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# Fabrication of $Bi_2Sr_2CaCu_2O_x$ films on metal substrates by the chemical process using metal alkoxides

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The formation behaviour of $Bi_2Sr_2CaCu_2O_x$ from compounds prepared by hydrolysis of metal alkoxides was studied and $Bi_2Sr_2CaCu_2O_x$ films on metal substrates were fabricated using a metal alkoxide solution. $Bi_2Sr_2CaCu_2O_x$ was formed through intermediate phases such as $Bi_2Sr_2Cu_1O_x$, $Bi_2CuO_4$, $SrCO_3$, $CaCO_3$ and CuO. $Bi_2CuO_4$ was initially formed with $SrCO_3$, $CaCO_3$ and CuO, and then reacted with $SrCO_3$ to form $Bi_2Sr_2Cu_1O_x$. $Bi_2Sr_2Cu_1O_x$ reacted with $CaCO_3$ and CuO to give $Bi_2Sr_2CaCu_2O_x$. $Bi_2Sr_2CaCu_2O_x$ films were successfully fabricated on nickel substrates using the metal alkoxide solution at the nominal composition of Bi:Sr:Ca:Cu = 2:2:2:3. $Bi_2Sr_2CaCu_2O_x$ was precipitated on Ni substrates at firing temperature of 770 °C or above, and a sharp $\Delta T_c$ was obtained at the firing temperature of 800 °C.

## 1. Introduction

The Bi–Sr–Ca–Cu–O system has at least two superconducting phases, $Bi_2Sr_2CaCu_2O_x$ and $Bi_2Sr_2Ca_2Cu_3O_x$, with a transition temperature, $T_c$, of around 80 and 110 K, respectively [1]. Therefore, the Bi–Sr–Ca–Cu–O system with high-$T_c$ superconductivities is a candidate for many applications. Applications of the high-$T_c$ Bi–Sr–Ca–Cu–O superconductor to electronic devices, magnetic shields, tapes for electric power transportation and magnets require the fabrication of films. A single-crystal MgO (100) has often been used as a substrate well-matched with films in the Bi–Sr–Ca–Cu–O system. However, ceramic substrates are not flexible so that they cannot be used for applications to superconducting tapes.

Metal substrates are most desirable for possible applications for these flexible tapes, but few reports exist regarding deposition of Bi–Sr–Ca–Cu–O films on metal substrates. While the fabrication of Bi–Sr–Ca–Cu–O films on Ag substrates by organometallic chemical vapour deposition was reported by Zhang *et al.* [2], it is inert but an expensive substrate for the applications described above and this process requires an expensive and specialized apparatus. Yoshida *et al.* [3] have prepared Bi–Sr–Ca–Cu–O films on Ni substrates coated with two buffer layers of an Ni–Al alloy and yttria-stabilized $ZrO_2$ by plasma spraying, but there are no reports that Bi–Sr–Ca–Cu–O films have been prepared directly on metal substrates. The deposition of Bi–Sr–Ca–Cu–O films directly on relatively cheap metal substrates is attractive; in general, however, the reactivity of metals with the film is higher at the firing temperature than that of ceramics. In the case of metal substrates, Bi–Sr–Ca–Cu–O films have to be fabricated at a temperature as low as possible to avoid reaction between film and metal. Consequently, it is considered that $Bi_2Sr_2CaCu_2O_x$ film should be deposited on metal substrates, since the $Bi_2Sr_2CaCu_2O_x$ phase is the stable and dominant phase at low temperature, and thus can be easily synthesized even at low firing temperatures.

The authors have successfully prepared an alkoxide solution in the Bi–Sr–Ca–Cu–O system by modification of the metal alkoxides, and fabricated Bi–Sr–Ca–Cu–O films on yttria-stabilized $ZrO_2$ and single-crystal MgO(100) substrates using this solution [4–6]; this method generally has the advantages of obtaining shaped ceramics such as fibres, films and bulks, as well as pure and homogeneous products at a relatively low temperature. In the present paper, the formation behaviour of $Bi_2Sr_2CaCu_2O_x$ was first studied in the hydrolysed powder product of the Bi–Sr–Ca–Cu–O system from a homogeneous metal alkoxide solution. On the basis of these results, $Bi_2Sr_2CaCu_2O_x$ films on metal substrates were fabricated using the metal alkoxide solution.

