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Development of ceramics, especially silicon carbide fibres, from organosilicon polymers by heat treatment

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[Plate 1]

From various new organosilicon polymers many useful ceramics are obtained by heat treatments. The new polymers that have been made in my Laboratory are called Mark I, II and III. High strength SiC fibre, SiC sintered bodies, refractory alloys, and refractory polymers have been obtained from those polymers.

In the process of converting organometallic polymers into SiC ceramics by heat treatment, an apparently amorphous state appears which has a parallel in the preparation of glassy carbon made by the pyrolysis of cross linked resins such as phenol-formaldehyde. This glassy state of SiC has many interesting features in the fields of physics and chemistry.

1. INTRODUCTION

The technique of making carbon by pyrolysis of organic material has existed from primitive ages. Science and technology today have been successful in producing high strength, high modulus of elasticity carbon fibres from such organic fibres as polyacrylonitrile or rayon by improving on the primitive carbonizing technique using synthetic fibres and applying tension during part of the pyrolysis process. Then, in order to obtain a ceramic composed of a metallic element and a non-metallic element, the pyrolysis of an organometallic polymer comes to mind. Human thinking is essentially conservative, and this appears to be a new concept. The step from producing carbon fibres to ceramic fibres by pyrolysis is a leap; it is discontinuity in human thought, leading to much research. Our work on the conversion of organosilicon polymers to silicon carbide was founded on the following postulates. The aim was to produce by simple processes materials with high melting points, high strengths and elastic moduli in forms suitable for modern technological applications.

1. In heat-treating organosilicon polymers under various atmospheres, there always remain ceramic skeletons. It may be appropriate to say that improved ceramics are created.
2. An organosilicon polymer before conversion may be formed into fibre or film and in the pyrolysis the original form is possibly retained. In that case, products of complicated shape can be obtained that are not possible otherwise.
3. In converting an organometallic polymer to a ceramic, the product is composed of ultra-fine particles or amorphous state material.
4. Because the ceramic is composed of such fine particles, a material such as silicon carbide, which normally does not sinter, is liable to cohesion and hence sintering. The mechanism will probably be evaporation and then condensation since the vapour pressure during pyrolysis will be relatively high.

[11]

5. An organosilicon polymer is converted into silicon carbide at a relatively low temperature, where formation by other means does not occur.

6. In the conversion of an organosilicon polymer into silicon carbide there is a stage when the material is amorphous. Mechanical strength in an amorphous state is generally high and chemical resistance for various environments is greater.

7. An organosilicon polymer may be dissolved in a solvent and mixed uniformly with the ceramic particles. The solvent can then be removed, and a green body formed which, on heat treatment, gives the sintered product. The binder as an inorganic is thus evenly distributed in the sintered body, which results in its high mechanical strength.

2. CONTINUOUS SILICON CARBIDE FIBRE PRODUCED BY THERMAL DECOMPOSITION OF ORGANOSILICON POLYMER

The first polycarbosilane made in my Laboratory was from dimethylpolysilane (figure 1). Dimethylpolysilane is heated in an autoclave at about 450 °C for about 8 h, and the polycarbosilane is obtained (Yajima *et al.* 1975, 1976*a, b, c*). The chemical formula of this polymer should be polysilapropylene, and is called Mark I.

