DEVELOPMENT OF NEW CARBONS BY ALLOYING WITH FOREIGN ELEMENTS

KAZUO KOBAYASHI
Department of Materials Science and Engineering
Faculty of Engineering, Nagasaki University
1-14, Bunkyo-machi, Nagasaki, 852 Japan

1. Old and new material "carbon"

Carbon materials have been used through human history. The first carbon materials were charcoal, soot etc. and those were used as fuel, painting and medicinal. After that various carbon materials were developed for industrial uses such as metallurgical coke, carbon black, activate carbon, electrodes, bearing and refractories, and they have contributed for progress of industrial technologies. In recent years high pressure synthetic diamond, glass-like carbon, carbon fiber and C/C composite were developed. The latest innovations on carbons are thought to be diamond film and C_{60}, fullerene etc. Those carbon materials are expected to be future materials toward 21 century.

2. What are the characteristics of carbon materials ?

Carbon material is situated at the position of the center among metal, ceramics and polymer. Carbon materials have properties of electric conductivity, thermal conductivity and variety in shape which are characteristics of metals. They have also high temperature strength and corrosion resistance which are popular properties of ceramics. They have also light weight and variety in shape which are fundamental properties of polymers. Among those properties high temperature specific strength and thermal shock resistance of carbons are the most prominent properties as a future high temperature structural materials. This is one of the main reasons that development of C/C composites is carrying on for the use as parts of space plane and air craft. On the other hand, carbon materials have a weak point for oxidation resistance. To improve the oxidation resistance is one of the major subjects for development of carbon materials for structural uses.

3. Creation of new carbons by concept of "carbon alloy"

"Carbon Alloys Research Group" started 2 years ago in the Carbon Society of Japan. Main purpose of the group is to carry on the researches and discuss on new functions which are given to carbon materials by alloying. Term of "Carbon Alloy" is defined as the material consisted of multi-components of the assembly of carbon atoms as a main component and the guest component, and physical and chemical interactions exist among the components. We also defined that carbons with different hybrid orbitals are regarded as different components.

Systematic researches on controlling of combination of chemical bondings, fundamental structure and microstructure of carbons, and doping of foreign elements into carbons are main subjects in carbon alloys.

4. Introduction of the researches on carbon alloys at Nagasaki University

4-1. Graphitization and sintering of carbons by boron doping

Addition of foreign elements is known to give an influence on graphitization behavior. Among them, boron atoms from addition of boron oxide or borides start to diffuse substitutionally into carbon structure above about 2000°C and accelerate graphitization. At the same time sintering and densification proceed under a pressure , and dense and strong boron-doped graphite block can be fabricated. Different graphitization behaviors are observed with different type of carbons and different additives.

4-2. Carbon/ceramics composites for improvement of oxidation resistance

Carbon/ceramic composites can be fabricated by pressureless sintering method from long-time ground coke powder mixed with non-oxide ceramic powders and also from calcined coke powder with boron compound under pressure. The characteristics of the composites are inherited from both carbon and ceramics. The most significant improvement is oxidation resistance. Oxidation behavior of carbon/B_4C/SiC composite showed that borosilicate layer formed on the surface under dry air condition and the oxide surface layer protected further oxidation. However, under wet condition B_2O_3 formed from B_4C reacted with H_2O to form HBO_2 or H_3BO_3 and dense uniform borosilicate protective layer could not form particularly at temperature range from 900°C to 1000°C because of high vapor pressure of boric acids.

4-3. Carbon fiber and C/C composite by alloying with boron or rare earth elements

After deposition of boron or some rare earth elements on the surface of carbon fiber or C/C composite, alloying of those elements was carried out by heat treatment above 2000° C. Oxidation resistance of various carbon fibers and C/C composites doped with boron or lanthanum improved 50° ~ 150° C higher in oxidation temperature than those of non-doped samples. However, degradation in strength was observed for the boron-doped carbon fibers. One of the future problems is to prevent the degradation in strength. The mechanism of improvement of oxidation resistance is not clear yet, but we consider some of the following mechanisms works on oxidation process in the case of boron doping, that is, 1) graphitization is accelerated by boron doping and high graphitizability prevent oxidation, 2) surface protective oxide layer formed and prevent oxidation, 3) active graphite edge sites are covered, and 4) electronic property is changed by substitutional solid solution.

4-4. Highly orientated graphite block from polyimide film by alloying with boron or rare earth elements

Polyimide block is known as a non-graphitizing carbon. However, a thin film of polyimide gives a carbon film with highly graphitized and orientated structure. Doping of boron or lanthanum accelerates graphitization of the film. With the aid of diffusion of those elements joining of multi-layered films proceeds under hot-pressing and highly orientated graphite block is obtained. The graphite block is expected to be used as a monochrometer.

4-5. Graphite microsphere from PF-resin carbon beads by alloying with rare earth elements

Spherical phenolformaldehyde(PF) resin beads with average diameter of 15μm transform to glassy carbon microsphere by heat treatment above 900 ° C. However, rare earth oxide such as Sm_2O_3 is added to the glassy carbon microsphere, it transforms completely to graphite microsphere by heat treatment above 2000° C. Growth of several graphite crystals was observed inside of the sphere without regular orientation. Graphite blocks with isotropic properties are expected to fabricate by sintering of those graphite microspheres.

4-6. Graphite/B_4C hybrid microsphere grown by heat treatment from mixture of carbon black and B_4C

Microsphere with 5~50 μm in size is obtained by heat treatment above 2400°C from mixture of carbon black and B_4C powder. Outer part of the spherical microsphere consisted of well orientated graphite layers and the inner part is occupied with mixture of graphite and B_4C. The spherical hybrid microsphere of graphite and B_4C is considered to be formed by resolution - precipitation process.

5. Approach to carbon alloys

Figure 1 illustrates the ways to develop carbon alloys. It is expected that new carbons with improved or new functions will be created by this idea through the efforts of cooperative research works.