## 2. Experimental procedure

### 2.1. Preparation of alkoxide solution

The starting materials for preparing the alkoxide solution were $Bi(O\text{-}iC_3H_7)_3$, $Sr(OC_2H_5)_2$, $Ca(OC_2H_5)_2$ and $Cu(OCH_3)_2$. $Bi(O\text{-}iC_3H_7)_3$ was commercially available (High Purity Chemicals Co.). $Sr(OC_2H_5)_2$ and $Ca(OC_2H_5)_2$ were prepared by reaction of the corresponding metal with ethanol and the ethanol solution of these alkoxides was used as the starting solution. $Cu(OCH_3)_2$ was synthesized by reacting $CuCl_2$ in methanol with $KOCH_3$ [7]. Commercially

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TABLE I Calcination products of compounds prepared by hydrolysis of metal alkoxide solution; hydrolysed compounds were calcined for 3 h in air

| Nominal composition (Bi:Sr:Ca:Cu) | Calcination temperature (°C) | | | |
|---|---|---|---|---|
| | 600 | 700 | 800 | 850 |
| 2:2:1:2 | $Bi_2CuO_4$<br>$CaCO_3$<br>$SrCO_3$<br>CuO | $Bi_2Sr_2CuO_x$<br>$CaCO_3$<br>CuO | $Bi_2Sr_2CaCu_2O_x$<br>$Bi_2Sr_2CuO_x$<br>$CaCO_3$<br>CuO | $Bi_2Sr_2CaCu_2O_x$ |
| 2:2:2:3 | $Bi_2CuO_4$<br>$CaCO_3$<br>$SrCO_3$<br>CuO | $Bi_2Sr_2CuO_x$<br>$CaCO_3$<br>CuO | $Bi_2Sr_2CaCu_2O_x$<br>CuO | $Bi_2Sr_2CaCu_2O_x$ |

available 2-dimethylaminoethanol (Kanto Chemical Co.) as a modifier of $Cu(OCH_3)_2$ was used without further purification. Ethanol as a solvent was dried over $Mg(OC_2H_5)_2$ and distilled.

$Cu(OCH_3)_2$ was modified using 2-dimethylaminoethanol in ethanol at a $Cu(OCH_3)_2$:2-dimethylaminoethanol molar ratio of 1:2 to make it soluble [8]. $Bi(O\text{-}iC_3H_7)_3$ was completely dissolved in an ethanol solution of $Sr(OC_2H_5)_2$ and $Ca(OC_2H_5)_2$ by the formation of a double alkoxide of Bi with Sr and Ca [4, 5]. Both solutions obtained by the above methods were mixed so as to obtain a homogeneous alkoxide solution (1.7–2.1 M alkoxide) at a desired molar ratio of Bi:Sr:Ca:Cu.

### 2.2. Preparation of hydrolysed powder and formation behaviour of $Bi_2Sr_2CaCu_2O_x$ during the heating process

Alkoxides in the ethanol solution at a molar ratio of Bi:Sr:Ca:Cu = 2:2:1:2 and 2:2:2:3 prepared by the above procedure were hydrolysed by an addition of water diluted in ethanol (0.19–0.23 M) to the solution at an $H_2O$/alkoxyl-group molar ratio of 1:1 and followed by refluxing for 15 h. The solvent was removed at 50 °C under reduced pressure to yield a hydrolysed powdery product. This powder was calcined at various temperature in air for 3 h in an electric furnace to study the formation behaviour of $Bi_2Sr_2CaCu_2O_x$.

