

# Mechanical properties of molybdenum coated with titanium carbide film

T. SHIKAMA, H. SHINNO, M. FUKUTOMI, M. FUJITSUKA, M. OKADA  
*National Research Institute for Metals, 1-2-1 Sengen, Sakuramura, Niihari-gun, Ibaraki-ken, Japan 305*

TiC-coated molybdenum is mechanically tensile tested. The 6  $\mu\text{m}$  thick TiC-coated molybdenum has a higher 0.2% proof strength with a slight decrease in uniform and rupture elongation than the uncoated one. This strengthening effect of the TiC coating can be explained by the constrained effect of the high strength TiC film. The 1.2  $\mu\text{m}$  thick TiC-coated molybdenum starts its plastic deformation at a lower stress than the uncoated one. Also, the coating makes the stress-strain curve more smooth. These effects are attributed to the surface effect, namely, that the interface between the molybdenum substrate and the strong and brittle TiC film acts as a strong dislocation source. The compressive stress in the TiC film will also help the start of plastic deformation at lower external stresses.

## 1. Introduction

In a tokamak type nuclear fusion reactor, some first-wall components, such as a limiter, are planned to be coated with some low- $Z$  ( $Z$  is the atomic number) materials. One can avoid the contamination of the fusion plasma with high- $Z$  impurities by a low- $Z$  coating. In Japan, the limiters, armour plates and protection walls, which will receive a high heat flux from the plasma, will be made of molybdenum coated with titanium carbide (TiC).

Under the operation, the first-wall components must stand the strong stress caused by the thermal expansion, the electromagnetic force and so on. At elevated temperatures, molybdenum itself is ductile and can stand up to the stress unless it is heavily radiation-damaged. However, the mechanical properties of molybdenum will be affected by the coating; molybdenum may become brittle due to the recrystallization and/or contamination with impurities in the coating process. The brittle surface film will also affect the mechanical behaviour of molybdenum. In some cases, it is unfortunate that molybdenum, coated with some brittle ceramics, is brittle-fractured during the operation.

Gomay *et al.* [1] reported that the chemical

vapour deposition (CVD) - TiC coated molybdenum had weaker strength than the uncoated molybdenum. Their reference specimen was cold-worked molybdenum and the weakening effect that they observed could be attributed to the recrystallization during the coating. Also, the CVD-TiC coated molybdenum is found to undergo less fracture elongation than the uncoated molybdenum [2].

In the CVD coating, the molybdenum substrate will be exposed to high temperature and corrosive gases, and it will recrystallize and may absorb some corrosive gas such as  $\text{Cl}_2$ . In such a case, the coating effect is difficult to separate from the degradation during the CVD coating.

Here, we examined the mechanical properties of molybdenum coated with a TiC film by magnetron-sputtering. The coating temperature is 870 K, far below the recrystallization temperature of molybdenum, and no reactive gas is used in the magnetron-sputtering. The specimens are fully annealed before coating to avoid the recrystallization during coating.

The TiC-coated molybdenum is found to have higher 0.2% proof strength as well as higher ultimate tensile strength with a slightly less rupture elongation than the uncoated molybdenum.

We will present the results concerning the mechanical behaviour of the TiC-coated molybdenum in the present report. The analysis of the coated TiC film, after the fracture of the molybdenum substrate, will be described in the following paper [3].

## 2. Experimental procedures

The tensile test specimens were punched out from 0.3 mm thick sintered molybdenum plates. The gauge size of the tensile specimen was 4 mm  $\times$  0.3 mm in cross-section and 12 mm long. After being mechanically polished by emery paper and ultrasonically cleaned in acetone, the specimens were fully annealed at 1850 K for 1 h in a vacuum of  $1 \times 10^{-4}$  Pa. These procedures make the uncoated molybdenum specimens references.

The TiC film was magnetron-sputter coated on the molybdenum specimen after annealing. The coating conditions were: the working gas was argon of  $5 \times 10^{-1}$  Pa with MRC (Material Research Co. Ltd)-made 99.8% TiC sintered target, and the temperature was 870 K. The deposition rate was 3 to 4  $\mu\text{m h}^{-1}$ . The thickness of the TiC film in the experiment was 1.2  $\mu\text{m}$  (thin coating) and 6  $\mu\text{m}$  (thick coating).

