor and acceptor abilities of coal were measured. The extent of the development of anisotropic texture in the coke is correlated closely to hydrogen transfer ability of the coal and coal blend.

Change of spin concentration as a function of charge (electron) transfer ability of iodine doped coal correlates with the maximum fluidity and temperature ranges of plastic stage of coal, respectively. The relationship between the extent of fine mosaic texture in the coke and the change of spin concentration for the iodine doped coal has been also recognized.

Hydrogen and charge (electron) transfer abilities of coal take a part of deep understanding for structure and carbonization reactivity of coal.

## Water gas reaction in coke gasification by H<sub>2</sub>O.

Yoshiaki KASHIWAYA, Kuniyoshi ISHII

(Received September 18, 1992)

## Abstract

Gasification reaction of metallurgical coke by Ar-H<sub>2</sub>-H<sub>2</sub>O mixtures at 1273, 1473 and 1673K was investigated. The determination of reaction rate was made by gas analysis method using both Quadrupole mass spectrometer (QMS) and Infrared gas analyzer. The gas analysis method is so useful for not only the quantifying the reaction rate but also the estimating the kinds of reactions occurring in H<sub>2</sub>O-coke gasification. The consideration of the kinds of reactions were made by using the thermodynamic characterization of produced gas composition and the variation of the amount of each produced gases (H<sub>2</sub>, CO, CO<sub>2</sub>) according to reaction temperature. The kinds of reactions in the region above 1273K were elucidated.

In coke gasification by  $H_2O$ , the main reaction is water gas reaction I. The generation of  $CO_2$  is caused by water gas reaction II and the possibility of water gas shift reaction is very low. Further, owing to produced  $CO_2$ , Boudouard reaction occurs and it becomes prominent in high temperature range.

## Mechanisms of Localized Corrosion in Copper Tubes

Takenori NOTOYA

(Received September 18, 1992)

### Abstract

The mechanisms of a localized corrosion in copper tubes, so-called "ant's nest corrosion", are reviewed. Corrosives are carboxylic acids such as formic acid and acetic acid which are decomposition products of chlorinated hydrocarbons used for detergents and for lubricant oil used for bending processes. Possible corrosives are also presented. The influence of such factors as temperature, moisture, oxygen, the type of corrosives and its concentration, pH, the catalytic activity of copper surface, stress, impurity of copper, bacteria and capillary forces are discussed. Corrosion processes are believed to be a micro anode-macro cathode type corrosion of copper. Corrosion reactions include copper complex formation and its oxidation to produce cuprous oxide deposited in microtunnels in copper tubes and release acids in the pits, which accelerate the corrosion.

## First-principles calculation of Diffuse Intensity Spectrum of Binary Alloys

Tetsuo MOHRI

(Received September 18, 1992)

### Abstract

The Short Range Order Diffuse Intensity Spectrum is obtained for Cu-Au and Cu-Pt systems from the first-principles which consists of electronic structure calculation and the Cluster Variation Method. The result clearly reproduces the observed intensity maxima for both the systems.

# Theoretical Study on the Phase Stability of Au–Pd System

Satoshi TAKIZAWA

(Received September 18, 1992)

## Abstract

Combining the electronic structure calculation and Cluster Variation Method, we study the phase stability of the Au–Pd system from the first-principles. Because of the small size mismatch between the constituents, the calculated mixing heats of formation agree well with the experimental results.

# Anisotropic Cyclotron Effective Mass and Local Fermi Surface Shape of lead

S. WATANABE and H. TAKAHASHI

(Received September 18, 1992)

## Abstract

The angular dependence of the Azbel'-Kaner Cyclotron Resonance Peaks in lead is Analyzed. All of the anisotropies in the cyclotron resonance peaks originating from the  $\langle 110 \rangle$  arms of the Fermi surface in the third band are shown to be characterized by a set of the three effective masses with one negative, corresponding to the hyperboloidal shape of the Fermi surface. This indicates the existence of the hole-electron mixed Landau state adjacent to the extremal points on the Fermi surface where the density of state becomes large. Referring to the 2-D limit of the cyclotron motion in a crystal, we discuss the dynamics of electrons on a hyperboloidal Fermi surface of Pb.

