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URANIUM SESQUICARBIDE FROM  
URANIUM DICARBIDE

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Effect of Stress on the Formation of Uranium  
Sesquicarbide from Uranium Dicarbide

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Three kinds of uranium carbides,  $UC_{1.87}$ ,  $UC_2$ -15w/o $U_2C_3$  and  $UC_2$ -C, in the form of particles, were heated under compressive stress up to about  $4,000 \text{ Kg/cm}^2$  below  $1,450 \text{ }^\circ\text{C}$  for up to 20 hrs. The formation of  $U_2C_3$  resulting from  $UC_2$  decomposition was detected quantitatively by X-ray diffraction analysis.

The amount of  $U_2C_3$  formed in the  $UC_2$  increased with increase of the stress and the heating time. The maximum formation rate appeared at about  $1,400 \text{ }^\circ\text{C}$ , and the minimum stress required for its formation seemed to exist, about  $600 \text{ Kg/cm}^2$ . These results could be explained by an assumption that the formation was controlled by the rate of change of the lattice arrangement of uranium atoms in  $UC_2$  into that of  $U_2C_3$ . It is considered that the plasticity of uranium carbides is related with the formation.

UC<sub>2</sub> からの U<sub>2</sub>C<sub>3</sub> 生成に関する応力の効果

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3種類のウラン炭化物 UC<sub>1.87</sub>, UC<sub>2</sub>-15W/O U<sub>2</sub>C<sub>3</sub> および UC<sub>2</sub>-C が, 粒状で, 1450 °C 以下の加熱温度, 約 4000 kg/cm<sup>2</sup> 以下の圧縮応力, 20 hr までの時間のもとに加熱された。UC<sub>2</sub> の分解による U<sub>2</sub>C<sub>3</sub> の生成が X線回析法により定量された。

UC<sub>2</sub> 中に生成する U<sub>2</sub>C<sub>3</sub> 量は応力および加熱時間の増すにつれて増加した。最大生成速度は約 1400 °C でみられ, また生成のために必要な応力の最小があつて, それは約 600 kg/cm<sup>2</sup> であつた。これらの結果は, 生成が UC<sub>2</sub> 中のウラン原子配列が U<sub>2</sub>C<sub>3</sub> 中のそれに変る速さに律速される, と考えることで説明された。さらに, ウラン炭化物の塑性も U<sub>2</sub>C<sub>3</sub> の生成に関連あるものと思われる。

目 次 な し

## 1. Introduction

Coated fuel particles with  $UC_2$  kernel have been chosen for use in a HTGR. The stability of  $UC_2$  under high temperature of a gas cooled reactor for a long period and also in high internal compressive pressure due to fission gas is not well elucidated. The phase diagram of U-C binary system reported by E. K. Storms<sup>(1)</sup> indicated that  $\alpha$ - $UC_2$  transforms to  $U_2C_3$  in the region below 1,514 °C and above the c/u ratio 1.87. This transformation, without any stress to the  $UC_2$  sample during heating, was confirmed by some workers<sup>(2)-(4)</sup>, but not by others<sup>(5)-(7)</sup>. M. C. Krupka<sup>(8)</sup> made the experiment by heating of  $UC_2$  under severe stress condition, and observed the formation of considerable amount of  $U_2C_3$  only by a short heating. Recently, F. H. Schneider<sup>(9)</sup> made the experiment on the decomposition of  $UC_2$  in which a mechanical energy was applied by crushing the  $UC_2$  material. He, then, proposed that the controlling factor for the formation of the  $U_2C_3$  was the diffusion of carbon liberated from the decomposition of  $UC_2$  rather than the change of lattice arrangement of uranium atoms from  $UC_2$  to  $U_2C_3$  structures.

The authors made an experiment on the stability of  $UC_2$  under stress at high temperature, and a part of the experimental results has already reported<sup>(10)</sup>. In the present study, the heating condition, under which the coated fuel particles would be irradiated in a gas-cooled reactor, was chosen, and the purpose is concentrated to observe the effects of stress on the stability of  $UC_2$  during out-of-pile heating.

