JOURNAL OF MATERIALS SCIENCE **34** (1999) 997–1001

Addition effects of aluminum and *in situ* formation of alumina in $MoSi_2$

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Phase composition change and mechanical properties at room temperature of $MoSi_2$ materials with the addition of aluminum were investigated. An explanation was given to the appearance of Mo_5Si_3 when hot pressing $MoSi_2$ raw powder containing oxygen. The mechanical properties including Vickers hardness, bending strength and fracture toughness were improved with the addition of aluminum up to the limit content needed for absorbing the oxygen in $MoSi_2$ raw powder. More aluminum addition than the limit content (in this study it is 5 wt %) will result in the formation of $Mo(Si, Al)_2$ and Si. The *in situ* formed Al_2O_3 could act as a crack pinning element. However, because the thermal expansion coefficients of Al_2O_3 and $MoSi_2$ are near and there is a strong bonding between them, the toughening effect by such *in situ* formed small Al_2O_3 particles (less than 2 μm) is limited.

1. Introduction

$MoSi_2$ exhibits high oxidation and corrosion resistance, high melting point (2020 °C) and excellent electrical conductivity with a moderate density of 6.31 g/cm^3. In the range of 1000 to 1700 °C, $MoSi_2$ forms a protective silica-glass surface layer. However $MoSi_2$ is brittle at room temperature and undergoes a brittle-to-ductile transition at about 1000 °C which offers stress relief by slip mechanisms. To overcome the disadvantages of $MoSi_2$ material, compositing is the most important way and much work has been done in this area in the past ten years [1–5]. For example, reinforcements such as SiC, ZrO_2, Si_3N_4, Al_2O_3, Mo_2B_5, TiB_2 and TiC are thermodynamically stable in $MoSi_2$ and composites reinforced with fibers, whiskers, platelets and particles have been produced. The properties of $MoSi_2$-based composites are better than that of $MoSi_2$ monolithic, for example, bending strength enhanced from 200–250 MPa to 300–550 MPa, fracture toughness enhanced from 2–2.5 MPa m$^{1/2}$ to 3–8 MPa m$^{1/2}$.

A good matrix material is needed for a successful composite. However, the $MoSi_2$ raw powders are generally contain some oxygen. This oxygen will change to glassy silica distributed at the grain boundary of the material after high temperature sintering. This glassy silica boundary has a detrimental effect on the mechanical properties of the materials at room and high temperatures. Petrovic *et al*. [6] investigated the effects of carbon to $MoSi_2$ for removing this oxygen and they found that only 2 wt % addition would greatly improve the high temperature mechanical properties. They also found there is a large weight loss (about 20 wt %) during hot pressing at 1830 °C in Ar when 2 wt % carbon was added. This large weight loose was attributed to the formation of MoO_3(g) and SiO(g). However, their recent work showed that the oxygen content in the samples with and without carbon addition almost remained unchanged [7]. Silva and Kaufman [8] studied the effects of aluminum addition on the microstructure and properties of $MoSi_2$. They found that the silica in $MoSi_2$ raw powder was changed to alumina and the hardness of the material was lowered with the addition of aluminum. In this work, a $MoSi_2$ powder with high oxygen content was used and addition of aluminum metal powder was selected to "absorb" the oxygen in $MoSi_2$ raw powder and *in situ* changed to Al_2O_3. The mechanical properties of these materials with the addition of aluminum were also evaluated.

2. Experimental

The raw powders were $MoSi_2$ (oxygen content 4.4826 wt %) and Al powder. After dry mixing, the uniformly mixed powders were hot pressed at 1600 °C for 60 min in a vacuum under a pressure of 20 MPa. The addition contents of Al for $MoSi_2$-Al materials were 0, 1, 2, 5 and 10 wt %.