The coated TiC film was found to have a (111) preferred orientation normal to the specimen surface. The chemical composition was found to be carbon-rich although no graphite phase was identified by the X-ray diffraction. No diffusion of titanium nor carbon into the molybdenum substrate was observed in the as-deposited condition. The hardness of the film was about 3300 VHN, about 1.5 times harder than the near-stoichiometric magnetron-sputter coated TiC.

The coated and uncoated specimens were tensile-tested to rupture at strain rates from  $1.4 \times 10^{-3}$  to  $1.4 \times 10^{-1} \text{sec}^{-1}$  at 300, 670, 870 and 1070 K.

## 3. Results

Fig. 1 shows plots of tensile stress against plastic strain for molybdenum coated with 1.2  $\mu\text{m}$  thick (thin coated) and with 6  $\mu\text{m}$  thick (thick coated) TiC, together with plots for uncoated molybdenum. The strain rate was  $1.4 \times 10^{-3} \text{sec}^{-1}$  at 300 K. Fig. 2 shows the same plot for thick coated and uncoated molybdenum, tensile-tested at 1070 K at a strain rate of  $1.4 \times 10^{-3} \text{sec}^{-1}$ .

When coated with the 1.2  $\mu\text{m}$  thick TiC film (thin coated), the plastic deformation started at a lower stress than the uncoated one and the stress-strain curve became smooth. This tendency can be observed at all strain rates adopted in the experiment at 300 K. When coated with a 6  $\mu\text{m}$  thick TiC film (thick coated), the tensile strength was found to increase appreciably. Also the stress-strain curve became smooth as in the thin coated case.

The smoothing of the stress-strain curve in the TiC-coated molybdenum can be seen more clearly in Fig. 3. Here, the stress and the plastic strain is log-log plotted at a strain rate of  $1.4 \times 10^{-3} \text{sec}^{-1}$  at 300 K. The uncoated molybdenum shows a change in slope in the curve at about 1% strain. On the other hand, the TiC-coated molybdenum does not show a change in slope up to 10% strain, having a larger slope than the uncoated one at strains less than 1%.

The 0.2% proof strength and the ultimate tensile strength at 300 K are plotted as functions of

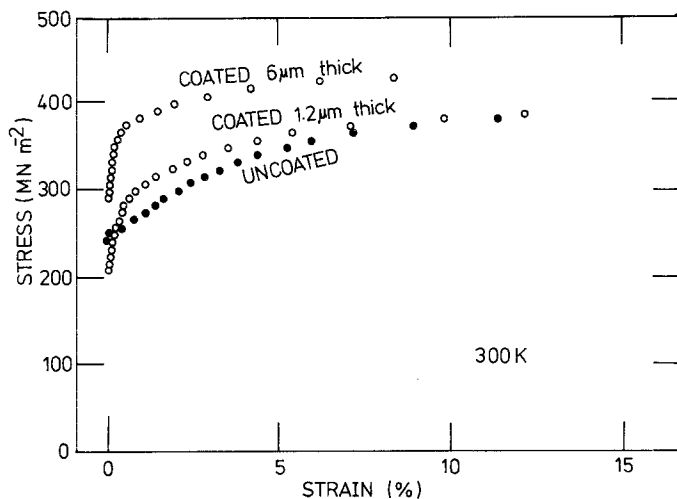


Figure 1 Stress-plastic strain curve of TiC-coated and uncoated molybdenum at 300 K and at a strain rate of  $1.4 \times 10^{-3} \text{sec}^{-1}$ .

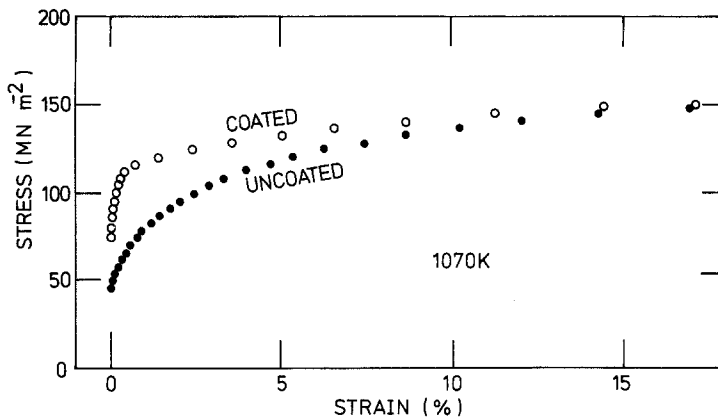


Figure 2 Stress-plastic strain curve of the thick coated and uncoated molybdenum at 1070 K and at a strain rate of  $1.4 \times 10^{-3} \text{ sec}^{-1}$ .

