JAERI-M
89-150

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October 1989

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編集兼発行　日本原子力研究所
印　　刷　山田軽印刷所

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(Received September 21, 1989)

Isothermal annealing tests with an alloy of 80% silver, 15% indium and 5% cadmium were performed in flowing argon atmosphere at temperatures ranging from 1073 to 1673 K to improve the understanding the vaporization behavior of the control rod material during the severe accidents of PWRs.

The alloy melted in the temperature range between 1123 and 1173 K. And very little vaporization was measured below the melting temperature. The weight loss due to vaporization was 0.5% at 1123 K and 8.2% at 1673K for the annealing time of 3600 s. Cadmium was completely released from the alloy at temperatures above 1173 K, while silver was not released below 1473 K. Cadmium was the most volatile and silver was the least volatile element of the alloy in the examined condition. The tests results indicated that both the release rate of component elements and the total amount of release were strongtly time-dependent.

Keywords: Ag-In-Cd, Control Rod, PWR, Severe Accident,
High Temperature, Vaporization, Release, Aerosol

アルゴン中における銀－インジウム－カドミウム制御棒材の高温蒸発

日本原子力研究所東海研究所燃料安全工学部
上塚　寛・大友　隆

（1989年9月21日受理）

加圧水型軽水炉のシビアアクシデント時における制御棒材料の蒸発挙動を調べるために，80％銀－15％インジウム－5％カドミウム合金を，アルゴン中で1073 K～1673 Kの温度に加熱し，60～3600秒間等温保持した。この合金の溶融温度は，1123 K～1173 Kの範囲であり，溶融温度より低い温度での蒸発量は極めて少量であった。高温における等温保持時間3600秒という条件に対して，蒸発による試料の重量減少は，1123 Kで0.5％，1673 Kで8.2％であった。カドミウムは，試料を1173 K以上に昇温させた場合，100％放出された。一方，銀は1473 K以下の温度では全く放出されなかった。試験条件の範囲においては，この合金の構成元素のうちで最も揮発性の高いのはカドミウムであり，低いのは銀であることが確かめられた。試験結果は，元素の放出速度と全放出量の時間依存性が強いことを示した。

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1. Introduction

In an unmitigated severe reactor accident, the fuel assembly may reach temperatures up to the melting points of Zircaloy cladding and fuel. A large quantity of fission product release is then expected in the reactor core. The fission product release and transport behavior is therefore one of the highly important items to be evaluated for the severe accident analyses of light water reactors(LWRs).

It has been proposed that high density aerosols in the reactor coolant system will interact with fission product vapors and co-agglomerate to attenuate any radioactive release to the environment(1). An alloy of 80% Ag, 15% In and 5% Cd clad in 304 stainless steel is used as control rods in most pressurized water reactors(PWRs). A typical PWR contains relatively much amount of control material in the core. In the Three Mile Island Unit-2(TMI-2) reactor core(2), for instance, there was about 2750 kg of Ag-In-Cd control material with cadmium being the most and silver the least volatile. Cadmium is the most volatile element of the core materials and is considered to be one of the main element of aerosol formation in a severe accident of PWR. Therefore special interest has been paid to the behavior of control material at very high temperatures since the first severe accident in a commercial nuclear power plant at TMI-2 reactor. Both the experimental and the theoretical studies(3)-(7) have already been made on the behavior of the

Ag-In-Cd control rods during severe reactor accident. However, there is still a great deal of uncertainty regarding the nature of the release of control rod materials in accident situations.

This paper describes the results of the silver-indium-cadmium control rod material annealing experiments conducted at temperatures ranging from 1073 to 1673 K in a flowing argon to improve the understanding of the high temperature vaporization behavior.

2. Experimental procedure

2.1 Specimen and apparatus

The chemical composition of the material used in the annealing experiments is listed in **Table 1.** Small disk specimens 2 mm in thickness were cut from PWR size control rod material of 7 mm in diameter. Prior to testing, the specimens were ultrasonically rinsed in acetone for degreasing. The test apparatus consisted of a 38 mm I.D. quartz reaction tube, an infrared furnace which had four tungsten filament heater lamps and a gas supply system as schematically shown in **Fig.1.** The infrared furnace was used in the present experiments because of its excellent capability of both the rapid heating and cooling rates, which allowed a short time isothermal annealing of specimen.

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2.2 Annealing tests

The specimen was set on a quartz holder in the center of the reaction tube in the furnace. Prior to the rapid heating-up of specimen, the apparatus was purged with a high purity argon gas. The specimen was then isothermally annealed in a flowing argon (3.3 ml/s) for a predetermined time between 60 to 3600 s at atmospheric pressure. In each test the temperature was measured with a Pt-Pt/13%Rh thermocouple attached to the specimen holder. The specimens were isothermally annealed at temperatures ranging from 1073 to 1673 K in steps of 50 or 100 K. The weight of each specimen was measured with a direct reading balance before and after annealing test, thereby the weight loss due to vaporization was calculated. Elemental analysis was performed on each residue of annealed samples using an inductively coupled plasma atomic emission spectroscopy(ICP-AES), following dissolution of the sample in 60% nitric acid. The release fraction of each component element was then calculated based on the results of the weight loss measurement and the elemental analysis. The control rod material contains very small amount of impurity elements such as Cu, Zn, Fe and Ni etc. These impurity elements were not analyzed in the present study and neglected in the calculation, since the total percentage of such impurities in the alloy is generally controlled at a negligible small level of about 0.05%(4).

3. Results and discussion

3.1 Weight loss due to vaporization

The extent of vaporization, i.e. total vapor release, at elevated temperatures can be evaluated by the weight loss measurement of annealed specimen. The weight loss of the specimens isothermally annealed in flowing argon at temperatures ranging from 1073 to 1673 K is listed in **Table 2** and is shown in **Fig.2** as a function of annealing time. The weight loss at 1073 and 1123 K are relatively small over the examined time range, e.g. 0.48% at 1073 K and 0.83% at 1123K for 3600 s. In contrast to this, strong change in weight loss with increase of annealing time is found in cases of temperatures above 1173 K. The data at 1173, 1273 and 1373 K show the big change in weight loss in times up to 300 to 900 s, afterwards the weight loss settles on a constant level of about 5%. The change in weight loss is more rapid at temperatures above 1473 K, it reachs about 5% in 60 s. This must be related with the very rapid release of volatile element from the specimen. The weight loss up to 5% is not difficult to imagine, since the specimen used in this experiment contains 5.1% cadmium of which normal boiling point is about 1040 K. The weight loss more than 5% was, however, measured at high temperatures and longer annealing times. This can not be explained without taking account of any additional vaporization of indium and/or silver.

The drastic change in weight loss of annealed specimens found in the temperature range between 1127 and 1173 K must be strongly related with the melting behavior of control rod material. The melting point of this alloy has been reported to be about 1100 K(4),(8). However, no complete melting of the specimen was observed at 1123 K in this study as shown in **Fig.3**. **Figure 3** shows photomicrographs of control rod material samples annealed at 1073, 1123 and 1173 K for 900 s in argon. The cooling rate from the isothermal annealing temperature to 900 K was about 10 K/s for every tests. The specimen annealed at 1073 K maintained its original shape after the test, while the specimen tested at 1123 K was apparently deformed and that heated to 1173 K was spheroidized as shown in the figure. The microstructure of the specimen annealed at 1073 K is a typical recrystalized structure of this alloy and no vestige indicating its melting at test temperature is seen. On the other hand, the microstructure at 1173 K is entirely dendritic, indicating the complete melting of the specimen at the test temperature. The microstructure at 1123 K seems to indicate the partial melting of the specimen. Therefore the melting point of this alloy is probably below 1123 K in a strict sense. However, the actual melting temperature of this alloy, above which the rapid vaporization occurs, is not below 1123 K but between 1123 and 1173 K. This can explain the drastic change in the weight loss observed between 1123 and 1173 K.

