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CONTAINING SMALL AMOUNT OF

URANIUM MONOSULFIDE

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Creep Strength of the Uranium Monocarbide Containing Small Quantity of Uranium Monosulfide

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Polycrystalline uranium monocarbide and containing 3.2 or 8.0 w/o of uranium monosulfide were prepared by arc-melting. By the stress-relaxation method, the primary creep strength was measured at temperatures up to 1460 °C in a vacuum. Hot hardness of the UC matrix was also examined at temperatures up to 1100 °C.

The stress-relaxation curves are in the logarithmic form with typical primary creep. The creep strength increases considerably with US content. The activation volume, defined by R. Chang, varies with temperature and US content; the values calculated are from about 2×10^{-21} to 1×10^{-20} cm^3. Hot hardness of the UC matrix increases with US content, especially at high temperatures.

少量の一硫化ウランを含んだ一炭化ウラン

のクリープ強度

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　多結晶一炭化ウランおよび3.2，8.0ｗ／ｏの一硫化ウランを含んだ一炭化ウラン（UC，UC–3.2ｗ／ｏUS，UC–8.0ｗ／ｏUS）がアーク溶解で調整され，応力緩和法による一次クリープ強度が，真空中，1460℃までの温度で測定された。また同試料の高温硬度が 1100℃までの温度で測定された。

　試料における応力緩和曲線は典型的な一次クリープにみられる対数型で表示された。クリープ強度は一硫化ウラン含有量の増加とともに増大した。温度およびUS含有量の函数として，R. Chang の定義にもとづく活性化体積の変化がみられ，計算の結果，それらは約 $2 \times 10^{-21} \sim 1 \times 10^{-20}$ cm³ の範囲にあることが判った。さらに，UCマトリックスの高温硬度はUS含有量の増加につれて増大され，特に高温においてその効果の著るしいことが判った。

目　次　なし

I. Introduction

Uranium monocarbide fuel has several advantages for fast-reactor use, compared with the uranium dioxide, including high uranium density, high thermal conductivity and excellent compatibility with sodium coolant and the cladding. However, the swelling of the fuel at high temperature under high burn-up during irradiation in the reactor is considered to be large. The swelling is caused by the accumulation of fission products inside the fuel, and is probably participated with the creep of fuel material. Therefore, the improvement in mechanical properties of the fuel may prevent the swelling.

For the purpose of increasing the mechanical strength of uranium monocarbide, J. J. Norreys[1] made the experiment on the compressive creep of uranium monocarbide with addition of tungsten, and found that the addition improved considerably the creep resistance. In the present study, uranium monosulfide was used as the additive, because the sulfide has the same structure as that of uranium monocarbide, while tungsten does not, and further it dissolves into the uranium monocarbide despite a small quantity of this additives. Furthermore, uranium monosulfide, compared with uranium monocarbide, has superior thermodynamical[2] and mechanical[3] properties, and also good compatibility with the cladding[4],[5]; and its vapor pressure is low at high temperatures. A UC-US mixed-anion

system has been studied to improve physical and chemical properties of the carbide fuel[6],[7]. However, no studies have ever been made on its mechanical properties. The purpose of the present study is to confirm the effect of US addition on such mechanical properties of uranium monocarbide as the primary creep strength and hardness at high temperature.

II. Experimental

1. Sample preparation

Three types of uranium monocarbide, that is, UC, UC-3.2 w/o US and UC-8.0 w/o US, were used in the experiment. These were prepared by the procedure shown in Fig. 1.

The powder of uranium monosulfide was obtained by the direct chemical reaction between uranium metal chips and sulfur powder; the mixture was sealed in a quartz tube evacuated to about 10^{-5} mmHg, and then heated at 160 ℃ for 24 hrs to cover the chips with gaseous sulfur, followed by the heating at 380 ℃ for 72 hrs. Heat treatment at 800 ℃ for 3 hrs yielded the mixture of several kinds of uranium sulfide, namely US, U_2S_3, U_3S_5 and US_2, which were identified by X-ray diffraction analysis. In order to remove the higher order uranium sulfides (U_2S_3 to US_2), the product was pressed into pellet and heat-treated at 1850 ℃ for 3 hrs in a vacuum. X-ray diffraction analysis showed that the final product thus obtained was mostly

uranium monosulfide, with trace amount of uranium sesquesulfide.

