

OXIDATION BEHAVIOR OF U-10 at% Zr ALLOY IN AIR AT 300-500 °C

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(Received 18 November 1997 • accepted 1 June 1998)

Abstract – The oxidation behavior of U-10 at% Zr alloy was studied using an X-Ray Diffractometer (XRD) and a thermogravimetric analyzer in the temperature range from 300 to 500 °C in air. From XRD, Infrared Spectroscopy (IR) and chemical analysis studies it was found that U-Zr alloy after complete oxidation was converted to U_3O_8 and ZrO_2 broken into several pieces of thin plates and some blocks. From the slope value ($1/n=0.562-0.872$) of the log-log plots of the weight gain against time, the oxidation kinetics was analyzed by a parabolic equation. The activation energy of 20 % conversion of U-Zr alloy to U_3O_8 and ZrO_2 was 57.02 kJ/mol and the oxidation rate per unit time and area was obtained to be :

$$dw/dt = 1.41 \times 10^6 e^{\left(\frac{-57.02 \text{ kJ/mol}}{RT}\right)} \text{ mg/min-cm}^2,$$

where w, t and T are weight gain, time and temperature, respectively.

Key words : Oxidation Behavior, U-10 at% Zr Alloy, XRD

INTRODUCTION

Uranium is used in a variety of applications because of its very high density (19.1 g/cm^3) and unique nuclear properties. However, unalloyed uranium exhibits poor corrosion resistance and sometimes undesirable combinations of strength and ductility. It is known that uranium alloyed with small quantities of elements such as titanium, molybdenum, niobium, and/or zirconium enhances the mechanical properties and corrosion resistance without greatly reducing its density. There have been some efforts to develop a new fuel material by replacing HEU (high enriched uranium) with LEU (low enriched uranium) to enhance what was enhanced in the research reactor. The U-Zr binary alloy is an important subsystem of the U-Pu-Zr ternary alloy, which has been recently recognized as a promising metallic nuclear fuel for the fast breeder reactor.

A knowledge of the oxidation behavior of U-Zr alloy is required to evaluate stability in long-term storage and disposal of spent fuels and to stabilize the metal chip waste which is generated during its manufacturing. There have been many studies on the oxidation of uranium metals [Loriers, 1959; Leibowitz et al., 1991a,b; Baker and Bingle, 1966; Bennett et al., 1974, 1975; Bennett and Myatt, 1977; Ritchie, 1981], UO_2 [Aronson et al., 1957; Kang et al., 1997; Scott and Harrison, 1963; Donald et al., 1992; Bae et al., 1994; You et al., 1995] and some uranium alloys [Antill and Peakall, 1961; Greenholt and Weirick, 1987; Kang et al., 1996; Barnartt et al., 1957; Matsui et al., 1993; Matsui and Yamada, 1994; Rama et al., 1994]. Loriers [1959] carried out the research on the oxidation of

metallic uranium. He reported that the rate of oxidation of uranium was nearly parabolic with temperatures at ordinary temperatures and was linear at burning temperatures. Leibowitz et al. [1961a,b] studied the oxidation rates in the temperature range from 125 to 250 °C in the oxygen pressures between 20 and 800 mmHg. They revealed some differences in oxidation behavior between the electropolished and the mechanically polished uranium samples. Bennett et al. [1974, 1995; Bennett and Myatt, 1977] carried out an experiment to investigate the influence of aluminum content and water vapor on uranium oxidation in air. They also investigated the influence of swelling on the rate of oxidation of irradiated and unirradiated uraniums by comparing with each other. There was no significant influence when the content of aluminum was 500-1,550 ppm. Ritchie [1981] reviewed the reactions of uranium with oxygen and water vapor under various conditions. He reported that the rate of reaction was strongly dependent on the nature of the uranium surface, i.e., on the thickness, adherence and stoichiometry of the surface oxide-layer and among various techniques to measure the rate of uranium corrosion weight gain measurements were the most common. Aronson et al. [1957] reported that UO_2 powder was oxidized up to $UO_{2.34}$ at temperatures below 260 °C, while above 260 °C UO_2 was oxidized up to U_3O_8 by a two step reaction through the phase U_3O_7 . Kang et al. [1997] carried out an oxidation experiment for UO_2 pellets in air at 300-550 °C. Scott and Harrison [1963] carried out the oxidation of uranium dioxides prepared by various methods in air at temperatures up to 800 °C. Bae et al. [1994] studied the oxidation behavior of unirradiated UO_2 pellets at 400 °C to characterize the oxidized powder and to establish a new spallation model. You et al. [1995] studied and compared the oxidation behaviors of irradiated and unirradiated UO_2 in the range of 250-400 °C. The oxidation rate

