On the Attribution of the Super Oxidation-resistance of Cemented Chromium Carbide

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Introduction

At present, the various kinds of the titanium carbide, TiC, or chromium carbide, Cr_3C_2, base sintered products have been successfully investigated as a superior heat-resistant material. Among them, the cemented chromium carbide, "CR", gives promise of many useful practices of chemical engineering because of its supper oxidation- and corrosion-resistance.

On the method of manufacture of the "CR" product and its properties, some valuable studies have been published[1]. Recently, the effect of the added chromium carbide on the oxidation-resistance of the other cemented carbide products was studied by J. Hinnüber and co-workers[2], yet much remains to be investigated on the cause of this remarkable oxidation-resistance.

Therefore the experimental work of this report has been to investigate the relationship between the structure of the surface oxidized film and the oxidation-resistance. Namely, the crystal structural change of the surface oxidized film at various temperatures was examined mainly by the electron diffraction method, and, at the same time, its microstructural change was also observed by electron microscope.

Experimental Method

The "CR" alloy was produced by sintering a compacted body of Cr_3C_2 powder mixed with 15 weight per cent of pure Ni powder with the same process reported by Y. Matsuyama, S. Kasahara and H. Hase[3]. The specimens of "CR" used here were given by Tungaloy Co.. Their characters were as shown in Table I.

Specimens for electron diffraction were prepared by the following procedures: making a bar with 4 mm. of diameter and about 10 mm. of length from this "CR" alloy, polishing the one end of the bar and then cleaning it with 10% HCl solution, distilled water, methyl alcohol and benzen in this order.

TABLE I

THE PROPERTIES OF THE "CR" ALLOY

Alloy / Properties	CR
Density	~ 6.9 g./cm^3
Hardness	at Room Temp. 84–88 Hr A.
	at 500°C 83–36
	at 900°C 73–31
Trans. Rupt. St.	70 kg./mm^2
Ther. Expans.	at 30–750°C 11.5×10^{-4}
Elect. Resist.	$\sim 4.3 \times 10^{-4} \Omega$ cm.
Magnetic Prop.	(non-magnetic)

CR: Cemented chrome-carbide, Cr_3C_2, contained 15% Ni.

This was oxidized in air up to 1000°C at every 100°C in a ceramic crucible to prevent contamination. These oxidized specimens were at once mounted on the spcimen holder of electron diffraction camera and surface film of them was examined by the reflection method. The diffraction unit used was attached to on the Simazu SM-C2 electron microscope, the camera length 15.9 cm. and acceleration voltage 50 kV.

At the same time, a micro structural change of the surface oxidized film at various temperatures was observed by electron microscope with the polysthylene-Al replica method. On the other hand, the process of oxidizing of the carbide powder itself was also observed by means of X-ray analysis and electron microscopy.

Moreover, the structure of the sintered product as determined with a special X-ray diffraction method and at the same time the Curie point of this specimen was also measured with magnetic balance.

Experimental Results

I. On the Oxidation Resistance of "CR" at High Temperature

According to J. Hinnüber's results, the "CR" alloy increased in weight by being heated in air at each temperature of 500, 600, 700, 800, 900 and 1000°C for one hour. As shown in Table II, the weight-gain was so small that the advancing of oxidation was not confirmed below 800°C. Though the weight-increase was small, it came to be measurable at 1000°C. In our results, the lustre of the polished surface changed little at 300°C, then faded gradually with the rise of temperature and vanished completely at

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[1] J.D. Kennedy, *Steel*, **131**, 92 (1952); P. Schwarzkopf and R. Kieffer, "Refractory Hard Metals", (1953) p. 122.

[2] J. Hinnüber and O. Rüdiger, *Archv. für Eisenhüttenwesen*, **24**, 267 (1953).

[3] Y. Matsuyama, S. Kasahara and M. Hase, Reported in the annual meeting of Japan-Kinzoku-Gakkai (1954).