Uranium monocarbide was prepared by arc-melting of reactor-grade uranium metal with high-purity graphite under the argon gas atmosphere of pressure +500 mmHg, using a non-consumable tungsten electrode. During the arc-melting, the UC "button" was turned over several times, to have uniformity in the matrix. The button was about 5 cm in diameter and about 8 mm in thick, containing 4.8 w/o of carbon and about 0.2 w/o of tungsten, both determined by chemical analysis. The button was divided into three portions; one was remelted, and the other two were mixed with uranium sulfide, followed by remelting in order to obtain the samples UC, UC-3.2 w/o US and UC-8.0 w/o US, respectively. Chemical analysis of these samples showed that there occurred no change in the carbon content by the procedures.

Microstructures of the samples are shown in Fig. 2(a), (b) and (c). By ceramographic observation and EPMA analysis, it was shown that uranium monosulfide was partly dissolved into the UC grains, the rest being precipitated in the UC grain boundaries for the two samples. To observe the existence of US solution in the UC matrix, the lattice parameters of the samples were measured by X-ray diffraction. The parameters for the samples UC, UC-3.2 w/o US and UC-8.0 w/o US were 4.96, 4.97 and 4.99 A, respectively.

2. Experimental procedure

The experimental apparatus for measuement of the primary creep strength is shown in Fig. 3. The specimen, cut into the size 5x5x5 mm by a diamond cutter in machine oil, was placed on the tungsten base rod. The temperature of the specimen was measured by optical pyrometer through a viewing port and also by Pt/Rh thermocouple attached to the sample. The experiment was made in a vacuum of about 10^{-4} mmHg. At the lowest temperature, the compressive stress was applied to the specimen at the constant stress load, 100 Kg/cm^2/sec, up to 700 Kg/cm^2. Then the stress released by primary creep of the specimen was measured against the time by means of the external-stress applying device. After the experiment, the residual stress was completely removed from the specimen, and then the specimen was heated to a higher temperature to remove the residual strain. After keeping at this temperature for 30 min, the stress was applied again in the same manner as before.

Hot hardness for the three samples was also measured with high-temperature micro-hardness tester EOF (Nippon Kogaku Co. Ltd.). The specimen of 5x5x5 mm in size was placed in a tantulum holder and heated in a vacuum. About five different impressions were made on the surface of the material grains by a diamond pyramid indentor; and the D. P. hardness was measured at the respective temperatures.

III. Results and Discussion

The amount of stress relaxation a_0-a vs. the relaxation time t are shown in Fig. 4, where a_0 is the initial stress and a the stress at time t. As seen in the figure, the amount of stress relaxation decreases with increase of the US content and with decrease of the temperature. Primary creep ceases in between 100 and 500 sec, followed by the secondary creep. The portion of curve for the primary creep is in a linear relation, and the respective curves converge at the delay time t_0 on the horizontal axis of relaxation time.

The results of hot hardness test are shown in Fig. 5. The hardness in the matrix of samples increases with increase of the US content, and decreases with increase of the temperature, the tendency being similar to the case of primary creep. It is to be noted that the effect of US addition appears remarkably at the high temperatures. As thus seen, the strength of UC matrix increases largely by addition of the US, especially at high temperature.

For the three samples, the primary creep phenomenon can be given in logarithmic expression, as follows:

$$a_0 - a = K \ln(1+t/t_0) \qquad (1)$$

and when $t \gg t_0$,

$$d(a_0 - a)/d(\ln t) = K \qquad (2)$$

where K is a constant indicating the primary creep strength

which is independent of the relaxation time.   The values of
K obtained as the slopes of curves in Fig. 4 are shown against
the temperatures, in Fig. 6.   It is seen that the value of K
increases with increase of the US content and with increase of
the temperature.   R. Chang[8] studied the stress relaxation
of polycrystalline uranium carbide, and expressed the constant
K as

$$K = 2.303 \frac{kT}{\mathscr{G}} + \text{a constant} \qquad (3)$$

where k is the Boltzman constant, T the absolute temperature
and $\mathscr{G}$ the activation volume.   The volume $\mathscr{G}$ corresponds to
the region of sample in which the dislocation has occurred and
moved due to the stress, whereby the primary creep is then
caused.   Therefore, this volume provided an indication of
the mechanical strength of materials.