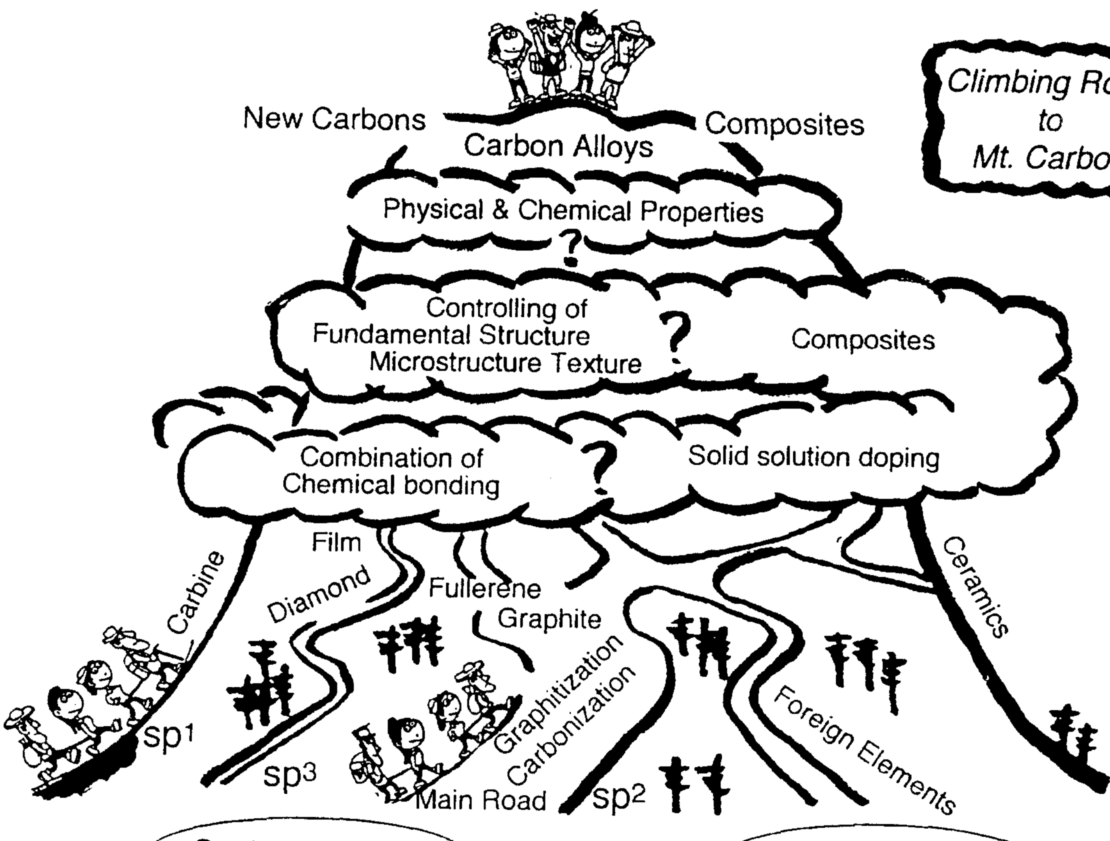

Fig. 1. Ways to climb new Mt Carbon

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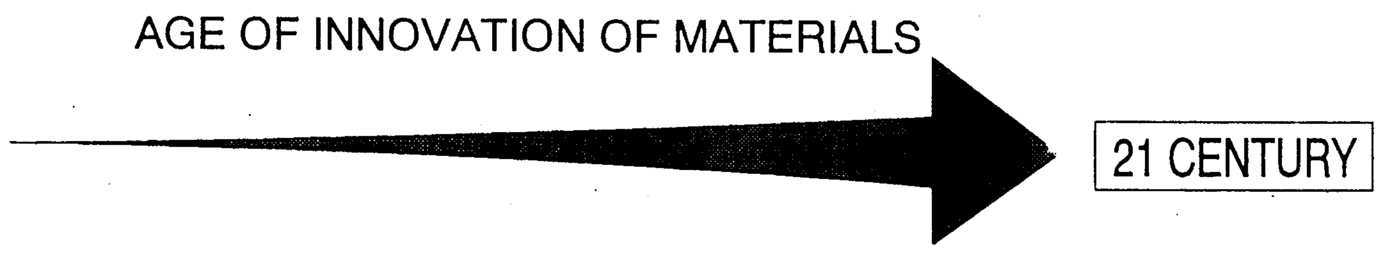
DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
FACULTY OF ENGINEERING
NAGASAKI UNIVERSITY

OLD AND NEW MATERIAL "CARBON"



- CHARCOAL
- SOOT, INK STICK
- COAL
- COKES
- PITCH, TAR
- CARBON, BLACK,
- ACTIVATED CARBON,
- ELECTRODE,
- BRUSH, BEARING,
- PENCIL,
- MECHANICAL SEAL,
- SYNTHETIC DIAMOND,
- PYROLYTIC CARBON, HOPG,
- GLASSY CARBON
- CARBON FILM
- HIGH DENSITY ISOTROPIC CARBON,
- GRAPHITE INTERCALATION COMPOSITES
- CARBON FIBER
- CFRP
- CFRM
- C/C COMPOSITE
- CARBON CERAMIC COMPOSITE
- CVD DIAMOND FILMS
- C_{60}, FULLERENE.

VARIETY OF STRUCTURES, MORPHOLOGIES, FUNCTIONS

Definition of "Carbon Alloy"

The <u>multi-components</u> materials consisted of <u>assembly of carbon atoms</u> as a main component and <u>guest component</u>, and <u>physical and chemical interactions</u> exist among their components.

Carbons with <u>different hybrid orbitals</u> are regarded as different components.

Carbon materials

1) consisted of different carbon components with different hybrid orbitals.

2) consisted of controlled space and textute.