The correlation between the weight loss and the annealing temperature is shown in **Fig.4** for three different conditions of annealing time ranging from 60 to 3600 s. The weight loss of specimens annealed at 1073 and 1123 K is less than 1% for all cases of annealing time. The way of change in weight loss with increase in annealing temperature is not the same in every case. For the case of 60 s annealing, the weight loss increases monotonously with an increase in temperature up to 1573 K. On the other hand, it sharply increases between 1123 and 1173 K for the cases of longer annealing times, afterward it settles on a almost constant level or increases gradually with temperature. The weight loss of specimens annealed for 3600 s was always higher than those of 60 and 900 s at every examined temperature. This results clearly indicate that the release rate and the total amount of release are strongly time-dependent.

There are many computer codes applicable for the severe reactor accident analysis. Some of them can calculate the fission products release and transport phenomena in the accident situation. However only a limited number of codes can calculate the release behavior of species from the control rod material. The CORSOR code(9) of STCP(Source Term Code Package) seems to be only one computer code at present which can be applicable for this purpose. In the CORSOR code the control rod release is calculated based on the following method:

(1) The control rods are assumed to fail at 1673 K and 0.05 of the inventory of Ag and In, and 0.5 of the Cd

are released from the nodes reaching this temperature.

(2) In the temperature range from 1673 to 2573 K, the cumulative fraction of the inventory released, F_{rel}, is calculated according to:

$F_{rel}(Ag)=0.0005x(T-1673)+0.05$

$F_{rel}(In)=0.00011x(T-1673)+0.05$

$F_{rel}(Cd)=0.00033x(T-1673)+0.5$

so that at 2573 K, 0.50 of the Ag, 0.80 of the Cd, and 0.15 of the In have been released.

(3) In the higher temperature range from 2573 to 3073 K, the cumulative fractions of the inventory released are calculated according to:

$F_{rel}(Ag)=0.001x(T-2573)+0.5$

$F_{rel}(In)=0.0017x(T-2573)+0.15$

$F_{rel}(Cd)=0.0004x(T-2573)+0.8$

which result in complete release at 3073 K.

This model is an extremely simplified one. No release rate is calculated and no physical process is assumed in the calculations. Although the calculation with this simple model may not be so reliable, it can be used as a first approximation for the comparison with the present data.

The weight loss data obtained for three different conditions of annealing time 60, 900 and 3600 s together with the calculation based on the CORSOR model is shown in **Fig.5** as a function of annealing temperature. As described above, the CORSOR calculation is valid for the temperature range above 1673 K. Therefore the comparison is not necessarily valid for the whole temperature range concerned, only the data at 1673 K is possible to compare. The extent of weight loss due to vaporization must be strongly influenced by some factors such as atmosphere, geometry of specimen and annealing time etc. Nevertheless the calculation with CORSOR model agrees with the present data at 1673 K.

The CORSOR model assumes the element release of control rods from the nodes which reaches at 1673 K. This temperature is based on the investigation(3),(4) on the failure temperature of the control rod cladding, which has been reported to be in the range of temperature between about 1600 and 1700 K. However, when the control rod failure, not only the release from the failure nodes but also the release from the adjacent nodes which reaches the melting temperature of the alloy should be taken into account, since no negligible release could be produced from the control rod material of nodes reaching at least the melting point.

3.2 Elemental vaporization

The vapor pressures of the component elements of the Ag-In-Cd alloy are shown in **Fig.6** as a function of temperature when considered as separate entities(7). The pressure of each element in the figure is the sum of the partial pressure of metal-bearing gases, M(g), $M_2(g)$, $M_3(g)$ and $M^+(g)$. This figure undoubtedly indicates that cadmium is the predominant element in the vapor in the concerned temperature range.

Powers(7) has made the comprehensive theoretical study of the Ag-In-Cd control rods during severe reactor accident. He calculated the speciation of the vapor over a 80% Ag, 15% In and 5% Cd alloy and predicted that the vapor is predominantly cadmium, monatomic Ag(g) and In(g), dimeric $Cd_2(g)$ and the mixed-metal AgIn(g) are the next most abundant species in the vapor. However this has not been confirmed experimentally.

In the present study, the release fraction of the component elements from the heated control rod samples was calculated by combining the results of the weight loss measurement and the elemental analysis. The release fraction, f, is defined by the following equation,

$$f = (W_0 - w)/W_0 \times 100, \qquad (1)$$

where W_0 is the initial inventory of element and **w** is the residual amount of element in the sample.

The calculated release fraction of cadmium is summarized in **Table 3** and is shown in **Figs.7** and **8**. **Figure 7** shows the correlation between the release fraction of cadmium from the samples annealed at temperatures ranging from 1073 to 1673 K and the isothermal annealing time. The release fractions at

1073 and 1123 K was relatively small. They were 7.3% and 15.2%, respectively, for the annealing time of 3600 s. On the other hand, one hundred percent of cadmium was released at temperatures above 1173 K. Not only the release fraction but also the release rate is very much dependent upon the annealing temperature. For instance, the fraction at 1173 K for the annealing time of 900 s is about 80%, while it reaches nearly 100% in 60 s at 1573 and 1673 K.

The correlation between the release fraction and the annealing temperature is shown in **Fig.8** for three different annealing times of 60, 900 and 3600 s. In the case of the shortest annealing time, 60 s, very small fraction of cadmium was released at temperatures below the melting point. It was only 0.6% at 1073 K and 1.9% at 1123 K. In the temperature range above the melting point, it increases monotonously with an increase in temperature, almost one hundred percent of release being reached at 1573 K. On the other hand, it sharply increases in the range just above the melting temperature for the cases of longer annealing times. This results indicate that the release fraction of cadmium from the alloy is strongly temperature-dependent and a complete release of cadmium in a relatively short time needs very high temperature.

Table 4 and **Figure 9** shows the release fraction of indium from the samples annealed at temperatures between 1073 and 1673 K as a function of isothermal annealing time. The release fraction is fairly low compared to the very high value of cadmium. Although the data considerably scatters in the range of annealing time to 600 s, it generally increases with increase in time and settles roughly constant level at 900 s except for the data at 1673 K. The release fraction at 1073 K is about 1.4% for the annealing time 900 and 3600 s, while it is about 5.4 and 7.7% for 900 and 3600 s, respectively. Also in this case, there is a tendency of higher release fraction at higher test temperatures. However the drastic change in release fraction, which was shown in **Fig.7** for the cadmium release, just above the melting temperature of the alloy was not measured on indium. This must be related with a much higher boiling temperature of indium. The normal boiling point of cadmium is 1040 K, which is lower than the melting temperature of Ag-In-Cd alloy. On the other hand, the normal boiling point of indium is 2343 K.