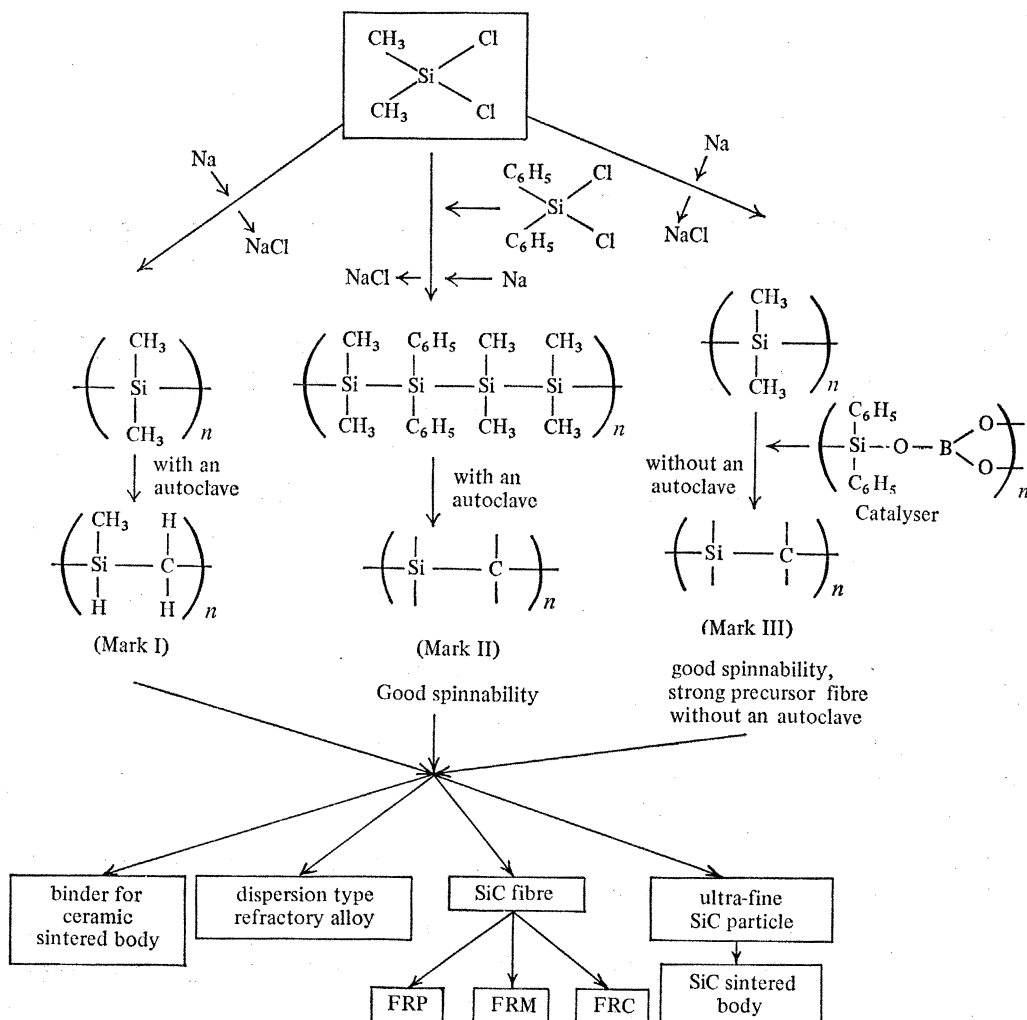


FIGURE 1. Prospect of industrial application of organometallic polymers.

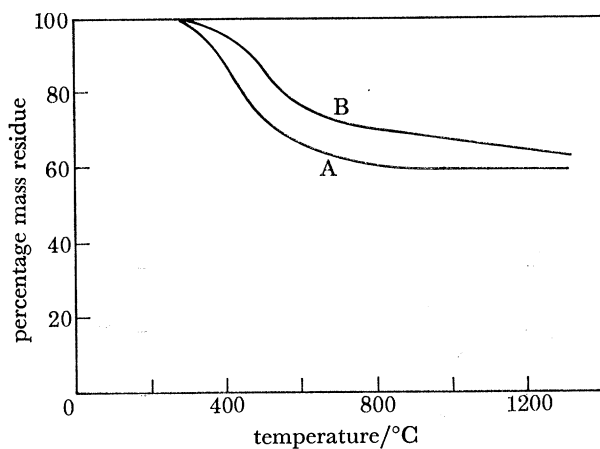


FIGURE 2. Thermogravimetric analysis of Mark I in (A) vacuum and (B) stream of Ar.