### 2.3. Fabrication of films on metal substrates

The alkoxide solution at a molar ratio of Bi:Sr:Ca:Cu = 2:2:2:3 (0.48 M alkoxide) prepared by the above procedure was dipcoated onto the sursurfaces of Cu and Ni substrates (20 mm × 10 mm × 1 mm) at a draw-up speed of 3 mm $s^{-1}$ in a nitrogen atmosphere. The coated substrates were subsequently heated at 200 °C for 5 min in air so that alkoxides were hydrolysed by the moisture in air. This coating and heating process was repeated 15 times to increase the film thickness. Finally, the films were fired in an electric furnace.

### 2.4. Characterization

The crystal structures of the samples were examined by the X-ray diffraction method (Rigaku Co.) using $CuK_\alpha$ radiation with a monochromator. Scanning electron microscopy (SEM) was performed on a JSM-840A (JEOL) to determine the morphology. Electrical resistivity of the films was measured by the conventional four-probe method.

## 3. Results and discussion

### 3.1. Formation behaviour of $Bi_2Sr_2CaCu_2O_x$

The X-ray diffraction patterns of hydrolysed powdery compounds with a nominal composition of Bi:Sr:Ca:Cu = 2:2:1:2 and 2:2:2:3 were amorphous. The hydrolysed compounds were calcined at various temperatures for 3 h in air to study the formation behaviour of the $Bi_2Sr_2CaCu_2O_x$ phase. Table I shows the products obtained by calcination of the hydrolysed compounds. For the nominal composition of Bi:Sr:Ca:Cu = 2:2:1:2, which is the same as a stoichiometric composition of $Bi_2Sr_2CaCu_2O_x$, $Bi_2CuO_4$ was formed with $SrCO_3$, $CaCO_3$ and CuO at 600 °C. At 700°C, $Bi_2CuO_4$ and $SrCO_3$ disappeared and $Bi_2Sr_2CuO_x$ was formed with $CaCO_3$ and CuO. At 800 °C, the fraction of $Bi_2Sr_2CuO_x$, $CaCO_3$ and CuO decreased and $Bi_2Sr_2CaCu_2O_x$ was formed. The intermediate phase of $Bi_2Sr_2CuO_x$ was completely converted into $Bi_2Sr_2CaCu_2O_x$ at 850 °C. For the nominal composition of excess Ca and Cu (Bi:Sr:Ca:Cu = 2:2:2:3), the formation process of $Bi_2Sr_2CaCu_2O_x$ was similar to that for the nominal composition of 2:2:1:2. The complete conversion of $Bi_2Sr_2CuO_x$ into $Bi_2Sr_2CaCu_2O_x$ for the nominal composition of 2:2:2:3 occurred at a lower temperature than that for the nominal composition of 2:2:1:2.

The formation behaviour of $Bi_2Sr_2CaCu_2O_x$ for the nominal composition of 2:2:2:3 was further studied between 750 and 800 °C. X-ray diffraction patterns of the calcined samples are shown in Fig. 1. Although $Bi_2Sr_2CaCu_2O_x$ was not obtained at 750 °C, it was slightly formed with $Bi_2Sr_2CuO_x$ at 770 °C. The complete conversion of $Bi_2Sr_2CuO_x$ into $Bi_2Sr_2CaCu_2O_x$ was achieved at temperatures as low as 800 °C, which is lower than that of $Bi_2Sr_2CaCu_2O_x$ prepared by the conventional solid-state reaction method [9]. This may be due to the fact that the crystal particles were small and homogeneously mixed with each other.