The three-point bending strength at room temperature was tested on $2 \times 4 \times 12$ mm specimens, outer span was 10 mm, cross head speed was 0.5 mm/min. Each data of bending strength was an average of 3 values. Vickers hardness and fracture toughness were tested by Vickers indentation method with indent load of 196 N, and Evans and Charles formula [9] was adopted to

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TABLE I Oxygen contents in raw powders and some samples

Sample	$MoSi_2$ raw powder	0%Al	5%Al	Al powder
Oxygen content (wt %)	4.4826	4.4397	5.4254	0.6758

calculate the fracture toughness. Each data of Vickers hardness and fracture toughness was an average of 6 values. The densities of the materials were measured by water displacement method. Oxygen contents of some specimens were tested by TC-436 analyzer (LECO Cooperation, USA). Phase compositions were analyzed by X-ray diffraction (XRD) technique using CuK_α radiation. A scanning electron microscope (SEM) equipped with energy dispersive X-ray analysis (EDAX) was used to observe the microstructures and determine the phase chemistry.

3. Results and discussion

The oxygen contents of the raw powders and some samples are listed in Table I. It can be seen that the oxygen content in $MoSi_2$ raw powder is high and it can be inferred that much glass phase will form during the high temperature sintering. If it is assumed that all the oxygen forms SiO_2 glass during the sintering process, the glass content in the specimen will be 8.4 wt %.

There are two oxidation reactions for $MoSi_2$:

$$2MoSi_2 + 7O_2 \rightarrow 2MoO_3 + 4SiO_2 \quad (1)$$

$$5MoSi_2 + 7O_2 \rightarrow Mo_5Si_3 + 7SiO_2 \quad (2)$$

Reaction 1 is the oxidation reaction of $MoSi_2$ at low temperatures (<800 °C) and reaction 2 is that at high temperatures (>800 °C) [10]. These two oxidation reactions are both thermodynamically possible, but reaction 1 has a lower Gibbs free energy and is more favoured [11]. According to the XRD results (Fig. 1 and Table II), there no other phase, including Mo_5Si_3, exists in the raw $MoSi_2$ powder, so it is considered that the oxidation of $MoSi_2$ at room temperature is in accordance with reaction 1 and the oxidation products MoO_3 and SiO_2 are amorphous. The X-ray photoelectron spectroscopy (XPS) results of Shaw and Abbaschian [12] also indicated that the $MoSi_2$ powder is covered with a duplex oxide layer of SiO_2 and MoO_3. However, after the raw $MoSi_2$ powder was hot pressed into ceramics, Mo_5Si_3 appeared. It is considered that SiO_2 easily forms a glass phase in the process of high temperature hot pressing, but that molybdenum oxide does not readily form a glass with SiO_2 and the dissolution of Mo in silica glass is small. This consideration is qualitatively confirmed by energy dispersive X-ray analysis (EDAX) as shown in Fig. 2. Fig. 2a is the SEM micrograph (backscattered image, BSI) of 0%Al specimen in which the grey matrix is $MoSi_2$, the light grey phase is Mo_5Si_3 and the isolated black areas are the glass phase. From Fig. 2b, c and d it can be seen that the Mo content in glass phase is small. It is worthy of note that, the small white dots in glass phase generally have higher