## 2. Experimental

### 2.1 Preparation of the samples

Three kinds of uranium dicarbide samples shown in Fig.1 were used in the experiments. The first sample, designated as  $UC_{1.87}$ , is the one of which the total and the combined c/u ratios obtained by chemical analysis are 2.02 and 1.87, respectively. The sample was prepared by carbo-thermic reduction and subsequent arc-melting, and care was taken to minimize such impurities as tungsten or oxygen. The micro-structure in Fig.1(a) indicates the precipitates of rod shaped free carbon and very fine UC in the  $UC_2$  matrix.

The second sample is uranium dicarbide containing about 15 w/o of  $U_2C_3$ , which is hereafter designated as  $UC_2-15w/oU_2C_3$ . This was prepared by arc-melting  $UC_{1.87}$  with about 20 w/o of UC, followed by heat treatment at 1,480 °C for 32 hrs in a vacuum. X-ray diffraction analysis showed that about 15 w/o of UC transformed to  $U_2C_3$  and the remainder to uranium dicarbide. The structure in Fig.1(b) shows that most of the  $U_2C_3$  precipitate at the  $UC_2$  grain boundaries.

The third sample shown in Fig.1(c) is uranium dicarbide containing small amount of rod-shaped free carbon, which is designated as  $UC_2-C$ . The sample was prepared by arc-melting UC with a pure graphite electrode, in order to prevent the impurities of oxygen or tungsten from entering into the system.

The amount of  $U_2C_3$  formed in the samples used in the

experiment was determined by X-ray diffraction. Pure uranium dicarbide and uranium sesquicarbide were prepared by each individual procedure, separately, and mixed together in several different ratios. The X-ray diffraction patterns for these mixture were taken, and the intensity ratios of independent peaks, from planes (110) and (112) for  $UC_2$  and (310) and (321) for  $U_2C_3$ , were calculated according to the formula shown in Fig.2. The relation between the intensity ratio and the concentration is shown in this figure.

## 2. Procedure of experiments

The stress-heating apparatus used in the experiments is shown in Fig.3. A sample crushed to particles in irregular sizes below about 0.5 mm was placed in a tungsten or molybdenum container, and the uniaxial compressive stress was applied by a tungsten push-rod, operated by an compressive strength testing machine, to the particles.

The apparatus in Fig.3(a) was used in the experiment for time and temperature dependencies of  $U_2C_3$  formation with  $UC_{1.87}$  sample, and that in Fig.3(b) for the experiments only on the stress dependency with  $UC_2$ -15w/o $U_2C_3$  and  $UC_2$ -C samples. In the latter apparatus, a special device to prevent heat loss in an axial direction was used, and so the temperature difference among three specimens was within about 10 °C.

The stress-heating was made in a vacuum of about  $5 \times 10^{-4}$  mm Hg, and the temperature of sample was measured by an optical micro-pyrometer during heating. The temperature fluctuation was within about  $\pm 10$  °C. In the stress applied, correction was made for its loss due to the stress relaxation



resulting from creep and compression of both the push-rod and the sample. The amount of the relaxation was recorded, continuously.

### 3. Results

The amount of  $U_2C_3$  formed from  $UC_{1.87}$  sample against heating time is shown in Fig.4. The loaded stress was corrected to the pre-determined value of  $750 \text{ Kg/cm}^2$  either once a hour (Fig.4(b)) or each time when the stress falls to  $712 \text{ Kg/cm}^2$  (Fig.4(c)). It is evident that no  $U_2C_3$  is formed without the stress as seen in runs E1 and E2 and the  $U_2C_3$  formation under stress-heating is proportional linearly to the time after a definite time, 8 or 2 hrs in this case, of the heating. Difference in this time arises from the method of stress correction and this means that the stress applied to the sample becomes effective after this time. Furthermore, the relaxation of stress is seen during heating and the relaxation rate after each stress correction decreases gradually with the elapse of time. Thus it is considered that the  $U_2C_3$  formation has a close connection with the effective stress comprising its relaxation rate. The typical microstructure and the typical X-ray diffraction patterns for the stress-heated samples are shown in Fig.5. The  $U_2C_3$  formation is clearly shown and the free carbon liberated from  $UC_2$  decomposition is seen to aggregate in large rod-shape in  $U_2C_3$  phase.