Assuming that $\mathscr{G}$ in Eq. (3) is not dependent on the tem-
perature, the differenciation of K with respect to T is given
as

$$dK/dT = 2.303k/\mathscr{G} \qquad (4)$$

In applying Eq. (4) to Fig. 6, it is seen that the dK/dT is
not constant but decreases with the temperature.   Thus the
activation volume is found to be a function of the temperature.
The reciprocal activation volume $1/\mathscr{G}$ is then plotted against
the temperature in Fig. 7.   It is seen that the reciprocal
activation volume decreases linearly with increasing tempera-
ture above 1093°K for sample UC and UC-3.2 w/o US, but not

so for sample UC-8.0 w/o US. In the case of the latter sample, the curve deviates from the straight line, which is considered to be the effect of the excess US at high temperature. The activation volumes for the three samples ranged from about 2×10^{-21} to 1×10^{-20} cm^3, and this range agrees with the results by R. Chang.

The results in Fig. 7 can be formulated as

$$\begin{aligned}
1/\beta &= 8.1 \times 10^{20} - 2.9 \times 10^{17} T \quad \text{for UC} \\
1/\beta &= 10.9 \times 10^{20} - 5.5 \times 10^{17} T \quad \text{for UC-3.2w/oUS} \\
1/\beta &= 15.5 \times 10^{20} - 9.7 \times 10^{17} T \quad \text{for UC-8.0w/oUS}
\end{aligned} \quad (5)$$

where the third equation corresponds to the straight line in the figure. For all the specimens, the lines of $1/\beta$ converge at 1093°K. Substituting Eq. (5) into Eq. (3), the value K is in parabolic form:

$$\begin{aligned}
K &= 2.303 kT (8.1 \times 10^{20} - 2.9 \times 10^{17} T) + \text{a constant} \quad \text{for UC} \\
K &= 2.303 kT (10.9 \times 10^{20} - 5.5 \times 10^{17} T) + \text{a constant} \quad \text{for UC-3.2w/oUS} \\
K &= 2.303 kT (15.5 \times 10^{20} - 9.7 \times 10^{17} T) + \text{a constant} \quad \text{for UC-8.0w/oUS}
\end{aligned} \quad (6)$$

As described already, the activation volume is a function of the temperature and the US content. However, in order to clearify the effect of US addition to UC on the primary creep strength, further studies have to be made under various stress conditions.

III. Conclusion

The followings were revealed for the primary creep strength of three samples UC, UC-3.2 w/o US and UC-8.0 w/o US.

1) The stress relaxation curve for the samples can be expressed in logarithmic form;

$$\sigma_0 - \sigma = K \ln(1 + t/t_0)$$

where σ_0 is the initial applied stress, σ the stress at time t, K the constant independent of the time and t_0 the delay time for the primary creep.

2) The value K equal to $d(\sigma_0 - \sigma)/d(\ln t)$ with $t/t_0 \gg 1$, is a function of the temperature, and can be given in parabolic form:

UC: $\quad K = 2.303kT(8.1 \times 10^{20} - 2.9 \times 10^{17}T) + $ a constant

UC-3.2w/oUS: $K = 2.303kT(10.9 \times 10^{20} - 5.5 \times 10^{17}T) + $ a constant

UC-8.0w/oUS: $K = 2.303kT(15.5 \times 10^{20} - 9.7 \times 10^{17}T) + $ a constant .

3) The primary creep strength of uranium monocarbide increases with increase of the US content.

4) The activation volume varies with temperature and the US content. The values calculated are from about 2×10^{-21} to 1×10^{-20} cm^3, which agrees with the result by R. Chang.

5) The D. P. hardness of the UC matrix is increased considerably by addition of the US, and this effect of the addition appears noticeably at the high temperatures.