The release fraction of silver is summarized in **Table 5** and shown in **Fig.10** as a function of annealing time. No or negligible small release of silver was measured in the present experiments except for the cases of the longest annealing, 3600 s, at temperatures 1573 and 1673 K. It was only about 1.4 and 2.5%, respectively. This shows that silver is still the least volatile element of the control rod alloy as predicted in the theoretical consideration for the vaporization of individual elements.

4. Conclusions

Isothermal annealing tests with small silver-indium-cadmium alloy specimens cut from the control rods of PWR were performed at temperatures from 1073 to 1673 K for times between 60 to 3600 s in a flowing argon atmosphere to understand the vaporization behavior of control rod material during severe accidents of PWRs. The following conclusions are drawn from the test results:

(1) The actual melting temperature of control rod alloy was found to be in the temperature range between 1123 and 1173 K. Very little vaporization was measured below the melting temperature.

(2) The weight loss of samples due to vaporization was 0.8% at 1123 K and 8.2% at 1673 K, respectively, for the annealing time of 3600 s.

(3) Cadmium was completely released from the alloy at temperatures above 1173 K.

(4) The release fraction of indium was 1.4% at 1073 K and 7.7% at 1673 K.

(5) Silver was not released below 1473 K. For the annealing time of 3600 s, the release fraction was 2.5% at 1673 K.

(6) Cadmium was the most volatile and silver was the least volatile element of the alloy in the examined condition.

(6) Both the release rate of component elements and the total amount of release were strongly time-dependent.

Acknowledgment

We would like to thank Dr.S.Hagen of Kernforschungszentrum Karlsruhe, Federal Republic of Germany, who kindly provided the control rod material. We would also like to thank Mr.H.Takeishi and Mr.K.Obara of the Department of Chemistry, JAERI, for the elemental analysis and the assistance in fabricating the test apparatus.

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Table 1 Chemical composition of Ag-In-Cd control material used in the present experiments.

Element	Nominal(wt.%)	Present Analysis(wt.%)
Ag	80	79.93
In	15	14.97
Cd	5	5.10

Table 2 Weight loss percentages of Ag-In-Cd control rod samples annealed in flowing argon.

	Annealing Time(s)				
Temp.(K)	60	300	600	900	3600
1073	0.05			2.24	0.48
1123	0.14			0.45	0.83
1173	0.44	2.27	3.44	4.17	5.25
1273	1.68	3.96	4.95	4.93	5.34
1373	3.03	4.97	5.25	5.32	5.55
1473	4.43	5.27	5.38	5.47	5.97
1573	5.25	5.56	5.68	5.70	6.90
1673	5.40	5.54	5.73	5.96	8.23

Table 3 Release fraction of Cd from control rod samples annealed in flowing argon.

	Annealing Time(s)				
Temp.(K)	60	300	600	900	3600
1073	0.64			6.11	7.31
1123	1.90			9.23	15.22
1173	8.05	42.90	64.41	81.40	99.81
1273	33.49	75.71	94.41	95.53	100.00
1373	60.83	95.71	99.44	100.00	100.00
1473	88.57	99.44	100.00	100.00	100.00
1573	98.51	100.00	100.00	100.00	100.00
1673	99.61	100.00	100.00	100.00	100.00

Table 4 Release fraction of In from control rod samples annealed in flowing argon.

	Annealing Time(s)				
Temp.(K)	60	300	600	900	3600
1073	0.45			1.44	1.34
1123	1.07			1.25	4.01
1173	2.17	1.09	0.54	1.87	3.03
1273	1.94	2.36	1.71	1.37	3.95
1373	1.67	2.05	3.10	2.73	2.96
1473	1.68	3.18	3.29	3.07	4.53
1573	1.96	3.29	3.03	4.69	4.85
1673	0.67	3.21	4.03	5.39	7.74

Table 5 Release fraction of Ag from control rod samples annealed in flowing argon.

	Annealing Time(s)				
Temp.(K)	60	300	600	900	3600
1073	0.00			0.00	0.00
1123	0.00			0.00	0.00
1173	0.00	0.00	0.00	0.00	0.00
1273	0.00	0.00	0.00	0.00	0.00
1373	0.00	0.00	0.00	0.00	0.00
1473	0.00	0.00	0.00	0.00	0.24
1573	0.00	0.00	0.16	0.00	1.36
1673	0.26	0.00	0.03	0.07	2.47

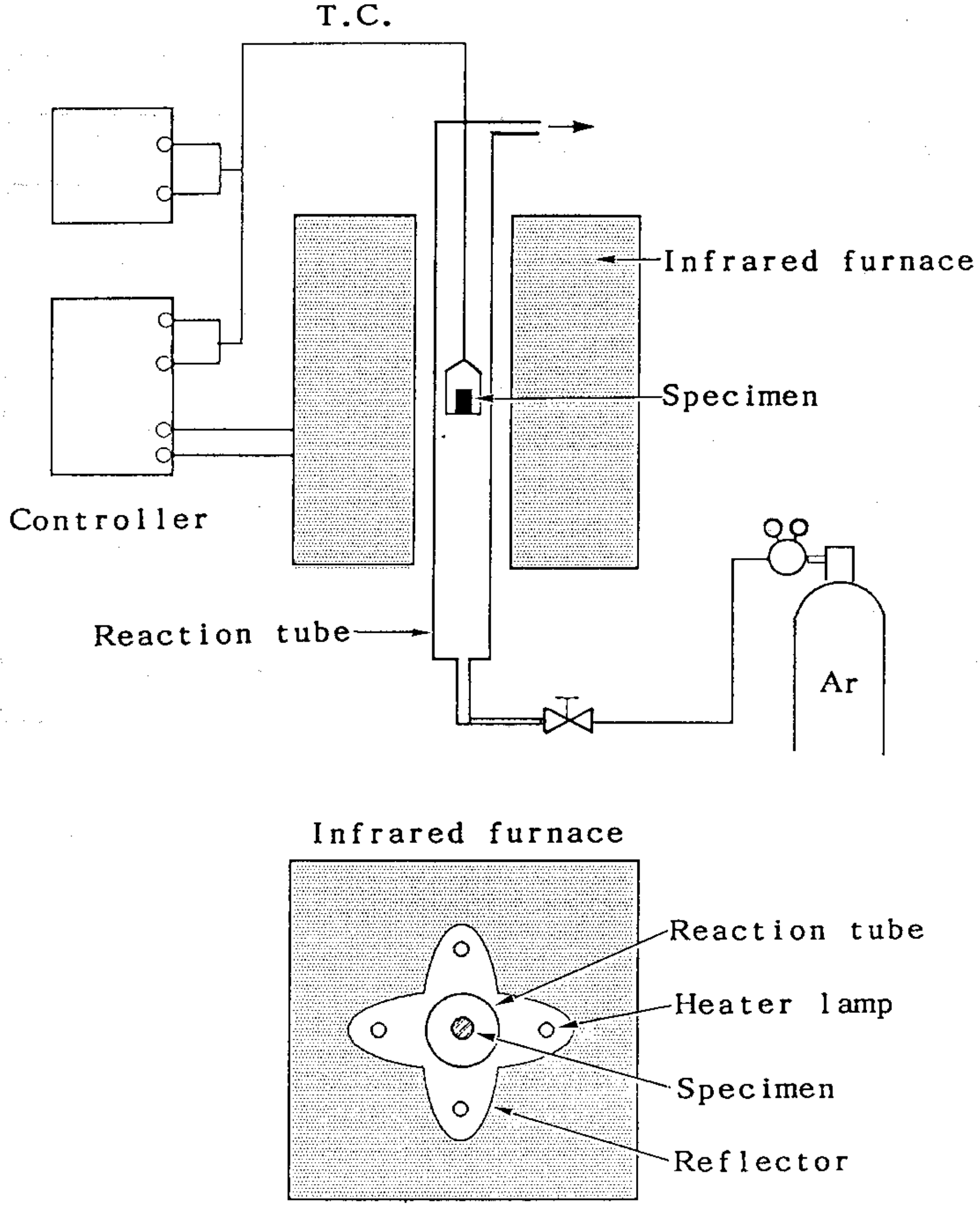

Fig. 1 Schematic illustration of apparatus.