3) doped with foreign atoms or compounds

<u>to improve or to create high functions.</u>

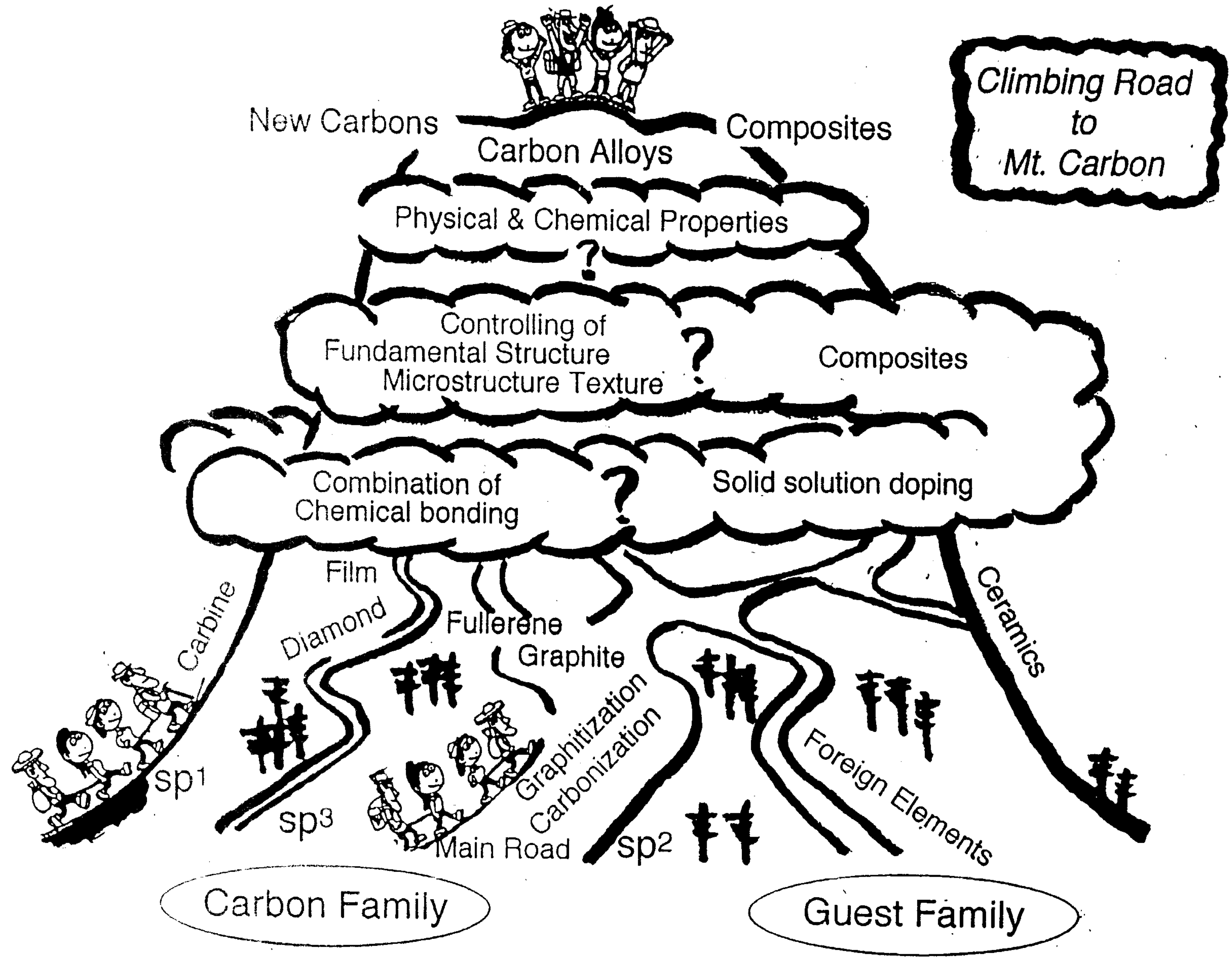


図. カーボンアロイの概念による新機能性炭素系材料の研究開発

IMPROVEMENT OF OXIDATION RESISTANCE OF CF AND C/C BY ALLOYING WITH BORON AND RARE EARTH ELEMENTS

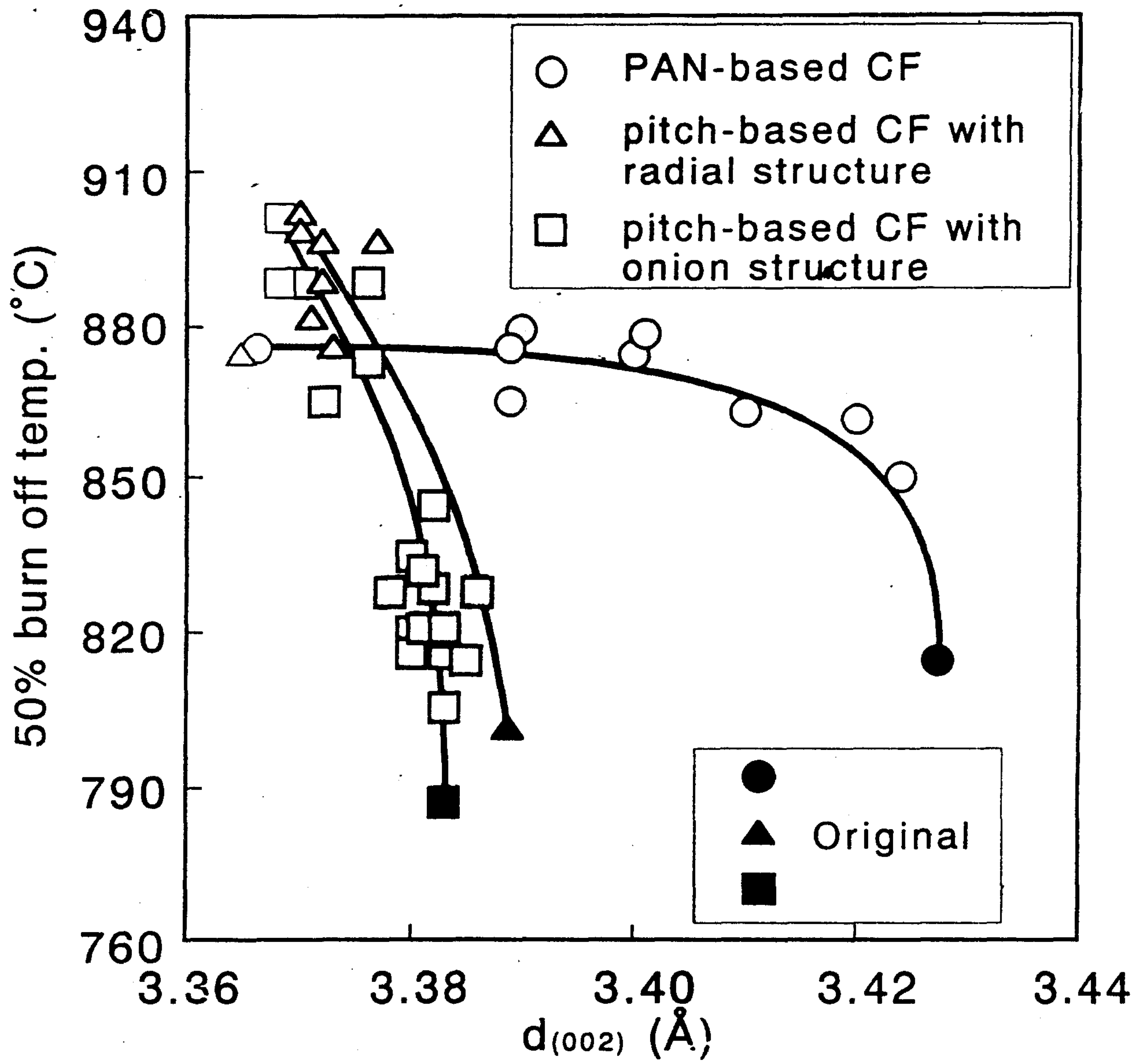
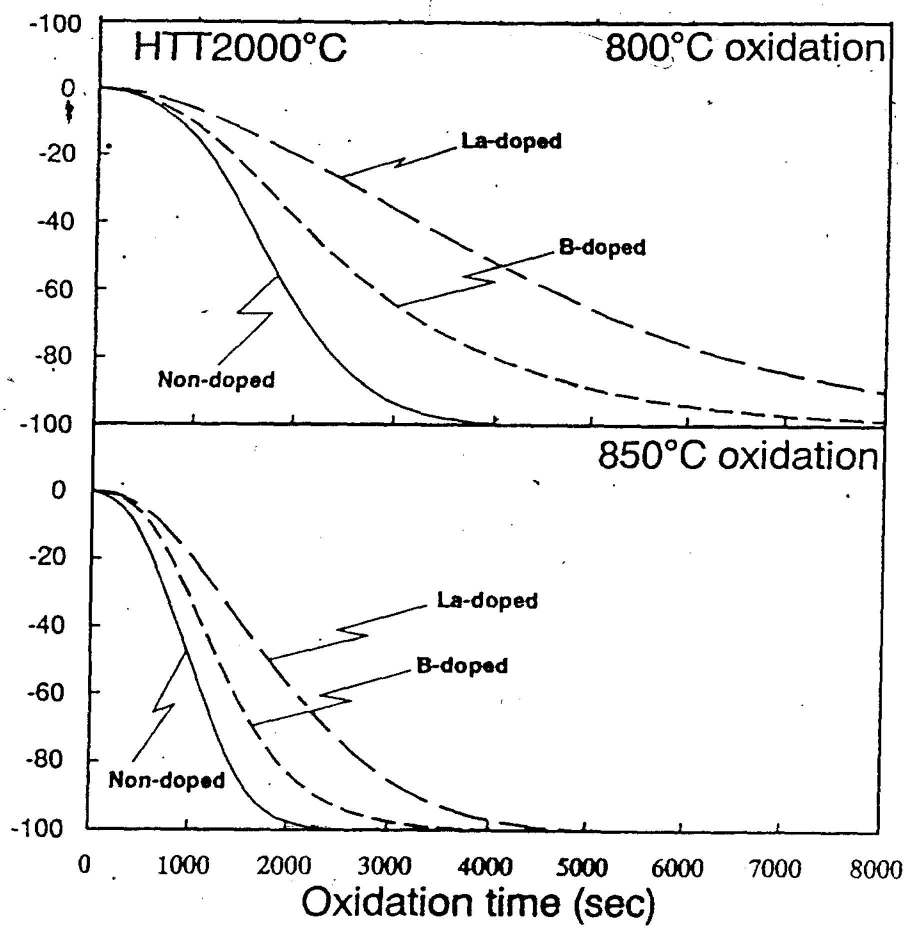
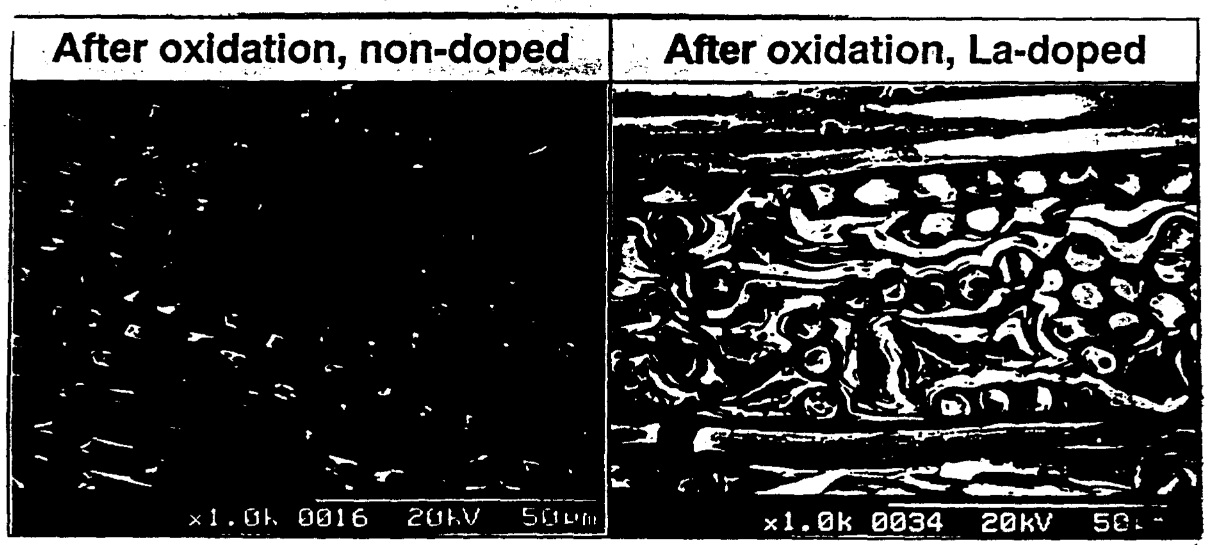