## Damage Rate Dependence of Electron-Irradiation Behaviors in Fe-Cr-Ni Model Alloy

Heishichiro TAKAHASHI, Naoyuki HASHIMOTO

(Received September 18, 1992)

### Abstract

To study the effects of damage rate on irradiation behaviors, a Fe-Cr-Ni alloy was electron-irradiated at the damage rates of  $1 \times 10^{-4}$  to  $2 \times 10^{-3}$  dpa/sec in the temperature range between 473K and 773K using a high voltage electron microscope. The composition changes (segregation) occurred at grain boundary sinks, i.e. Ni segregation and Cr depletion. The maximum segregation and swelling peak appeared at higher temperature with the increasing of damage rate. The amount of swelling was higher at lower damage rate. On the other hand, the maximum compositional change was recognized at a medium damage rate of  $1 \times 10^{-3}$  dpa/sec. This damage rate dependence of segregation and swelling can be explained by considering the recombination rate and sink density in the grain.

## The effect of Precipitated MnS on Recrystallization in Low Carbon Martensite Steel

Hiroshi TAUMI, Yoichi ITO and Toshio NARITA

(Received September 18, 1992)

### Abstract

Primary recrystallization of the deformed martensite steel was studied with interest on the effect of precipitated MnS. In this study, specimens with or without precipitated MnS were prepared by solution heat-treatment. It was found by optical and transmission electron microscopic observations that the depletion area of sulfur in a cold worked matrix was recrystallized preferentially. It is, therefore, suggested that dissolved sulfur in the matrix was a more effective inhibitor for recrystallization.

## Martensitic Transformation of Antiferro-magnetic Fe Particles Embedded in a Cu Matrix in a Magnetic Field

Yoshimi WATANABE\*, Masaharu KATO\*\* and A. SATO\*\*

(Received September 18, 1992)

### Abstract

Martensitic transformation of antiferro-magnetic Fe particles embedded in a Cu matrix has been studied in the presence of a magnetic field at low temperatures. The saturation magnetization increased when a magnetic field of 4.44MA/m was applied during deformation at 4.2K. Electron microscopic observation indicated that the increment of the transformed fraction by the magnetic field was greater for larger particles, in which transformation by plastic deformation is easier. Cooling down to 4.2K after deformation at room temperature induced additional transformation by a few percent. On the other hand, the application of a magnetic field during simple cooling did not cause any effect on the additional transformation. Since the chemical free energy difference between the  $\gamma$  and  $\alpha$  phases has a maximum around the Neel temperature, the transformation of Fe particles below this temperature may be promoted by a magnetic field only when it is superimposed with a mechanical driving force.

## Microstructural change of Al on Hydrogen or Deutrium ion implantation

Hiroshi KINOSHITA and Heishichiro TAKAHASHI

(Received September 18, 1992)

### Abstract

Microstructural changes of Al on 30keV H<sup>+</sup> or D<sup>+</sup> ion implantation to fluence of 0.5~4 × 10<sup>17</sup> H<sup>+</sup> or D<sup>+</sup>/cm<sup>2</sup> at room temperature were investigated by transmission electron microscopy (TEM). In the case of D<sup>+</sup> implantation, bubbles were formed with high number density and small mean size compared to the case of H<sup>+</sup> implantation.

At fluences greater than 4 × 10<sup>17</sup> H<sup>+</sup>/cm<sup>2</sup>, tunnel structure and blisters were observed. When the electron beam was focused around a blister, we recognized that some part of the bright region which is the tunnel structure, changed into dark contrast. It can be thought that the phenomena was the evidence for high pressure fluid motion of implanted H<sup>+</sup> atoms.