The temperature dependency of  $U_2C_3$  formation from  $UC_{1.87}$

sample is shown in Fig.6. In the case, the stress was corrected every time when the initial stress  $750 \text{ Kg/cm}^2$  falls to  $712 \text{ Kg/cm}^2$ . The maximum  $\text{U}_2\text{C}_3$  formation is seen to occur at about  $1,400 \text{ }^\circ\text{C}$ .

Fig.7 shows the effect of external compressive stress on  $\text{U}_2\text{C}_3$  formation for two different samples under different temperatures. The stress was corrected in the manner shown in Fig.4(c). Due to the stress loading to the three specimens at the same time, the stress applied differed among the three specimens. Value of the applied stress were calculated from the diameters of the samples and the loadings. It is seen in Fig.7 that the threshold stress for the formation of  $\text{U}_2\text{C}_3$ , for  $\text{UC}_2\text{-15w/oU}_2\text{C}_3$ , exists at about  $600 \text{ Kg/cm}^2$  and the formation increases gradually after the threshold, while the formation in the case of  $\text{UC}_2\text{-C}$  increases gradually with increase of the stress, and that the amount of  $\text{U}_2\text{C}_3$  formation in  $\text{UC}_2\text{-15w/oU}_2\text{C}_3$  is larger than that in the sample  $\text{UC}_2\text{-C}$ .

#### 4. Discussion

Concerning the  $\text{U}_2\text{C}_3$  formation from  $\text{UC}_2$  decomposition, F.H.Schneider<sup>(9)</sup> pointed out that the rate of  $\text{U}_2\text{C}_3$  formation was controlled by either of the following : (1) the rate of lattice arrangement of uranium atoms from  $\text{UC}_2$  to  $\text{U}_2\text{C}_3$  structure, or (2) the removal rate of excess free carbon liberated from  $\text{UC}_2$  decomposition. Further he considered that the growth rate of  $\text{U}_2\text{C}_3$  would finally depend on the transportation of

liberated carbon to sinks by diffusion in  $U_2C_3$  matrix, because of its less diffusion rate in  $U_2C_3$  than in  $UC_2$ . In his experiments, the sample was crushed into particles of various sizes ; so he supposed that the new types of sinks for the carbon diffusion had been formed and the path of the diffusion was shortened. The present experiment differs from Schneider's ones in the method of supplying mechanical energy to the dicarbide particles ; the energy was given directly to the particles during heating. The results are interpreted, as follows.

The linear relationship seen in Fig. 4(a) makes it possible to assume that the rate of  $U_2C_3$  formation is controlled by the rate of lattice rearrangement of uranium atoms from  $UC_2$  to  $U_2C_3$ , since the linear relation may not appear if the carbon diffusion process controls the rate. This assumption is also supported by the data shown in Fig. 6. That is, the difference in carbon diffusion coefficients between 1,370 and 1,400 °C, reported in Schneider's paper, is not sufficient to explain the difference, i.e. 20w/o, in  $U_2C_3$  formation between two temperatures. It was already pointed out that the process of stress relaxation above a certain value of stress had a connection with  $U_2C_3$  formation. The relaxation necessarily leads to the relative displacement of uranium atoms in the lattice.

In Fig. 8(a), Schneider's geometrical model in the transformation of  $UC_2$  lattice into  $U_2C_3$  is shown, where A represents a uranium atom in  $UC_2$  lattice and B that in  $U_2C_3$ . Then the stress is regarded as effective for displacement

of a uranium atom from A to B at the  $UC_2-U_2C_3$  lattice boundary. From this assumption the formation rate of  $U_2C_3$  can then be expressed by referring to Fig.8(b), where  $\Delta F_a$  is the activation energy in movement of a uranium atom in  $UC_2$ ,  $\Delta F_{tr}$  the potential energy at the point B,  $\Delta F_f$  the formation energy in decomposition from  $UC_2$  to  $U_2C_3$  and carbon, and  $\Delta E_s$  the energy, which is not known well yet at present, given to the uranium atom displaced to a point between A and B. The rate R, i.e. the difference in transformation rate of  $UC_2$  to  $U_2C_3$  and vice versa, is expressed as