Fig. Relation betw)en 50% burn–off temperature and d(002) spacing of boron–doped an·! original carbon fibers with defferent type (HTT 2500°C)

C／C複合材の耐酸化性とホウ素、ランタンのドーピングの影響



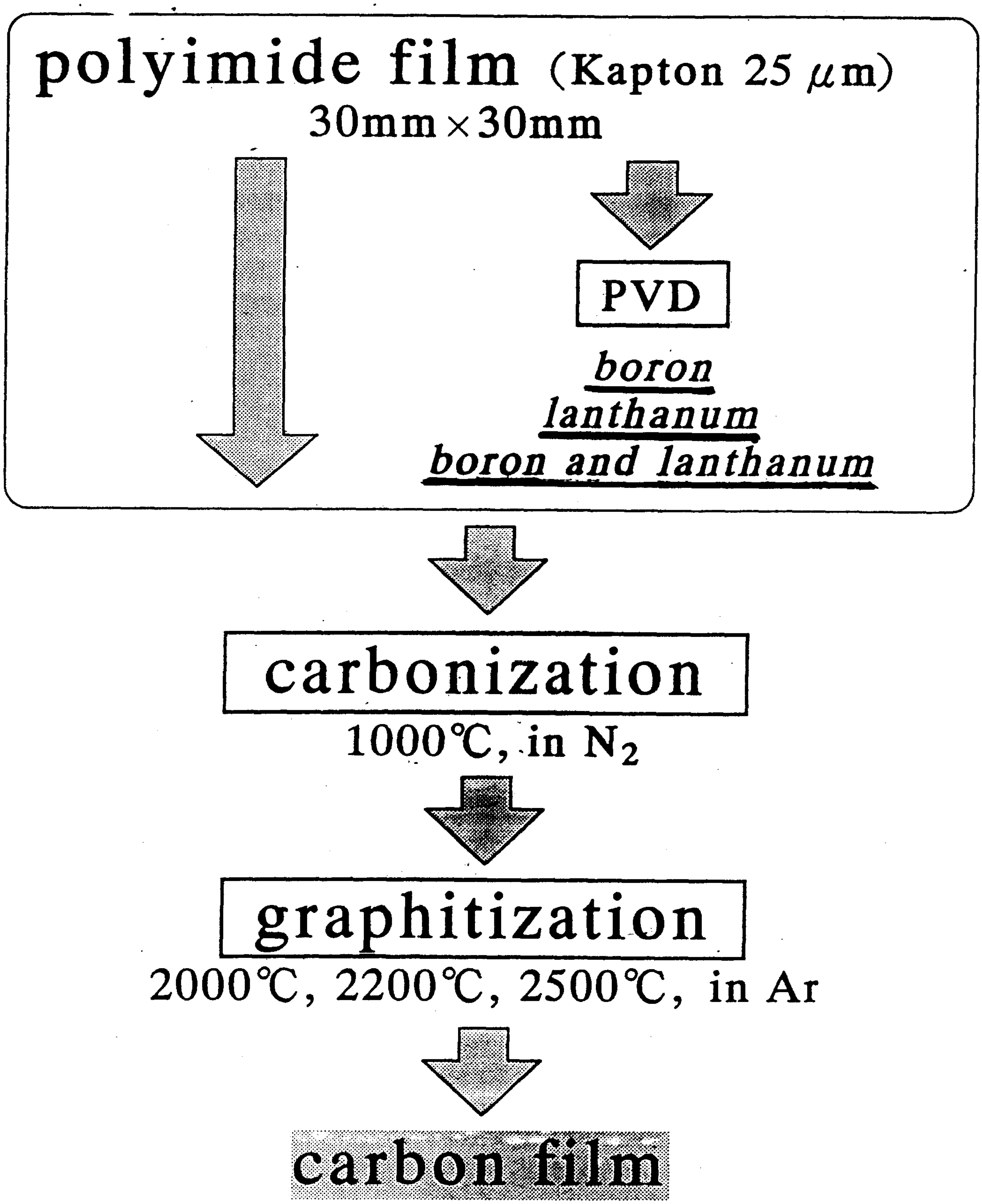
Weight change of doped C/C composites (HTT2000°C) with oxidation time