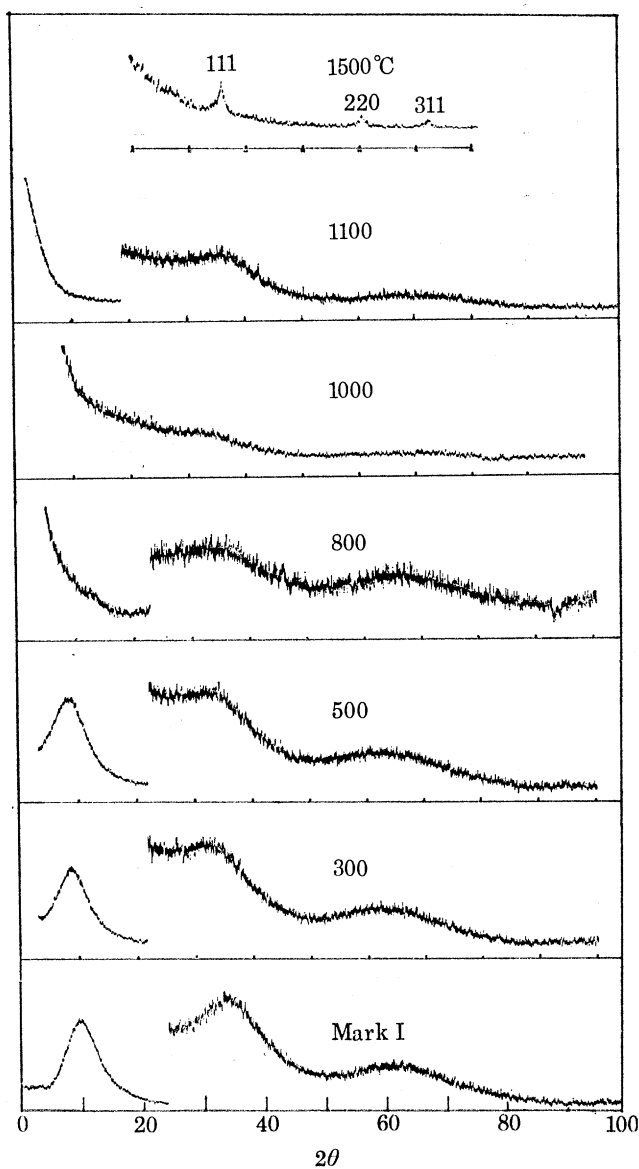


FIGURE 3. X-ray diffraction patterns of Mark I fibres heat-treated at several temperatures.

Mark I can be melt-spun into fibres of tensile strength 9.8 MPa. The fibre is cured by heating in air up to 200 °C or by oxidation with ozone gas at room temperature. The cured precursor fibre is heated to 1300 °C in a vacuum or nitrogen atmosphere and gives a fibre of β -SiC, of average tensile strength 2.94 GPa, and average Young modulus 245 GPa (Yajima *et al.* 1975, 1976*b, c*) (figures 2, 3, and 4).

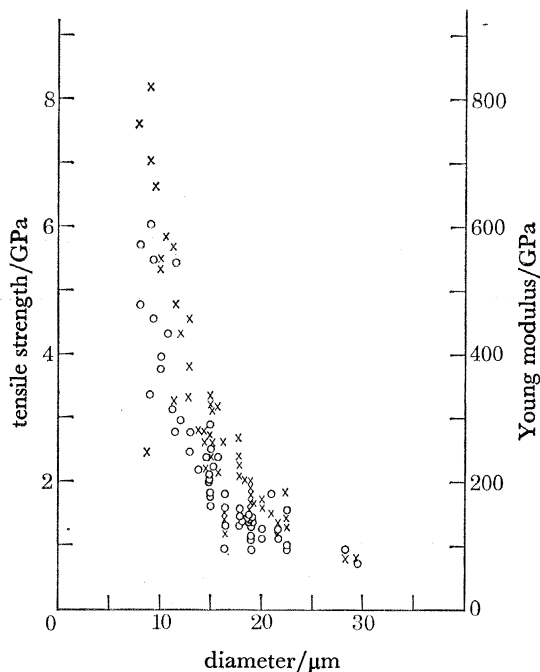


FIGURE 4. Variation of tensile strength and Young modulus with fibre diameter (\times , tensile strength; \circ , Young modulus).

By addition of a small percentage (by mass) of diphenyldichlorosilane to dimethyldichlorosilane as shown in figure 1, we can obtain Mark II polymer. This polymer has better spinnability compared with Mark I, so that precursor fibres of lower diameter can be obtained, which give β -SiC fibres of higher strength and Young modulus, namely 3.43 and 245 GPa, respectively.

In the cases of Mark I and II polymers, an autoclave is necessary for the polycarbosilane preparation. This may be unsuitable for industrial production. Mark III can be made in an open vessel covered with nitrogen gas by addition of a small percentage (by mass) of polyborodiphenylsiloxane to polydimethylsilane (Yajima *et al.* 1978). The structure of Mark III is considerably different from Mark I and II by the examination of DTA in air, but the fibre obtained from Mark III is still β -SiC fibre. The study of Mark III polymer and its final product is continuing.

The SiC fibres from Mark I, II and III contain approximately 20% (by volume) of free carbon. In spite of such a large amount of free carbon, the fibres are not oxidized in air at 1250 °C for long time, as shown in figure 5. This is surprising, and the reason for the high oxidation resistance is considered to be due to the amorphous state of the uniform mixture of β -SiC and carbon.