$$R \propto \exp \left( -\frac{\Delta F_{tr} - \Delta E_s}{kT} \right) \left[ 1 - \exp \left( -\frac{\Delta F_f}{kT} \right) \right] \quad (1)$$

where k is the Boltzman's constant and T the absolute temperature. In the equation, it can then be shown that a maximum value of R appears necessarily at a certain value of T when  $\Delta E_s$  is a constant or zero, since the formation rate decreases both with increase of T until the value of  $\Delta F_f$  is zero and with decrease of T. This tendency agrees with the result shown in Fig.6 ; the maximum appears at about 1,400 °C under the stress of 750 Kg/cm<sup>2</sup>.

The effectiveness of the stress in  $U_2C_3$  formation rate,  $\Delta R$ , is given by

$$\Delta R = \left[ R \right]_{\Delta E_s = \Delta E_s} - \left[ R \right]_{\Delta E_s = 0} \quad (2)$$

$$\propto \exp \left( \frac{\Delta E_s}{kT} \right) - 1$$

where  $\Delta E_s = 0$  means that no stress is applied. The results shown in Fig.7 suggest that the applied stress is not directly proportional to the energy  $\Delta E_s$ . This seems to be related with the plasticity of the carbide. According to

M. Tokar's survey<sup>(11)</sup> on the mechanical properties of uranium carbides, no data are given of the compressive strength of  $UC_2$  at any temperature. However, a plastic deformation of the carbides seemed to have occurred under stressing at high temperature, since the experimental temperature is over half the melting point of  $UC_2$  and the stress relaxation has occurred sufficiently. Moreover, the uranium atom near the position B in Fig.8 in the  $UC_2$  lattice may be regarded as existent in the plastic region when the slip at the  $UC_2$ - $U_2C_3$  boundary is considered, since the distance (equal to  $d \times \sin 19.4^\circ = 0.35d$ , where  $d$  is the lattice distance of  $UC_2$ ) between the position A and B is considered to be much larger than the distance, supposed to be about  $0.2d$ , of elastic deformation from A. The plastic deformation would influence directly the displacement of uranium atom, and furthermore makes the diffusion of the liberated carbon atoms easier by an acceleration of the carbon removal to the sinks or by a formation of new sinks. However, the effectiveness of the stress in terms of  $\Delta E_s$ , for example, could not be elucidated in the present experiment. Further studies are necessary on the mechanism of the  $U_2C_3$  formation from the dicarbides under stressing.

## 5. Conclusion

Three types of uranium dicarbide samples,  $UC_{1.87}$ ,  $UC_2$ -15w/o $U_2C_3$ , and  $UC_2$ -C, were heated at temperature up to  $1450^\circ C$  under the externally applied stresses of up to  $4000 \text{ Kg/cm}^2$ .

The following were revealed.

(1) The formation of  $U_2C_3$  is not observed when stress is not applied, but observed when stress is applied during heating. The experimental results suggest that the uranium dicarbide as the kernel may decompose during use in a HTGR, when the temperature is higher than about 1350 °C and the pressure due to fission gas is several hundreds atmosphere.

(2) The yield of  $U_2C_3$  from the dicarbide increases with increases of the stress and the heating time, and the yield is about 90% by heating at 1400 °C for 20 hrs under the stress of 750 Kg/cm<sup>2</sup>. The minimum stress required for the formation of  $U_2C_3$  seems to exist, about 600 Kg/cm<sup>2</sup>.

(3) The yield of  $U_2C_3$  under stress at 750 Kg/cm<sup>2</sup> by heating for a period attains a maximum value at about 1400 °C.

(4) The experimental results on the  $U_2C_3$  formation under stressing is interpreted by an assumption that the formation is controlled rather by the rate of change of the lattice arrangement of uranium atoms in  $UC_2$  into that of  $U_2C_3$ , than by the rate of removal of excess carbon liberated from the formation reaction. The stress is assumed to be especially effective when the plastic deformation of the uranium dicarbide appears to make the uranium atoms in  $UC_2$  lattice move to the positions of  $U_2C_3$  lattice and to make the diffusion of the liberated carbon easier.