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of the irradiated uranium dioxide was higher than that of un-irradiated. Antill and Peakall [1961] reported for the oxidation of uranium alloys in carbon dioxide and in air that additions of titanium, molybdenum, niobium and copper reduced the attack in air at 500°C by factors up to 200, whereas the silicon alloys had a high rate of attack in carbon dioxide at most temperatures. Greenholt and Weirick [1987] carried out the oxidation of uranium-0.75 wt% titanium in environments containing oxygen and/or water vapor at 140°C. They reported that U-0.75 wt% Ti reacted with oxygen to form uranium dioxide and the reaction rate which was approximately 3.2×10^{-3} mg/cm²·h was linear and independent on the oxygen partial pressure between 0.067 and 133.3 kPa. Barnartt et al. [1957] carried out the oxidation of 50 wt% uranium-zirconium alloy with oxygen gas at 1 atm pressure over the range of 200-500°C. They reported that the alloy oxidized somewhat more rapidly than pure Zr, but very much more slowly than uranium. Matsui et al. [1993; Matsui and Yamada, 1994] investigated the oxidations of U-10 at% Zr and U-20 at% Zr in air at 432-1,028 K and 423-1,063 K, respectively. Rama Rao et al. [1994] observed the oxidation behavior of U-Zr alloys having different concentrations from 10 to 90 wt% Zr in atmospheric condition. The reaction rate decreased with the concentration of Zr.

In the present paper, the oxidation behavior of U-10 at% Zr alloy was studied by XRD and thermogravimetry in the temperature range of 300-500°C in air for evaluating stability in the long-term storage and disposal of spent fuels. An oxidation rate equation was proposed and verified by the results of XRD for oxidized product. The activation energy and the preexponential factor in the reaction rate equation for the oxidation of U-10 at% Zr alloy were determined.

EXPERIMENTAL

1. Materials

Specimens having the dimensions of 11.45 mm in diameter and 0.85-1.05 mm in thickness were prepared by cutting off an ingot of U-10 at% Zr alloy made by induction melting with depleted uranium and zirconium metal at 1,650°C under 0.133 Pa for 10 min. The initial average weight and surface area of the specimen were 1,361 mg and 240.1 mm², respectively. Before testing, the specimens were abraded with a 600 grit silicon-carbide paper, washed in acetone under an ultrasonic cleaner and rinsed with ethyl alcohol. All the specimens were stored in a dry environment and tested with their surfaces covered with oxide films formed in air at room temperature.

2. Apparatus

The experimental apparatus (thermogravimetric analyzing device) for oxidation mainly consists of a furnace, an electric balance, a control and data acquisition system and a conditioning system for the furnace. Fig. 1 is a schematic diagram of the apparatus. Temperature of the furnace could be controlled with any mode of heating by a programmable microprocessor. The crucible was made of alumina to avoid reaction of the specimen with the crucible during the experiment.

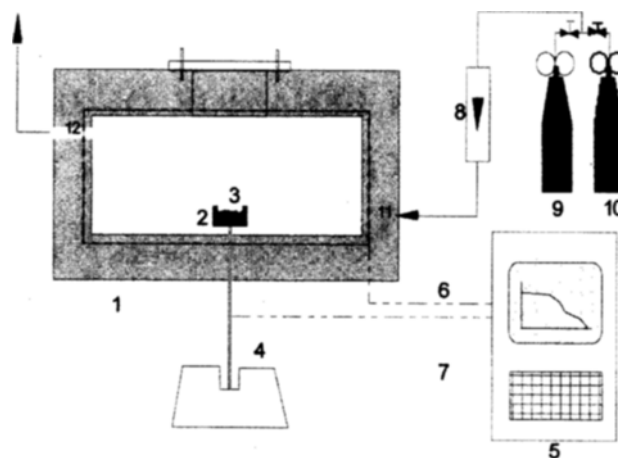


Fig. 1. A schematic diagram of the thermogravimetric furnace.