TABLE II

WEIGHT INCREASES OF "CR" BY OXIDATION AT VARIOUS TEMPERATURS FOR TWO HRS. IN AIR, FROM J. HINNÜBER AND CO-WORKER'S RESULTS

Temperature °C	Weight increase g./m², hr.
500	<0, 1
600	<0, 1
700	0, 2
800	0, 2
900	0, 75
1000	1, 2

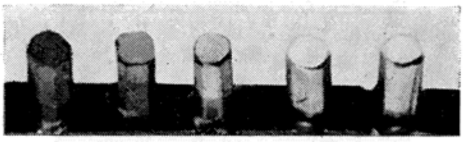


Photo. I. The lustre change of the polished surface by oxidation at various temperatures for 1 hr. in air.

TABLE IV

WEIGHT INCREASES OF Cr_3C_2 POWDER BY HEATING AT VARIOUS TFMPERATURES FOR ONE HOUR IN AIR

Temperature °C	Weight increase	By X-ray※ diffraction
300	−5 mg./g. hr.	—
500	5 〃	3%
800	150 〃	60%
1000	——	90%

※ The estimation was measured by comparing the observed intensities of oxide lines with the standards.

1000°C or up (Photo. I), while a faint color appeared first at 300°C for two hours, then changed with the rise of temperature. These results were described in Table III. These changes of lustre and color corresponded with the above weight-increase.

TABLE III

THE CHANGES OF THE COLOR, THE STRUCTURE AND THE COMPOSITION OF THE OXIDE FILM DURING OXIDATION

Temperature °C	Color	The composition of the oxide-film	Remarks
100	Metallic lustre	Imperfect Cr_2O_3	
200	Metallic lustre	Imperfect Cr_2O_3	
300	Metallic lustre, Very faint bronze-like color	Cr_2O_3	Little oriented crystals
350	Metallic lustre, Faint bronze-like color	Cr_2O_3	Little oriented crystals
500	Lustre, Bronze-like color	Cr_2O_3	At random orientation
800	Faded lustre, Green black color	Cr_2O_3	〃
1000	Non-lustre Green and gray	Cr_2O_3 and NiO–Cr_2O_3	〃

From these results, it shoult be concluded that the "CR" alloy is useful for practical purposes of long time operation at such high temperature as 800°C in air. It must be studied whether such an excellent oxidation-resistance is based on these starting materials themselves or any characteristic structure of these oxidized films. Firstly, oxidizing the chrome carbide powder, Cr_3C_2, itself at various temperatures, the weight-increase was measured as shown in Table IV, and also, the crystal structural change of its powder was observed by the X-ray method such as illustrated in Photo II. This indicated that Cr_3C_2 had begun to change into Cr_2O_3 at 500°C already, and then the weight-gain step by step increased with rising temperature. On the other hand, the oxidation-resistance of nickel, which was the binder of "CR", was checked: Ni plate was heated in air and the structure of surface was examined by the electron diffraction. The patterns obtained were shown in Photo. III. It also indicated that the formation of NiO are faintly observed at 300°C and clearly at 500°C. It is worth being discussed that, as understood from these above results, though each component of "CR" alloy, Cr_3C_2 and Ni becomes unstable at even lower temperature than 500°C, the sintered products were stable for oxidizing for a long time at such a high temperature as about 800°C. This result suggests that the oxidation-resistance of "CR" alloys is attributed to the formation of some desirable protective film.

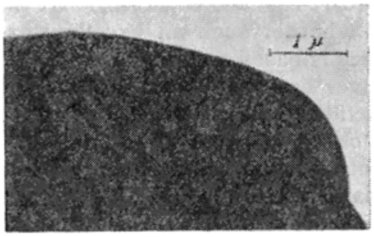
II. The Structure of Oxide Film

Therefore, to confirm the formation of such protecting surface film, the variations of the surface structure with oxidizing at various conditions were examined by the electron diffraction.

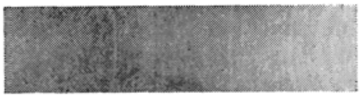
The abstract of the main results from these observations were enumerated in Table III.

Phot. II. The shape and structural change of chrome-carbide powder during oxidation process.

(a)

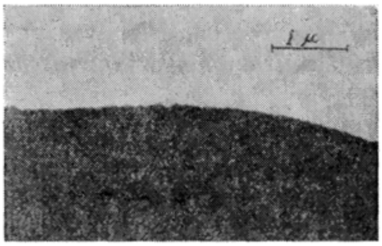


at 300°C for 1 hr.