SEM photographs of the C/C composites(HTT2000°C) before and after oxidation at 830°C.

HIGHLY ORIENTATED GRAPHITE BLOCK FROM POLYIMIDE FILM BY ALLOYING WITH BORON OR RARE EARTH ELEMENTS

Experimental procedure



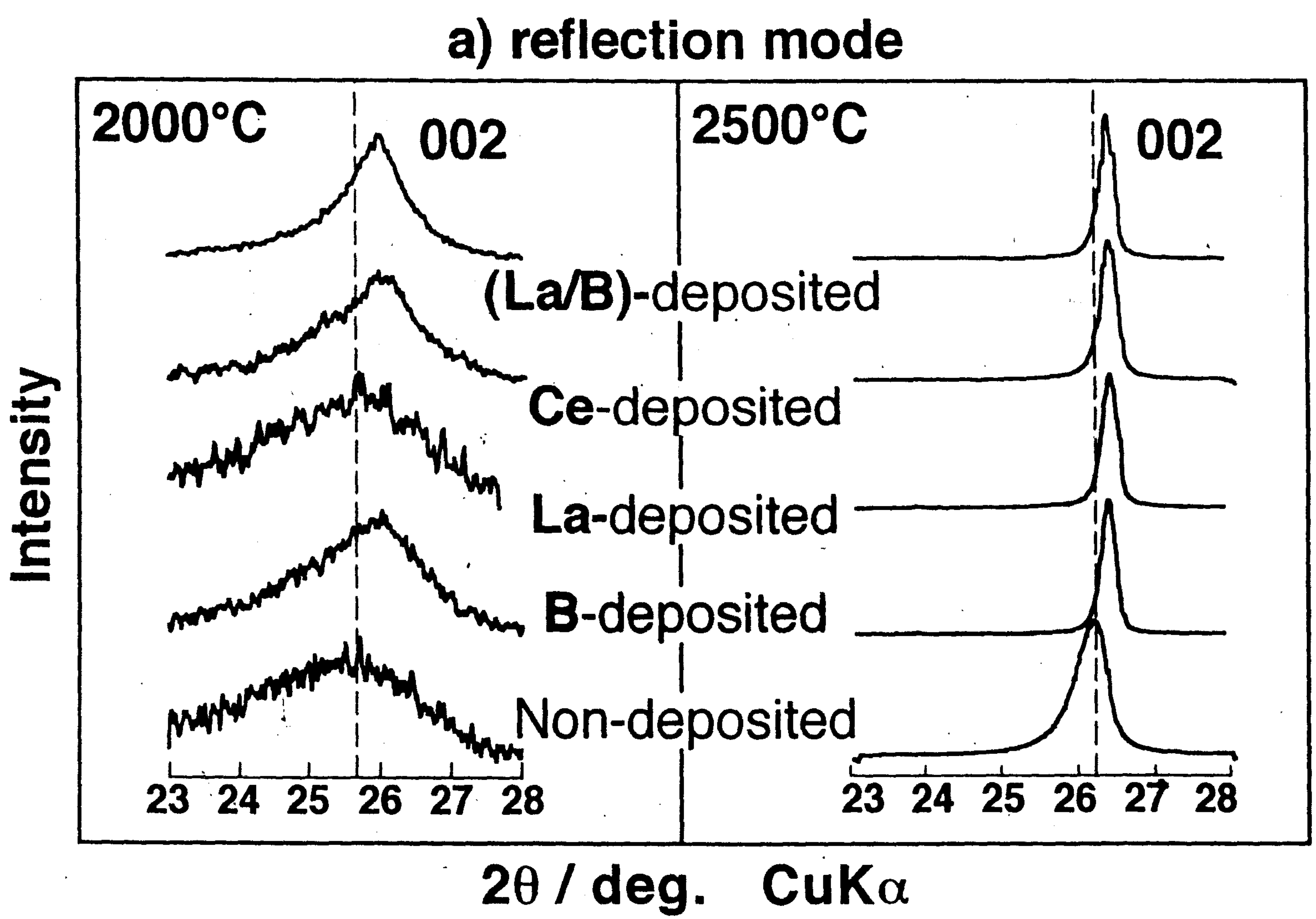


Fig. X-ray diffraction patterens of polyimide carbon powders after heat-treatment at 2000°C and 2500°C

