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OF OXIDE FILM OF THE STRUCTURAL
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THERMAL CYCLES

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Composition variation of the corrosion product spalled during oxidation in simulated HTR coolant under temperature cycling has been examined by activation analysis. Comparison was made among three heats having different Mn, Al, Si and Co contents, which influence the behaviour of the material. The heat with better protective oxide film and without intergranular attack was found to cause minimum release of the radioactive products. There is intimate relation between chemical composition of the oxide film and corrosion resistance. Discussion is made on the factors controlling the release rate of Co into the environment.

Key Words : Hastelloy-X, HTR Type Reactor, Oxidation Kinetics,
Thermal Cycling, Oxide Spallation, Helium,
Very High Temperature, Corrosion Products,

高温ガス炉構造材料のヘリウム中熱サイクル下の
腐食挙動と腐食生成物のはく離

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高温ガス炉一次系の化学的条件を近似したヘリウム気流中で、耐熱合金の熱サイクル下の腐食試験を腐食生成物の元素構成の変化の測定を中心に行った。熱サイクル条件は室温と1,000°Cを高温部保持時間300hr、平均加熱速度3°C/min、平均冷却速度40°C/minで行い、試験時間は最長約5,000hrとした。

供試材として用いたハステロイ-X基の合金は腐食挙動に重要な役割を果す、Mn, Si, Al, Coの微量成分の含有量の異なる三種を用い、主としてヘリウム中の耐食性の改善と腐食生成物のはく離で放出される放射化ポテンシャルの大きい元素の量との関係を追跡したが、あわせて酸化膜構成元素の時間的推移と腐食挙動との関連も考察した。

Mnを添加して防護膜の保護性を改善することと、Alを低減して、局部侵食を抑制する二つの防食手段がCo, Niなどの元素の放出の低減に実質的に有効であるという先報までの結論を長時間試験においても再確認した。また、酸化抵抗の良否と形成される酸化膜の構成元素との間に密接な関係が認められ、なかでもMnとSiが大きい役割を果すことを明らかにした。

CONTENTS

1. INTRODUCTION	1
2. EXPERIMENTAL METHODS	2
2.1 Materials	2
2.2 Apparatus and test procedure	2
2.3 Neutron irradiation and γ -ray spectrometric analysis	3
3. RESULTS AND DISCUSSION	3
3.1 Composition of the spalled oxide	3
3.2 Change in Cr content in the oxide	4
3.3 Co content in the spalled oxide	4
3.4 Oxidation kinetics under thermal cycling	5
3.5 Evaluation of the total release rate	6
4. CONCLUSIONS	6
REFERENCES	7

目 次

1. 諸 言	1
2. 実験方法	2
2.1 材 料	2
2.2 装置と試験手法	2
2.3 中性子照射とガンマ線分光分析	3
3. 結果と考察	3
3.1 はく離酸化物の組成	3
3.2 酸化物中のクロム濃度の変化	4
3.3 はく離酸化物中のコバルト濃度	4
3.4 熱サイクル下の酸化速度	5
3.5 総放出率の評価	6
4. 結 論	6
文 献	7

1. INTRODUCTION

The consideration of nuclear properties of structural metal has not customarily given to the off-core structures. The experience of the power reactor operation, however, has shown that the radiotransport due to the activation of corrosion products released from the metal component in the primary circuit can cause a serious radiation exposure problems to the personnels who work for maintainance and repair.

In HTR system, the radiotransport problems have been handled in terms of the fission product plateout. It is blieved that there can be an another area to be explored. The structural metals used in high temperature regions are generally composed of Ni, Cr, Fe, and are frequently accompanied by Co, Mn, Ta etc that are potential in being transmuted to radioactive isotopes. The assesment of possible release of corrosion products including these elements may be required as the system assumes to operate for very long time and at higher temperatures.

Metals are generally protected with oxide film in the oxidizing gaseous environments, while as the operational cycles are accumulated, the associated stress cycles can spall off the film to form oxide dust and contaminate the walls of the primary circuit.

In the previous work¹, the authors demonstrated that such oxide spallation occurs during exposure of certain structural alloys, and radioactivation analysis indicated the existence of various radioactive species involving ^{60}Co . Major conclusions drawn were as the followings;

- 1) Noble elements, Co, Ni and Fe, that are not expected to be oxidized in the HTR helium can be incorporated into the spalled oxide.
- 2) Elimination of intergranular attack by proper alloy modification is one of the key issues to reduce the incorporation.
- 3) Minimizing Co content in alloys is a basic exercise to be recommended, but is an expensive and give only partial benefit.