Acknowledgment

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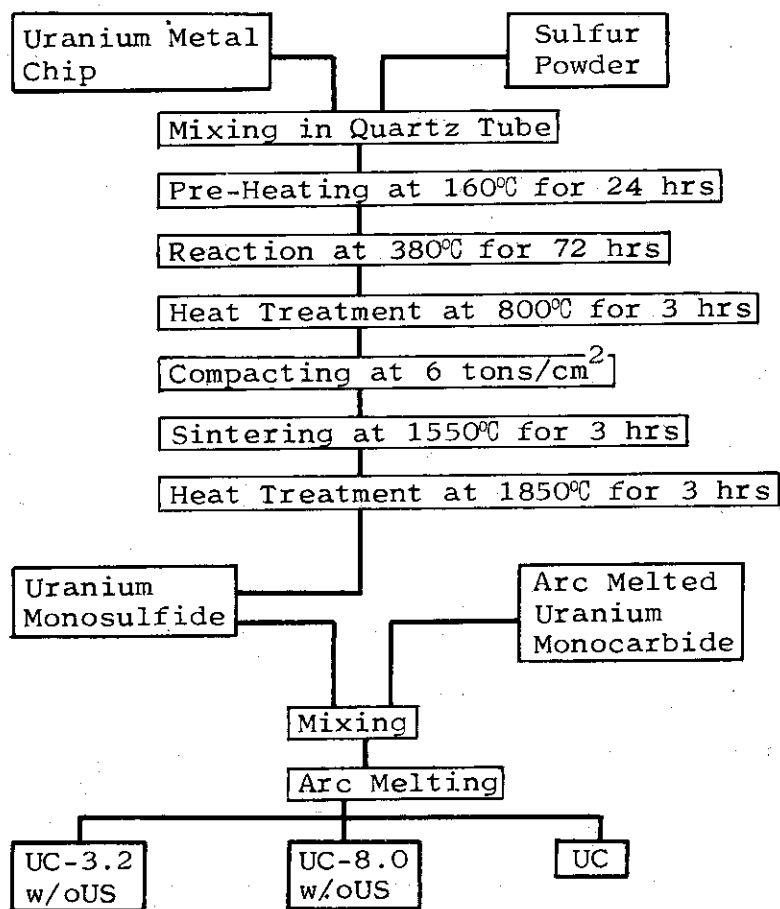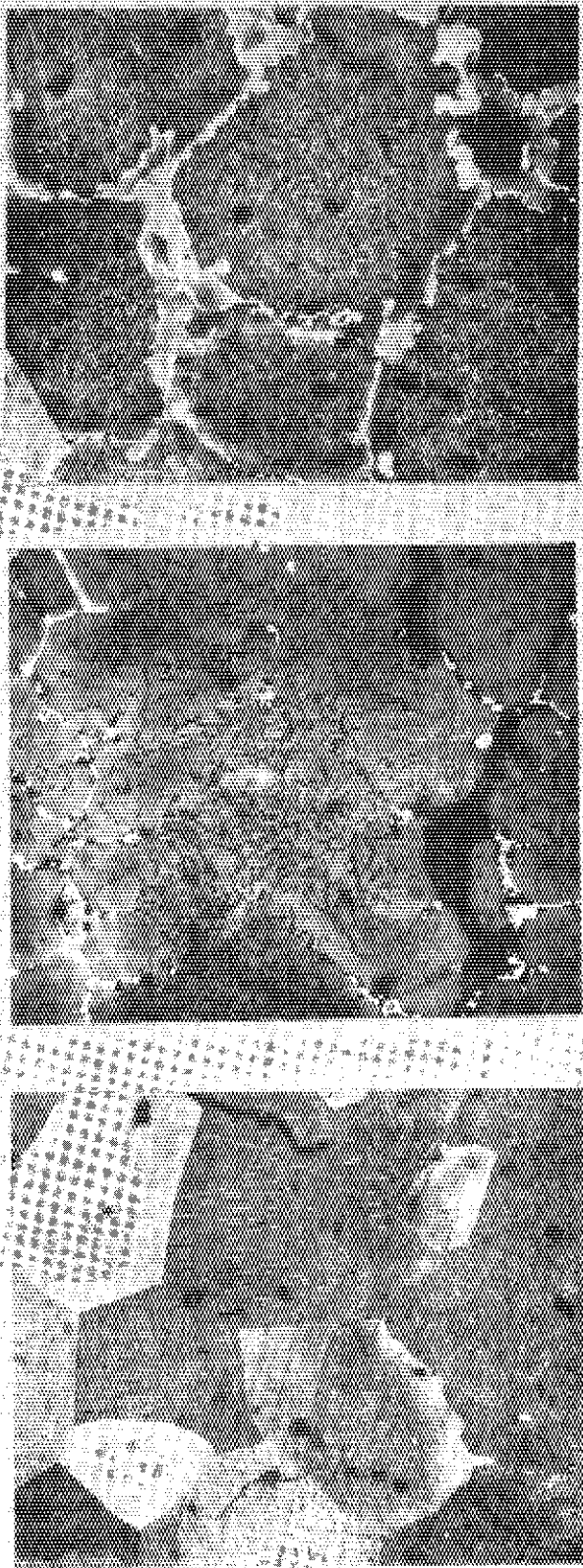
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┌──────────────────┐                    ┌──────────────┐
│ Uranium Metal    │                    │  Sulfur      │
│ Chip             │                    │  Powder      │
└──────────────────┘                    └──────────────┘
         ┌─────────────────────────────────────┐
         │ Mixing in Quartz Tube               │
         └─────────────────────────────────────┘
         ┌─────────────────────────────────────┐
         │ Pre-Heating at 160℃ for 24 hrs      │
         └─────────────────────────────────────┘
         ┌─────────────────────────────────────┐
         │ Reaction at 380℃ for 72 hrs         │
         └─────────────────────────────────────┘
         ┌─────────────────────────────────────┐
         │ Heat Treatment at 800℃ for 3 hrs    │
         └─────────────────────────────────────┘
         ┌─────────────────────────────────────┐
         │ Compacting at 6 tons/cm²            │
         └─────────────────────────────────────┘
         ┌─────────────────────────────────────┐
         │ Sintering at 1550℃ for 3 hrs        │
         └─────────────────────────────────────┘
         ┌─────────────────────────────────────┐
         │ Heat Treatment at 1850℃ for 3 hrs   │
         └─────────────────────────────────────┘

