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An organo-metallic polymer used in powder metallurgy: The effect of polycarbosilane in iron-chromium alloy

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A new material was developed by introducing an organo-metallic polymer into powder metallurgy. In the uniform mixture of Fe–13Cr* alloy powder and polycarbosilane (PC) using *n*-hexane, the Fe–13Cr particles were coated with PC. The product of Fe–13Cr + 10 wt % PC, obtained by hot-pressing the mixture, was subjected to an oxidation test, high-temperature hardness measurement and a wear resistance test, and found to be superior in all respects to that without the PC addition. The structure was observed by transmission electron microscope and it was found that grains of $CrSi_2$ and Cr_7C_3 about 0.1 μm in size, dispersed uniformly in the Fe–13Cr + 10% PC, contributed to improvement of the mechanical properties. Observation by scanning electron microscope showed some difference in the formation of the oxidation film between Fe–13Cr and Fe–13Cr +10% PC. This new alloy, while adding an organo-metallic polymer to powder metallurgy, has several outstanding features with the possibility of many applications in the future.

1. Introduction

Research on organo-metallic polymers has advanced greatly over the past ten or so years, to such an extent that the "organo-metal chemistry" is now termed the "third chemistry" as against organic and inorganic chemistry. The present authors worked on the process of converting organosilicon polymer, as an organo-metallic polymer, to silicon carbide, as an inorganic, by heating the former and this led to the synthesis of a continuous SiC fibre [1–3]. The starting material was polycarbosilane (PC), a space polymer [1–3]. Particles of the Fe–13Cr alloy powder are coated with this PC. The powder is then pressure-molded, and heat treated. The organo-metallic polymer is thus thermally decomposed, resulting in reactions between the released elements and the alloy metals. In this way, a heat-resistant Fe–Cr material with a uniform dispersion of fine-grain compounds, having excellent mechanical and thermal properties, can be obtained, which would be impossible by any conventional method. This introduction of an organo-metallic polymer to powder metallurgy is the first such attempt in the world.

2. Materials

Polycarbosiliane was produced using dimethyldichlorosilane as the starting material [1–3]; the number-average molecular weight of the PC used

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*i.e. Fe–13 wt % Cr.

being 1500. The Fe–13Cr alloy powder was produced by a water-spray process; the mean particle size being 3 μm and the wet chemical analysis 12.48% Cr, 0.86% Si, 0.06% Mn, 0.07% Ni, 0.01% C, with the rest Fe.

3. Experimental

Fe–13Cr alloy powder and polycarbosilane were taken in weight ratio 9:1. After mixing well *n*-hexane was added, and the mixture was stirred again. The *n*-hexane evaporated off in dry air. The resulting mass was crushed and the powder was passed through a 100-mesh screen. PC had been dissolved in the *n*-hexane to give viscous substance, so the particles of Fe–Cr alloy powder after sieving were thinly coated with PC. The alloy powder was hot-pressed in a carbon die of 50 mm inner diameter under an argon atmosphere. Heating was by induction using a 20 kW high-frequency oscillator. The temperature of the compressed powder was raised at rate 300° C h^{-1} to 1100° C and kept there for 30 min. The pressure was released, the high-frequency power source was cut off, and the compact was allowed to cool by standing. A flowchart of the process is shown in Fig. 1. The specimen was cut and subjected to structural observation, oxidation resistance and mechanical tests.