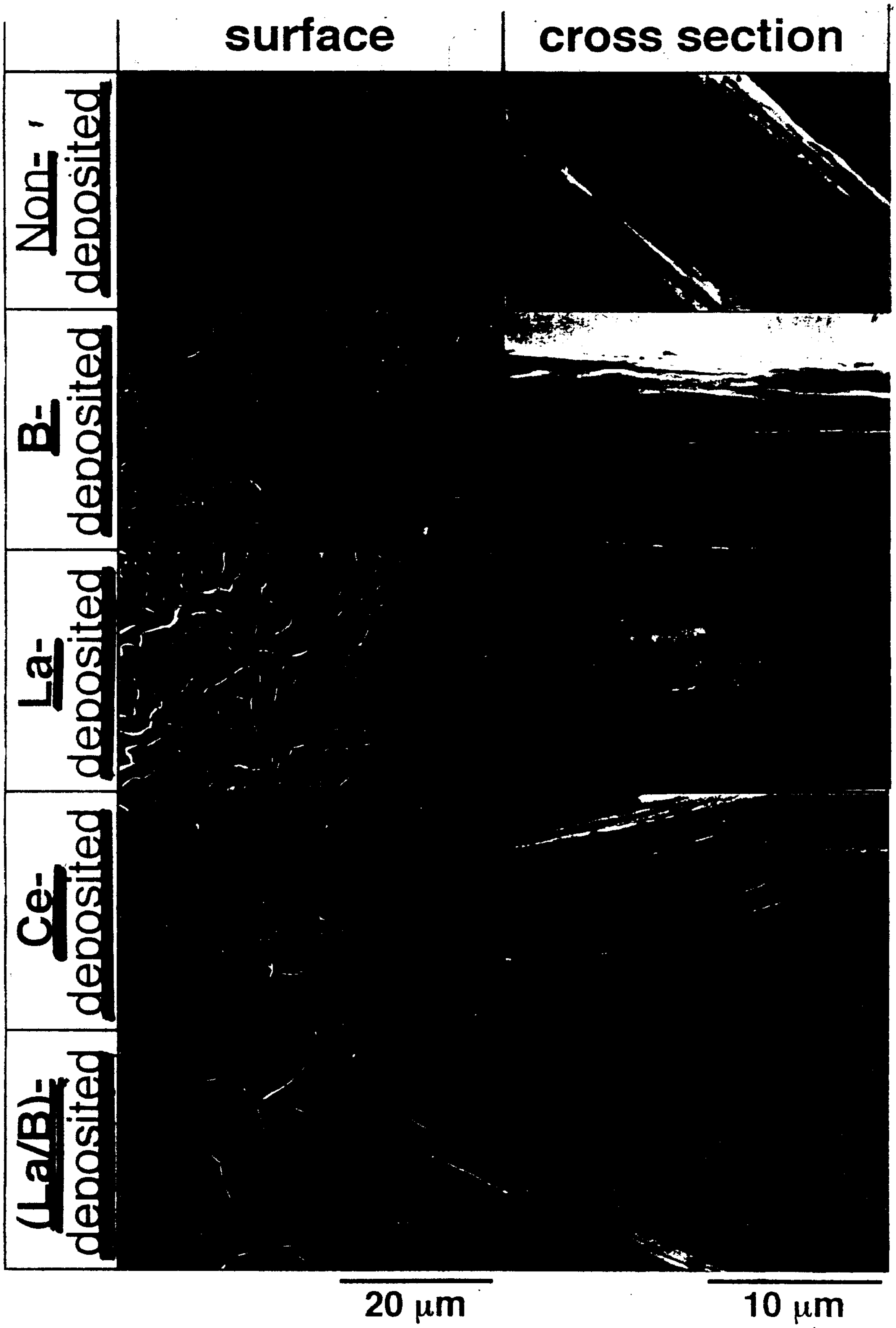


Fig. SEM photographs of the film suface and cross section of polyimide carbon films after graphitization at 2500°C