The $Bi_2Sr_2CaCu_2O_x$ phase is formed through the intermediate phases as described above. $Bi_2CuO_4$ is already formed at 600 °C and reacts with $SrCO_3$ to

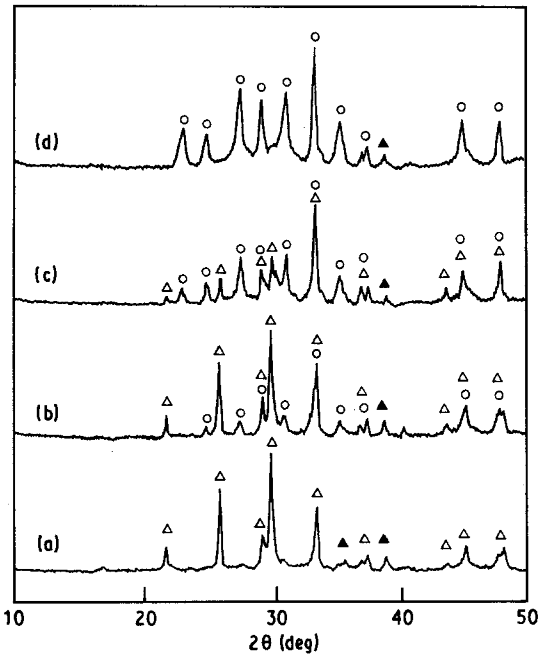

*Figure 1* Cu$K_\alpha$ X-ray diffraction patterns of samples with a nominal composition of 2:2:2:3 calcined at (a) 750 °C, (b) 770 °C, (c) 790 °C and (d) 800 °C for 3 h in air. (○) $Bi_2Sr_2CaCuO_x$, (△) $Bi_2Sr_2CuO_x$, (▲) CuO.

form $Bi_2Sr_2CuO_x$ at temperatures above 600 °C. Also in the case of this chemical process using metal alkoxides, $Bi_2Sr_2CuO_x$ may be formed by the incorporation of Sr cation into $Bi_2CuO_4$ having a channel structure, as suggested by Beltran *et al.* [10]. $Bi_2Sr_2CuO_x$ subsequently reacts with $CaCO_3$ and CuO to form $Bi_2Sr_2CaCu_2O_x$. For the formation of $Bi_2Sr_2CaCu_2O_x$ by reaction of $Bi_2Sr_2CuO_x$ with $CaCO_3$ and CuO, the reaction process may be similar to the formation of $Bi_2Sr_2Ca_2Cu_3O_x$ by diffusion of Ca and Cu into $Bi_2Sr_2CaCu_2O_x$, because the structure of $Bi_2Sr_2CaCu_2O_x$ is constructed by adding extra layers of Ca and CuO to the $Bi_2Sr_2CuO_x$ matrix [11, 12]. It is therefore considered that formation of $Bi_2Sr_2CaCu_2O_x$ from $Bi_2Sr_2CuO_x$ may occur due to the intercalation of extra layers of Ca and CuO into $Bi_2Sr_2CuO_x$, as suggested by Dietderich *et al.* [13]. This speculation seems reasonable in that the diffusion process is obviously enhanced by increasing Ca and Cu content in the normal composition.

For promoting the formation of $Bi_2Sr_2CaCu_2O_x$, therefore, the nominal composition of excess Ca and Cu (Bi:Sr:Ca:Cu = 2:2:2:3) should be adopted due to a large amount of the diffusion species, as in the case of promoting the formation of $Bi_2Sr_2Ca_2Cu_3O_x$ discussed in previous papers [6, 14, 15].

### 3.2. Fabrication and characterization of $Bi_2Sr_2CaCu_2O_x$ films on metal substrates

As described above, the nominal composition of excess Ca and Cu (Bi:Sr:Ca:Cu = 2:2:2:3). in alkoxide solution brought about the complete conversion of $Bi_2Sr_2CuO_x$ to $Bi_2Sr_2CaCu_2O_x$ at temperatures as low as 800 °C. Therefore, the nominal composition of 2:2:2:3 was adopted to make films on metal substrates.