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(a)  $UC_{1.87}$ , showing the precipitates of rod-shaped free carbon and very fine UC in the  $UC_2$  matrix

(b)  $UC_2-15w/oU_2C_3$ , showing the precipitates of  $U_2C_3$  at the  $UC_2$  grain boundaries

(c)  $UC_2-C$ , showing the precipitates of rod-shaped free carbon in the  $UC_2$  matrix

Fig.1 Microstructures of the starting materials for the stress-heating experiments



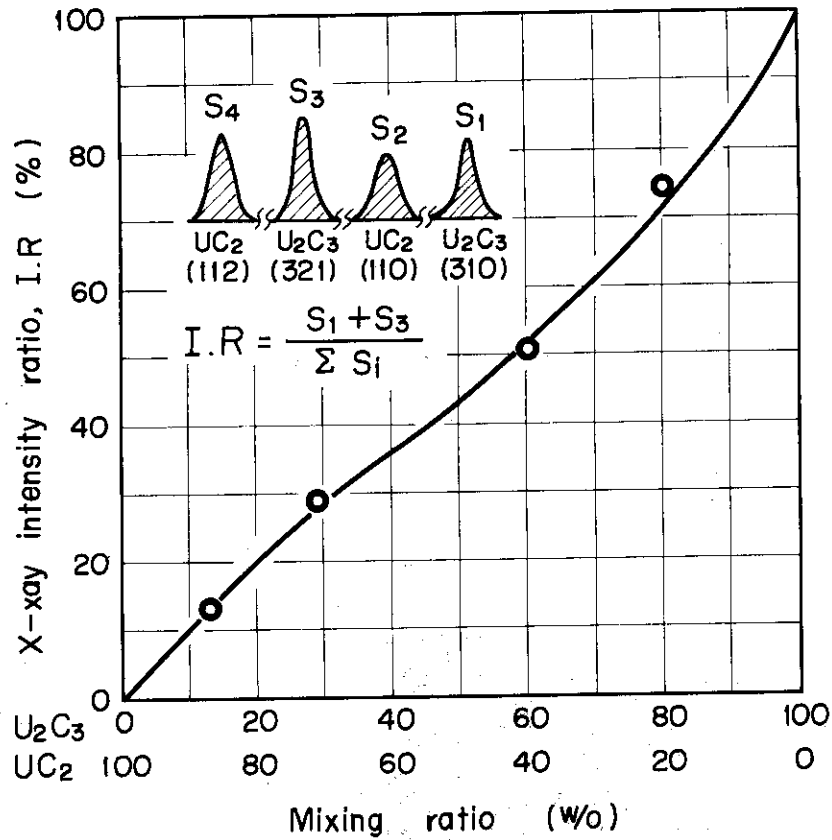


Fig.2 Calibration curve for determining the amount of  $U_2C_3$  formed in  $UC_2$

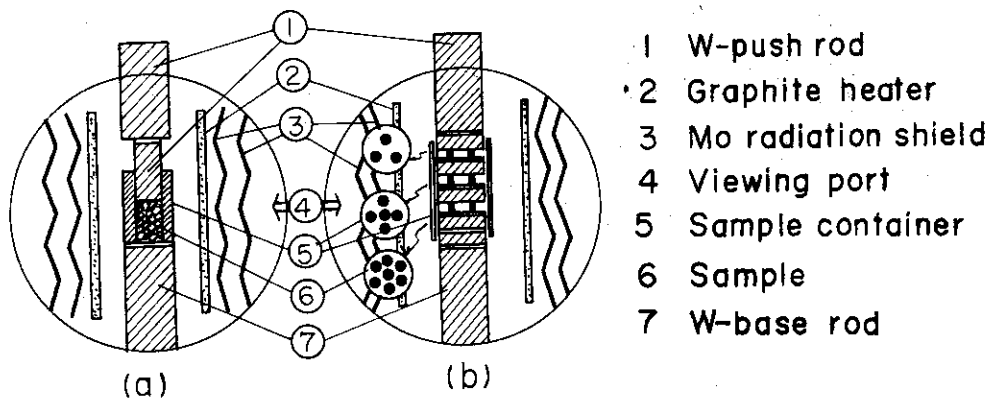


Fig.3 Schematic diagram of the stress-heating apparatus ( a ; temperature and time dependencies, and b ; stress dependency )