The present work aims at the further close follow on the kinetics of oxidation and spallation under thermal cycling, and the sequence of compositional changes in the oxide film during extended time exposures.

2. EXPERIMENTAL METHODS

The basic method and procedure of the experiments are the same as the previous work.¹

Specimens were exposed to the simulated HTR helium flow at atmospheric pressure under thermal cycles between R.T. and 1000 °C up to 5000 hr. Oxide spallation and weight change were followed at appropriate intervals. The analysis of the oxide composition was made by γ spectrometry after activation in a reactor.

2.1 Materials

The chemical composition of the sample materials are shown in Table 1. All three heats have the basic composition of the Hastelloy alloy-X. The heat-B is a commercial heat, while the others are those modified by controlling Al, Mn, Si and Co contents for uses in the HTR helium environments. In this particular study, contents of these four minor elements have special significance. Heat-B is characterized by its susceptibility to intergranular attack mainly due to its Al content. Heat-G is the heat with minimized Co, Al and Si.

It has been conformed in the preliminary studies that excessive reduction of Si content leads to enhanced oxide spallation. Heat-0 is the heat with optimized Mn and Si contents for improved corrosion resistance in the HTR environment. The Al and Co contents in this heat are nearly equivalent to Heat-G. The specimens were taken from the rolled and solution annealed sheets and formed to the coupons of $2 \times 10 \times 20$ (mm) size. Prior to the test the surface was wet abraded with #1200 carborandom paper, degreased with reagent grade acetone and vacuum-dried.

2.2 Apparatus and test procedure

Each single specimen was placed in a quartz tube, which was designed to expose the specimen to continuously refreshed helium stream with close monitoring of temperature and impurity levels. The test apparatus used were connected to a helium recirculating system with continual purification and impurity injection operated at 0.5 kg/cm²G above the atmospheric pressure.

The flow rate of helium was maintained at or above 100 cc/min per square cm of the reacting surfaces. The impurity levels were monitored by gas chromatography and hygrometry through sampling gas at inlet and

outlet of each test apparatus. The analysis of the test environment was shown in Table 2, which was maintained throughout the tests.

The test samples were exposed under heating cycles between room temperature and 1000 °C, and held at 1000 °C for 300 hr per each cycle. The average heating and cooling rates at temperatures above 400 °C were 3 and 40 °C/min. respectively. The oxide powder spalled was collected in high purity acetone under ultrasonic vibration. After removing the specimen the powder suspended in the solvent was precipitated by centrifugal separation technique.

The collected powder of the spalled oxide was finally vacuum-dried for gravimetric measurement. The specimens after the ultrasonic cleaning were also subject to the gravimetry, and returned to clean containers at the test section and further exposure was given.

2.3 Neutron irradiation and γ -ray spectrometric analysis

The collected powder of the spalled oxide was irradiated by neutron for activation analysis.

The irradiation was made by pneumatic shooting through the core of the JRR-2 (10 Mwt) reactor giving two levels of neutron flux, 3×10^{13} (n/cm²·sec) \times 5 min. and 3×10^{12} (n/cm²·sec) \times 260 hr.

The former was applied to utilize the reaction $^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$, and the latter was for reactions $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$ and $^{50}\text{Cr}(n,\gamma)^{51}\text{Cr}$.

The activated spalled oxide was analyzed by a 1K channel pulse height analyzer equipped with a Ge(Li) detector.

3. RESULTS AND DISCUSSION

3.1 Composition of the spalled oxide

The results of neutron activation analysis of oxide spalled from the three heats of materials after exposure for different time steps up to nearly 4000 hours are shown in Table 3.

The form of the spalled oxide was the mixture of whisker-shaped strings and fine platelets. In the results reported previously, the form of the oxide was mainly of the latter type, and Cr occupied about 50 to 60 % of the total weight of the oxide. The present results in Table 3 show substantially lower values than the previous results.