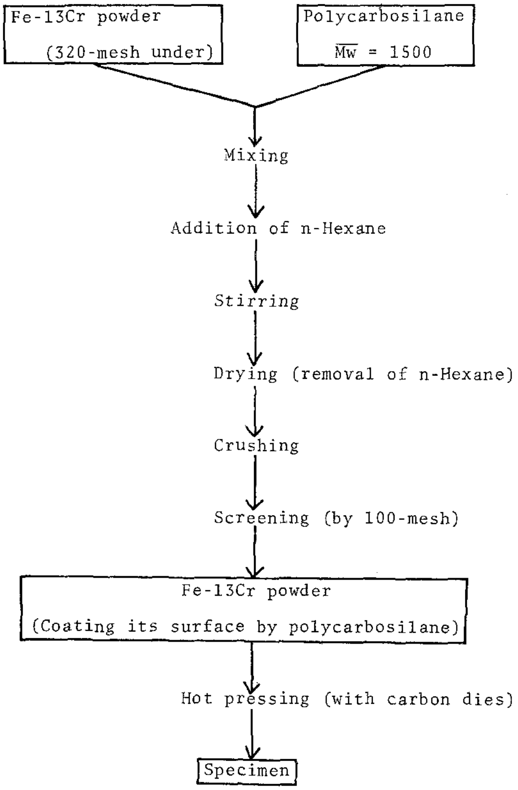

Figure 1 Flowchart for the preparation of specimens.

4. Results and discussion

4.1. Structure

Structure of the sintered Fe–Cr body was observed by transmission electron microscope. The specimen was made into a thin film by jet polishing at 60 V, 3 A with a solution of 1 part perchloric acid to 7 parts ethyl alcohol. The electron microscope used was JEM-200A using an acceleration voltage 200 kV. Micrographs are shown in Figs. 2 and 3; the Fe–13Cr + 10% PC alloy has observable spherical and ellipsoidal in-

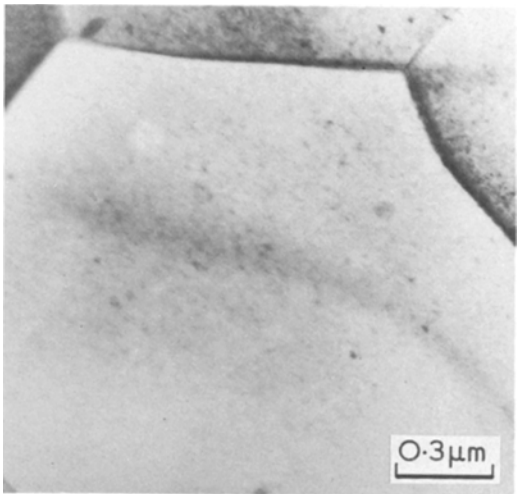

Figure 2 Transmission electron micrograph of Fe–13Cr alloy.

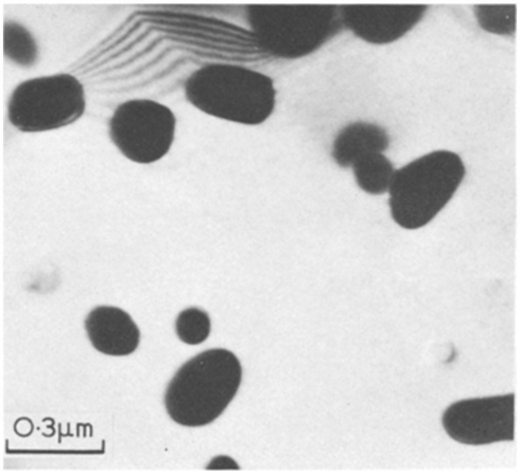

Figure 3 Transmission electron micrograph of Fe–13Cr + 10% PC alloy.

clusions. X-ray and electron diffractions show the spherical compound to be $CrSi_2$ and the ellipsoidal one to be Cr_7C_3. The inclusion diameter distribution is shown in Fig. 4; inclusions of about 1500 ~ 2500 Å are most numerous.