Tunnel structure was also formed at  $4 \times 10^{17} \text{D}^+/\text{cm}^2$  implantation. When the electron beam was focused on some tunnel structure, small defect clusters were formed only in the bright contrast region. It might be because of the sub-threshold electron irradiation damage caused by charged  $\text{D}^+$  atoms.

## TEM OBSERVATION OF MAGNETITE REDUCTION WITH IMPLANTED HYDROGEN

K. ISHII\*, M. KATSUMI\*\*, Y. TAMURA\*\*\*,  
Y. KASHIWAYA\*, and S. SATOH\*

(Received September 18, 1992)

### Abstract

In order to make clear the crystallographic mechanism of  $\text{H}_2$  reduction of iron oxide, hydrogen ion was implanted into the magnetite and microstructural changes were investigated by a transmission electron microscope (TEM). Magnetite sample was prepared by oxidizing thin foils of pure iron with  $\text{CO}_2$  gas at  $1300^\circ\text{C}$ . The samples for TEM observation were finally thinned by Ar ion milling. Hydrogen implantation was conducted at room temperature after Ar ion thinning. The energy of implantation was 50 KeV and the doses were 1 and  $2 \times 10^{17}$  ion- $\text{H}_2/\text{cm}^2$ . In the spot where the defect cluster introduced by Ar thinning was concentrated, wustite phase was formed in the magnetite matrix as soon as hydrogen was implanted. Wustite was also formed by cooperation of hydrogen implanted and electron irradiation during TEM observation.

**Key words:** Magnetite, ion implantation, crystallographic mechanism, hydrogen reduction

## **Balling-up Phenomena of Native Oxide Film on Poly-Si/Single-crystal-Si Interface**

Somei OHNUKI, Michiya KIMURA, Heishichiro TAKAHASHI  
Koji KIMURA and Kuniaki KUMAMARU

(Received September 18, 1992)

### **Abstract**

Annealing behavior of native oxide and crystal growth in poly-Si/SiO<sub>2</sub>/substrate-Si were investigated by means of high resolution electron microscopy. The grain growth and crystal orientation between poly- and substrate-Si were affected by the doped impurities. By the doping of either of As or B, the grain growth and the balling-up of the oxide were enhanced, and an Epitaxial relation was predominate. However, by the doping of both of As and B, the grain growth was predominate, but the Epitaxial relation and the balling-up were suppressed. From these results the reliability was discussed on the glass reflow model, and the importance of the impurity segregation and the lattice mismatch around the interface was emphasized.

## **Coloring Behavior of Stabilized Zirconia in the Reaction with Active Metal Solder**

Toshiki MITSUEDA and Toshio NARITA

(Received September 18, 1992)

### **Abstract**

A stabilized zirconia ceramics becomes colored brown near the interface when it is joined to metals with an active metal solder. To clarify this coloration mechanism, joining of ZrO<sub>2</sub>/Ti·Ag·Cu/ZrO<sub>2</sub> was carried out in vacuum at temperatures between 1073 and 1273K for up to 14.4ks. It was found that the colored zone grew parabolically and the activation energy was 201kJ/mol. The reaction product of TiO was determined by the X-ray diffraction method. The diffusional analysis of oxygen showed that the colored zone appeared in the part of zirconia with oxygen pressures below 10<sup>-6</sup>Pa. When the colored zirconia was heat-treated in air, a reversible color change was observed from brown to white.

The coloration seems to be due to the transition of electronic states between Zr<sup>4+</sup> and Zr<sup>3+</sup>. This energy change is caused by the electrons accompanied by the formation of the

oxygen vacancies when the oxygen of the zirconia transfers toward the interface and reacts with titanium.