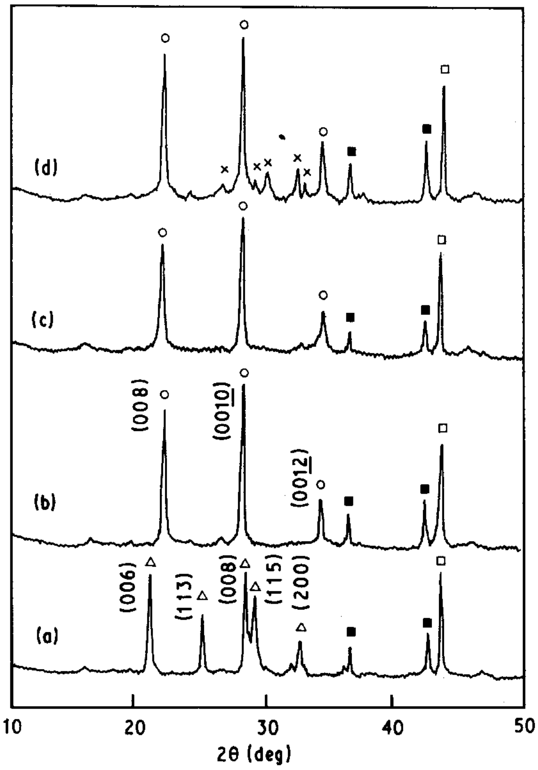

*Figure 2* Cu$K_\alpha$ X-ray diffraction patterns of films on an Ni substrate fired at (a) 750 °C, (b) 770 °C, (c) 800 °C and (d) 830 °C for 3 h in air. (○) $Bi_2Sr_2CaCuO_x$, (△) $Bi_2Sr_2CuO_x$, (□) Ni, (■) NiO, (×) unknown.

Films were coated on Cu and Ni metal plates using a metal alkoxide solution. The coated films, which were amorphous according to the X-ray diffraction analysis, were fired at 800 °C for 3 h. In the case of the Cu plates, a part of the fired film exfoliated and the metal surface was exposed. The remaining part of the film could be easily peeled away. The X-ray diffraction pattern of the film on the Cu plates had peaks of $Bi_2Sr_2CaCu_2O_x$, CuO, $Cu_2O$, and Cu with unknown weak peaks. In the case of the Ni plates, the fired film adhered strongly to the substrate. Consequently, Ni plates were employed as a substrate in subsequent experiments.

The films on the Ni substrates were fired at 750–850 °C for 3 h. $Bi_2Sr_2CaCu_2O_x$ film on the Ni substrate was not obtained at 850 °C due to the reaction of film with the substrate. The X-ray diffraction pattern of the film fired at 850 °C had strong NiO peaks with weak peaks of Ni and undefined phases. X-ray diffraction patterns of films fired at 750, 770, 800 and 830 °C are shown in Fig. 2. The presence of NiO was recognized in the X-ray diffraction pattern of all films, as well as Ni of the substrate. The surface of the Ni substrate was oxidized during firing. The film fired at 750 °C had the $Bi_2Sr_2CuO_x$ phase having relatively strong (0 0 *l*) reflections. The (0 0 *l*) reflections attributed to the $Bi_2Sr_2CaCu_2O_x$ phase were observed above 770 °C. These indicate a preferred orientation of the *c* axis perpendicular to the substrate, despite the use of the metal substrate.

The formation temperature of $Bi_2Sr_2CaCu_2O_x$ was lower for film than for powder. This is assumed to arise as follows. In the case of film, a homogeneous gel film is formed by supplying $H_2O$ from the moisture in the atmosphere. The homogeneous gel film gives a film with fine mixed crystal particles of intermediate phases, in which a better and larger area of interface between $Bi_2Sr_2CuO_x$ and diffusion species is built up. Consequently, $Bi_2Sr_2CaCu_2O_x$ is smoothly formed in the case of film.