When polycarbosilane is heated up to 1000° C in a gas (argon) atmosphere CH_4 and H_2 are evolved due to thermal decomposition, leaving behind the skeletal SiC; the result is formation of amorphous SiC [1–3]. As already described, in the present experiment, particles of the Fe–Cr alloy powder were uniformly coated with PC. The powder was cold-pressed, and then heated up to 1100° C, so that the amorphous SiC reacted with Fe and Cr in the matrix to produce the silicides and carbides of the respective metals, which were distributed uniformly throughout the alloy. On the other hand, when α- or β-SiC is admixed with commercial Fe–Cr alloy and hot-pressed, the resulting alloy does not have a uniform dispersion of silicide and carbide. The grain sizes of silicides and carbides are larger than those in dispersion-type alloys like Cu–SiO_2, TD–Ni and SAP. It was reported recently that cobalt and nickel alloys and 316 stainless steel having a dispersion of relatively large-grain stable intermetallic compounds (such as CoMoSi and Co_3Mo_2Si) exhibit excellent chemical- and abrasion-resistance characteristics [5, 6]. Grain sizes of the precipitate compounds in the present experiment were relatively large, about 0.1 μm, but oxidation resistance and wear resistance of the Fe–Cr alloy were extremely high. The possible applications of the organo-metallic polymer are significant since no complicated process is required to condition diameters of the dispersion grains, and the grains of the compounds can be dispersed uniformly throughout the alloy at a relatively low temperature.

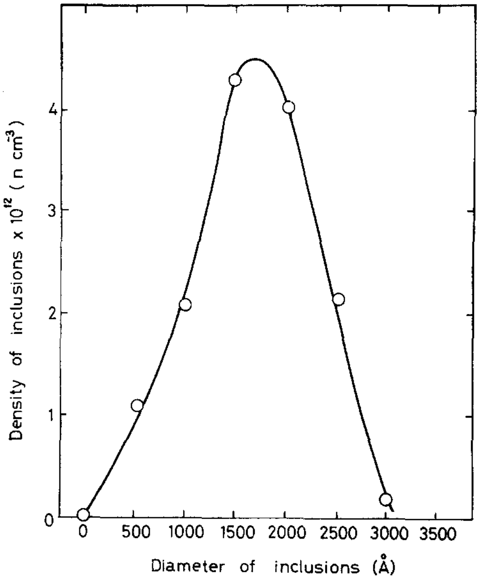

Figure 4 Diameter distribution of the inclusions in Fe–13Cr + 10% PC alloy obtained by transmission electron microscope observation.

4.2. Grain size

Fe–13Cr alloy and Fe–13Cr + 10% PC alloy hot-pressed at 1100° C were heated at 1000° C for

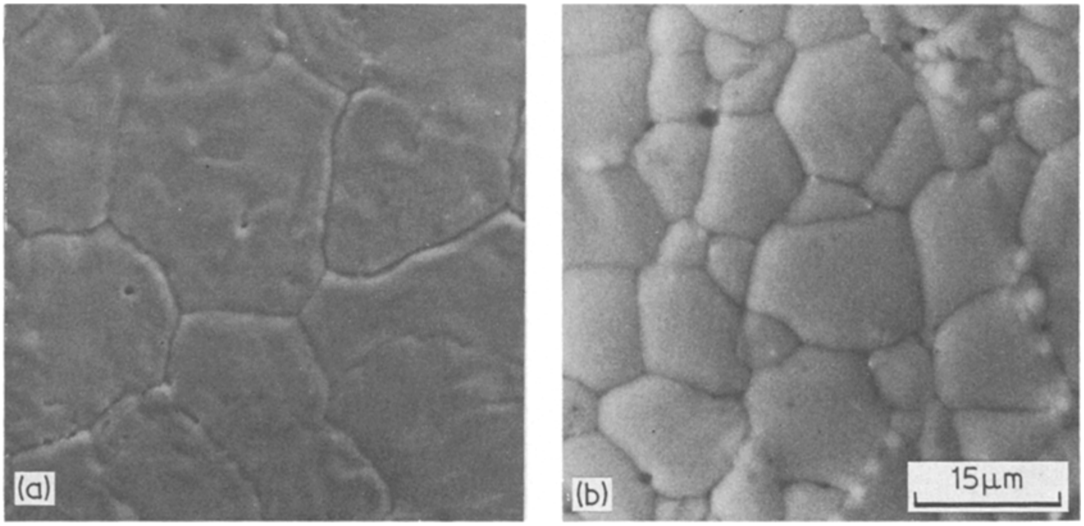

Figure 5 Scanning electron micrographs of surface substrates formed by thermal etching of (a) Fe–13Cr and (b) Fe–13Cr + 10% PC alloys.