strain rate in Figs. 4 and 5 respectively. The thickly coated molybdenum has a stronger 0.2% proof strength than the uncoated one. The ultimate tensile strength also seems to increase with the thick coating, which is not as clear as the increase of the 0.2% proof strength. The thin coating does not increase the 0.2% proof strength nor the ultimate tensile strength appreciably. Rather, the 0.2% proof strength has a trend to decrease in comparison with the uncoated one at higher strain rates.

Concerning the ductility change, the rupture elongation, as well as the uniform elongation, apparently decreases with the TiC coating as shown in Figs. 6 and 7 at 300 K.

Table I summarizes the results obtained at the strain rate of  $1.4 \times 10^{-3} \text{ sec}^{-1}$  at various elevated temperatures on the thick coated molybdenum. At all temperatures, the 0.2% proof strength increases with the TiC coating, with a slight decrease in the rupture elongation. The increase in the ultimate tensile strength is not so clear as in the 0.2% proof strength.

The specimen, which was heat treated at 1500 K for 5 h in a vacuum of  $5 \times 10^{-5} \text{ Pa}$  after the

thick coating, was also tensile-tested at a strain rate of  $1.4 \times 10^{-3} \text{ sec}^{-1}$ , at 300 and 1070 K. The results are tabulated in Table I. The present heat treatment would improve the adhesive strength of the film but does not affect the general results as shown in Table I.

#### 4. Discussion

From the present results, it is clear that the thick coating increases the 0.2% proof strength. The ultimate tensile strength will also be increased by the thick coating but it is not so clear. The coating also changes the shape of stress-strain curve in the lower strain region.

The strengthening effect of the coating can be attributed to the constrained effect of the film, proposed by Ochiai and Murakami [4, 5].

As will be reported in the following paper [3], the present TiC film is considered to be adhesive to the molybdenum substrate. The film does not actually exfoliate until the strain of the molybdenum substrate exceeds more than 10%. Although many cracks are formed through the coated TiC film at quite a small strain, the TiC film will bear some portion of the applied stress

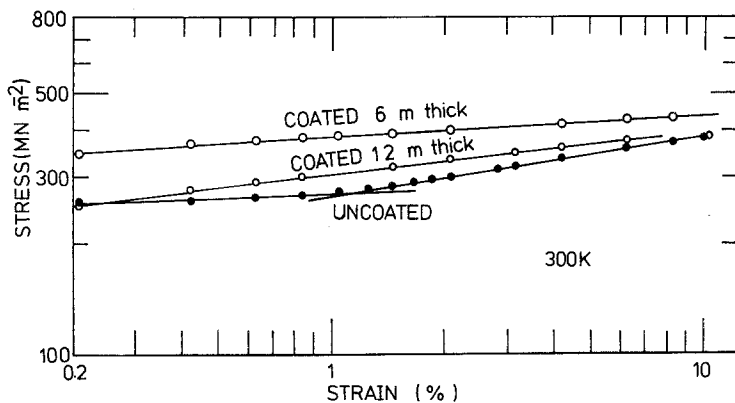


Figure 3 Log-log plot of stress and plastic strain of TiC-coated and uncoated molybdenum at 300 K and at a strain rate of  $1.4 \times 10^{-3} \text{ sec}^{-1}$ .

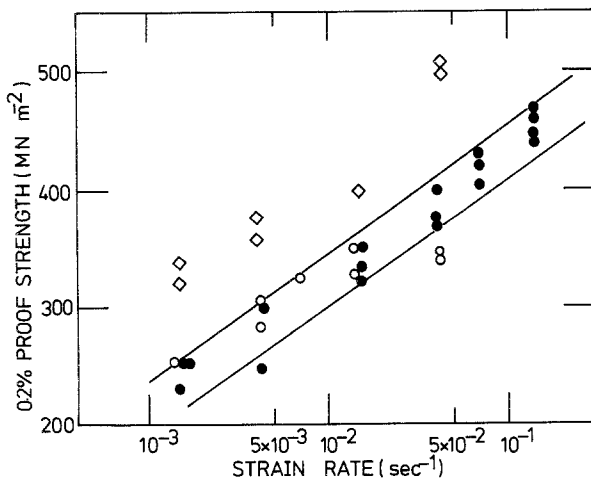


Figure 4 0.2% proof strength as a function of strain rate at 300 K: closed circle – uncoated; open circle – thin coat; open square – thick coat.