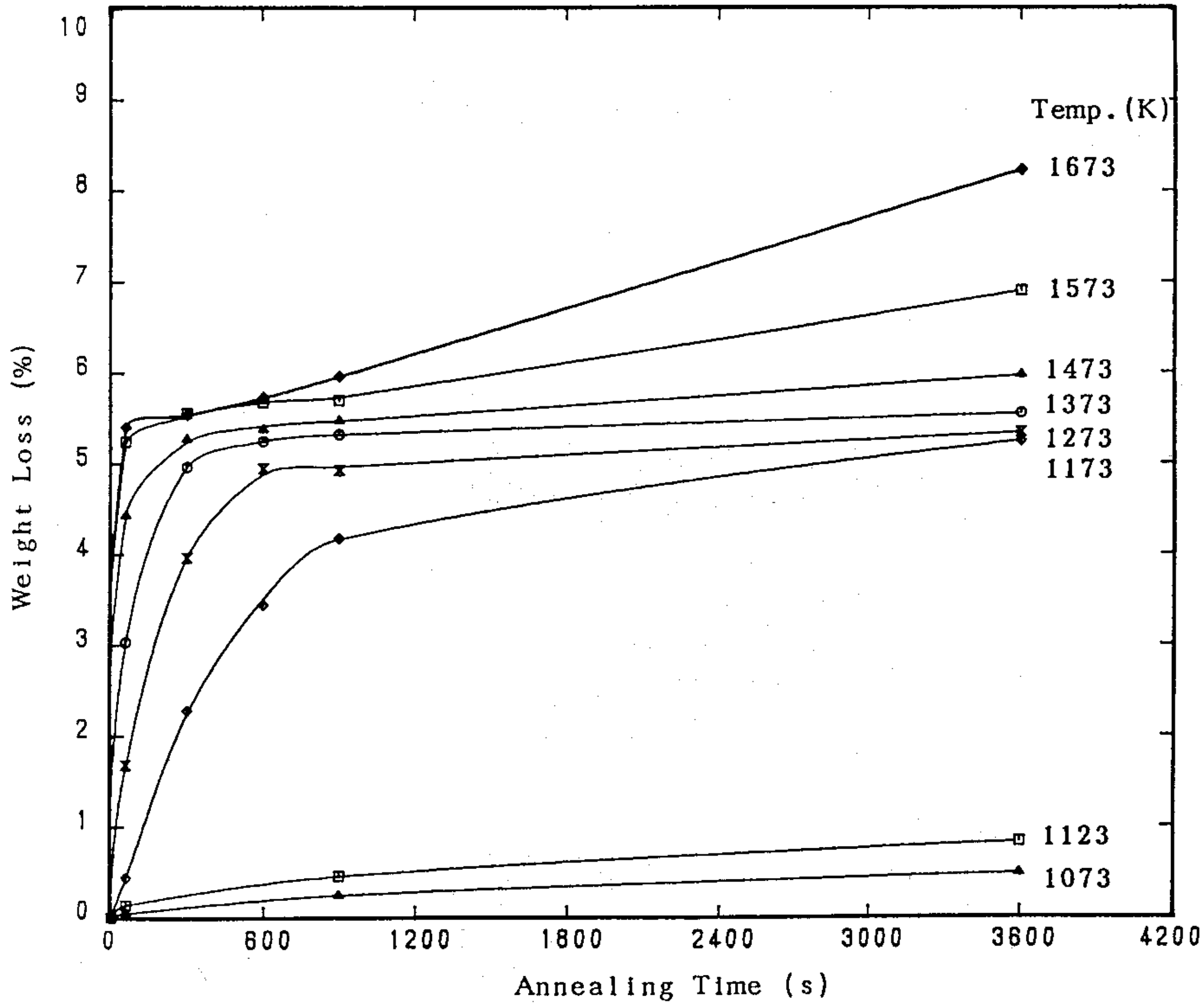

Fig. 2 Correlation between annealing time and the weight loss percentage of control rod specimens annealed at various temperatures.