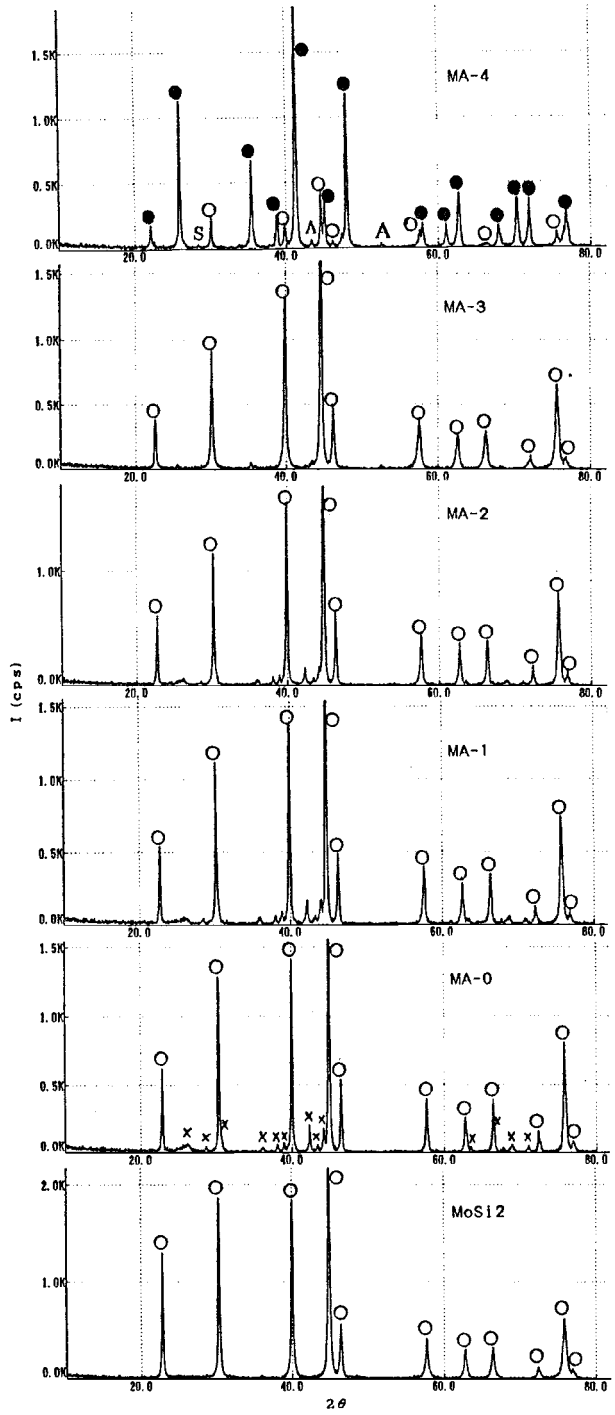
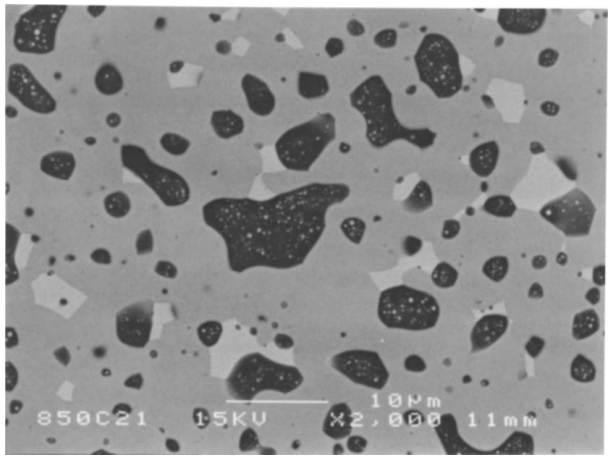


Figure 1 XRD patterns of the hot pressed $MoSi_2$-Al specimens with various aluminum addition content (○—$MoSi_2$; ●—$Mo(Si, Al)_2$; ×—Mo_5Si_3; A—Al_2O_3; S—Si).

TABLE II Effect of Al addition on the phase composition of $MoSi_2$ determined by XRD

Sample	$MoSi_2$ raw powder	0%Al	1%Al	2%Al	5%Al	10%Al
Phase composition	$MoSi_2$	$MoSi_2$, Mo_5Si_3	$MoSi_2$, Mo_5Si_3	$MoSi_2$, Mo_5Si_3	$MoSi_2$, Al_2O_3	$Mo(Si, Al)_2$, $MoSi_2$, Al_2O_3, Si



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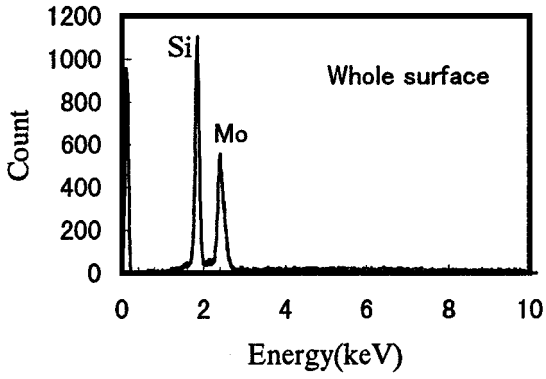

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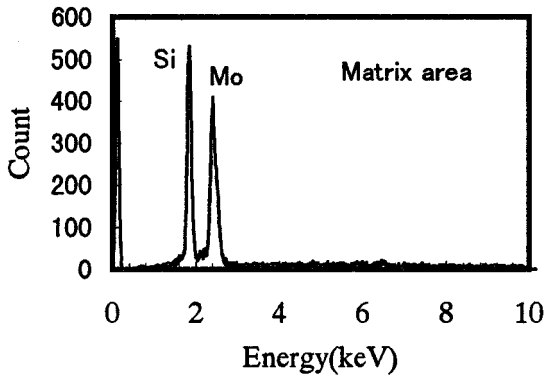