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is lower than that in the film directly peeled off from the solid oxide layer. The whiskers of this sort have been observed frequently in the previous works, and are believed to be the result of evaporation and deposition of the metals or oxides at the surface under comparatively slow helium flow. The whiskers are known to contain Cr, Mn, Ni, Fe, Co and Si.^{2,3}

From the view point of the radioactivation, the most important species among those noted above are ^{60}Co and ^{51}Cr , the former being the strong γ -ray emitter and the latter being the most in abundance.

3.2 Change in Cr content in the oxide

Cr in the oxide was found to change depending on time of exposure and the alloy composition. Figure 1 shows the sequence as a function of time.

Heat-0 and B is comparatively low in Cr at the early stage, but the latter makes a shift to a higher Cr composition to the level equivalent to Heat-G. The common feature of the product with lower Cr content is the coincidence with the form of oxide. The spalled product rich with the whiskers showed lower Cr. In Heat-G, the spalled oxide changed from the early whisker-like to the later flaky platelet form at the transition between 1500 and 2000 hrs. The form of the spalled oxide in Heat-G is a mixture of whiskers and flakes of platelets throughout the test period since the stage at 1500 hr. The observed feature is interpreted as the followings; the oxide scale formed on the surface is basically high in Cr, but in the alloy with good oxide film stability such as Heat-0 suffers rather limited spallation and the majority of the collected oxide is occupied by the whiskers that had been grown on the outer surface of the oxidized metal. The higher levels of Cr in Heats G and B are due mainly to the oxide film grown directly from the metal and broken down from the surface upon thermal cycling.

3.3 Co content in the spalled oxide

Figure 2 shows the results of Co determination. In Heat-B, the commercial heat, showed a steady increase of Co with increasing the time of exposure in the range of testing. While in the other heats no such trend was observed, and eventually, both tended to fall into very low levels.

It has already been pointed out by the authors that the elimination of Al, is the elimination of the susceptibility to the intergranular

attack, effectively reduce the incorporation of Co into the spalled oxide. The behavior of Heats O and G is reasonably understood because of their immunity to the intergranular attack, and also because of the effective blockage of any possibility of Co evaporation by the formation of protective Mn-Cr spinel oxide film.⁴ The evidence of the formation of the islands of the unoxidized noble metals in the oxide film on Heat B can be seen in Fig. 3. The major mechanism that governs the incorporation of Co into the spalled oxide in Heat-B, therefore, is confirmed to be the intergranular attack, by which the Co content in the oxide may tend to increase as the Co content in the base metal adjacent to the metal-oxide interface increases with time. Generally speaking, the alloys containing both Al and Co ought to be checked critically in this respect.

3.4 Oxidation kinetics under thermal cycling

Separate evaluation only of the amount of spallation is made in Fig. 4. The spallation from Heats G and B were nearly linear functions of time, while gradually decreasing trend was the case for Heat O. The summation of the weights of the spalled oxide and the specimen gave the total weight gain. Figure 5 summarizes the parabolic plots of the three heats. It should be of special attention that the plots of the gross total gave excellent straight lines, which means that the overall reaction maintained the same diffusion-controlled kinetics regardless of the spallation. Here, again, the rate of corrosion is the lowest with Heat-O. Figure 6 shows the comparison of the three heats with respect to the total amount of reaction and the associated oxide spallation. The beneficial effects of increasing Mn and optimizing Si are evident. The authors have already observed and interpreted the effects of these minor elements in the previous paper.⁴

The observed independence of the parabolic kinetics from the spallation seemed to disagree with the former⁴ observation that the formation of MnCr_2O_4 spinel in the outer part of the oxide layer was essential feature of the protection by Mn addition. The authors presently assumes that the diffusion barrier to the Cr ions is some inner layer adjacent to the metal, while the outer layer serves as another barrier for the reach of oxidizing species to the interface where the combination of oxygen and metal elements take place. The areas of partial spallation was seen as high as approximately 10 %.

3.5 Evaluation of the total release rate

The release of potential radioactive species is clearly dependent on the total amount of oxide spallation per given surface area and the percentage of the problem species in the oxide. The amount of essential release can be evaluated by the products of multiplying these two values.

Figures 7 and 8 were obtained in such a manner for Cr and Co respectively. In these two figures the benefit of improving corrosion resistance is clear. The increase of resistance to the spallation definitely reduce the release rate in the most severe case seen in Fig. 5 when Cr_2O_3 formation is assumed. The spalled oxide, however, is composed of the deposited whiskers in its major portion. It is also possible that the spalled areas are continually repaired, although the cumulative plots show as if the amount of observed deviation represented the area remaining uncovered.