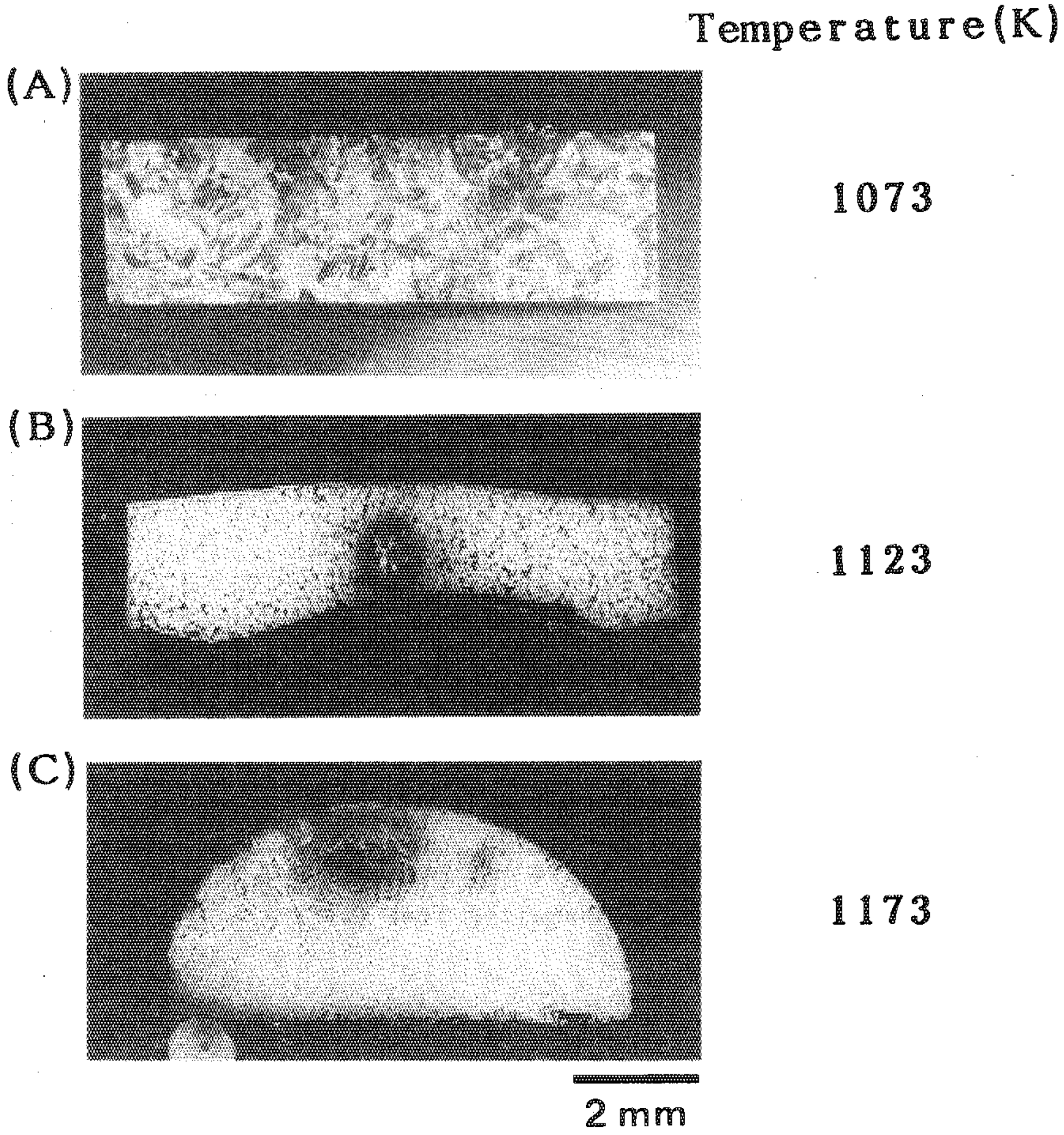

Fig. 3 Photomicrographs of Ag-In-Cd control rod material annealed at 1073, 1123 and 1173 K for 900 s in flowing argon.

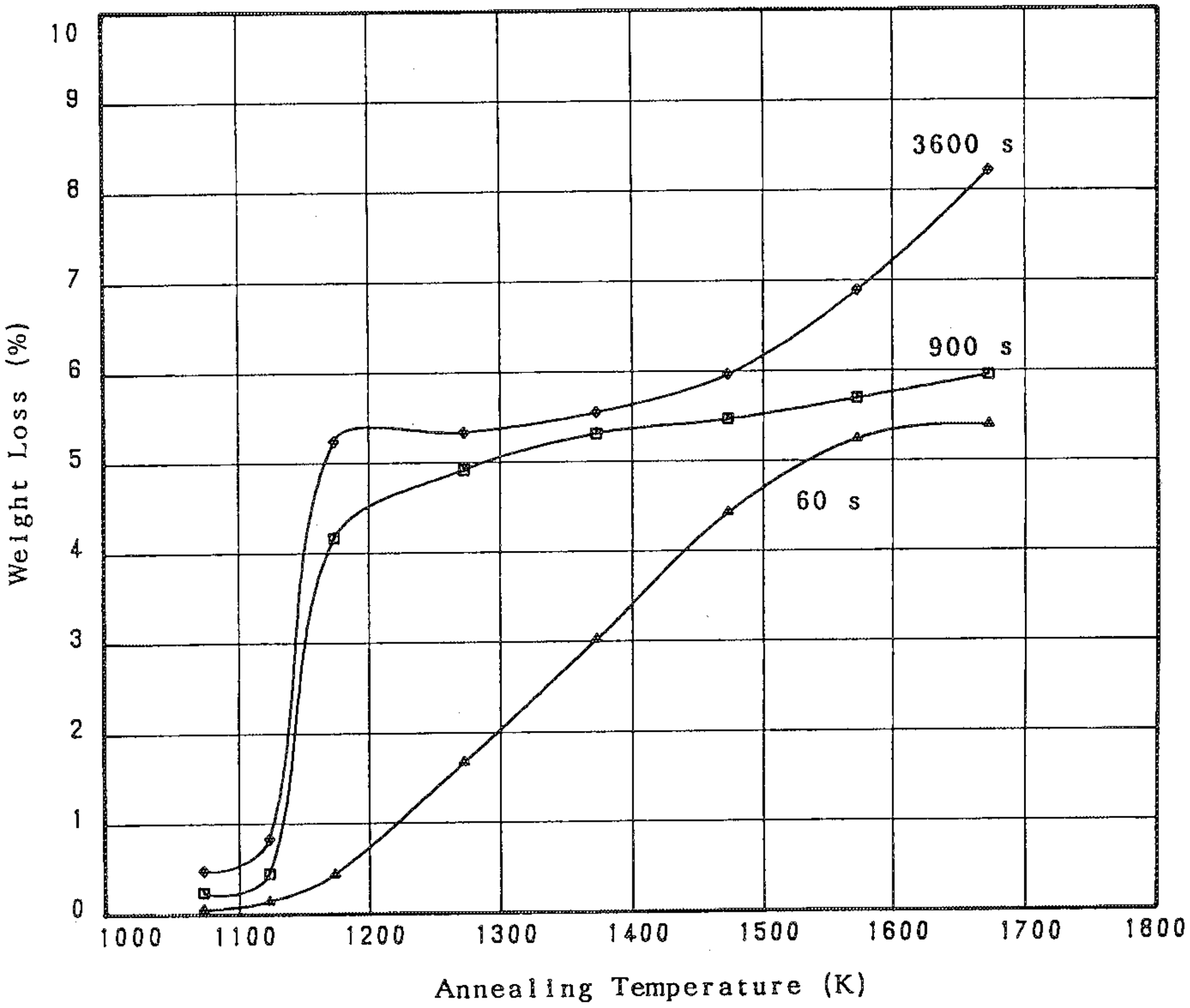

Fig. 4 Weight loss percentages of control rod specimens annealed for three different times of 600, 900 and 3600 s as a function of annealing temperature.