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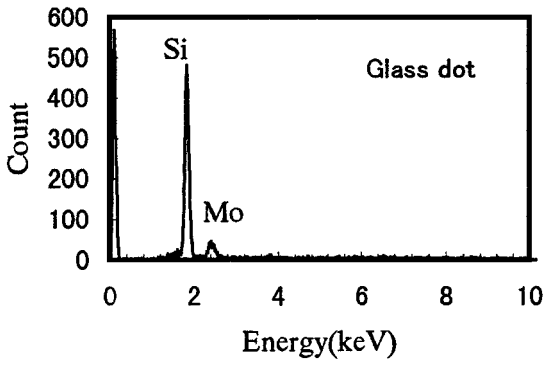


(d)

Figure 2 SEM micrograph (BSI) and EDAX patterns of 0%Al specimen: (a) SEM micrograph; (b) EDAX pattern of the whole surface; (c) EDAX pattern of the matrix area; (d) EDAX pattern of the glass dot.

Mo content than that in other areas of the glass phase. The oxygen contents of $MoSi_2$ compacts before and after hot pressing are almost not changed (see Table I). So, it is suggested that in the process of hot pressing the following reaction takes place and Mo_5Si_3 is formed:

$$3MoSi_2 + 2MoO_3 \rightarrow Mo_5Si_3 + 3SiO_2 \qquad (3)$$

The above reaction is thermodynamically possible in the temperature range of interest according to the data provided by reference [11]. From a general point of view, MoO_3 is easy to vaporize and the oxygen content in the sample will decrease. However, in this study an electrical discharge hot pressing apparatus was used and only about 5 min was needed to raise the temperature to 1600 °C. Hence it is considered that reaction 3 took place before any MoO_3 vaporization and kept the oxygen content in the sample unchanged.

According to the oxygen content in the $MoSi_2$ raw powder and reactions 1 and 3, it can be calculated that the amount of Mo_5Si_3 formed in the 0%Al specimen is about 11.3 wt %. When Al was added, it reacted with the oxidation products of $MoSi_2$ in reaction 1:

$$3MoO_3 + 6SiO_2 + 14Al \rightarrow 3MoSi_2 + 7Al_2O_3 \qquad (4)$$

If all of the oxygen in $MoSi_2$ powder used in this work reacts with the added Al powder and forms Al_2O_3, the content of Al that must be added is 5 wt % and about 9.5 wt % of Al_2O_3 will form *in situ* in the specimen. This is just the composition of 5%Al sample. That is, in 1%Al and 2%Al samples the addition of Al is not enough to absorb all of the oxygen in the $MoSi_2$ powder and reaction 3 will also take place. The above analysis is proved by the XRD results (Table II). The higher oxygen content in 5%Al sample may result from oxygen-absorbtion by aluminum in the processing. However, when more Al than 5 wt % was added, such as in 10%Al sample, the extra Al would react with $MoSi_2$ to form $Mo(Si, Al)_2$ and Si:

$$MoSi_2 + 2xAl \rightarrow Mo(Si_{1-x}Al_x)_2 + 2xSi \qquad (5)$$

Of course, according to the phase diagram of Mo-Si-Al system, some aluminum will dissolve into $MoSi_2$ before changing to $Mo(Si, Al)_2$.

Fig. 3 is the BSI micrograph of 5%Al sample. It can be seen that the glass areas have disappeared and are replaced by Al_2O_3 (dark region) after the addition of aluminum. Also, the Mo_5Si_3 phase is not present in this specimen in accordance with the XRD result.

Fig. 4 is the relationship between the density of the alloy and the aluminum content. The lower density of 0%Al sample is thought to be caused by the high glass content of the material. With the addition of aluminum up to 5% the density increased, but higher aluminum addition than 5% lowered the density of the alloy. The reason for the former is considered to be the change of glass phase to Al_2O_3 with the addition of aluminum and the later is to be formation of $Mo(Si, Al)_2$.