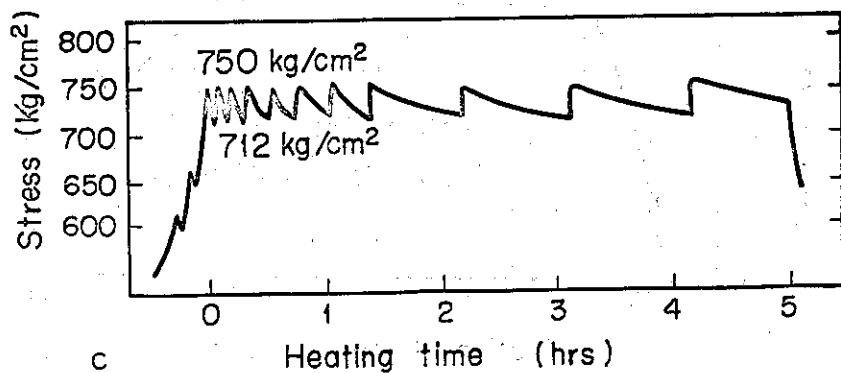
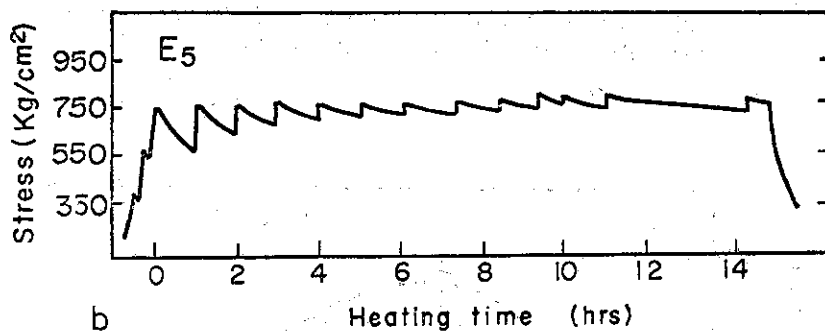
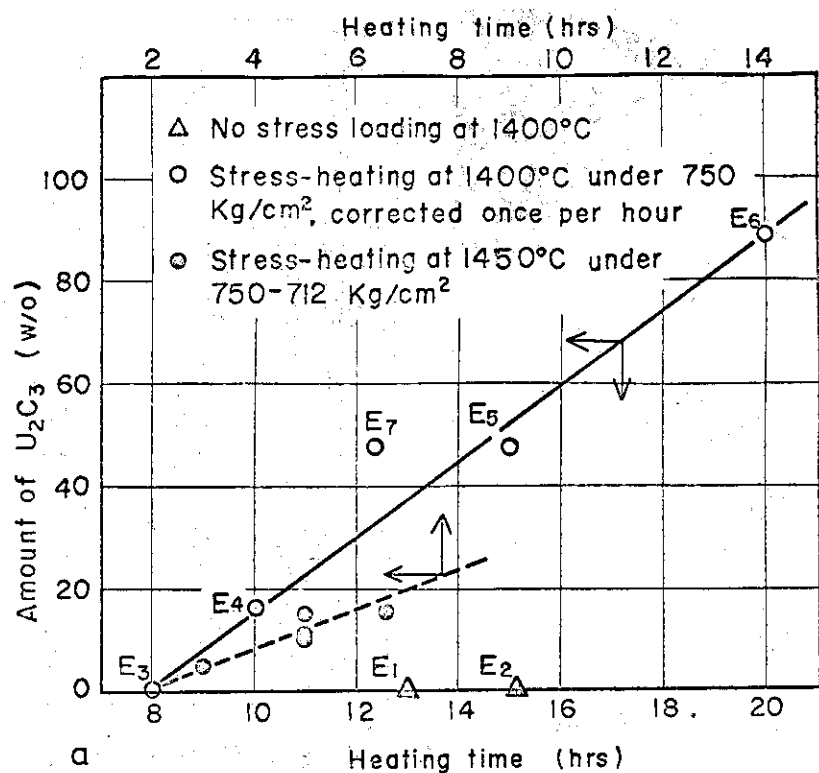