Cr_3C_2

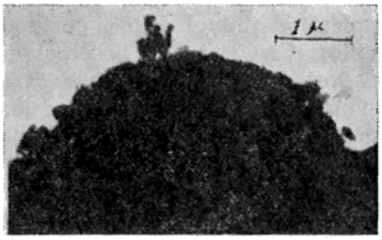
(b)



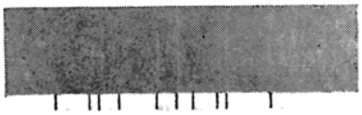
at 500°C for 1 hr.

Cr_3C_2

(c)

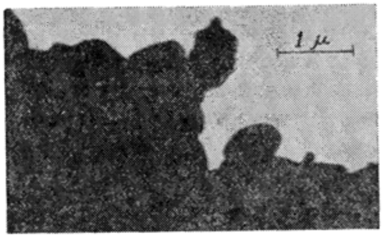


at 800°C for 1 hr.

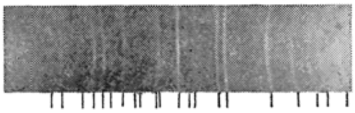


Cr_2O_3

(d)



at 1000°C for 1 hr.



Cr_2O_3

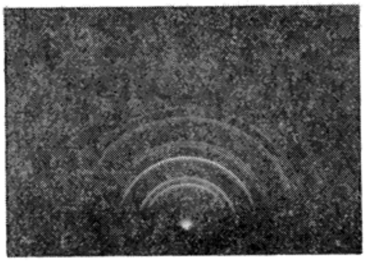


Photo. III. The electron diffraction pattern of the oxidized Ni plate at 500°C for 1 hr. in air.

Among them, the interesting results would be reviewed as follows.

i) The surface film consisted of one kind of chromic oxide, Cr_2O_3, only and not of other chromium oxide or nickel oxide below 800°C. When at such higher temperature as about 1000°C, remarkable oxidation was observed by weight-increasing, then both Cr_2O_3 and the chromium-nickel spinel, $NiO \cdot Cr_2O_3$, were first observed in the oxide film.

ii) Concerning the chromic oxide filme below 800°C, the variation of its structure corresponding to the rise of temperature was so remarkable as not to be expected previously. Namely, the surface films heated from the room temperature to 250°C for one hour consisted of very fine and imperfect crystallites of Cr_2O_3 and, moreover, were very flat. Heating it at 300°C in air continuously, the imperfect crystallites of Cr_2O_3 in the oxide film altered into perfect ones and tended to be oriented, their basal planes being parallel to the surface. This tendency was observed up to 500°C. However, in the oxidized film at higher temperature than 500°C, such orientation became at random and, the surface, also, became rough step by step. On these problems, the further sufficient explanations must be supplied as follows.

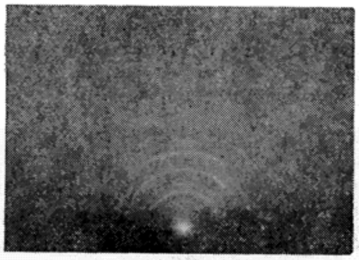
a) The confirmation that the oxide film at lower temperature was composed of imperfect and minute crystallites was based on the experimental evidences of the diffraction patterns. The diffraction patterns as Photo. IV (1) and Fig 1, are interpreted to be two-dimensional-like patterns diffracted by imperfect crystallites of Cr_2O_3 with the crystal basal planes slipped at random as observed in the polished graphite pattern4). At the same time, the diffuse ring patterns indicated that the crystallites were very minute. In the sample, oxidized at higher temperature,

Photo. IV. The electron diffraction patterns of oxide film formed on the surface of "CR" by oxidation at various temperatures for 1 hr. in air.

(1)

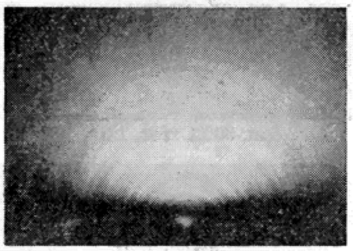
at 300°C for 1 hr.

(2)



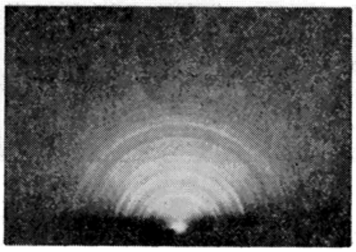
at 300°C for 2 hr.