through the adhesive interface [4]. The shear stress,  $\tau$ , along the adhesive interface will be born by the bulk stress,  $\sigma$ , of the film following the relation [3, 4],

$$\sigma = \frac{2L}{t} \tau. \quad (1)$$

Here,  $L$  is the distance between two cracks (the interdistance), and  $t$  is the thickness of the film.

In the present experiment, the adhesive strength of the TiC film is considered to be greater than the shear stress,  $\tau$ , generated along the interface [3]. Then, the stress, which the TiC film can bear, must be determined by the bulk strength of the film,  $\sigma_t$ . Actually, the bulk strength,  $\sigma_t$ , will be the fracture strength of the film,  $\sigma_{tf}$ .

Thus, approximately the TiC-coated molybdenum whose cross-section and strength are  $S_m$  and  $\sigma_m$ , and of TiC whose cross-section and strength are  $S_t$  and  $\sigma_{tf}$ , respectively. The apparent strength of the composite,  $\sigma_c$ , can be written as follows

$$\sigma_c = S_m \sigma_m + S_t \sigma_{tf}. \quad (2)$$

When this relation can be applied to the present results, the apparent strength of the TiC film can be obtained. Here, we assumed that the molybdenum substrate did not change its mechanical properties during the coating process. This assumption can be justified when considering the present coating conditions as described in the previous section. The apparent strength of the film obtained is depicted in Fig. 8 as a function of the deformation temperatures. The reported temperature dependence of the Vickers Hardness Number (VHN) of the bulk TiC [6] is also shown in Fig. 8. The present results show a weaker temperature dependence.

The increase of the tensile strength due to the thick coating is about  $80 \text{ MN m}^{-2}$ . So, the thin coating will increase the strength by about  $16 \text{ MN m}^{-2}$ . This degree of the increase is difficult to distinguish from the scatter of the results as one can see from Figs. 4 and 5. Also, the weakening effect of the coating, which will be described in

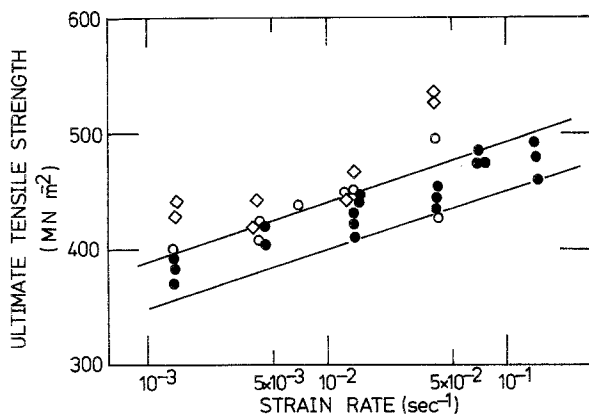


Figure 5 Ultimate tensile strength as a function of strain rate at 300 K: closed circle – uncoated; open circle – thin coat; open square – thick coat.

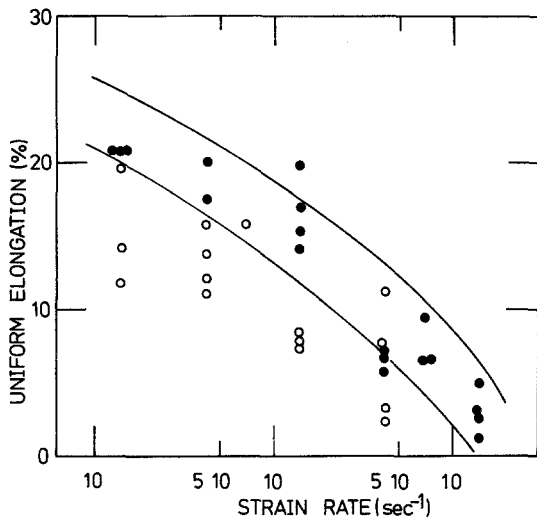


Figure 6 Uniform elongation as a function of strain rate at 300 K: closed circle – uncoated; open circle – coated.

the following, will cancel this small increase of the 0.2% proof strength. At a higher strain rate, the weakening effect may exceed the strengthening effect.