50h in a vacuum of 10^{-5} mm Hg. After thermal etching, grain sizes of both the alloys were observed by scanning electron microscope. Fig. 5 shows typical micrographs. Grain sizes in the Fe–13Cr alloy are 25 μm, and in the Fe–13Cr + 10% PC alloy they are very small (9 μm). This is possibly because in the latter, fine grains of $CrSi_2$ and Cr_7C_3 resulting from PC decomposition are dispersed in the alloy matrix, thereby suppressing grain growth of the alloy.

4.3. Oxidation test

4.3.1. Weight gain

Specimens of size 5 mm x 5 mm x 10 mm, buff-polished, were kept in air at 1000° C for specific periods of time, and weight gains due to the oxidation were measured with a Mettler balance. The results are shown in Fig. 6. As seen in the figure, the weight gain increases in a parabolic manner in the Fe–13Cr alloy, but in the Fe–13Cr + 10% PC alloy it hardly increases at all.

4.3.2. Spalling

Specimens of size 5 mm x 5 mm x 10 mm, buff-polished, were kept at 1000° C in air for 250 h. The oxide film was observed to adhere on to the matrix alloy (see Fig. 7). In the Fe–13Cr alloy, spalling is very considerable, but in the Fe–13Cr + 10% PC alloy, a thin oxide film adheres firmly without spalling.

4.3.3. Scanning electron microscope observation and EPMA measurement of the oxide film

Formation of the oxide film was observed with JSM-U3 (DDS) scanning electron microscope and X-ray microanalyser. In the X-ray microanalysis, the electron acceleration voltage was 25 kV and

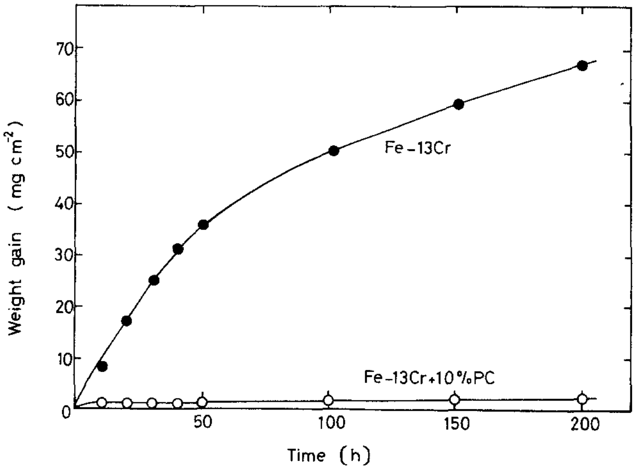

Figure 6 Oxidation curves of Fe–13Cr and Fe–13Cr + 10% PC alloys in air at 1000° C.