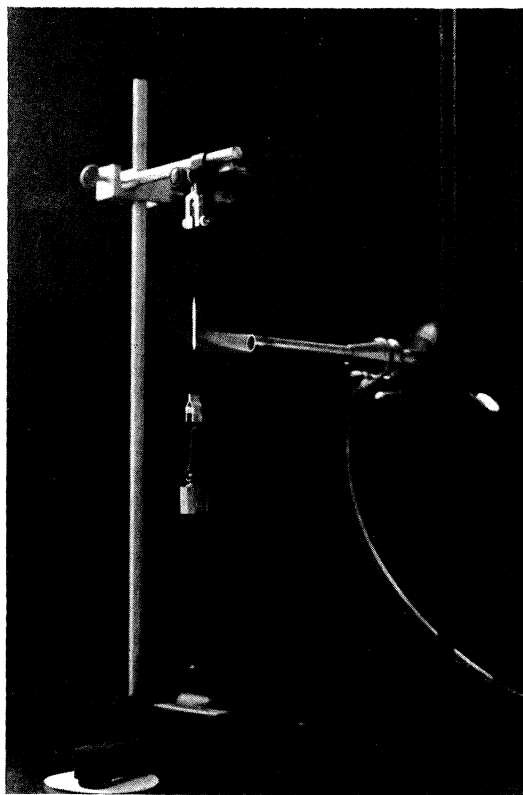


FIGURE 5. Heat-resisting test on SiC fibre for 72 h at 1250 °C in air, tensile load 1.9 GPa.

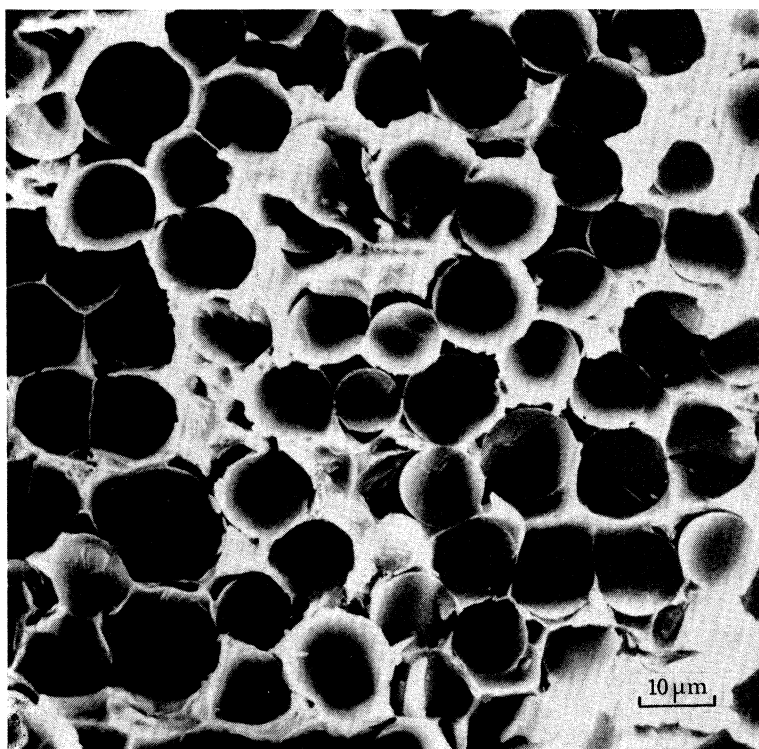


FIGURE 7. Scanning electron micrograph of fracture surface in 50% (by volume) SiC fibre reinforced aluminium composite.

3. FEASIBILITY OF SiC FIBRE FOR FIBRE REINFORCED METALS

Various metallic powders have been mixed with the SiC fibres and sintered at suitable temperatures. By these experiments an understanding of the compatibility of the fibre with the metals has been obtained, as shown in table 1 (Yajima 1977).

TABLE 1. REACTIVITY OF THE SiC FIBRE WITH VARIETY OF METALS AT HIGH TEMPERATURES

metal	melting temperature/°C	temperature/°C for 1 h in H ₂ gas									
		450	530	620	650	750	850	950	1000	1100	1200
Al	660	○	○	○	—	—	—	—	—	—	—
Ag	961	—	—	—	○	○	○	—	—	—	—
Cu	1083	—	—	—	—	○	○	○	—	—	—
Ni	1453	—	—	—	—	—	—	—	○	×	×
Co	1495	—	—	—	—	—	—	—	○	△	×
Fe	1537	—	—	—	—	—	—	—	○	○	○
Ti	1668	—	—	—	—	—	—	—	△	△	△
Cr	1875	—	—	—	—	—	—	—	○	○	△
Mo	2610	—	—	—	—	—	—	—	○	○	○

○, no reaction; △, slight reaction; ×, reaction.

The tensile strength of the composite of Al and SiC fibre increases with increasing percentage (by volume) of SiC fibre as shown in figure 6. The fracture surface of the composite specimen (Al+SiC fibre) is shown in figure 7. There is no pull-out of the SiC fibres at the fracture surfaces showing that there is good adhesion between the Al and SiC fibre. The tensile strength of the silicon carbide fibres shows no variation with temperature (figure 8) and maintain this strength for long periods at high temperatures (figure 5).