When thin coated, the plastic deformation is found to start at a lower stress than that in the uncoated one. Talia *et al.* [7] have shown that molybdenum single crystal decreases its flow stress when it is covered with the thin oxide film, at 213 and 295 K. This softening effect of the thin surface brittle film was also observed in niobium single crystal by Nagakawa and Meshii [8]. The softening effect was interpreted to be due to the

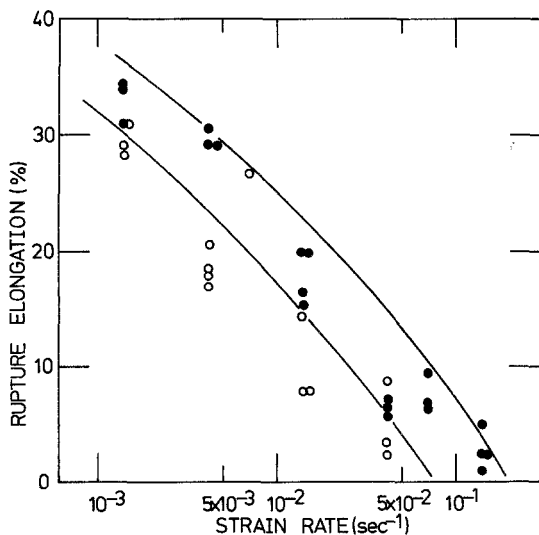


Figure 7 Rupture elongation as a function of strain rate at 300 K: closed circle – uncoated; open circle – coated.

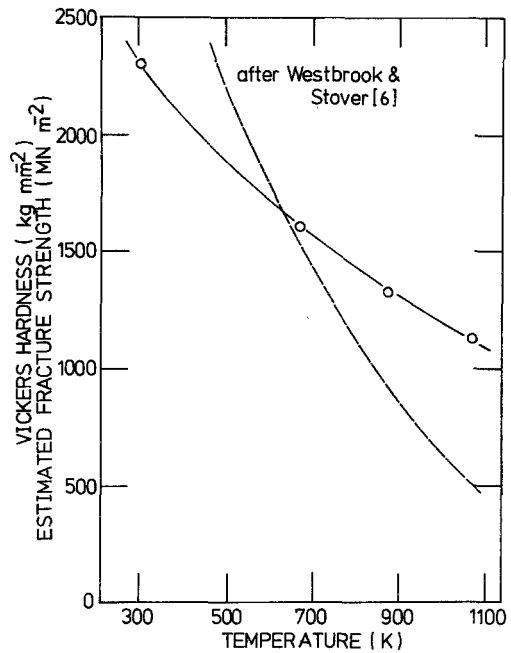


Figure 8 Estimated fracture strength of the present TiC film as a function of temperature, with the reported temperature dependence of VHN of bulk TiC [6].

interface acting as a strong dislocation source. [6, 8]. In this experiment, the interface of the molybdenum and the brittle TiC film can become a strong dislocation source.

Especially, the present TiC film was found to have a strong compressive stress. From the bending curvature measurements, we can estimate the magnitude of the compressive stress to be about 100 to 200 N [9]. This compressive stress is comparable to the 0.2% proof strength of the present specimen, about 300 N. This compressive stress generates a strong shear stress along the interface, which will assist the premature beginning of the plastic deformation.

This interface acting as a dislocation source, and the compressive stress in the film, will also change the stress-strain curve to be smooth at the initial stage.

With the increase of strain, the uncoated surface region will increase due to plastic deformation and the strengthening effect of the film will decrease. Also, some portion of the film will exfoliate as the deformation proceeds. As a result, the TiC film will bear less strength and the increase of the ultimate tensile strength in the coated molybdenum is not so apparent as that in the 0.2% proof strength.