GRAPHITE MICROSPHERE
FROM PF-RESIN CARBONS BEADS
BY ALLOYING
WITH RARE EARTH ELEMENTS

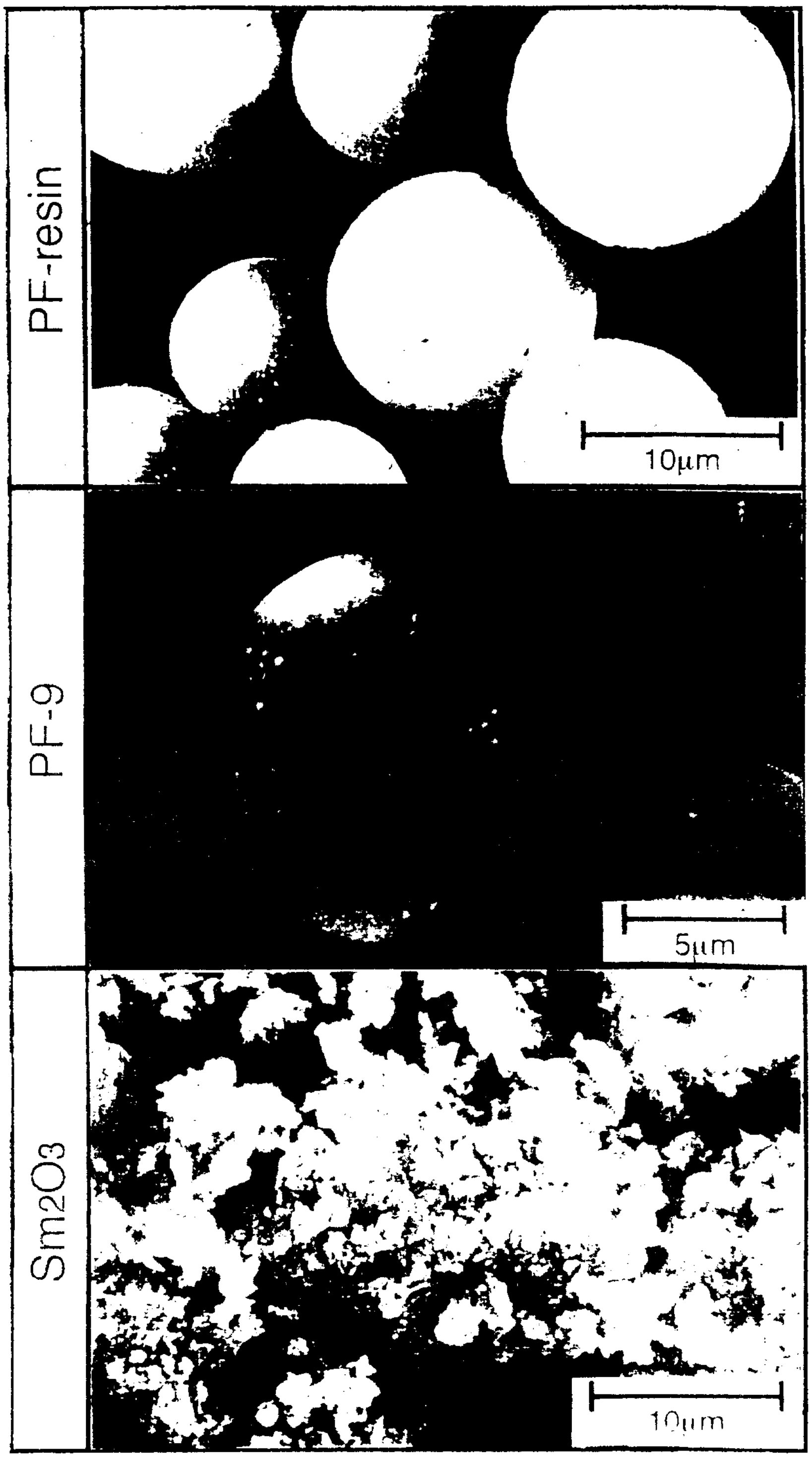


Fig. SEM micrographs of PF-resin,PF-9 and Sm_2O_3

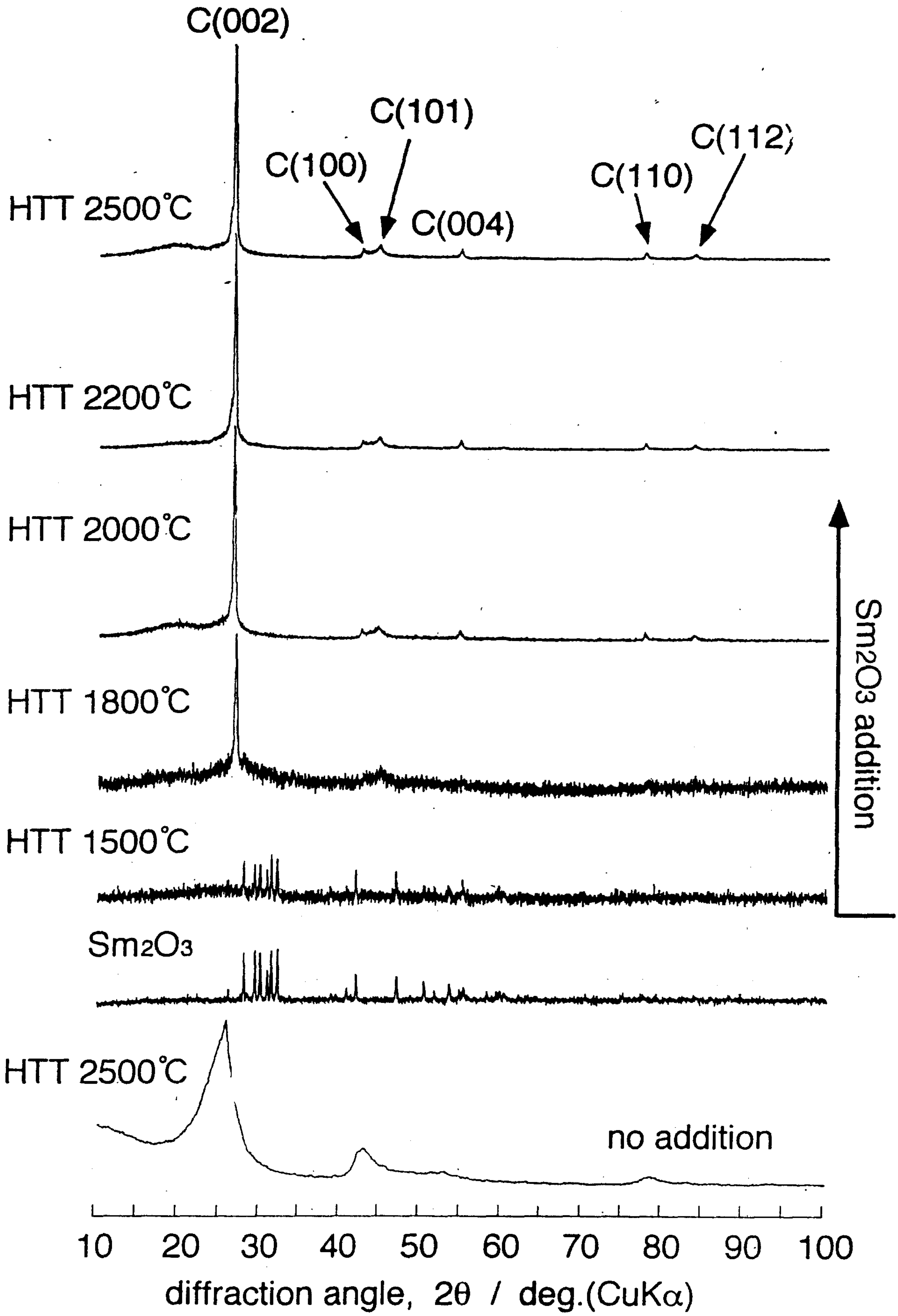


Fig. Effect of heat treatment temperature on Xray diffraction profile.