Fig. 5 shows the effect of the aluminum addition content on the Vickers hardness, bending strength and

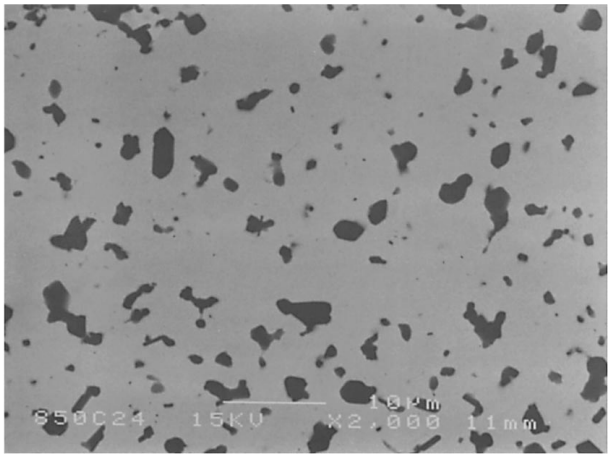


Figure 3 SEM micrograph (BSI) of 5%Al specimen.

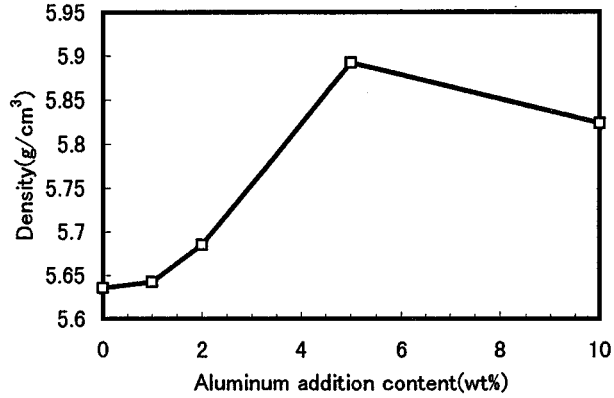


Figure 4 Effect of aluminum addition content on the density of $MoSi_2$ alloy.

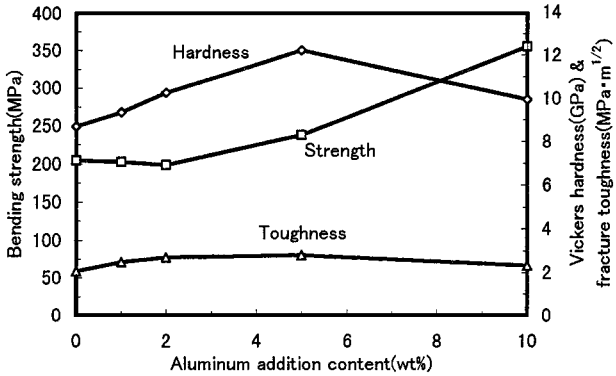
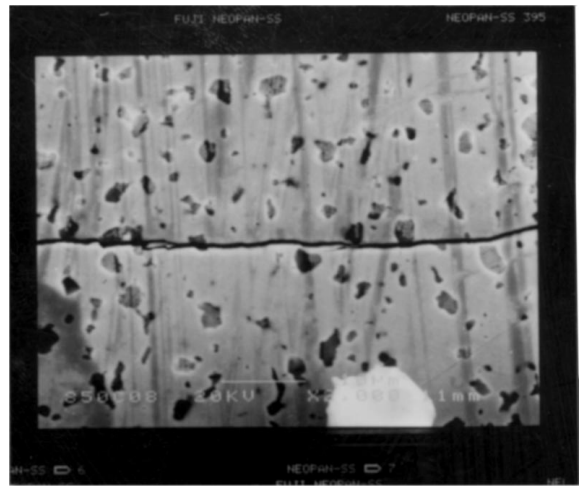
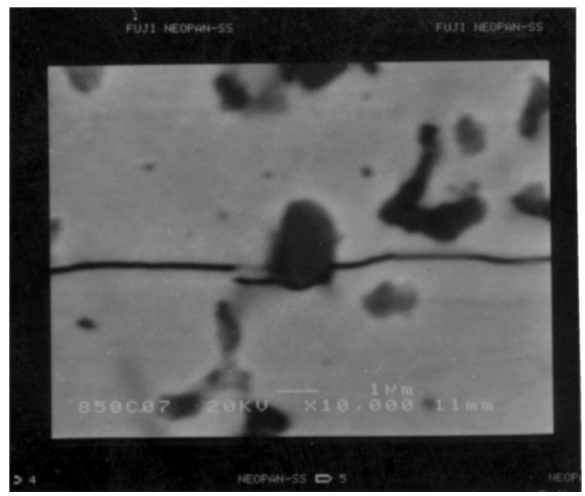