The fact that the heats with less spallation gave lower parabolic rate constants is also worth noting. Cr as seen in Fig. 7, and it is also noted that the expensive effort of reducing Co as in Heat G relative to Heat-0 was rather easily substituted by the optimization of Mn and Si contents in Heat 0 as seen in Fig. 8. The avoidance of intergranular attack by simply reducing Al can be another essential means of protecting the system from contamination by Co as seen in Fig. 8.

4. CONCLUSIONS

- (1) Mn in Hastelloy-X acts to improve the adherence and the protective function of the oxide film formed in the simulated HTR coolant.
- (2) The possible release of potential radioactive species through oxide spallation can be avoided by optimizing Mn and Si contents and minimizing Al and Co in the alloy.
- (3) The spallation itself did not affect the basic time dependence of the oxidation kinetics during the thermal cycling in the simulated HTR helium environment.

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Table 1 Chemical compositions of specimen materials.(wt%)

	C	Mn	Si	P	S	Cr	Co	Mo	W	Fe	Ni	Al
Heat-B	0.06	0.60	0.43	0.007	0.005	21.55	1.01	8.92	0.45	17.76	Bal.	0.42
Heat-G	0.08	0.65	0.03	<0.005	<0.005	21.98	0.008	8.81	0.54	18.38	Bal.	<0.02
Heat-0	0.07	0.88	0.27	<0.005	<0.005	21.90	0.04	9.13	0.47	18.23	Bal.	<0.03

Table 2 Levels of impurities in the test environment.

impurity	H ₂	H ₂ O	CO	CO ₂	CH ₄
partial pressure (μ atm)	200-210	0.8-1.2	100-110	2-3	5-6

(Practically no O₂ to affect the experiment results.)

Table 3 Results of neutron activation analysis on oxide spalled from three heats surface.

Time(hr)	Heat	Content in Spalled Oxide (wt%)		
		Cr	Mn	Co
1455	Heat-B	9.28	3.08	0.0047
	Heat-G	35.37	3.65	0.0036
	Heat-0	6.14	2.60	0.0078
2189	Heat-B	34.90	13.71	0.0163
	Heat-G	35.57	4.29	0.0020
	Heat-0	19.48	7.86	0.0028
2911	Heat-B	40.30	10.61	0.0317
	Heat-0	21.57	9.58	0.0076
3768	Heat-B	47.24	9.46	0.043
	Heat-G	44.73	6.51	0.0007
	Heat-0	15.56	7.01	0.0024

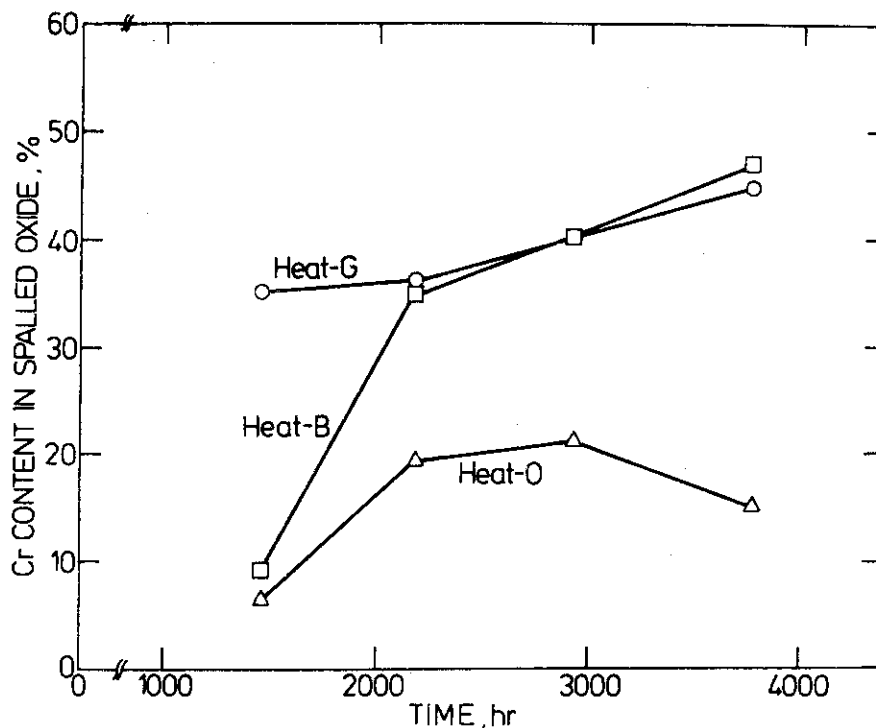


Fig.1 Comparison of Cr content change in spalled oxide of three heats as a function of time.