## High temperature oxidation of MoSi<sub>2</sub>-based materials

Kazuya KUROKAWA<sup>\*)</sup>, W. L. WORRELL<sup>\*\*)</sup>

(Received September 18, 1992)

### Abstract

The background of MoSi<sub>2</sub>-based materials as a new heat-resistant structural material which is usable in oxidizing atmospheres at ultra-high temperature was described. Moreover, the oxidation tests of pure MoSi<sub>2</sub> materials and MoSi<sub>2</sub>-based materials reinforced with WSi<sub>2</sub>, SiC or SiC-ZrO<sub>2</sub> were carried out in a pure oxygen gas at 1773K. For the heating to 1773K, two heating schedules were applied; i. e. an extremely rapid heating procedure to obtain the isothermal oxidation behavior and a relatively slow heating procedure to clarify the oxidation behavior under this condition. All MoSi<sub>2</sub>-based materials used in the present study had intrinsically outstanding resistance to oxidation as far as the isothermal oxidation is concerned, although the MoSi<sub>2</sub>-based composite materials were inferior to pure MoSi<sub>2</sub>. Moreover, it was suggested that the addition of WSi<sub>2</sub> into MoSi<sub>2</sub> matrix promotes "pest" reaction and the reaction is suppressed by the use of high-density materials, the decreasing of WSi<sub>2</sub> concentration and the increasing of heat-up rate.

## Analysis of Solidification Path of Aluminum Base Ternary Alloy

Kenichi OHSASA, Mitsuhiro OHMIYA,  
Masayuki KUDOH and Tatsuya OHMI  
(Received September 18, 1992)

### Abstract

Solidification paths of Al-Ge-Si and Al-Cu-Si ternary alloys under the conditions of the equilibrium and non-equilibrium solidification were analyzed on the basis of thermodynamic calculation. Sub-regular solution model was used to describe the Gibbs free energy of the phases in the ternary alloys. The excess free energy of the phases were calculated from the interaction parameters of the binary systems which construct the ternary systems. The changes in fraction solid and compositions of ternary solution phases during the solidification of the ternary alloys were calculated. As a result, the experimentally obtained temperatures such as the start of solidification, the start of eutectic and the end of solidification agreed well with the calculated non-equilibrium solidification path.

## Refining Mechanism of Primary Crystals in Hypereutectic Al-Si Alloy Ingots by the Duplex Casting Process

Tatsuya OHMI\*, Yasuhiro TANAKA\*\*,  
Masayuki KUDOH\* and Ken-ichi OHSASA\*  
(Received September 18, 1992)

### Abstract

Recently, the authors reported the refinement of primary silicon crystals in the hypereutectic Al-22mass%Si alloy ingots produced by the Duplex Casting process with the combination of Al-12mass%Si alloy as the first melt and Al-32mass%Si alloy as the second melt. In this study, three possible origins of the refined primary crystals were examined: (1) detachment of eutectic silicon crystals during the remelting process of solidified shell of the first melt, (2) nucleation in the second melt during the mixing process of the first and second melts, and (3) nucleation after complete mixing.

In order to examine the first origin, two combinations of alloy compositions were selected for the Duplex Casting process: (a) Al-33mass%Cu and Al-32mass%Si; and (b) Al and Al-44mass%Si. As a result, the primary silicon crystals were refined even though the

first melt was free from silicon in either case. Therefore, the first origin is concluded to be not dominant in the refinement of primary crystals.

The combination of Al-51mass%Ge alloy and Al-32mass% Si alloy was selected to examine the second and third origins. The germanium concentration in the refined primary crystals was lower than the possible minimum concentration predicted on the assumption that the primary crystals came from the third origin. Therefore the second origin, i. e. nucleation in the second melt, is confirmed as the predominant one.

Based on these results, a refining mechanism of primary crystals by the Duplex Casting process is presented.