Fig.4 The relationship between the amount of  $U_2C_3$  formed in the sample  $UC_{1.87}$  and heating time, and the aspect of applied stress

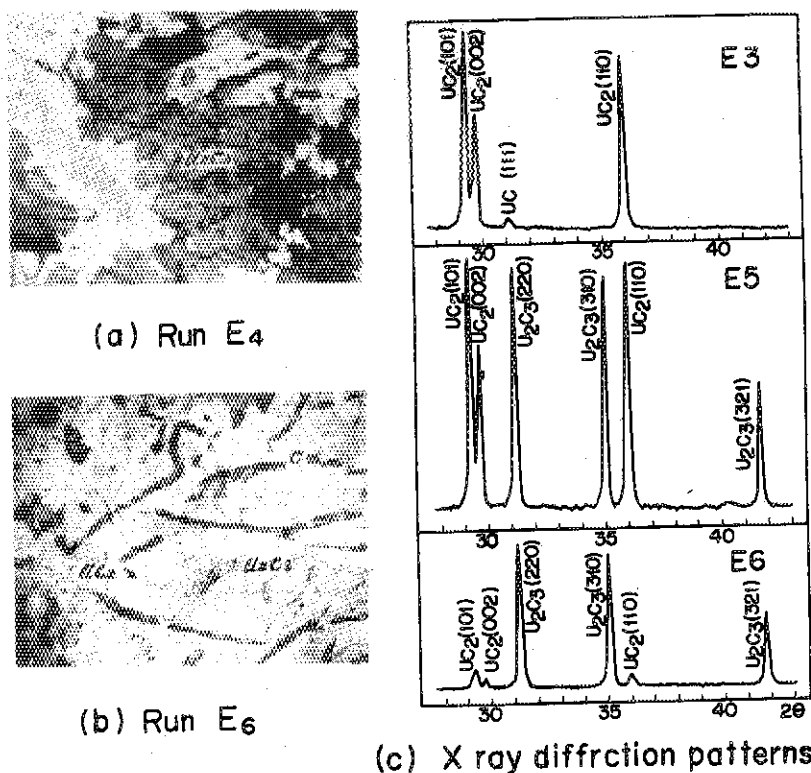


Fig.5 Typical microstructures and X-ray diffraction patterns of the stress-heated samples