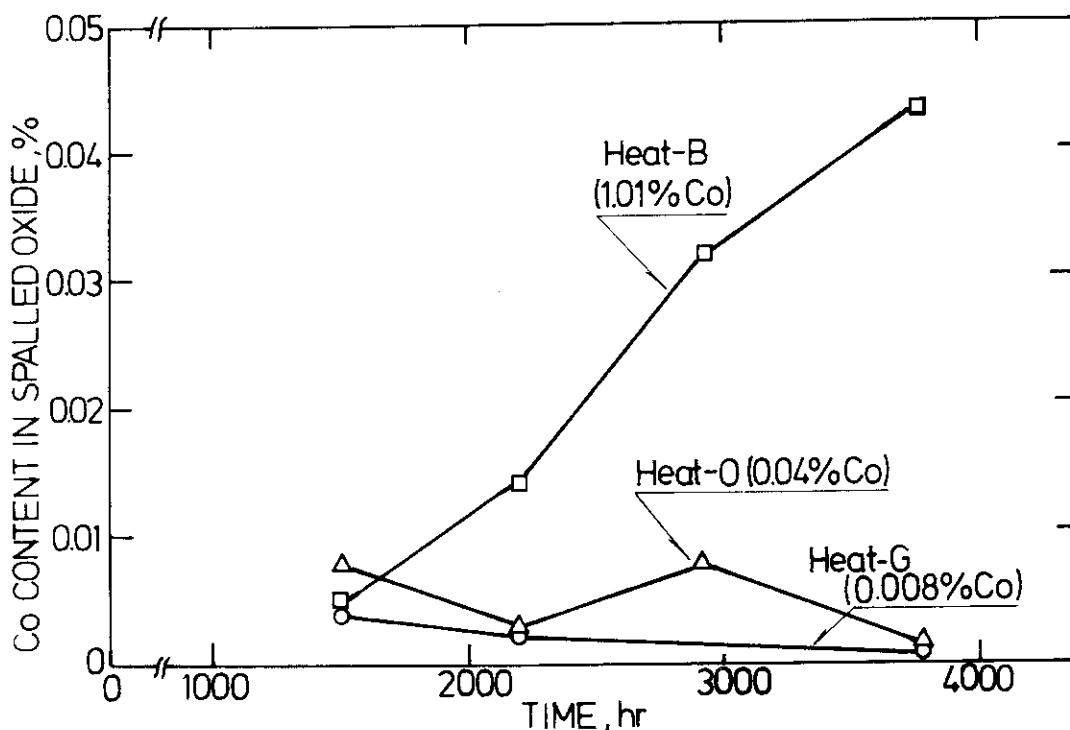


Fig.2 Comparison of Co content change in spalled oxide of three heats as a function of time.