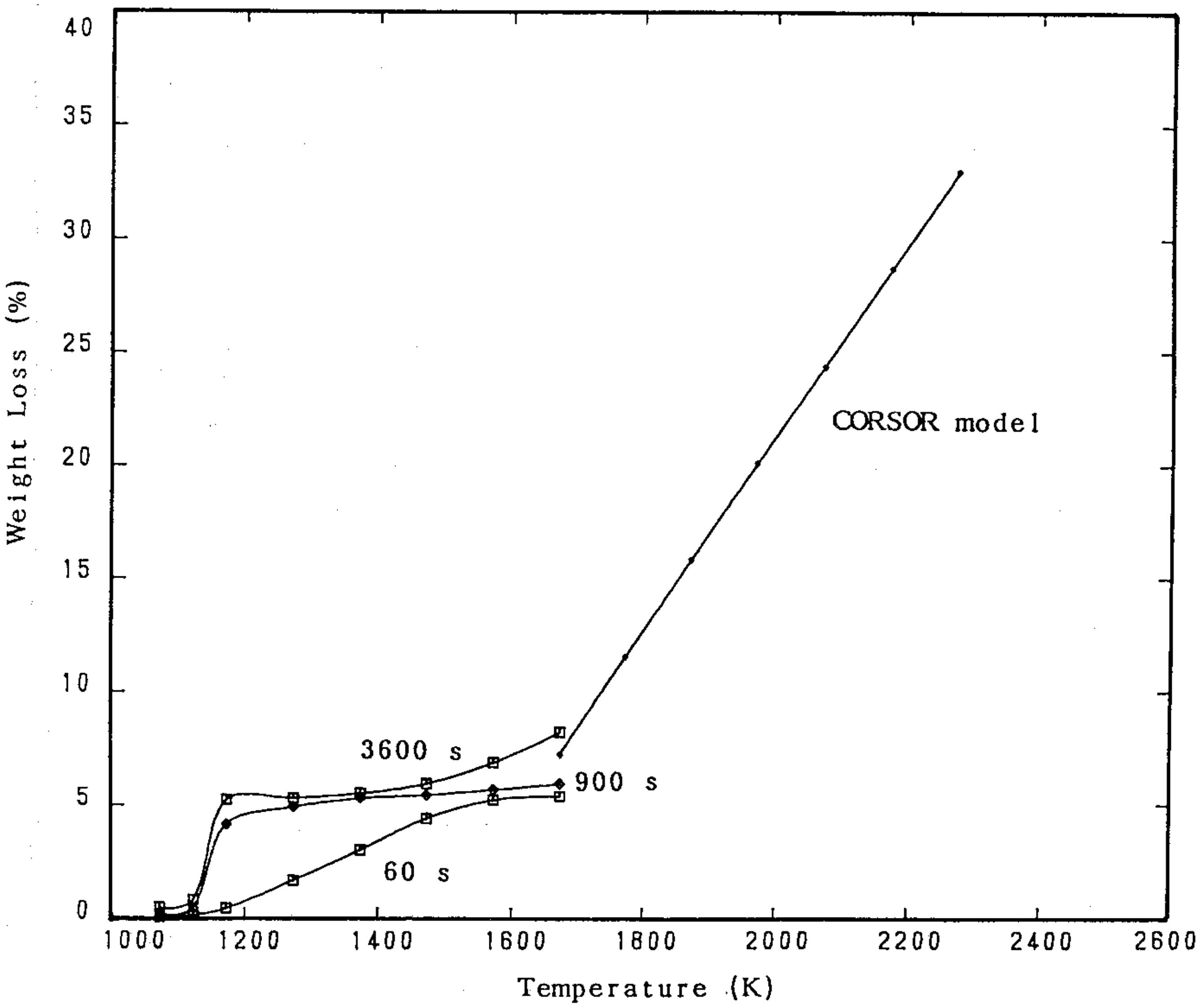

Fig. 5 Weight loss percentages of control rod specimens annealed for times of 60, 900 and 3600 s as a function of annealing temperature together with the calculation based on the CORSOR model.

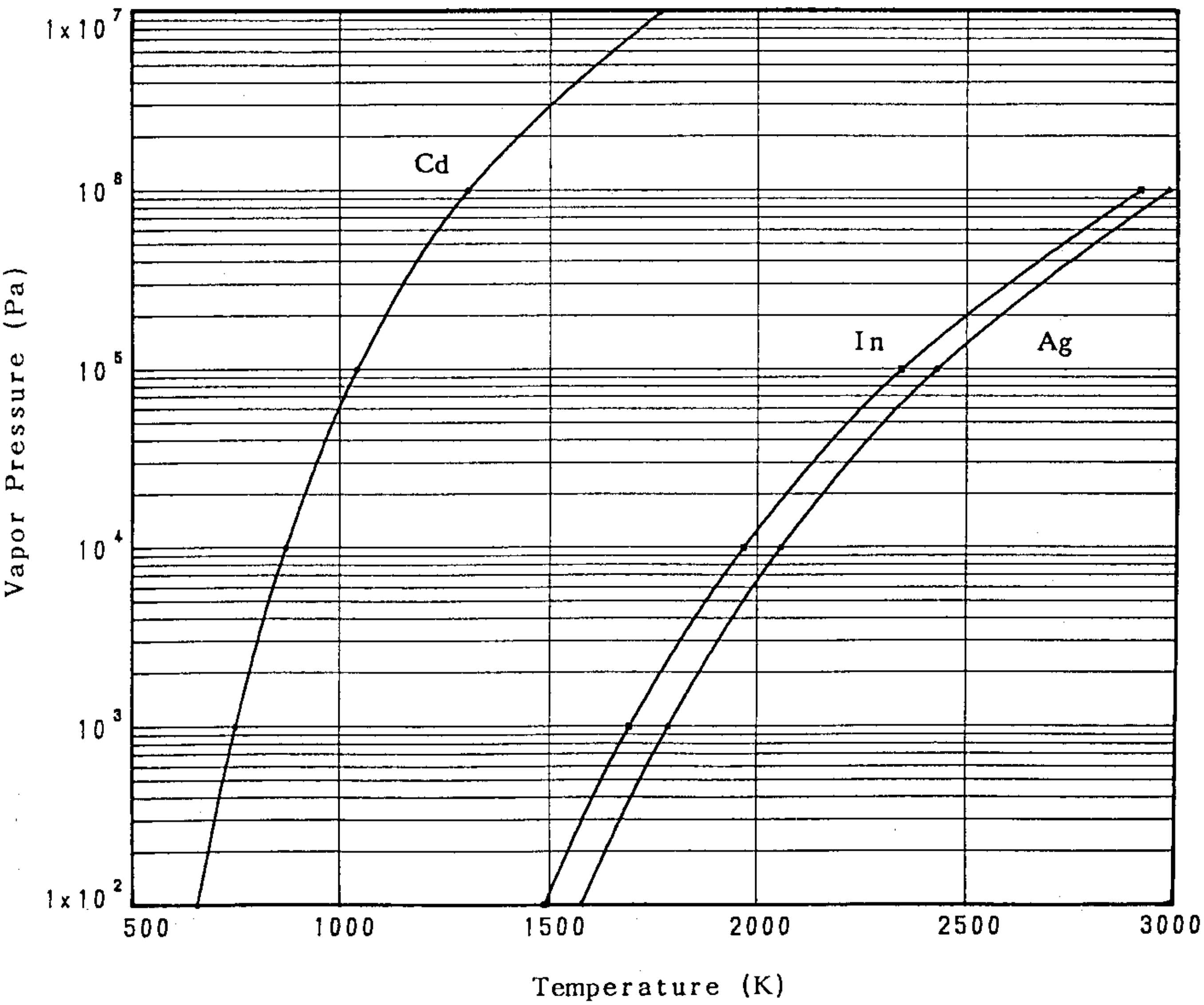

Fig. 6 Vapor pressure of the individual control rod elements as a function of temperature.