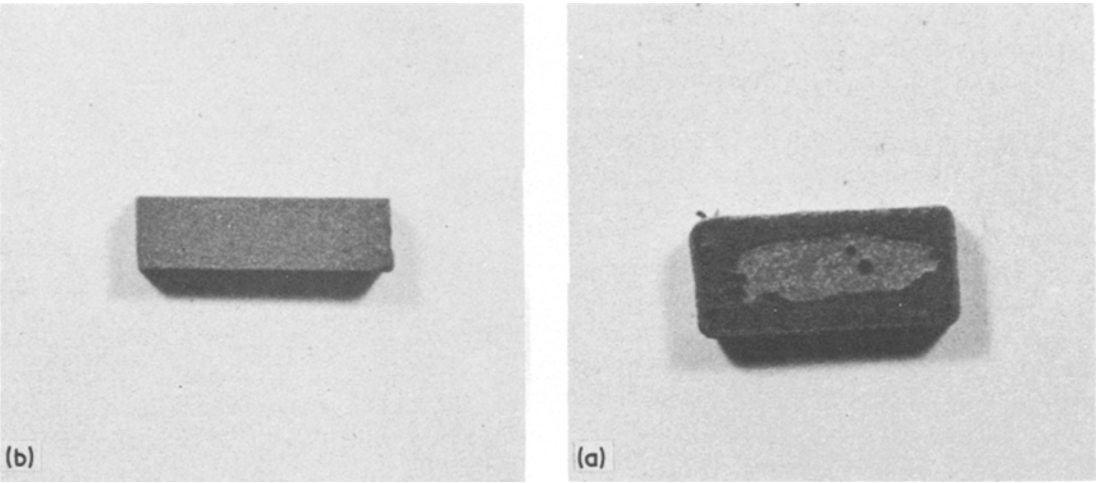

Figure 7 Photographs of (a) Fe–13Cr and (b) Fe–13Cr + 10% PC alloys after oxidation in air at 1000° C for 50 h.

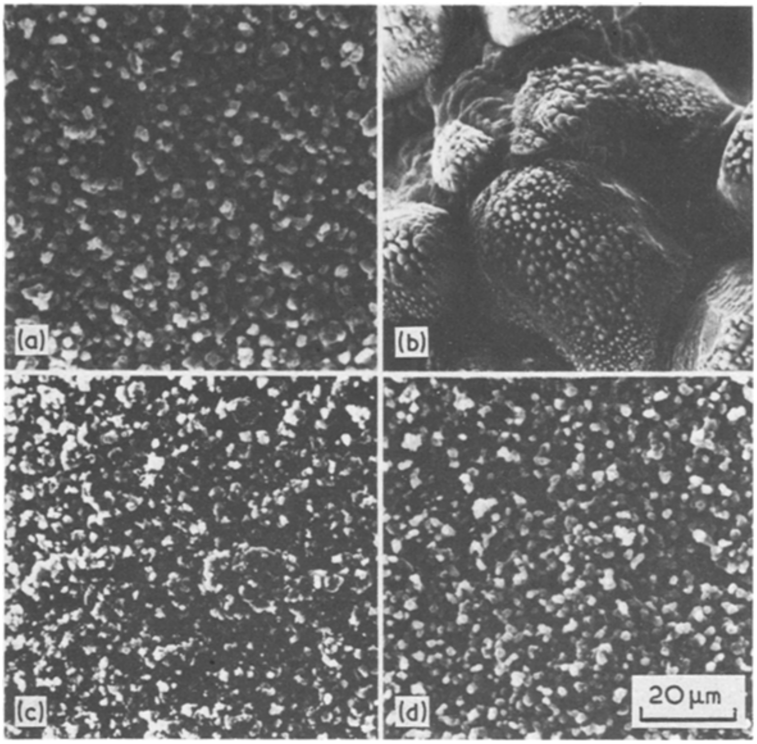

Figure 8 Scanning electron micrograph of surface oxides of Fe–13Cr and Fe–13Cr + 10%PC alloys. (a) and (b); Fe–13Cr alloy oxidized for 100 h at 800 and 1000° C respectively. (c) and (d); Fe–13Cr + 10%PC alloy oxidized for 100 h at 800 and 1000° C respectively.

the absorption current 1×10^{-8} A. 5 mm × 5 mm × 10 mm specimens of Fe–13Cr alloy and Fe–13Cr + 10% PC alloy were kept in the air at 800 and 1000° C for 100 h, and surface of the oxide film was observed by SEM. Micrographs are shown in Fig. 8. There was not a large difference between the alloy surfaces oxided at 800° C for 100 h, but after heating at 1000° C for 100 h, the oxide film of the surface of Fe–13Cr alloy protruded, while the oxide film of Fe–13Cr + 10%PC alloy still retained a smooth surface. A cross section of the cut specimens was observed using SEM. As seen in Fig. 9, in the alloy without PC the oxide film was thick and had cracks, but in the alloy with PC, on the other hand, the oxide film was thin and adhered firmly to the matrix. Fig. 10 shows EPMA measurement of the Fe–13Cr + 10%PC alloy. Its oxide film was composed of Fe, Cr and Si. The formation of the oxide film in two phases was characteristic. The Cr phase largely existed at surface of the matrix and in middle of the oxide film, while the distribution of Fe phase was complementary; i.e. where Cr phase was concentrated, Fe phase was less. The Si phase existed mainly at lower side of the respective phases.