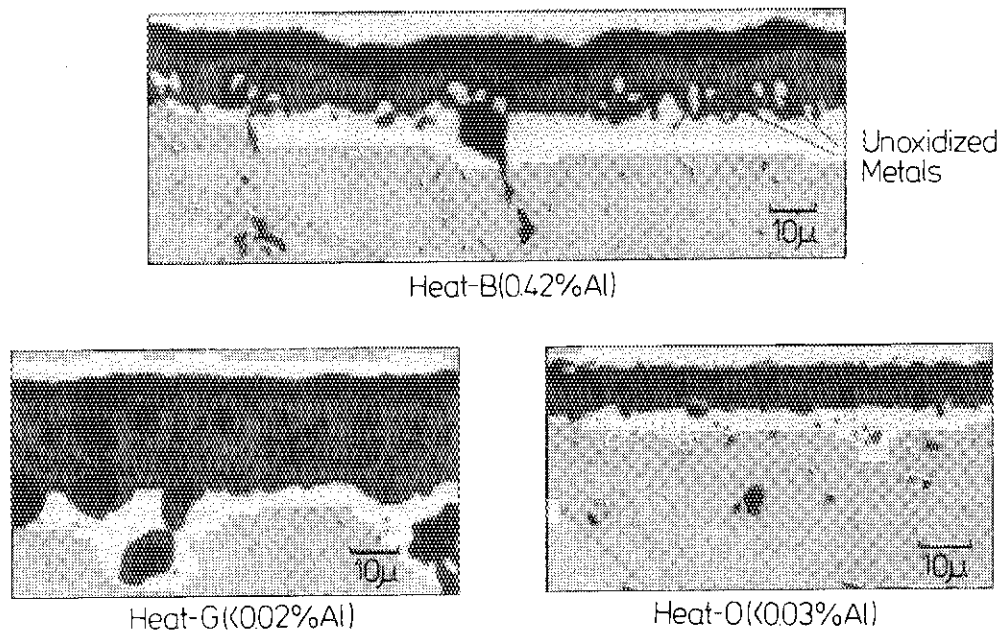


Fig.3 Cross sections of the oxide specimens after exposure for cumulative 1900 hr.

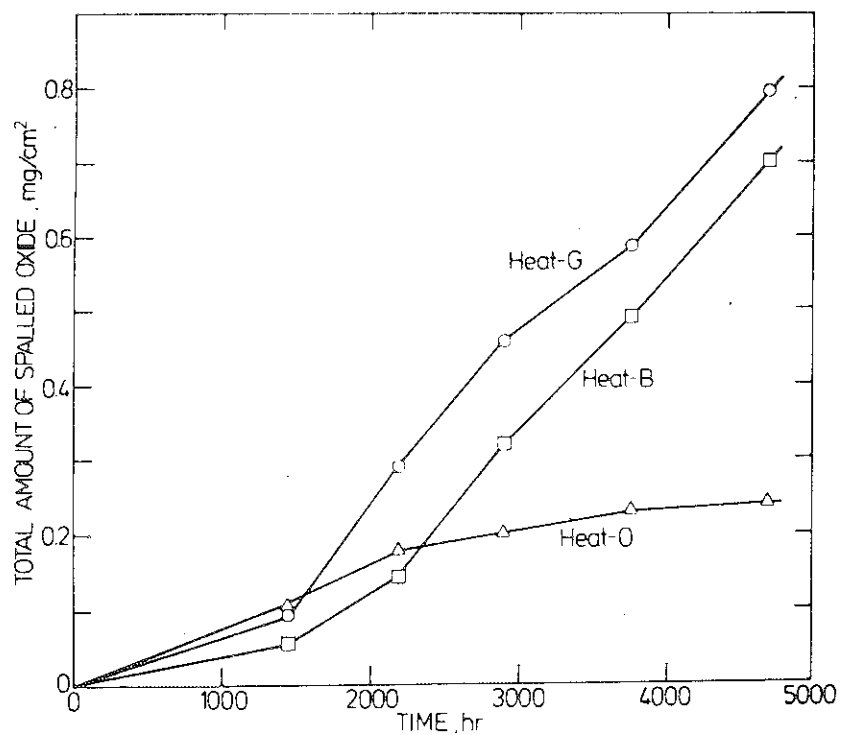


Fig.4 Cumulative amount of spalled oxide of three heats as a function of time.