┌──────────────┐                        ┌──────────────────┐
│ Uranium      │                        │ Arc Melted       │
│ Monosulfide  │                        │ Uranium          │
│              │                        │ Monocarbide      │
└──────────────┘                        └──────────────────┘
              ┌──────────┐
              │ Mixing   │
              └──────────┘
              ┌──────────────┐
              │ Arc Melting  │
              └──────────────┘
    ┌──────────┐   ┌──────────┐      ┌──────┐
    │ UC-3.2   │   │ UC-8.0   │      │ UC   │
    │ w/oUS    │   │ w/oUS    │      └──────┘
    └──────────┘   └──────────┘
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Fig. 1 Flow chart for preparation of the sample
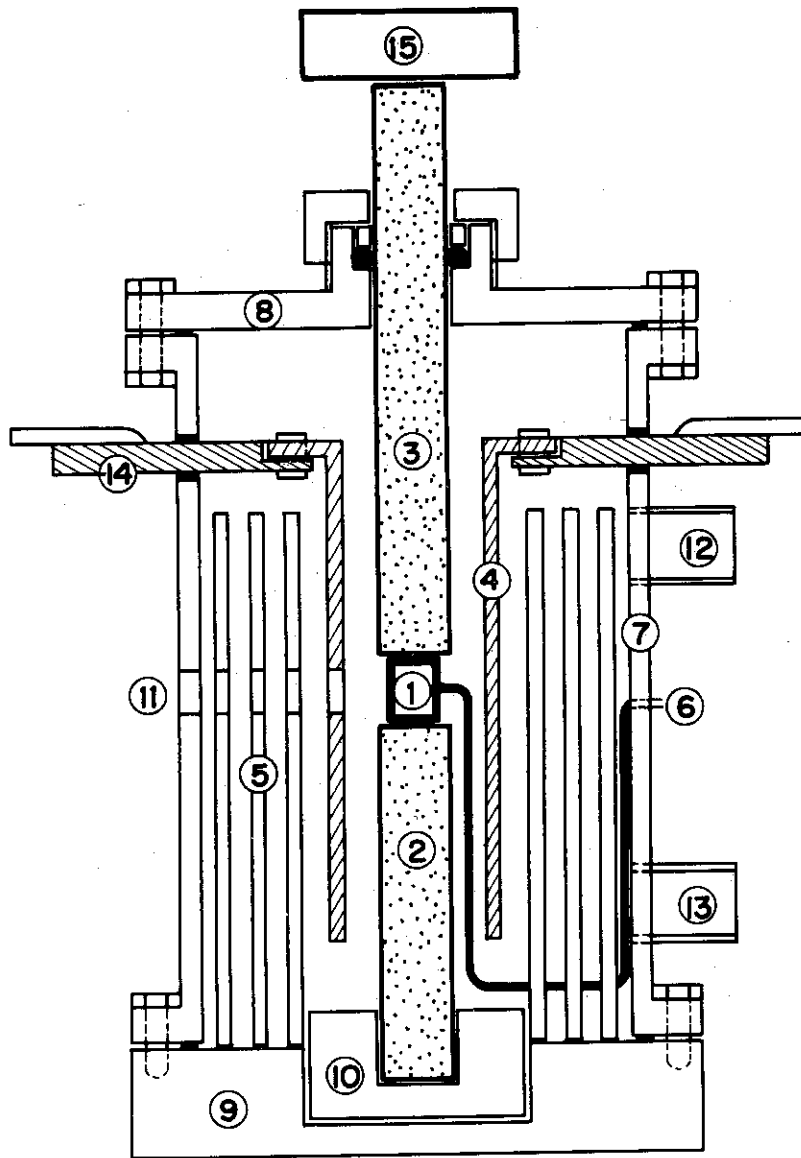
(a) UC   (b) UC-3.2w/oUS   (c) UC-8.0w/oUS