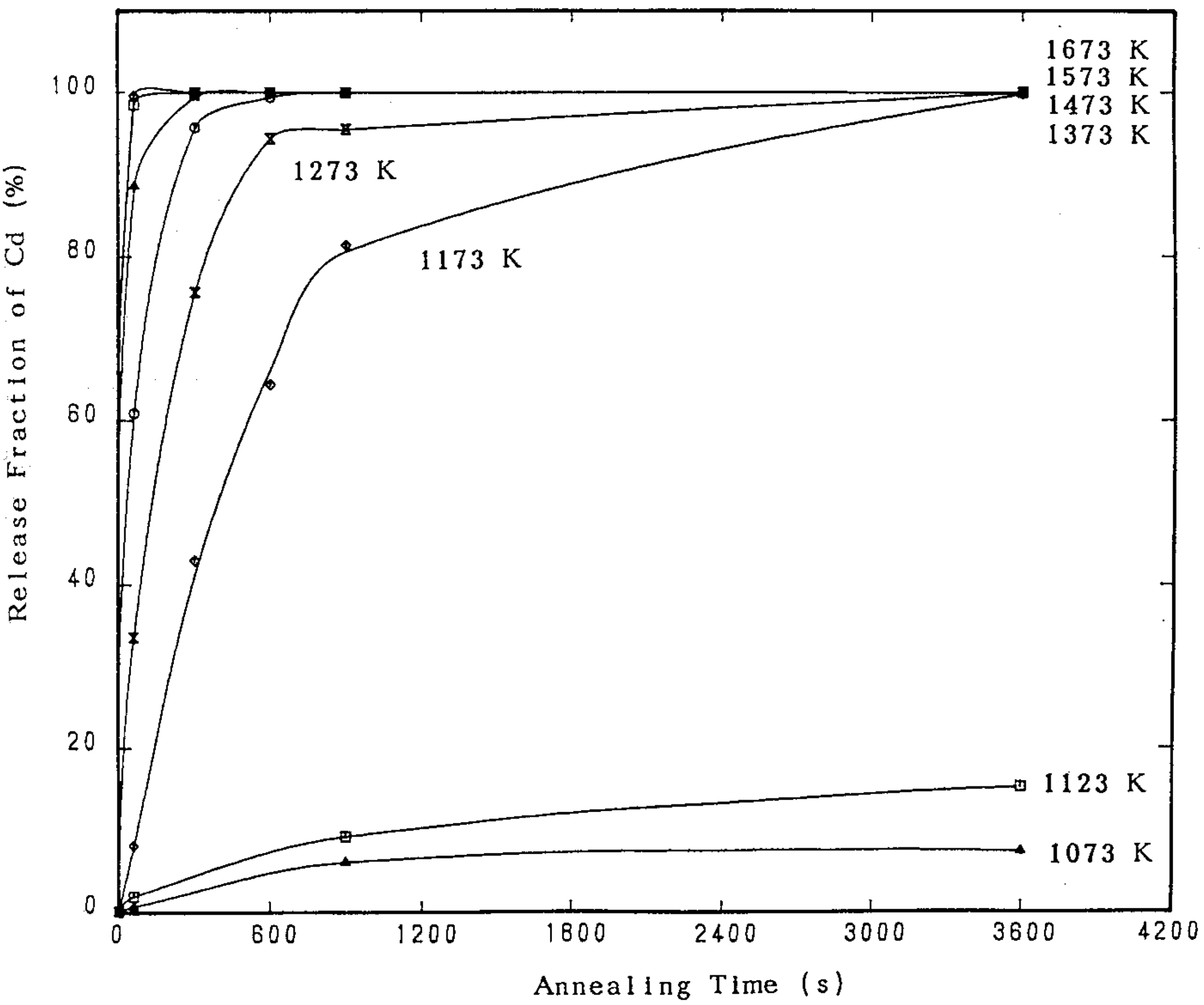

Fig. 7 Release fraction of Cd from the control rod samples annealed at temperatures between 1073 and 1673 K as a function of isothermal annealing time.

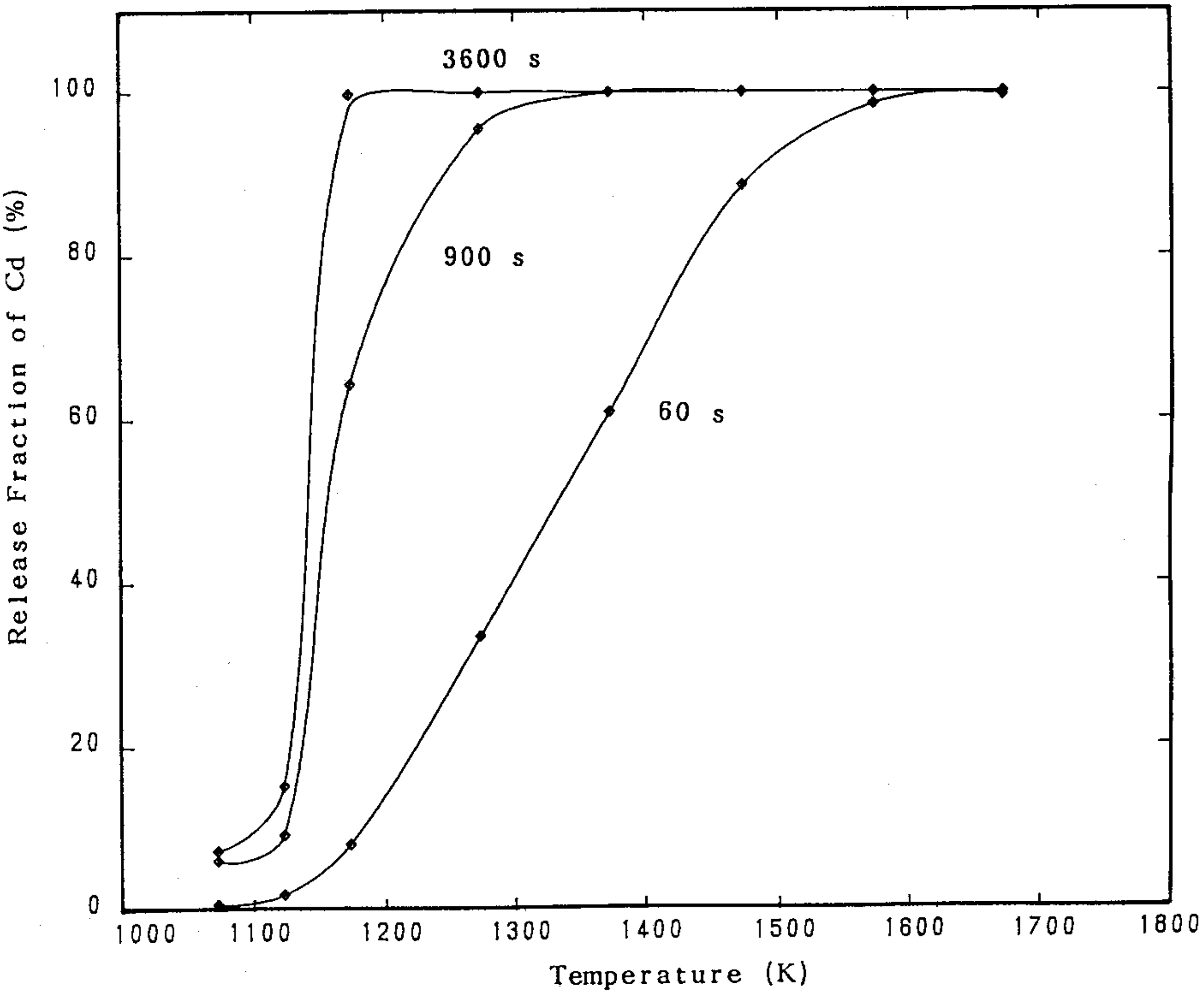

Fig. 8 Correlation of the release fraction of Cd and the annealing temperature for three different annealing times of 60, 900 and 3600 s.