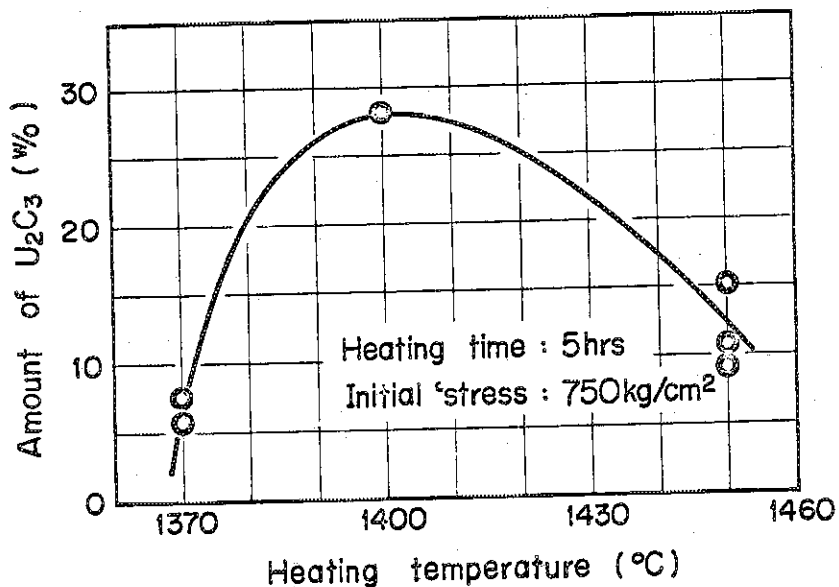


Fig.6 Temperature dependency of U<sub>2</sub>C<sub>3</sub> formation

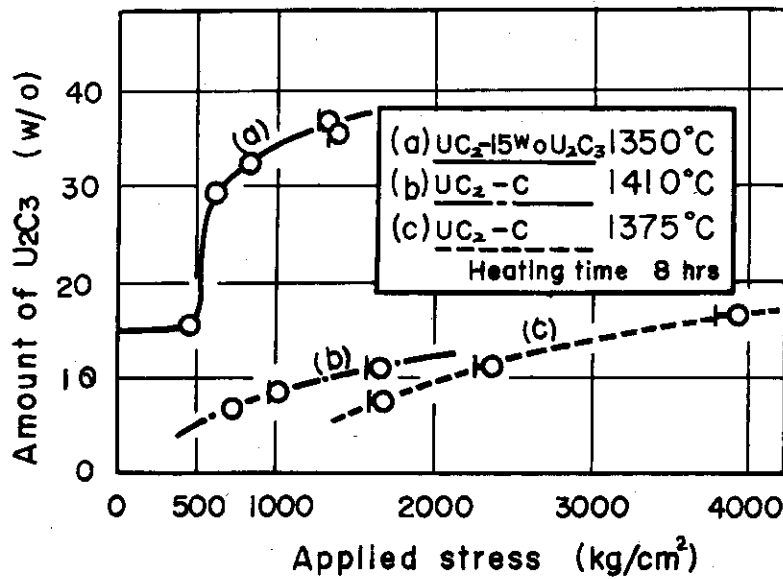


Fig.7 Stress dependency of  $U_2C_3$  formation

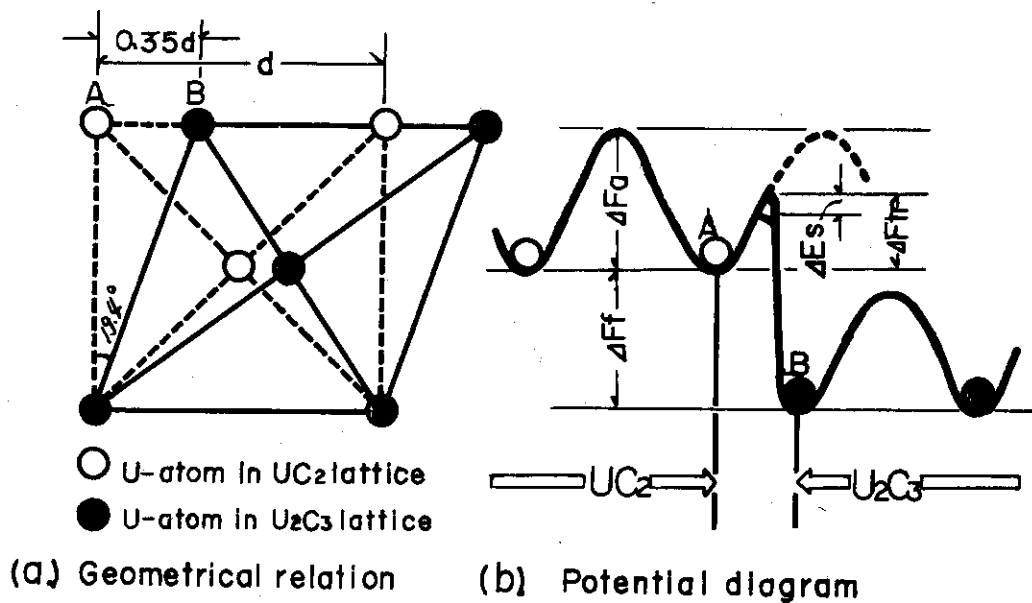


Fig.8 Interpretative diagrams for the effect of stress on  $U_2C_3$  formation from  $UC_2$