## Measurement of Growth Rate of Austenitic Phase during Peritectic Reaction in an Fe-C System

Kiyotaka MATSU-URA, Youichi ITOH and Toshio NARITA

(Received September 18, 1992)

### Abstract

$\delta$ -iron and melted high carbon steel, with the carbon content of the solvus and liquidus lines in an iron-carbon equilibrium phase diagram, were held at 1423°C in contact with each other, and the thickness of  $\gamma$ -phase formed between  $\delta$  and liquid phases was measured. The relationship between the thickness  $x$  ( $\mu\text{m}$ ) and time  $t$  (s) was regressed such that  $x = 85.7t^{0.50}$ .

The distribution of carbon concentration over those three phases was also measured. The result gave a gradual decrease of carbon concentration in  $\gamma$ -phase from  $\gamma$ /liquid interface toward  $\delta/\gamma$  interface and the equilibrium conjugation relationships at both interfaces.

The experimental results of growth rate of  $\gamma$ -phase and the distribution of carbon concentration were both in good agreement with the results of the simulated peritectic reaction based on the diffusion-controlled mechanism.

## Large Undercooling due to Oxide Flux in Plain Carbon Steel

Masayuki KUDOH, Jun-ichi TANAKA,  
Kohjiroh OKUYAMA and Ken-ichi OHSASA

(Received September 18, 1992)

### Abstract

In this study, a new flux for achieving high undercooling in plain carbon steel was developed. The flux made was by mixing of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{CaO}$ . Carbon steel weighing 100g, was inserted into an alumina crucible and covered with the flux, was melted and frozen with a slow cooling rate. Then, it could be statically undercooled and the undercooling in the carbon steel was changed with the flux composition. In this experiment, carbon steel was cooled down to 232K by using the flux of 14%  $\text{Al}_2\text{O}_3$ -57%  $\text{SiO}_2$ -29%  $\text{CaO}$ . The microsegregation abruptly reduced to below the undercooling of around 50K resulting from the rapid increase in partition coefficient, and the hardness profile in the plain carbon steel undercooled till 213K was uniform according to a short period from the start to end of the solidification. It is considered as a mechanism to obtain high undercooling that alumina inclusions are eliminated from molten steel to the flux and that soluble oxygen in the molten steel is decreased with reduced Si from  $\text{SiO}_2$  in the flux.

## Effect of Rolling Temperatures on the Deformation Texture of Hypo-eutectic Mg-Li Alloy

Youichi ITOH, Kiyotaka MATSUURA, Hiroshi TAUMI,  
Noboru YONEZAWA and Toshio NARITA

(Received September 18, 1992)

### Abstract

Hot-extruded flat bars of hypo-eutectic Mg alloy containing 6.3 mass% Li were rolled at 230K, 300K, 420K and 520K, and the deformation textures for Mg-rich phase, which had possessed on h. c. p lattice, were investigated.

The texture for a sheet rolled at 230K was composed of two components. The predominant component was  $(0001)\langle 11\bar{2}0 \rangle$  and  $(0001)\langle 10\bar{1}0 \rangle$  rotated  $\pm 15\sim 20^\circ$  about a transverse direction and the subsidiary component was  $(0001)\langle 10\bar{1}0 \rangle$  rotated  $\pm 30\sim 40^\circ$  about a rolling direction. As the rolling temperature rised, the former component became gradually weak,

while the latter component about rolling direction became strong and approached to an orientation  $\{11\bar{2}0\}\langle 10\bar{1}0\rangle$ .

It is supposed from the above results that active deformation mechanisms are changed from (0001) slip and  $\{10\bar{1}2\}$  twin at low temperature to  $\{10\bar{1}0\}$  and  $\{10\bar{1}1\}$  slips at high temperature.