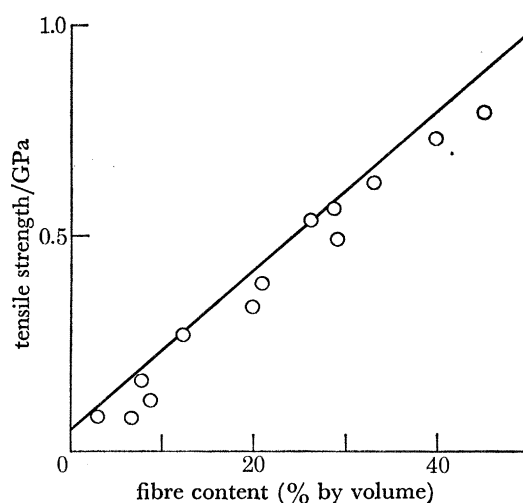


FIGURE 6. Tensile strength plotted against SiC fibre volume fraction for SiC fibre reinforced aluminium composite. The straight line indicates the rule of mixture.

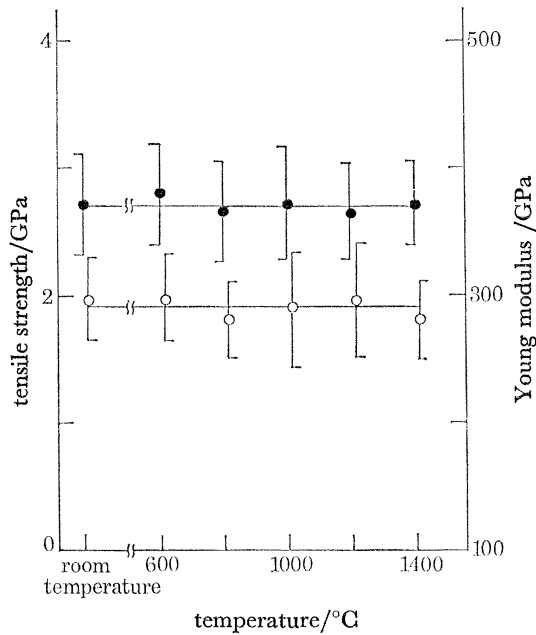


FIGURE 8. Variation of tensile strength and Young modulus with temperature (●, tensile strength; ○, Young modulus).

4. PREPARATION OF SILICON CARBIDE MATERIALS BY SINTERING WITH ORGANOSILICON POLYMERS

Mark I, II and III polymers can be used as binders of α -SiC particles for the sintering of SiC body. The apparent densities of the bodies are low but the mechanical properties are high. Also, those sintered bodies can be impregnated and resintered using molten Mark I, II or III polymer repeatedly giving sintered SiC with mechanical properties increasing with the repeated impregnation and sintering, as shown in figures 9 and 10.

All α -SiC particles in the SiC bodies sintered at 1100–1500 °C are fully covered and strongly bound with the amorphous β -SiC from the thermal decomposition of Mark I, II or III.

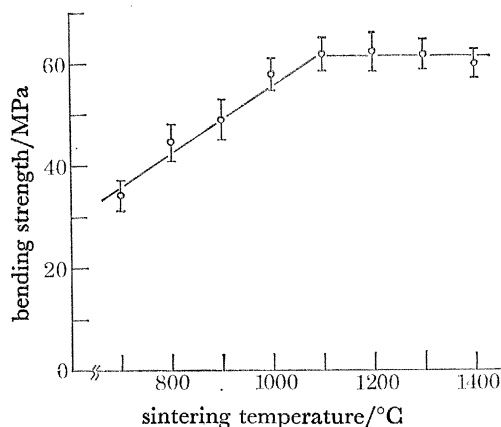


FIGURE 9. Bending strength plotted against sintering temperature in SiC sintered with Mark I.

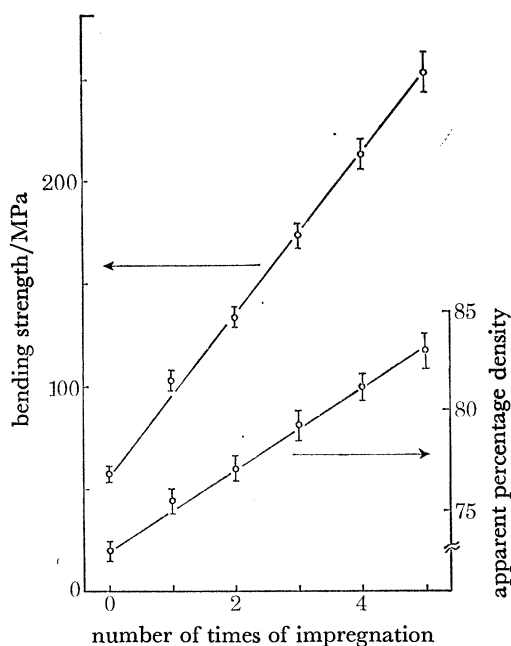


FIGURE 10. Bending strength and apparent density of SiC sintered and reimpregnated with Mark I plotted against repetition of the Mark I impregnation cycle; sintering temperature 1000 °C under flow of N₂, without heating in air.