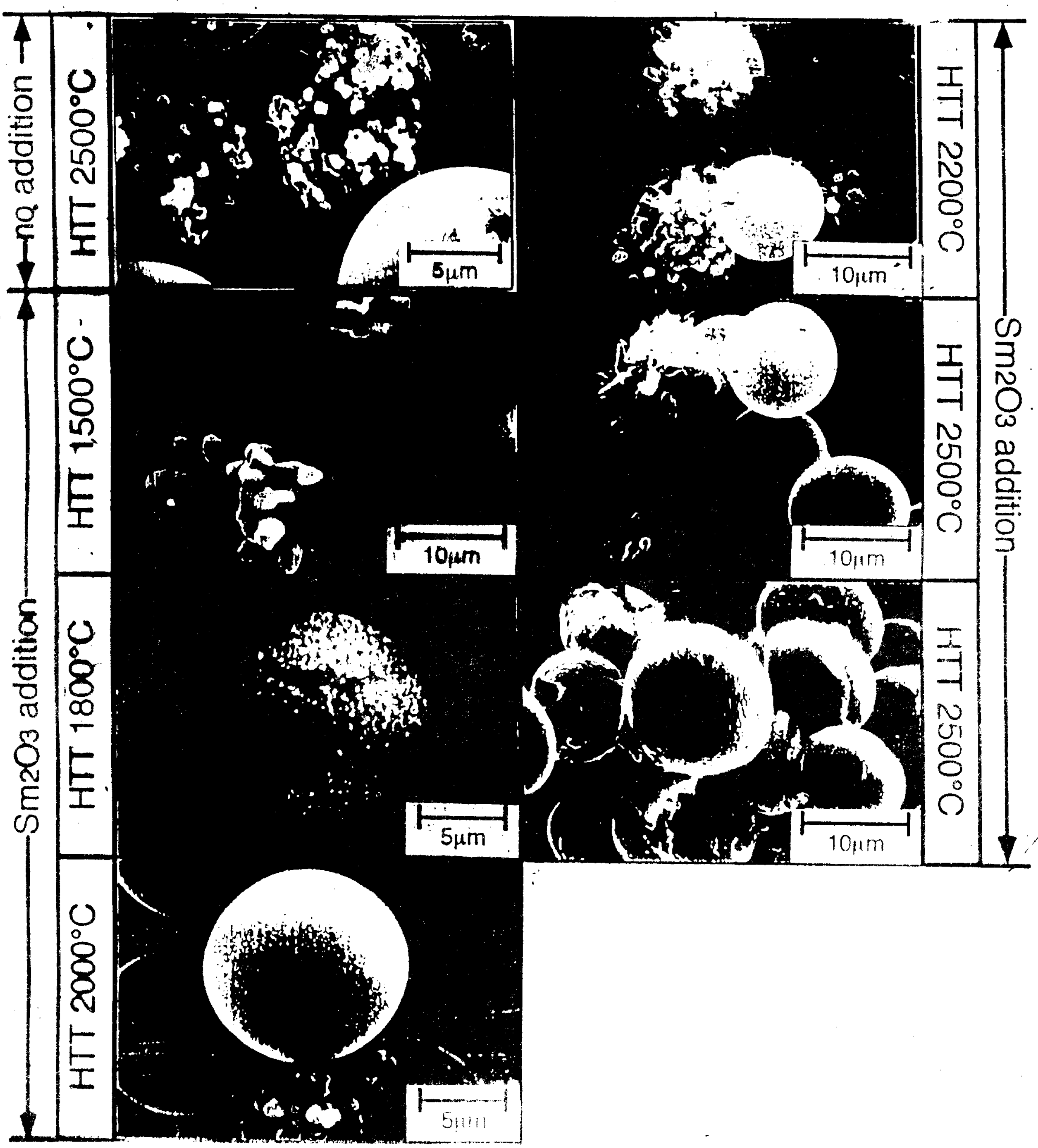


Fig. SEM micrographs of heat treated PF-9 with and without Sm_2O_3

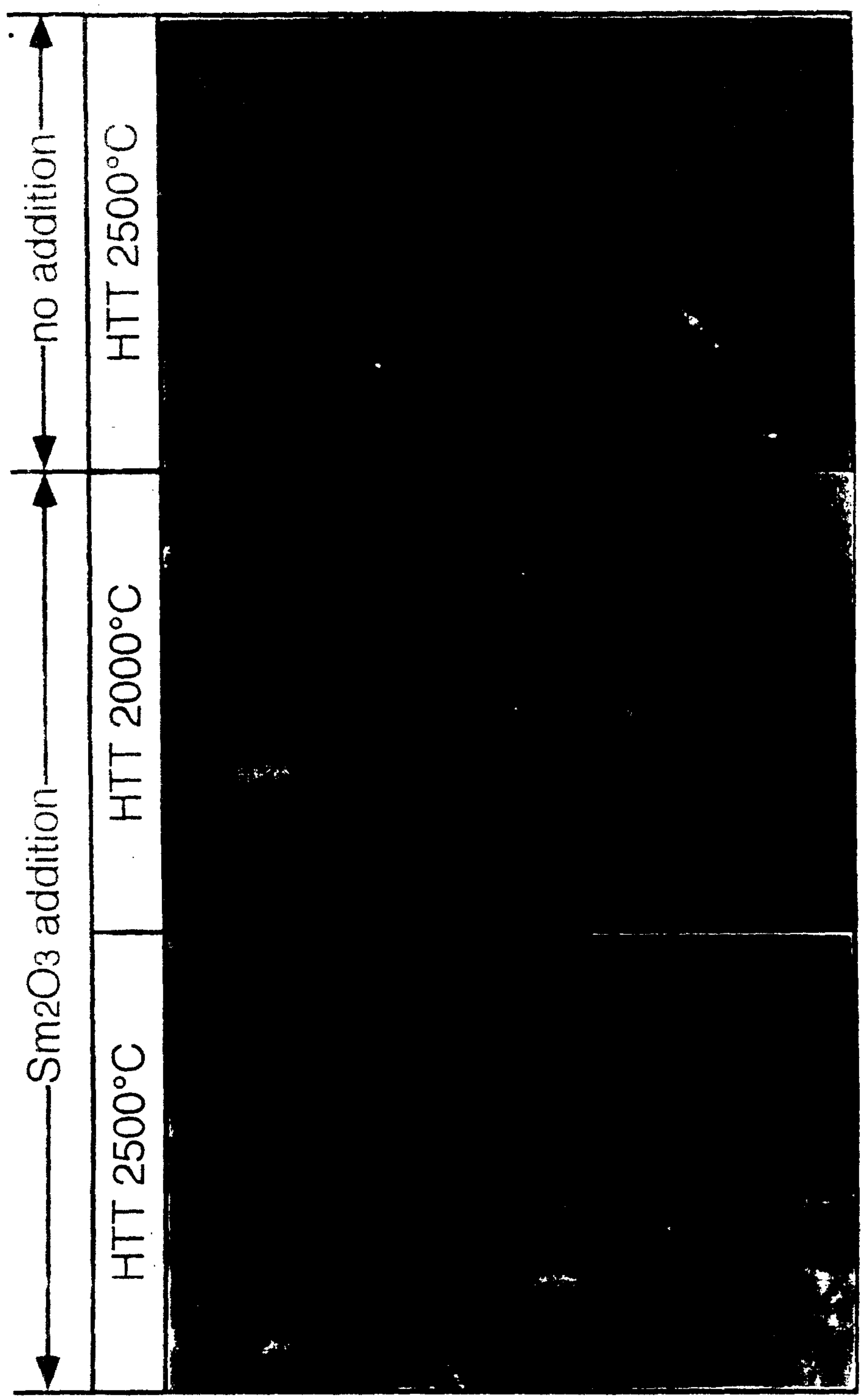


Fig. Polarizing microscope photograph of heat treated PF-9 cross section with and without Sm_2O_3.

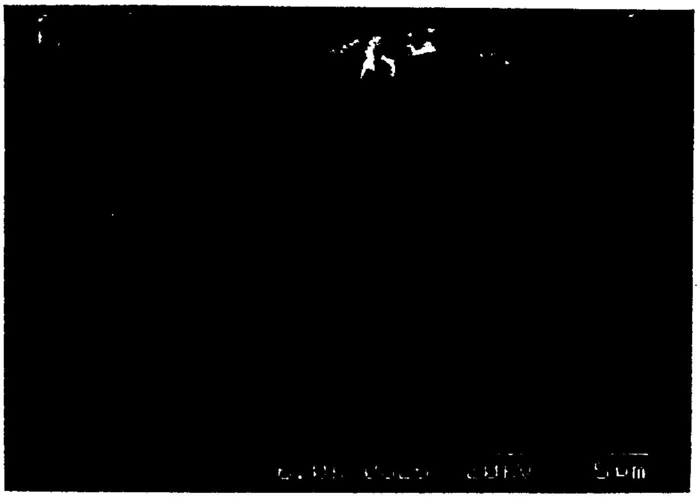


図　PF-9にCeを10wt%添加した試料を2500℃熱処理した炭素試料粉末のSEM写真