## Functionally Gradient Materials of Ni-NiO, Ni-Si<sub>3</sub>N<sub>4</sub>, Ni-AlN and Al-AlN Systems.

Koji ATARASHIYA

(Received September 18, 1992)

### Abstract

Generally speaking, the preparation of FGM-blocks, especially in the metal-metal nitride systems, by the method of powder metallurgy requires an extremely high temperature and high pressure. But, in this work using a ductile nickel metal or an aluminum ultrafine particle, the FGM-blocks were easily prepared by powder metallurgy at a lower temperature. In the system Ni-NiO and Ni-Si<sub>3</sub>N<sub>4</sub>, a mixture of a metallic powder and a non metallic powder whose contents were gradually changed was pressed in a steel die under a pressure of 200-320 MPa. These green compacts were heated at 900-1573 K in controlled atmosphere under null pressure. In the case of Ni-AlN and Al-AlN systems, a compositionally gradient mixture of a coarse metallic powder and an aluminum ultrafine powder were pressed under 200 MPa in a steel die followed by heating at 873-1473 K in flowing nitrogen. In this process, the metallic ultrafine particle was reacted with nitrogen into metal nitride, but the coarse metallic powder did not react with nitrogen. Thus, the FGM-blocks of metal-metal nitride systems were completely accomplished. The FGM-blocks of Ni-NiO, Ni-Si<sub>3</sub>N<sub>4</sub>, Al-AlN and Ni-AlN systems prepared by this method were characterized by their properties and were used in joinings. The joining of metal/FGM/ceramics, metal/FGM and ceramics/FGM were completely accomplished at 900-1573 K.

## A Solid Feeder of Fluidised Agglomerates of Fine Particles

Tadatoshi CHIBA

(Received September 18, 1992)

### Abstract

In an effort to examine gas fluidisation and transportation of several different kinds of non-fluidisable and fluidisable fine particles such as submicron ceramics, commercial carbon black and catalyst particles, pressure drop and expansion of the particle beds were measured in a 50mm i. d. fluidised column. It was shown from the measurements that smooth fluidisation is obtainable even for some submicron particles if they grow to agglomerates with mean diameters of ca.  $100\mu\text{m}$  by gas passage through the bed. Entrainment of these fluidised particles out of the column, particularly of carbon black and FCC catalyst, was also examined equipping a gas jet tube and a riser tube inside the column. The rate of particle entrainment was shown to depend on the gas velocity in the riser tube, the diameter of the riser tube, the depth of the riser bottom in the bed and the distance between the nose of the jet tube and the bottom of the riser tube. Existing theories were applied to estimate the effective diameter of agglomerates and the rate of entrainment.

## A Fundamental Study of the Production of Fine Platinum Powder by Hydrogen Reduction of a Chloro-Platinum Acid Aqueous Solution

Hikomichi KIUCHI, Hiroaki SAKASITA and Takuo YASUDA

(Received September 18, 1992)

### Abstract

Twice the amount of NaOH that is required for neutralization was added to a chloro-platinum acid aqueous solution. It was treated by heating for 12 hours, and then it was reduced by hydrogen pressure.

The induction period occurred on the reduction without the heating treatment. However the reaction resistance disappeared through the heating of the solution, and the pH of the solution changed from 12.5 to 3. The platinum complex in the solution after the treatment was considered to be one hydroxide ion coordinated into one platinum atom.

The reaction curves were the straight lines which did not depend upon the concentration change of platinum in the solution. The reaction rates obtained from the slope were

corrected by the temperature dependency of the hydrogen solubility, and these corrected rates gave 3.75kcal/mol as an activation energy. The dependency of the reaction rate upon the hydrogen pressure was of the first order. The reaction rate was proportional to the surface area of solution. Therefore the rate determining process may be the diffusion of the dissolved hydrogen through the liquid laminar film at the interface between the gas and the liquid.

The reduced platinum powder were fine spherical particles (0.2~1.5 $\mu$ m in diameter). The powder gave the broadening of the peaks on X ray diffraction. The broadening showed that the spherical particle consisted of very small crystallites, and the diameter of the crystallite was calculated to be about 13nm according to Scherrer's equation.