- | | | |
|-------------|-------------------|-------------------|
| 1. Furnace | 5. Computer | 9. Argon canister |
| 2. Crucible | 6. Temp. control | 10. Air canister |
| 3. Sample | 7. Data record | 11. Gas inlet |
| 4. Balance | 8. Flow regulator | 12. Gas outlet |

3. Experimental Procedure

The specimens were contained in alumina crucibles and heated up to the test temperature in a flow of purified argon before the oxidation. While the oxidation tests were performed, the oxidant, air, was continuously injected. The weight gains of the specimens were measured by microbalance having a load-carrying capacity of 5 g of samples and sensitivity of 1 µg; the data were automatically acquired and stored along with the time and the temperature during the oxidation. The flow rate of oxidizing gas was 10 l/min at an atmospheric pressure.

RESULTS AND DISCUSSION

1. Reaction and XRD Patterns

It is generally known that a specimen of uranium and its alloy are broken and pulverized during oxidation due to the volume change resulting from the phase transformation of uranium to the intermediate phases and finally U₃O₈. Baker and Bingle [1966] reported for metallic uranium that in the low temperature region below 400°C, there was a thin adherent layer, covered by an oxide which is loose and flaky tending to form well-defined plates. For the high temperature runs above 625°C, the underlying oxide was very adherent, but appeared somewhat sintered, while the surface oxide powdered off quite readily.

In this study, the specimens broke into several pieces of thin plates and blocks. After complete oxidation, the change in the specimen shape observed in this study was similar to that of pure uranium metal and U-20 at% Zr alloy, respectively, as reported by Baker and Bingle [1966] and Matsui et al. [1993]. But this result is different from that observed in our previous study for the oxidation of UO₂ in air at 300-550°C [Kang et al., 1997]. For UO₂ the specimen after complete oxidation at the temperature range from 300 to 550°C broke into fine powder. Typical examples of the specimen shape after complete oxidation at 350, 450 and 500°C in air

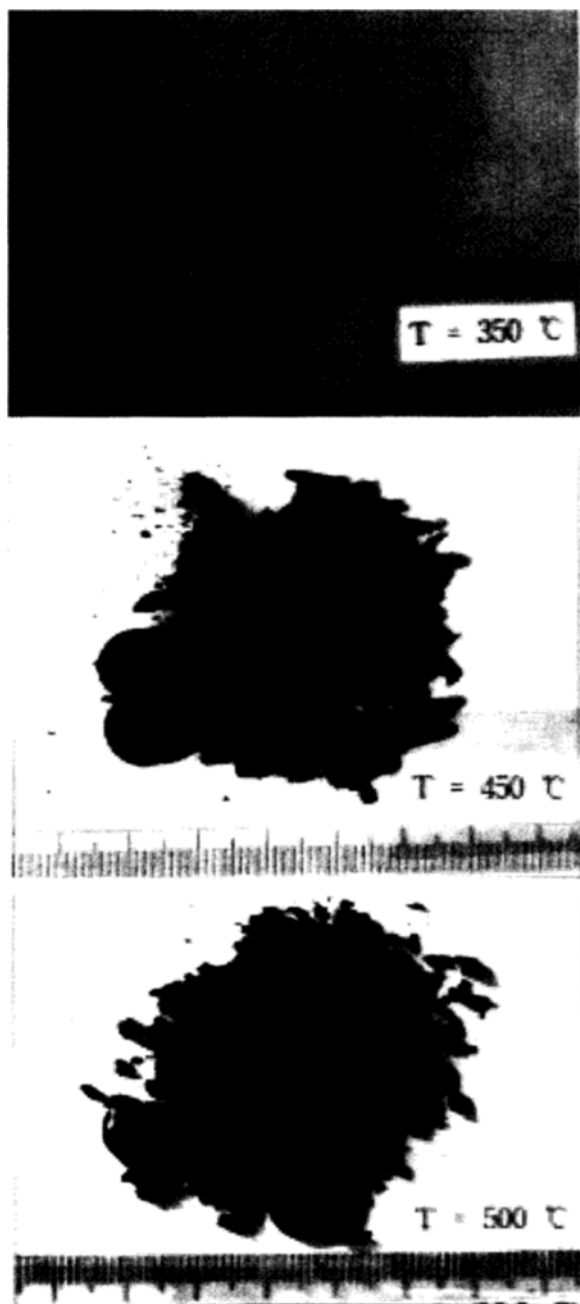


Fig. 2. Shapes of the specimens after complete oxidation in air at 350, 450 and 500 °C.

are shown in Fig. 2.