Although films fired at 770 and 800 °C had the $Bi_2Sr_2CaCu_2O_x$ phase as a single phase, essentially, the X-ray diffraction pattern of the film fired at 830 °C had unknown peaks with peaks of $Bi_2Sr_2CaCu_2O_x$ possibly because of a slight reaction between the film and substrate. The temperature dependences of electrical resistance normalized to that at 300 K for films on Ni substrates fired at 770, 800 and 830 °C are shown in Fig. 3. The film fired at temperatures as low as 770 °C exhibited $T_c$ (onset) around 90 K. Whereas $T_c$ (onset) of the film fired at 770 °C was similar to that of the film fired at 800 °C, $T_c$ (zero) increased as the firing temperature increased. This behaviour may result from a better contact among the grains grown at higher temperatures. $T_c$ (onset) and $T_c$ (zero) of the film fired at 830 °C were lower than those of the film fired at 800 °C. The decrease of $T_c$ (onset) and $T_c$ (zero) at the firing temperature of 830 °C is assumed to be due to slight impurity phases formed by the reaction between the film and substrate. In the fabrication of $Bi_2Sr_2CaCu_2O_x$ films on Ni substrates using a metal alkoxide solution, therefore, firing at 800 °C was required to yield a sharp $\Delta T_c$ without an excessive reaction between the film and substrate.

The temperature dependences of electrical resistance normalized to that at 300 K for films on Ni substrates fired at 800 °C for 1, 3 and 10 h are shown in Fig. 4. There was no change in the X-ray diffraction patterns of these films. Although $T_c$ slightly decreased from 1 to 3 h, it was approximately constant between 3 and 10 h. The decrease of $T_c$ between 1 and 3 h may be due to the reaction of film with substrate. The constancy of $T_c$ between 3 and 10 h may suggest no proceeding reaction between the film and substrate.

SEM photographs for the film on Ni substrates fired at 800 °C for 3 h are shown in Fig. 5. Fig. 5a shows the surface morphology of the film, where plate-like crystals with the $c$ axis oriented perpendicular to the substrate were observed. Fig. 5b shows the fracture surface produced due to excessive bending. The film was about 1 μm in thickness. Spherical grains with a size of ~ 0.5 μm were observed under the film. It is assumed that the grains are NiO crystals formed by oxidation of a part of the Ni substrate on the basis of the X-ray diffraction data. Remarkably, bending did not produce a fracture between the NiO and Ni metals, but between NiO and $Bi_2Sr_2CaCu_2O_x$ film.

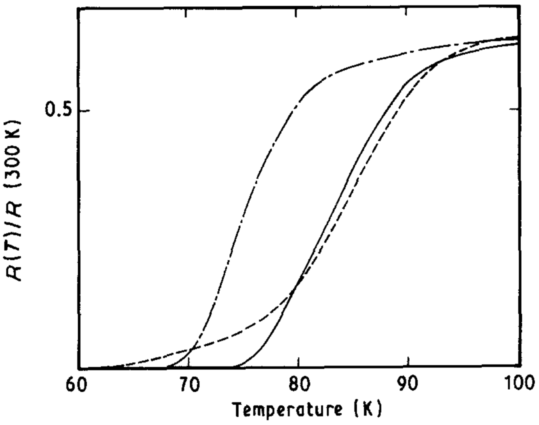

*Figure 3* Temperature dependences of the electrical resistance normalized to that at 300 K for films on Ni substrates fired at (- - -) 770, (——) 800 and (— — —) 830 °C for 3 h in air.

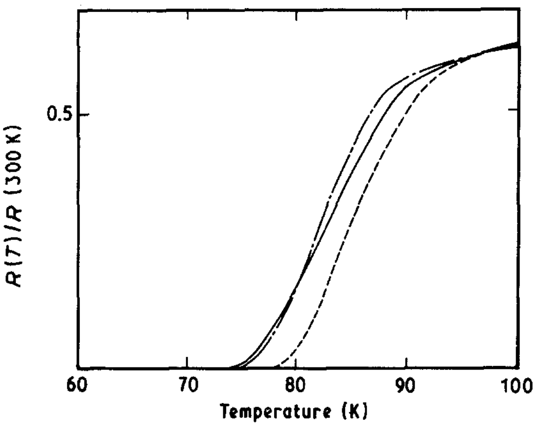

*Figure 4* Temperature dependences of the electrical resistance normalized to that at 300 K for films on Ni substrates fired at 800 °C for (- - -) 1, (——) 3 and (— — —) 10 h in air.