## Production of Fine Copper Powder by Disproportionation Reaction of Cuprous Sulfate Solution using a Continuous Type Autoclave

Hitoshi SASAKI and Tadao NAGAI

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### Abstract

Disproportionation reaction of cuprous sulfate solution was studied to obtain fine copper powder suitable for conductive paste using a continuous type autoclave.

Cuprous sulfate solution was made in the autoclave containing fine copper wire and cupric sulfate solution by mutual reaction of ( $\text{Cu}^{2+} + \text{Cu}^0 \rightarrow 2\text{Cu}^+$ ) at high temperature, e. g., 220°C. Cuprous solution, thus formed, was dropped continuously into first reservoir through an over flow pipe. The fine copper powder was obtained by disproportionation reaction of ( $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}^0$ ) proceeded by cooling.

Cooling temperature of the reservoir had a large effect on the diameter of the powder. Fine copper particles of 1~2 $\mu$ m in diameter were obtained in the reservoir kept at low temperature, e. g., 0°C, while large particles more than 10 $\mu$ m in diameter were obtained in the reservoir kept above 70°C.

The shape of copper powder obtained was greatly altered by time to time. The copper powders withdrawn from the second reservoir at an earlier period had flat crystal surface planes and showed an excellent oxidation resistance, while that obtained from latter stage consists of aggregates of fine particles and were oxidized after drying.

## Development of Graphite Cathodes for an Aluminum-Chlorine Fuel Cell in High Temperature Chloride Melts

Tatsuo ISHIKAWA, Takeshi SASAKI, and Shoichi KONDA

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### Abstract

An aluminum-chlorine fuel cell for manufacturing aluminum chloride was proposed as one process of an electrochemical cycle for the production of high-purity aluminum from aluminum scraps. To develop cathodes for the fuel cell, several graphite electrodes with many holes of the same size were tested by changing the hole sizes and numbers, and the performance for the reduction reaction of chlorine was estimated in terms of the discharge characteristics of the cell in a mixture of  $\text{MgCl}_2$  25 mol%- $\text{NaCl}$  75 mol% at  $750^\circ\text{C}$ . The voltage drops due to the resistance of the reduction reaction decrease with the decrease in the size of the holes, but in small holes such as those 2 mm in diameter hardly all holes worked equally, showing the difficulty of enlarging the reaction zone. To overcome this disadvantage of drilled electrodes, grooved electrodes were developed and an output current of 4 A at an output voltage of 1.5 V was attained using electrodes with a diameter of 68 mm.

## Electrodeposition Forms of Solid Aluminum and Estimation of their Smoothness in Low-Temperature Chloride Melts containing $\text{AlCl}_3$ .

Shoichi KONDA, Takaaki MATSUDA, Tatsuo ISHIKAWA

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### Abstract

This report is concerned with the morphology of solid aluminum electrodeposited in chloride melts containing  $\text{AlCl}_3$  of over 50 mol% at  $200^\circ\text{C}$ . The rotation of electrodes has a leveling effect on such deposits, especially at linear velocities over 0.5 m/sec, and compact polycrystalline aluminum is more easily formed in melts with  $\text{AlCl}_3$  concentrations of over 55 mol%. The ratio of the quantity of electricity for deposition ( $Q_c$ ) to dissolution ( $Q_a$ ) of the aluminum on a nickel electrode is a criterion for the smoothness of the deposits.

## Effects of Porosity and Slag Former Amount on Rate of Heating-up Reduction of Self-fluxed Pellet.

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### Abstract

Six kinds of self-fluxed pellets were used in heating-up reduction experiments. It was found that the reducibility of pellet increased with the increase of porosity, increase of CaO/SiO<sub>2</sub>, and decrease of slag former amount. Starting temperature of slag flowing-out decreased with increase of slag former amount and sintering temperature and increased with the increase of porosity. If the original characteristics of pellets (porosity, sintering temperature and slag former amount) are known, then starting temperature of slag flowing-out can be calculated under certain experimental conditions. It was also found that the shrinkage was controlled by the reduction rate at high temperature over 1000°C.