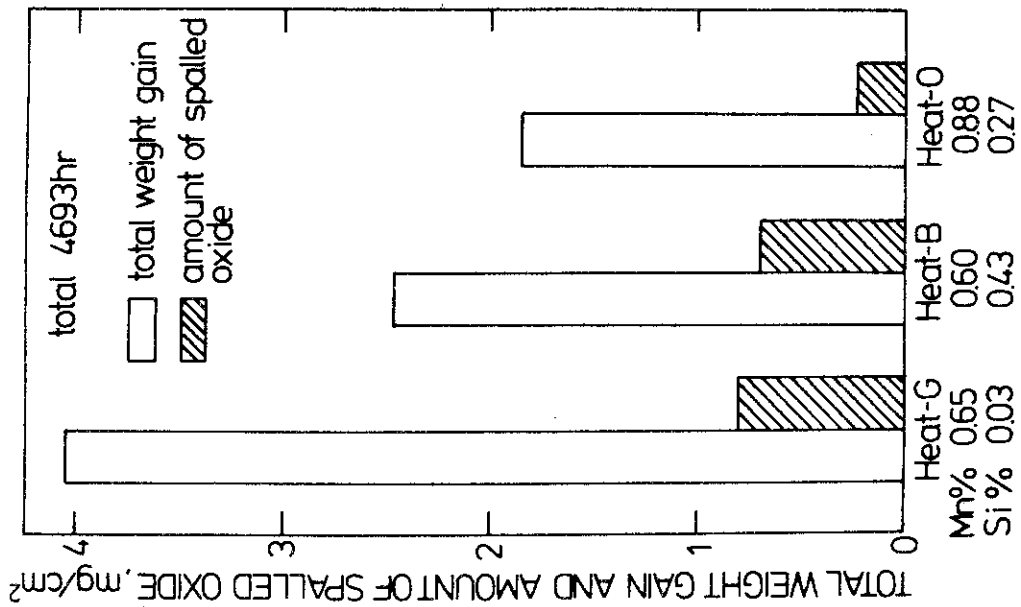


Fig.6 Comparison of total weight gain and total amount of spalled oxide of three heats for total 4693 hr.

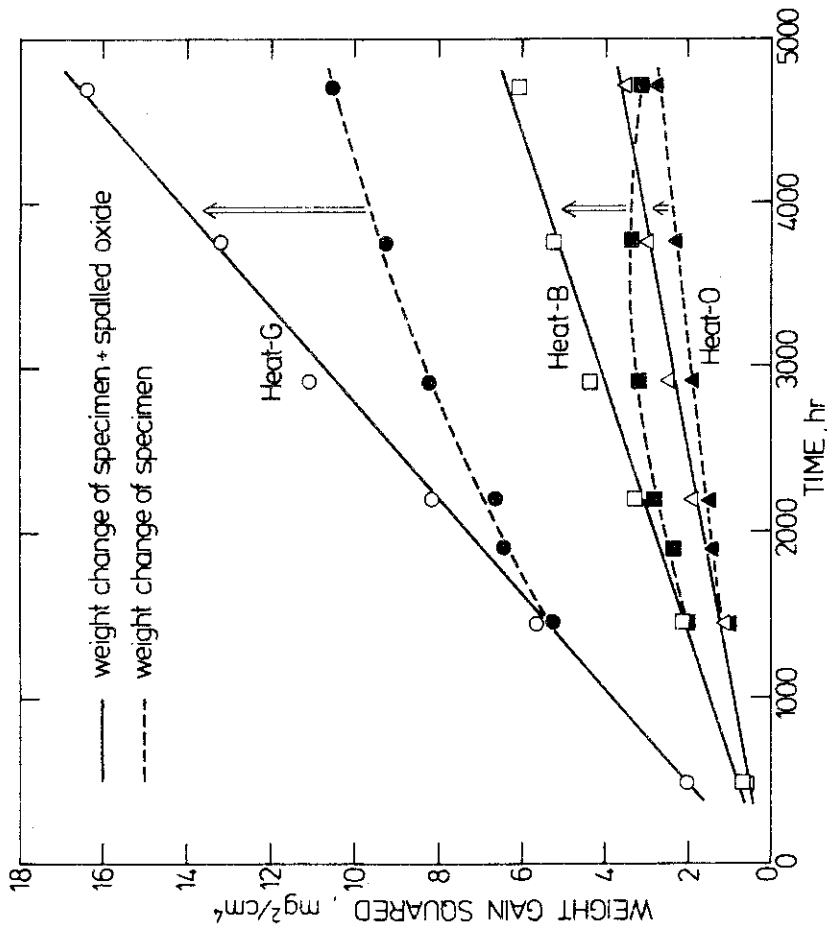


Fig.5 Oxidation kinetics of total weight gain of three heats.