Those sintered SiC bodies can be used not only for refractory structural materials but can be applied as a refractory supporter for catalysts by the reason of their porosities.

When the polymers Mark I, II and III are heated up to approximately 1700 °C in nitrogen gas, very fine and equiaxial particles can be obtained.

Those ultra-fine β -SiC crystalline powders are sinterable and very strong bodies can be obtained. By hot pressing these powders at 1800–2000 °C, SiC materials of high bending strength (900 MPa) and high density (3.1 g cm⁻³) are obtained.

The Mark I, II or III impregnated SiC bodies have surprising good resistance to attack by molten iron compared to the SiC sintered bodies as shown in figure 11. The reason for this has not been clarified but it is considered that it is due to the amorphous state of β -SiC. The SiC sintered bodies which are developed in my Laboratory can be applied to iron and steel production process.

A powder of Fe-13Cr alloy is mixed with the solution of Mark I in xylene, and after evaporation of the xylene the resulting powder is cold pressed to form a green body (Yajima *et al.* 1978a). The body is heated up to 1000 °C in nitrogen gas. By this treatment, a sintered

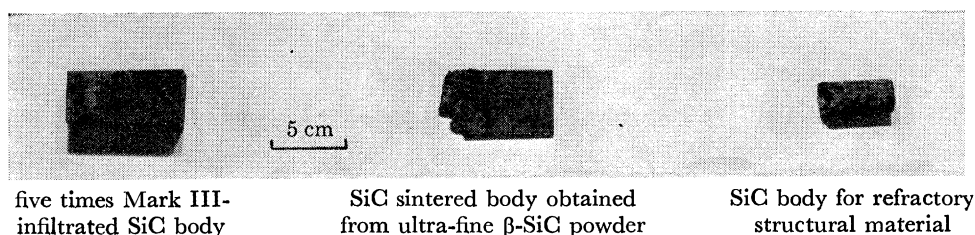


FIGURE 11. Corrosion test of some SiC bodies to molten iron.

material is obtained which has high oxidation resistance and hardness at high temperatures (figure 12). In the matrix of the alloy specimen, fine chromium silicide and chromium carbide are uniformly dispersed. The introduction of organometallic polymers to powder metallurgy is a new field of study at present.

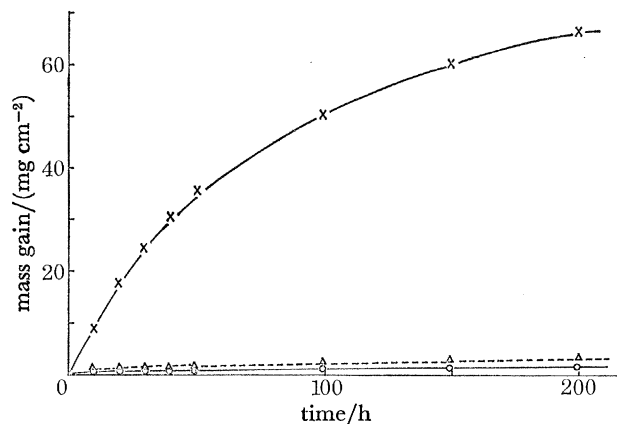


FIGURE 12. The mass gain plotted against the heating time in air at 1000 °C for the Fe-Cr alloy (×), the Fe-Cr (10% (by mass) Mark I alloy (○) and Ni-22Cr reference (Δ).

5. CONCLUSION

The conversion of organometallic polymers into inorganic compounds and useful technological materials is a new field of basic and technological study. There are many interesting phenomena in this field, and the study and the development will be expanded not only for refractory materials but also to materials with interesting magnetic and electronic properties.