At the fracture strain, the effective area of the

TABLE I Results of tensile test on molybdenum uncoated and coated with TiC\*

Temperature (K)	Specimen	0.2% proof strength (MN m <sup>-2</sup> )	Ultimate tensile strength (MN m <sup>-2</sup> )	Total elongation (%)	Per cent of exfoliation of coated film (%)
RT	Uncoated	245	380	34 (21) <sup>†</sup>	
	Coated	329	437	30 (13) <sup>†</sup>	12.3
	Coated and Heat treated <sup>§</sup>	321	412	27 (17) <sup>†</sup>	—
670	Uncoated	64	206	35	
	Coated	128	206	32	4.6
870	Uncoated	62	179	36	
	Coated	115	192	31	3.0
1070	Uncoated	58	157	38	
	Coated	103	157	27	2.5
	Coated and Heat treated <sup>§</sup>	96	185	27	—

\*TiC thickness; 6 to 8  $\mu\text{m}$  on both sides of 300 m molybdenum.

<sup>†</sup>Uniform elongation in parentheses.

<sup>‡</sup>Per cent of weight loss against total weight of coated film.

<sup>§</sup>Heat treatment; 5 h at 1470 K in vacuum,  $1 \times 10^{-4}$  Pa, after coating.

coated surface will still be more than a few tens per cent. The coated region will deform less with the result of a slight decrease in the rupture elongation as well as in the uniform elongation.

Considering the application of the TiC-coated molybdenum to the first-wall component, a several per cent decrease in the rupture elongation does not affect the safety problem. The mechanical strength increase in the coated molybdenum will be rather beneficial. However, the specimen used was a 0.3 mm thick molybdenum substrate with 1.2 and 6  $\mu\text{m}$  thick TiC film, emphasizing the coating effect. In actual application, the molybdenum thickness will be a few hundreds mm with 10 to 20  $\mu\text{m}$  thick TiC. In this case, the strengthening increase due to the coating will be negligible. All in all, the TiC coating by magnetron-sputtering does not have bad effects on the mechanical properties of molybdenum.

## 5. Conclusion

The TiC-coated molybdenum was mechanically tensile-tested. It is planned to use this composite as the first-wall component in the tokamak type nuclear fusion reactor in Japan. The 6  $\mu\text{m}$  thick TiC-coated molybdenum has a higher 0.2% proof strength with a slight decrease in uniform and rupture elongation as compared to the uncoated molybdenum.

These can be explained by the constrained effects of the high strength TiC film.

The 1.2  $\mu\text{m}$  thick TiC-coated molybdenum starts its plastic deformation at a lower stress than

the uncoated one. Also the coating make the stress-strain curve more smooth. These effects may be attributed to the surface effect: the interface between the molybdenum substrate and the strong and brittle TiC film acts as a strong dislocation source. The compressive stress in the TiC film may also help the start of plastic deformation at lower stresses.

These effects of the coating will not be a serious problem in the actual application where the thickness of the molybdenum substrate is more than  $10^4$  times than that of the TiC coating.

## Acknowledgement

The authors wish to express their gratitude to Drs Y. Hiraoka and J. Nagakawa in NRIM and Dr S. Ochiai at the University of Kyoto for their encouraging discussions.

## References

1. Y. GOMAY, H. KOIZUMI and K. SHIBUKI, *J. Nucl. Sci. Tech. (Japan)* **19** (1982) 214.
2. M. FUJITSUKA, T. SHIKAMA, M. FUKUTOMI and M. OKADA, to be published.
3. T. SHIKAMA, H. SHINNO, M. FUKUTOMI, M. FUJITSUKA and M. OKADA, *J. Mater. Sci.* **18** (1983) 3099.
4. S. OCHIAI and Y. MURAKAMI, *Met. Sci.* **10** (1976) 401.
5. *Idem*, *Trans. JIM* **18** (1977) 384.
6. J. H. WESTBROOK and E. R. STOVER, in "High Temperature Materials and Technology", edited by I. E. Campbell and E. M. Sherwood, (Wiley, New York, 1967) p. 312.

7. J. E. TALIA, L. FERNANDEZ and R. GIBALA, *Scripta Metall.* **12** (1978) 737.

8. J. NAGAKAWA and M. MESHII, *Phil. Mag.* **A45** (1982) 983.

9. T. SHIKAMA, H. SHINNO, M. FUKUTOMI, M.

FUJITSUKA, M. KITAJIMA and M. OKADA, *Thin Solid Film* **101** (1983) 233.

*Received 6 January*

*and accepted 24 February 1983*