Ritchie [1981] reported in his review of the reaction rates of uranium with oxygen and water vapor that uranium reacted with oxygen according to the following equation:



He also reported that at temperatures up to 200 °C, the oxide formed was hyperstoichiometric uranium dioxide with x in the range of 0.2 to 0.4, while U_3O_8 was formed at higher temperature (>275 °C). In our previous study for oxidation of U_3Si in air [Kang et al., 1996], U_3Si reacted with oxygen

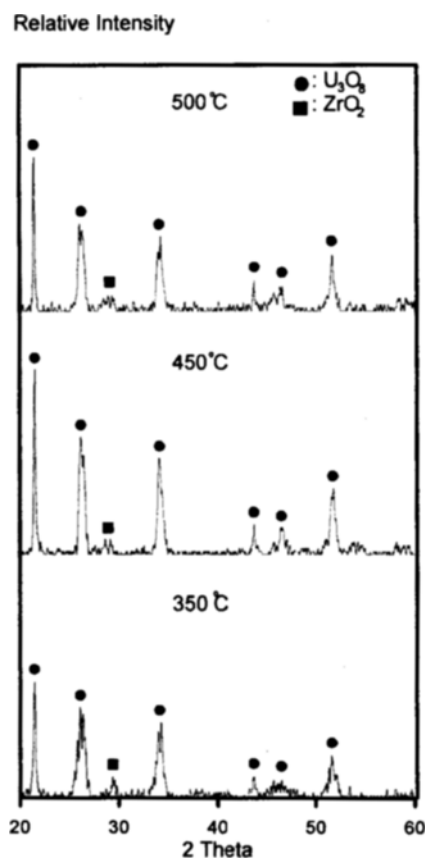
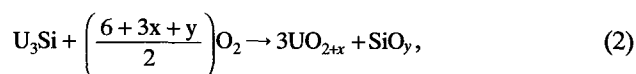
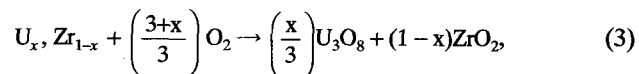


Fig. 3. XRD patterns of products after complete oxidation.

according to the following equation :



U_3Si was converted to UO_2 , U_2O_5 and Si after 200 hours at temperatures up to 275 °C and UO_2 , U_3O_7 , SiO and SiO_2 after 400 hours at the temperature of 300 °C. U_3O_8 began to be detected at temperature 325 °C. Rama Rao et al. [1994] reported for U-Zr alloy that U-Zr alloy reacted with oxygen according to the following equation :



From Eq. (3) U-10 at% Zr alloy were supposed to react with oxygen in the temperature range from 300 to 500 °C according to the following equation:

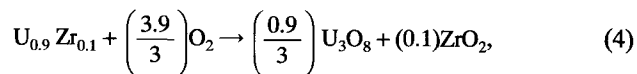


Fig. 3 shows the XRD, IR and chemical analysis results after oxidation at temperatures of 350, 450 and 500 °C, respectively. From these XRD patterns it was confirmed that U-10 at% Zr alloy was converted to U_3O_8 and ZrO_2 by oxidation.

2. Oxidation Rates

The oxidation rates of uranium and its alloys have been analysed by various equations such as linear, parabolic and parabolic, depending on oxidation conditions. The factors that