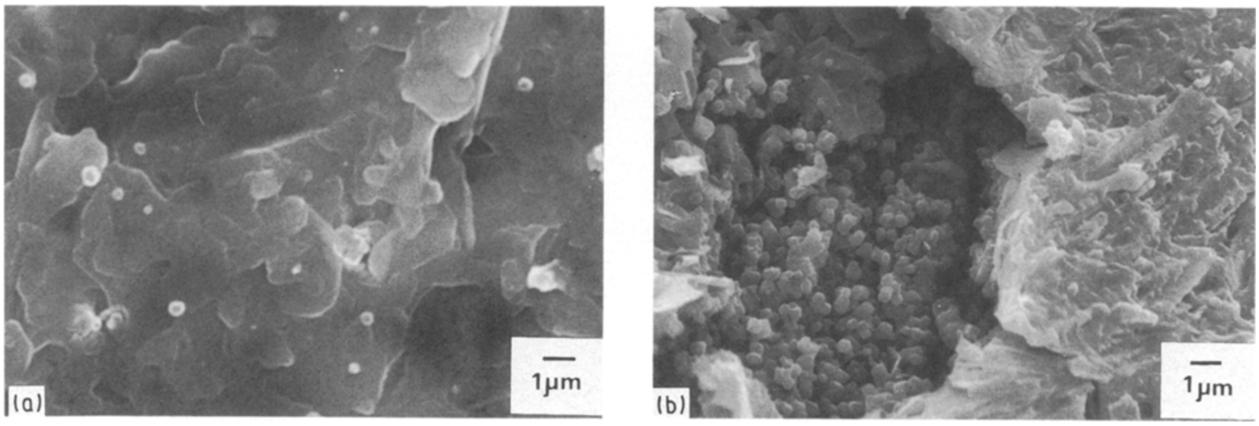

*Figure 5* SEM photographs of film on an Ni substrate fired at 800 °C for 3 h in air: (a) surface of film, (b) fracture surface produced by excessive bending.

On the other hand, it was very easy for the film on the Cu plate to exfoliate at the interface between the copper oxides and copper metal. It is considered that the formation of NiO between $Bi_2Sr_2CaCu_2O_x$ film and Ni substrate acts as a buffer layer so that $Bi_2Sr_2CaCu_2O_x$ film strongly adheres to the substrate.

## 4. Conclusions

The formation behaviour of $Bi_2Sr_2CaCu_2O_x$ from compounds prepared by hydrolysis of metal alkoxides were studied and $Bi_2Sr_2CaCu_2O_x$ films on metal substrates were fabricated using a metal alkoxide solution.

1. $Bi_2Sr_2CaCu_2O_x$ was formed through intermediate phases such as $Bi_2Sr_2Cu_1O_x$, $Bi_2CuO_4$, $SrCO_3$, $CaCO_3$ and CuO. $Bi_2CuO_4$ was initially formed with $SrCO_3$, $CaCO_3$ and CuO, and then reacted with $SrCO_3$ to form $Bi_2Sr_2Cu_1O_x$. $Bi_2Sr_2Cu_1O_x$ reacted with $CaCO_3$ and CuO to give $Bi_2Sr_2CaCu_2O_x$.
2. The complete conversion of $Bi_2Sr_2Cu_1O_x$ into $Bi_2Sr_2CaCu_2O_x$ occurred at a lower temperature for the nominal composition of Bi:Sr:Ca:Cu = 2:2:2:3 than Bi:Sr:Ca:Cu = 2:2:1:2.
3. Although $Bi_2Sr_2CaCu_2O_x$ films on Cu substrates exfoliated, films were successfully fabricated on Ni substrates. The formation temperature of $Bi_2Sr_2CaCu_2O_x$ was lower for the film than for powder.
4. $Bi_2Sr_2CaCu_2O_x$ was precipitated on Ni substrates at a firing temperature of 770 °C or above. A sharp $\Delta T_c$ was obtained at the firing temperature of 800 °C. Firing at 830°C or above resulted in a decrease in $T_c$.

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