Figure 5 Effect of aluminum addition content on the mechanical properties of $MoSi_2$ alloy.

fracture toughness of the materials. The hardness reached its highest value at 5% aluminum addition. This result was different from that of Silva and Kaufman [8] because of the different oxygen content in the $MoSi_2$ starting powder. The low hardness of 0%Al specimen maybe also due to the high glass content in the alloy. The toughness of 0%Al specimen was about 2 MPa $m^{1/2}$ and with the addition of aluminum slightly higher toughness values were obtained. The highest toughness about 2.8 MPa $m^{1/2}$ was obtained at 5% aluminum addition. That is, density, Vickers hardness and toughness of the alloy has the same trend with the addition of aluminum. The *in situ* formed Al_2O_3 should give some good contribution to the Vickers hardness and toughness. However, the bending strength of the material almost did not change (keeping at about 200 MPa) when the aluminum addition was less than 2%, and then gradually increased to about 350 MPa when aluminum addition reaching 10%. This may be resulted by the formation of $Mo(Si, Al)_2$ and actually formed a $MoSi_2$-$Mo(Si, Al)_2$-Al_2O_3 composite with a higher strength.



(a)



(b)

(c)

Figure 6 Crack propagation path of 5%Al specimen under Vickers indentation: (a) crack path; (b) crack deflected by Al_2O_3 particle; (c) crack passed through Al_2O_3 particle.

Fig. 6 shows the crack propagation path of cracks associated with the Vickers indentation. It can be seen that, generally, the *in situ* formed Al_2O_3 did not significantly change the crack propagation direction (Fig. 6a) but could act as a crack pinning element. Although sometimes the propagating crack was deflected by the *in situ* formed Al_2O_3 particle (Fig. 6b), generally it passed through these particles (Fig. 6c). It was considered that the reason was that the interface bonding between the matrix of $MoSi_2$ and the *in situ* formed Al_2O_3 particles was strong and the thermal expansion coefficients of these two phases were similar. Thus, the toughening effect by such *in situ* formed small (less than 2 μm) Al_2O_3 particles was limited.

4. Conclusions

1. Aluminum metal powder is a good additive for "absorbing" the oxygen in $MoSi_2$ raw powder when making $MoSi_2$ ceramic. Furthermore, the *in situ* formed Al_2O_3 can become a reinforcing phase. However, more Al addition than that needed for absorbing the oxygen will react with $MoSi_2$ to form $Mo(Si, Al)_2$ and Si.

2. When with no aluminum addition, the oxidation products of $MoSi_2$ at room temperature, MoO_3 and SiO_2, will change to SiO_2 glass in high temperature hot pressing process, during which MoO_3 will react with $MoSi_2$ and form Mo_5Si_3 and more SiO_2 glass.

3. The room temperature mechanical properties (Vickers hardness, bending strength and fracture toughness) of $MoSi_2$ with aluminum addition, which were better than that of $MoSi_2$ with no aluminum addition, up to the limit content needed for absorbing the oxygen in $MoSi_2$ raw powder. Because the interface bonding between $MoSi_2$ and the *in situ* formed Al_2O_3 was strong and the thermal expansion coefficients of these two phases were similar, the toughening effect by the small *in situ* formed Al_2O_3 particles was limited.

Acknowledgements

This study was supported by the STA Fellowship program of Japan International Science and Technology Exchange Center (JISTEC) of Science and Technology Agency of Japan. The authors gratefully acknowledge Dr. K. Shobu, Dr. M. Komatsu, Dr. C. N. Xu and Dr. P. Sun for their kind help in experiments.

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Received 12 January
and accepted 8 October 1998