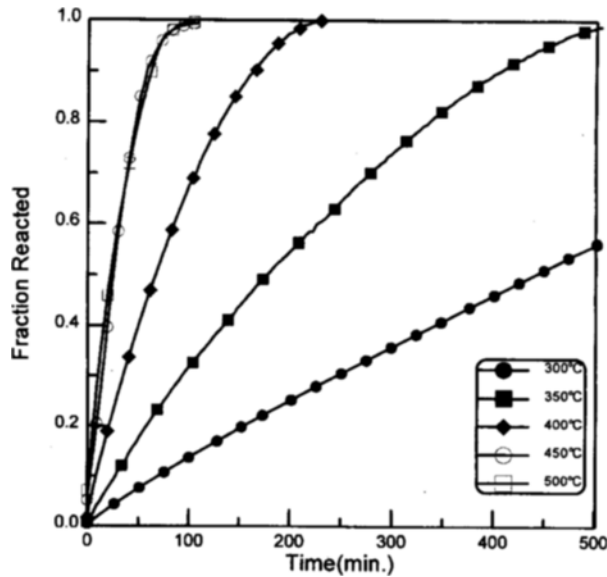


Fig. 4. Fraction reacted-time curve for the oxidation of U-10 at% Zr in air at 300-500 °C.

affect the oxidation rate are temperature, moisture content, impurity, oxygen potential, roughness of surface, surface area versus volume ratio, irradiation-induced swelling and so on. Bennett et al. [1974, 1975; Bennett and Myatt, 1977] reported that temperature had the most pronounced effect and the temperature change from 50 to 300 °C increased the rate of oxidation by a factor of over 10^6 . Matsui and Yamada [1994] reported for U-10 at% Zr that the oxidation kinetics was able to be analyzed by a parabolic equation in the low temperature region below 242 °C and a linear equation in the middle and high temperature regions above 455 °C. Rama Rao et al. [1994] reported for U-Zr alloy that the reaction rate was linear in the case of alloy samples containing Zr up to 31.2 at%. Fig. 4 shows oxidation data obtained in this study over the temperature range of 300-500 °C. At 300 °C the rate of oxidation was nearly linear, and for the temperature range higher than 350 °C the rates decreased with time. This is because the product layer formed at an initial stage of the reaction is not very porous and acts as a protective barrier to the entry of oxygen. Therefore, the oxidation process can be said to be controlled by the diffusion of oxygen into the surface of the solid phase rather than chemical surface reaction kinetics as one of the typical phenomena of the solid-gas reaction at the temperatures used in this study. The weight gain (mg/cm^2), Δw , during oxidation is plotted against time (t) in log-log scale in Fig. 5. The slopes of the lines in the figure, n , were obtained from the following empirical rate law:

$$\Delta w^n = kt, \quad (5)$$

where t is time (min) and k is a constant for each temperature. In this study, the slopes, $1/n$, were determined to be 0.562-0.872 depending on temperature. Thus, the oxidation kinetics can be described by an equation containing the parabolic ($1/n=0.5$) and linear ($1/n=1$) terms, which is known as a parabolic equation as follows [Matsui et al., 1993; Matsui and Yamada, 1994]:

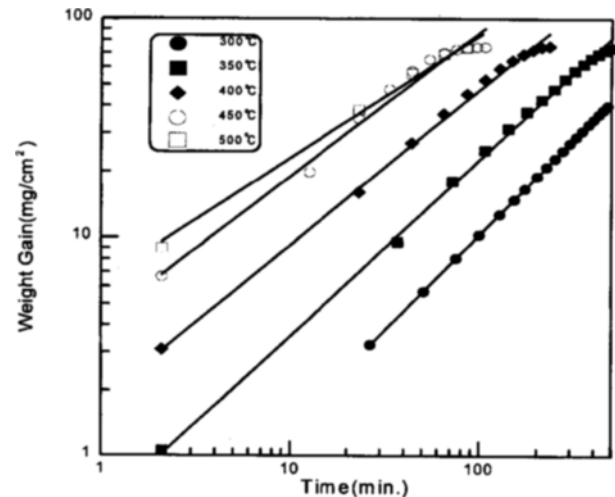


Fig. 5. Time dependence of the weight gain at 300-500 °C.

$$\Delta W = k_p t^{1/2} + k_l t + c, \quad (6)$$

where k_p and k_l are the parabolic rate constant (diffusion-controlled mechanism) and the linear rate constant (surface reaction-controlled mechanism), respectively and c is a constant. The values of k_p and k_l calculated from Eq. (6) are presented in Table 1. To observe the reaction rates of U-10 at% Zr versus temperature, the reaction rates at weight gains equating to 20 % and 40 % of the specimen weight are shown in Table 2. The weight gain per unit time and area at 20 % weight gain against the inverse of temperature is plotted and shown in Fig. 6. With an Arrhenius type of expression for