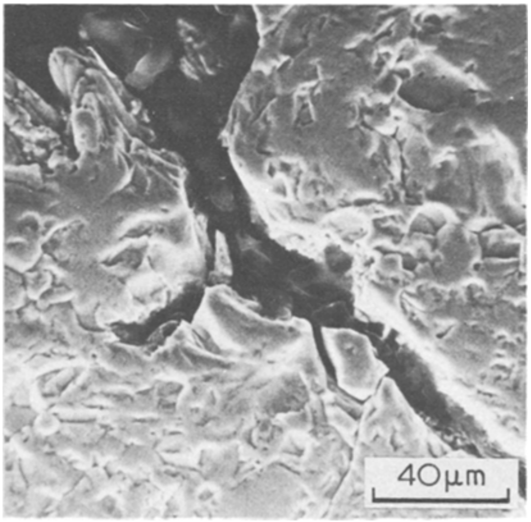

Figure 9 Scanning electron micrograph of the cross-section of oxide layers on Fe–13Cr alloy oxidized for 300 h in air at 1100° C.

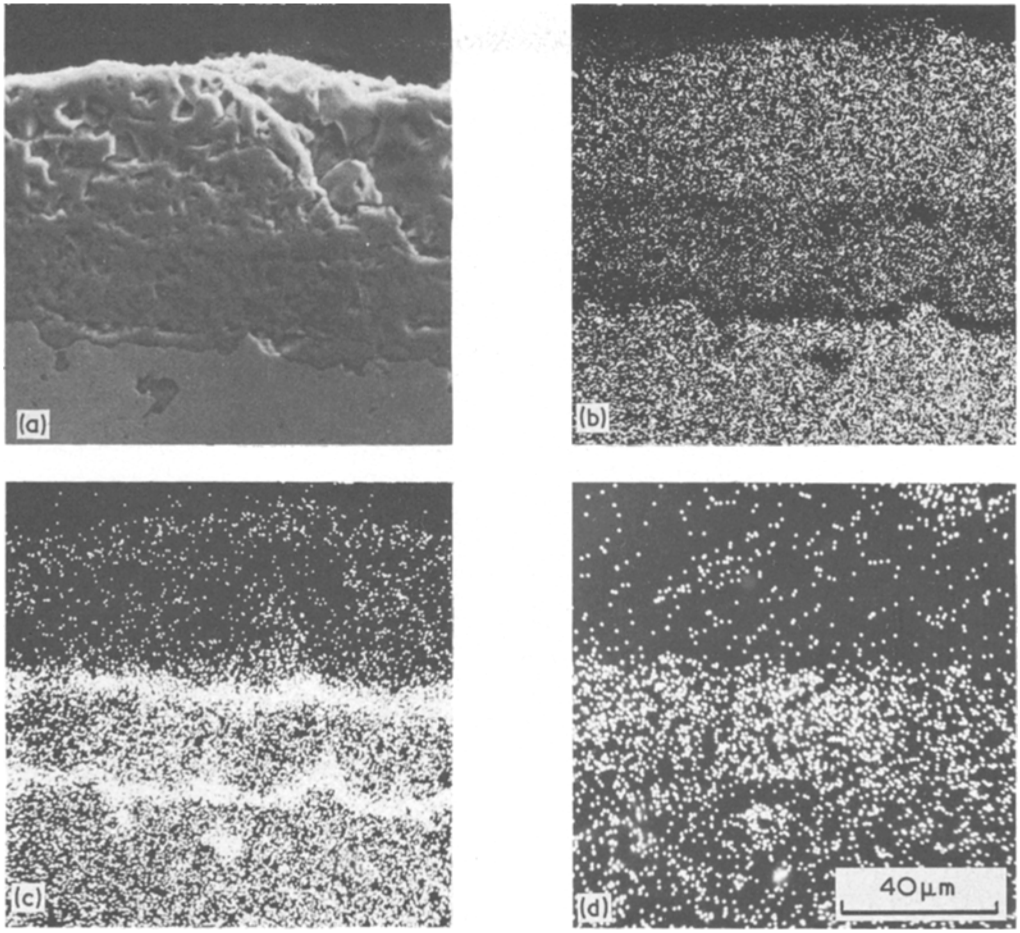

Figure 10 X-ray images on the cross-sections of oxide layers formed on Fe–13Cr + 10% PC alloy oxidized for 300 h in air at 1100° C: (a) Secondary electron image, (b) Fe $K\alpha$ X-ray image, (c) Cr $K\alpha$ X-ray image, (d) Si $K\alpha$ X-ray image.

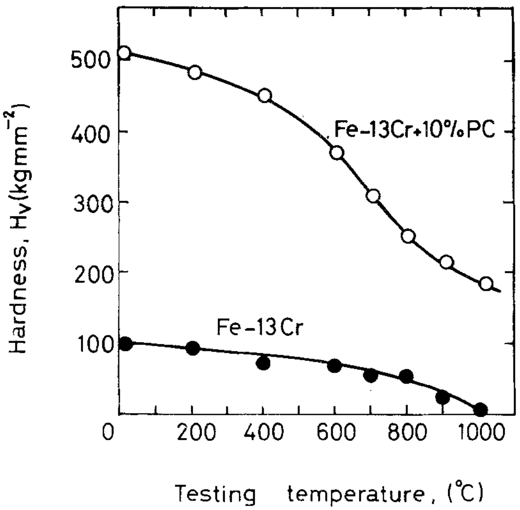

Figure 11 Hardness of Fe–13Cr and Fe–13Cr + 10% PC alloys at various temperatures from room temperature up to 1000° C.

4.4. High-temperature hardness

Vickers microhardness of Fe–13Cr alloy and Fe–13Cr + 10% PC alloy was measured at room temperature to 1000° C. The results are shown in Fig. 11. As seen, the hardness of the Fe–13Cr + 10% PC alloy was much higher than that of the Fe–13Cr alloy, especially at room temperature. This is possibly because in the former, extremely hard precipitated fine-grain $CrSi_2$ and Cr_7C_3 were distributed uniformly at high density in the matrix alloy.

4.5. Wear resistance test

A wear resistance test was made with Okoshi's testing apparatus. At room temperature, a disc 30 mm diameter and 3 mm thick was rotated at a peripheral speed 1 m sec^{-1} on the surface of a rectangular alloy specimen 40 mm x 40 mm x 10 mm with a 7 kg load. Specific abrasion was

7.10×10^{-6} mm^2 kg^{-1} in the Fe–13Cr alloy and 1.24×10^{-6} mm^2 kg^{-1} in the Fe–13Cr + 10% PC alloy, the difference being numerically close to six times. The increase in wear resistance by PC addition was probably due to the cause outlined in Section 4.4.

5. Conclusion

A new sintered alloy was developed by coating particles of Fe–13Cr powder with polycarbosilane as an organo-metallic polymer and then heating. Both the method and product have several remarkable features:

(1) At relatively low temperatures, the organo-metallic compound PC decomposes to give amorphous SiC with loose bonding, which reacts with the matrix alloy. The reaction temperature to obtain the product can thus be low.

(2) Particles of the alloy powder coated with the organo-metallic polymer are heated, so fine grains of the compounds having similar sizes are dispersed uniformly in the alloy. Growth of the alloy grains is consequently suppressed, resulting in greater hardness at both room and high temperatures, and high wear resistance.

(3) Because of the above reason, corrosion resistance of the alloy at high temperature is very large; no spalling of the oxide film takes place.

A number of applications can be expected of the developed product. In this report, only the results by hot-pressing reactions have been described. Experiments with the ordinary sintering method are also in progress, with good results which will be reported in future.

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