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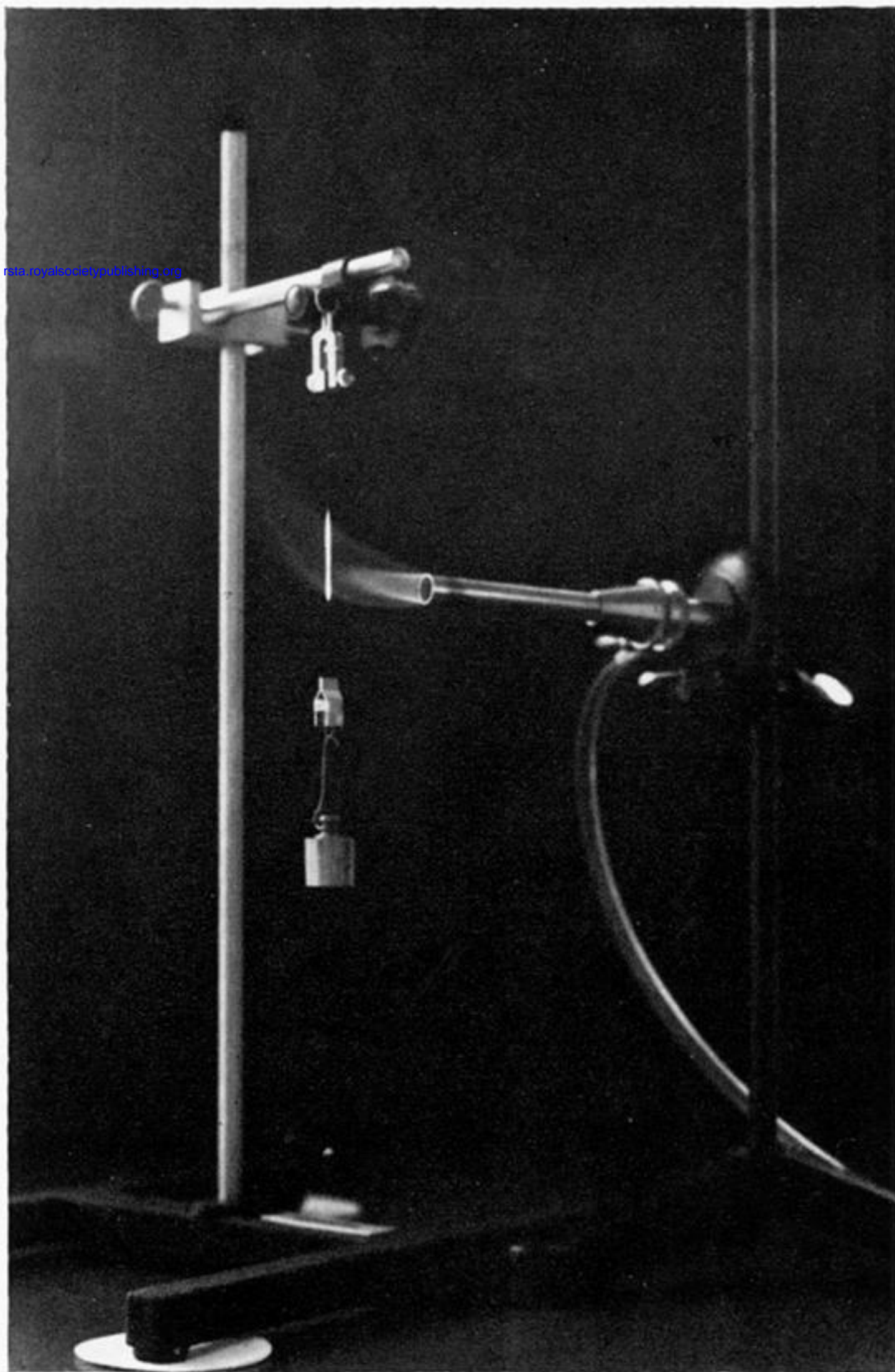


FIGURE 5. Heat-resisting test on SiC fibre for 72 h at 1250 °C in air, tensile load 1.9 GPa.