Fig. 2 Microphotographs of the samples UC, UC-3.2w/oUS and UC-8.0w/oUS used in the experiments

Fig.3 Experimental apparatus for the measurement of primary creep strength

1 : sample
2 : W-base rod
3 : W-push rod
4 : Mo-heater
5 : Mo-radiation shield
6 : Pt/Rh thermocouple
7 : SUS-bessel
8 : upper cover
9 : lower cover
10 : spacer
11 : viewing port
12 : gas out-let
13 : gas in-let
14 : elevtrode
15 : pushing machine
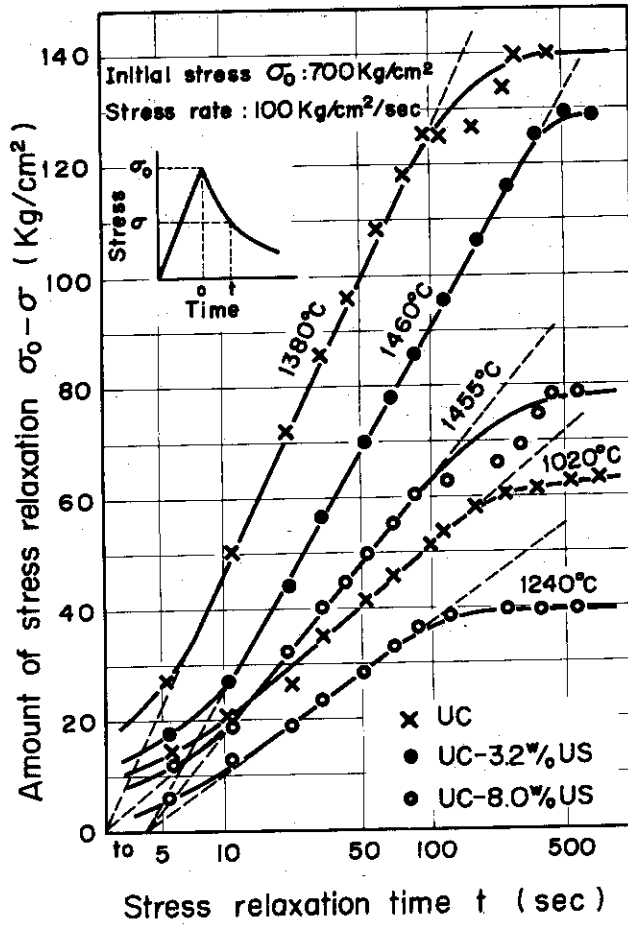
Fig.4 Typical results of the primary creep
strength against relaxation time
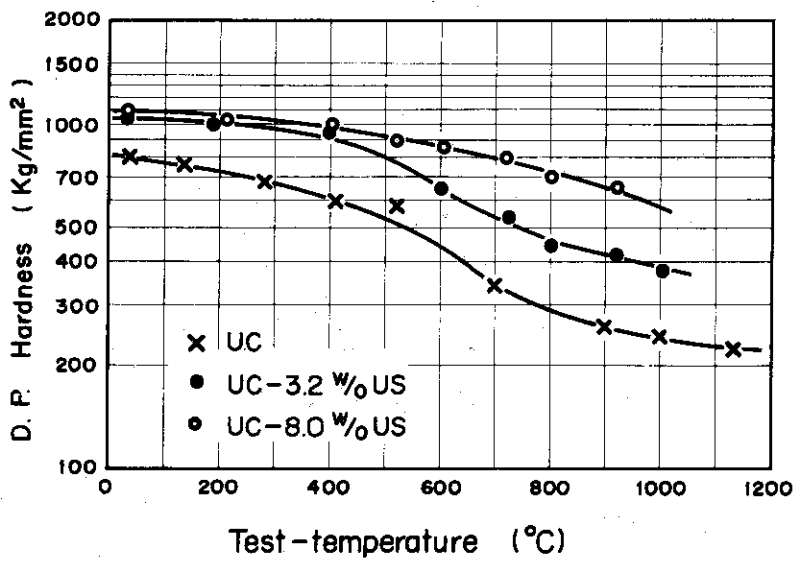
Fig.5 The changes of hot-hardness against temperature
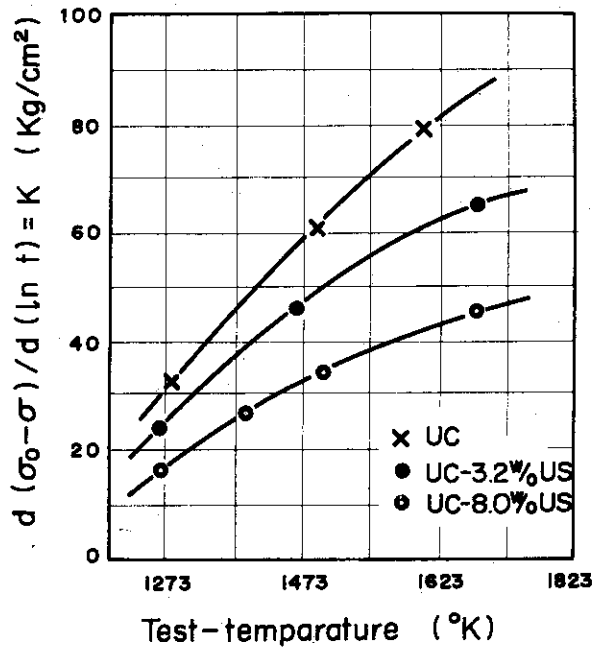
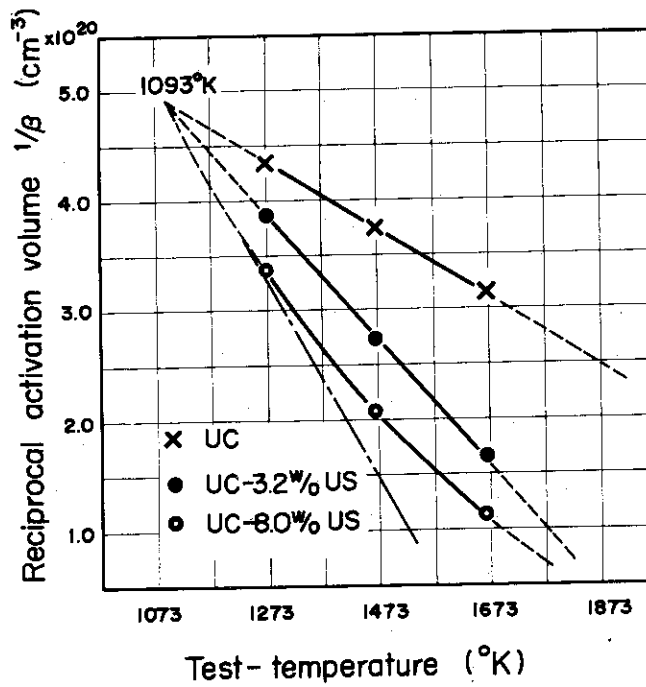Fig.6   The relationship between K-value and test
        temperature

Fig.7   Reciprocal activation volume against test
        temperature