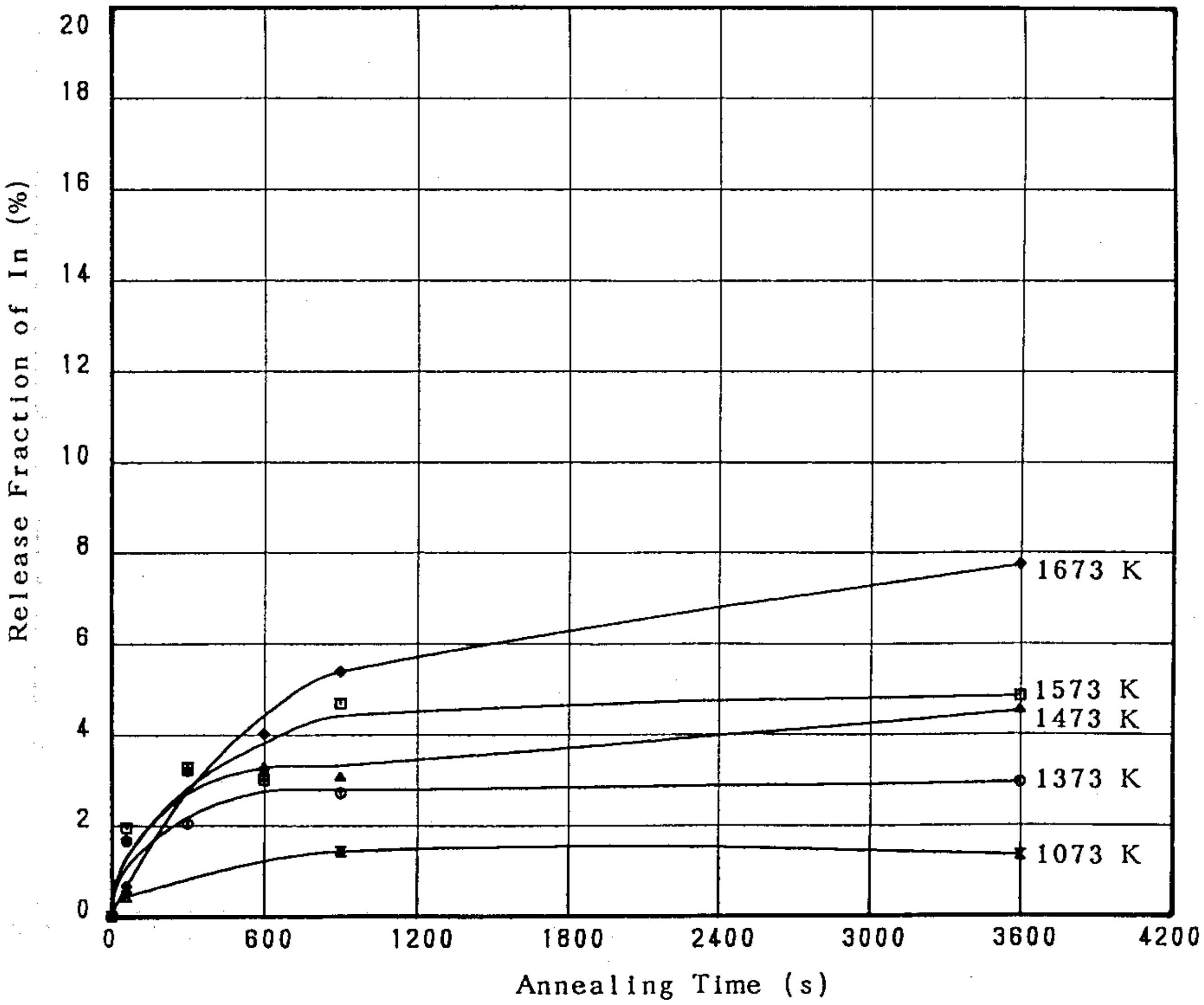

Fig. 9 Release fraction of In from the control rod samples annealed at temperatures between 1073 and 1673 K as a function of isothermal annealing time.

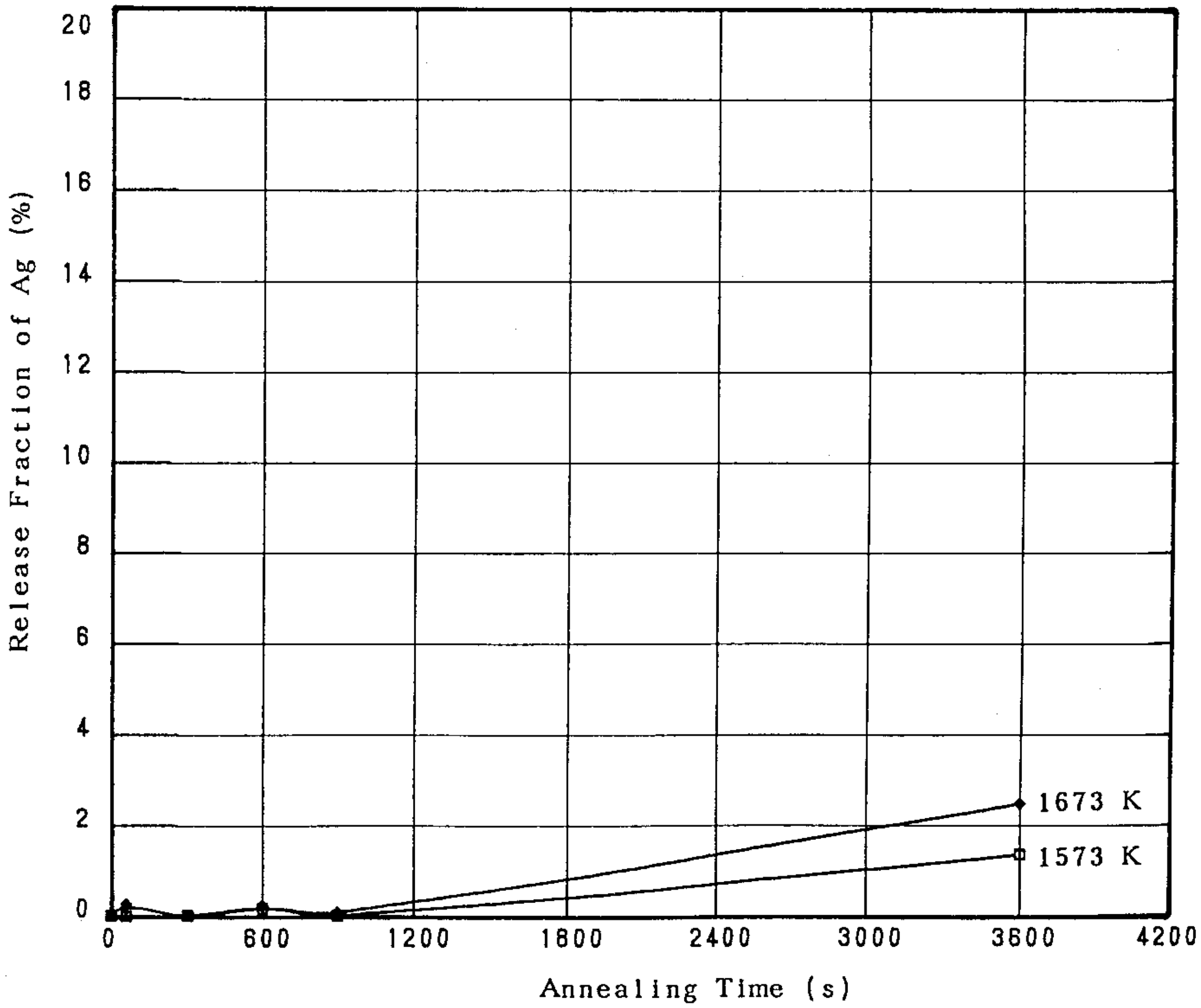

Fig. 10 Release fraction of Ag from the control rod samples annealed at 1573 and 1673 K as a function of isothermal annealing time.