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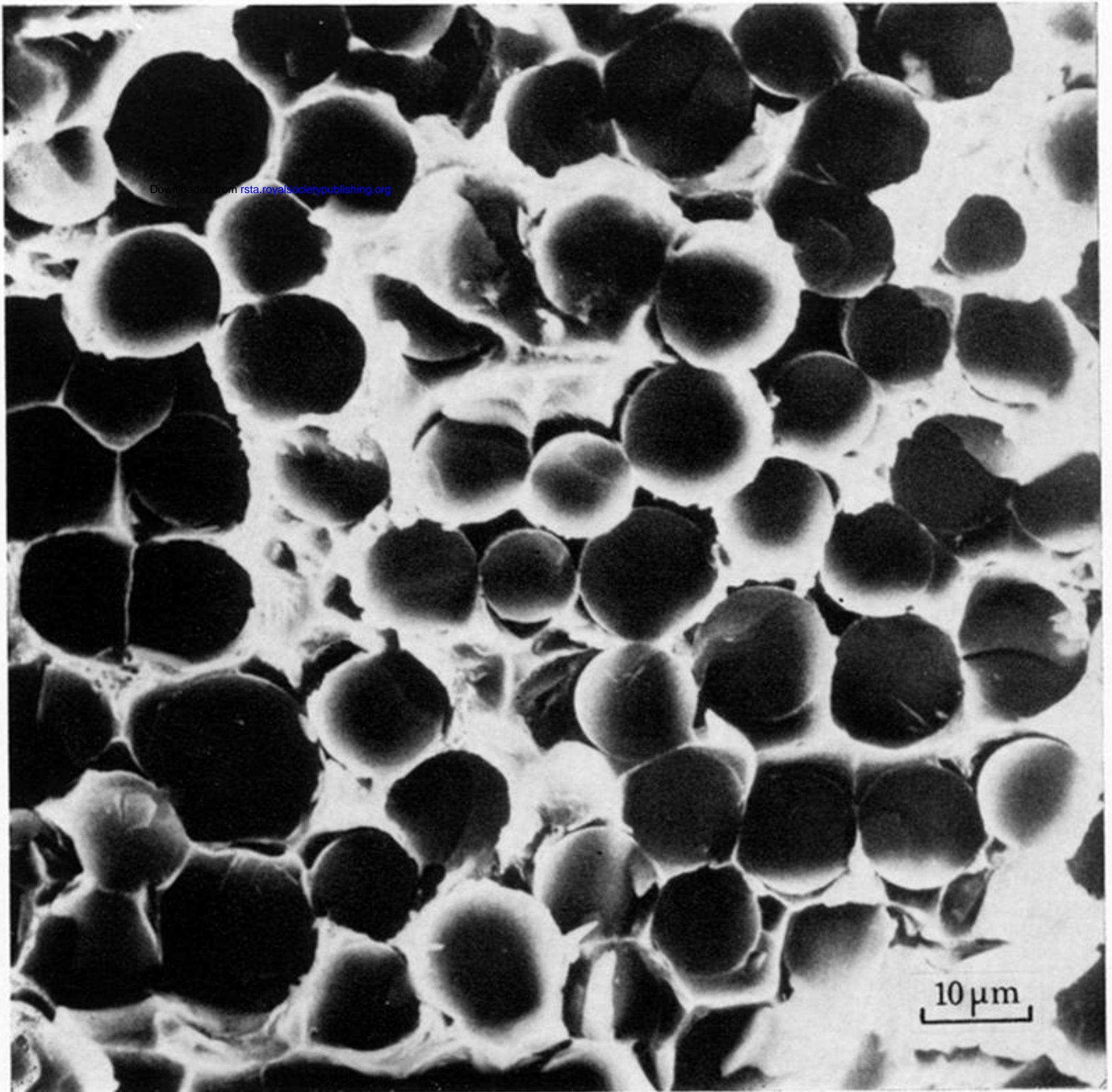
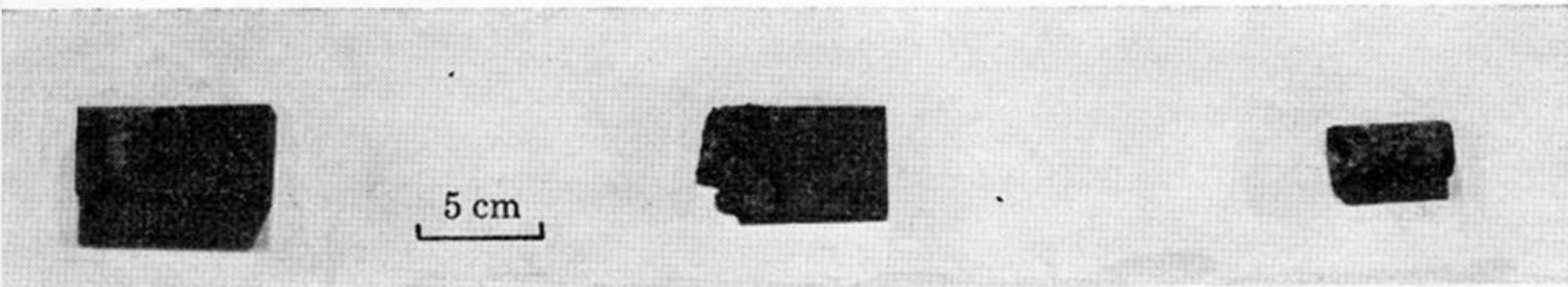


FIGURE 7. Scanning electron micrograph of fracture surface in 50% (by volume) SiC fibre reinforced aluminium composite.



Five times Mark III-
infiltrated SiC body

SiC sintered body obtained
from ultra-fine β -SiC powder

SiC body for refractory
structural material

FIGURE 11. Corrosion test of some SiC bodies to molten iron.