Table 1. Reaction rate constants for the oxidation of U-10 at% Zr in air

Temp. (°C)	Rate constant	
	k_p ($\text{mg}/\text{cm}^2\text{-min}^{1/2}$)	k_l ($\text{mg}/\text{cm}^2\text{-min}$)
300	0.373	6.761×10^{-2}
350	2.689	4.734×10^{-2}
400	3.931	1.360×10^{-1}
450	2.844	8.198×10^{-1}
500	5.082	4.399×10^{-1}
370 [19]*	0	2.67×10^1
410 [19]*	0	6.28×10^1
450 [19]*	0	1.10×10^2
502 [19]*	0	7.35×10^1
242 [20]**	1.080	5.21×10^{-1}
455 [20]**	0	9.46×10^1

*U-20 at% Zr

**U-10 at% Zr

Table 2. Oxidation rates of U-10 at% Zr in air

Temp.	Rate of oxidation, $\text{mg}/\text{cm}^2\text{-min}$		
	20 %	40 %	U [Baker and Bingle, 1996]
300	0.085	0.076	0.066
350	0.237	0.204	0.350
400	0.550	0.476	1.370
450	1.247	1.458	1.270
500	1.717	1.240	1.460

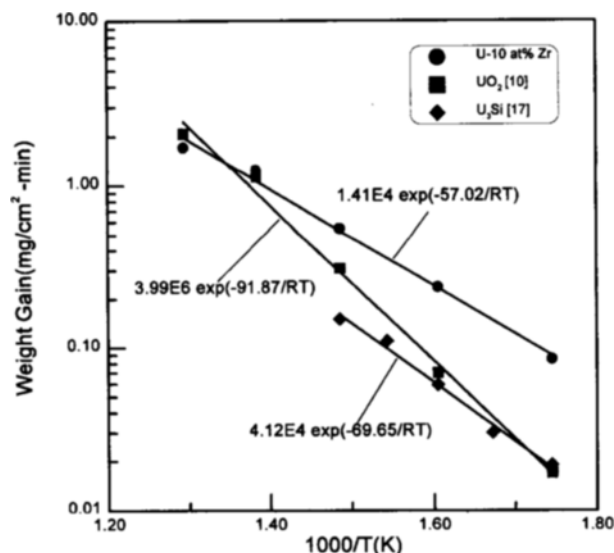


Fig. 6. Rate of weight gain versus $1000/T$.

the rate equation, the frequency factor and activation energy were calculated. Activation energy for the 20 % weight gain was 57.02 kJ/mol in the temperature range 300-500°C. Ritchie [1981] reported for uranium metal in his review of the reaction rates of uranium with oxygen that the activation energy in the temperature range 40-300°C is 75.312 kJ/mol. In our previous study [Kang et al., 1996, 1997] the activation energy of UO_2 in the temperature range 300-500°C was 91.87 kJ/mol and the activation energy of U_3Si in the temperature range 300-400°C was 69.73 kJ/mol. The activation energy of U-10 at% Zr was smaller than that of UO_2 which was obtained at the same experimental condition. In this study, the reaction rate per unit time and area can be expressed as follows:

$$dw/dt = 1.41 \times 10^6 e^{\left(\frac{-57.02 \text{ kJ/mol}}{RT}\right)} \text{ mg/min-cm}^2 \quad (300 \leq T(^{\circ}\text{C}) \leq 500), \quad (7)$$

where w , t and T are weight gain, time and temperature, respectively.

CONCLUSION

Analyses of XRD patterns and thermogravimetry in order to observe the oxidation behavior of U-10 at% Zr pellet have been carried out and the following conclusions are made.

1. The specimens after complete oxidation break into several pieces of thin plates and blocks.
2. From XRD, IR and chemical analysis studies, U-10 at% Zr alloy is converted into U_3O_8 and ZrO_2 in the temperature range of 300-500°C
3. From thermogravimetry analysis, the oxidation kinetics is parabolic.
4. The activation energy of 20 % weight gain is 57.02 kJ/mol and the oxidation rate per unit time and area is found:

$$dw/dt = 1.41 \times 10^6 e^{\left(\frac{-57.02 \text{ kJ/mol}}{RT}\right)} \text{ mg/min-cm}^2,$$

where w , t and T were weight gain, time and temperature, respectively.

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