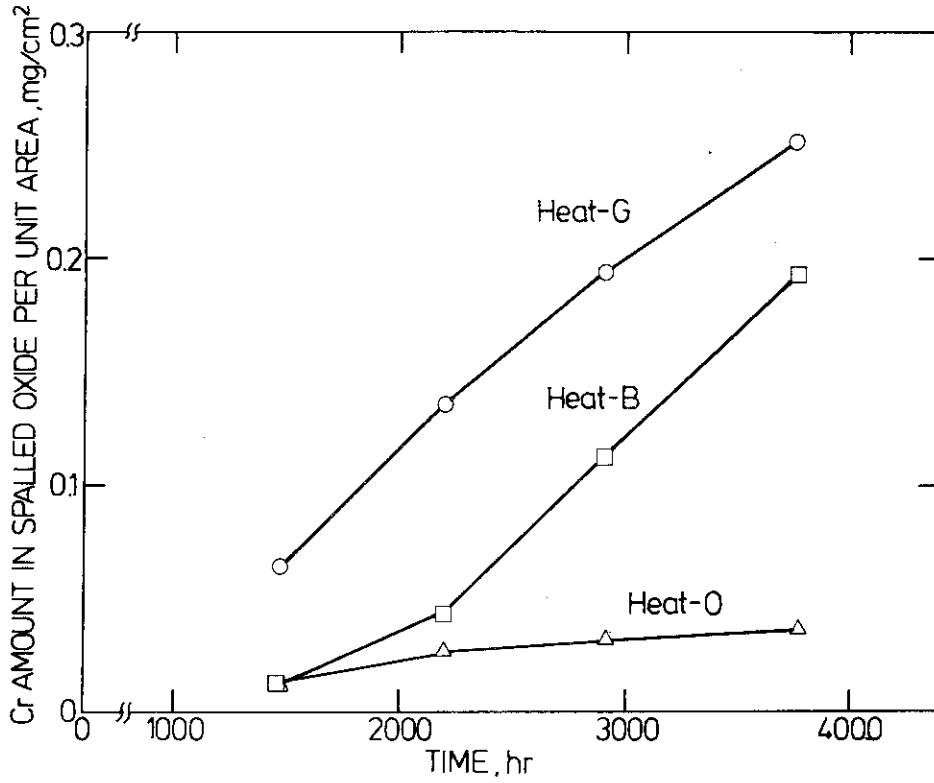


Fig.7 Release rate of Cr from unit area of three heats surface.

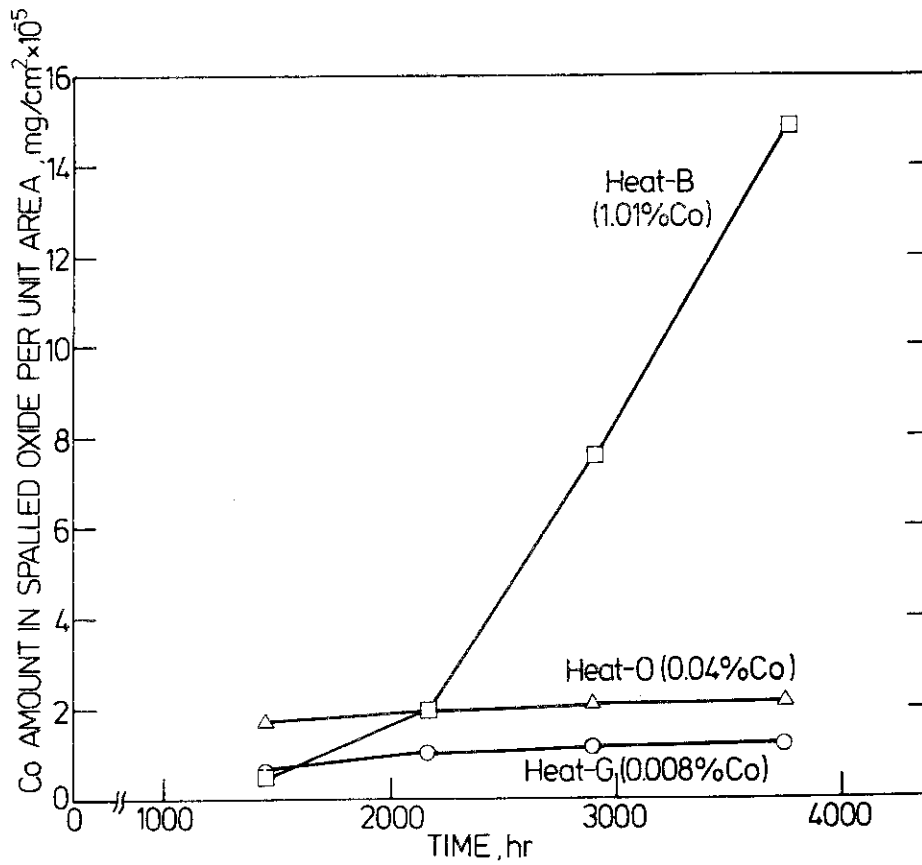


Fig.8 Release rate of Co from unit area of three heats surface.