(3)



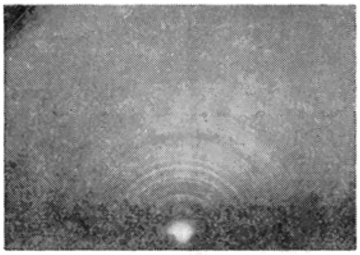
at 350°C for 1 hr.

(4)



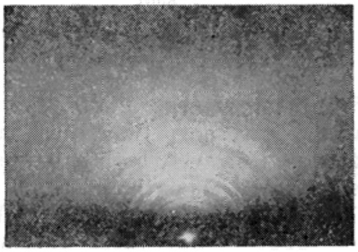
at 350°C for 8 hr.

(5)



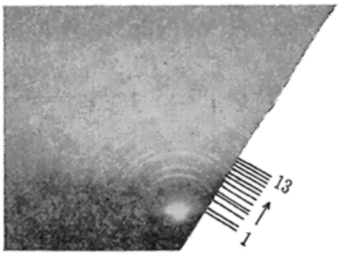
at 500°C for 1 hr.

(6)



at 800°C for 2 hr.

(7)

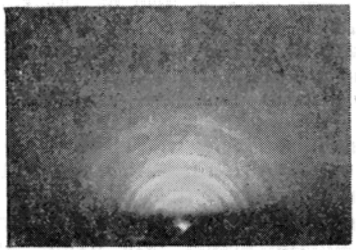


at 1000°C for 1 hr.

Comparison between observed spacing and the spacing of spinel oxide, Cr_2O_3NiO

	Observed	Spinel
1	4.75 A	4.79 A
2	4.26	4.15
3	2.96	2.94
4	2.52	2.50
5	2.40	2.40
6	2.12	2.10
7	1.92	1.91
8	1.73	1.77
9	1.64	1.63
10	1.50	1.50
11	1.44	1.445
12	1.347	1.345
13	1.299	1.297

(8)



Previously heated at 350°C for 1 hr. and again at 800°C for 1 hr.

Fig. 1. The sketch of the electron diffraction pattern of the polished surface.

the diffraction patterns Photo. IV, (6) were *more remarkably sharp than* those at lower temperature. However, both patterns always coincided with Cr_2O_3 patterns.

b) The appearence of arcing in Photo. IV (2) must suggest that these chromic oxide crystallites were oriented. Orientation was determined by the ordinary method, using the reciprocal lattice as illustrated in Fig. 2.

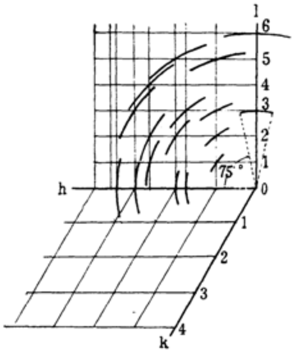


Fig. 2. The schematic diagram of the diffraction pattern of oriented chromic oxide crystals with their C-axis inclined 75°C to the matrix surface, in reciprocal lattice.

This figure shows the diffraction pattern of oriented Cr_2O_3 crystals with their C-axis inclined at the angle of 75° to the matrix surface.

c) Film-thickness or flatness can be estimated from the electron-microscopic photographs substantially, also by the ring width or diffusing behavior of the electron diffraction pattern. The arcs of the diffraction patterns obtained from the specimens below 500°C, diffused toward the centre of the ring. This diffused ring was different from the usual halo pattern and interpreted to be originated from a refraction of electrons because of the very flat surface.

d) In the oxidized film at 1000°C, the existence of the spinel type oxide, $NiO \cdot Cr_2O_3$ was confirmed with the result of Photo. IV (7). This pattern and spacing showed a good agreement with the spinel type oxide observed previously on the surface oxide film of Ni–Cr alloy. It has been reported by several workers[5,6] that the oxidation-resistance of this alloy at high temperature took place because of the formation of the densed and flexible oxide film of $NiO \cdot Cr_2O_3$.

However, in this experimental result, the oxide film composed of this spinel oxide did no longer act the most effective part in preventing the oxidation. Though it is interesting to consider why this spinel oxide was formed on the surface of this product, this will be discussed in the later.

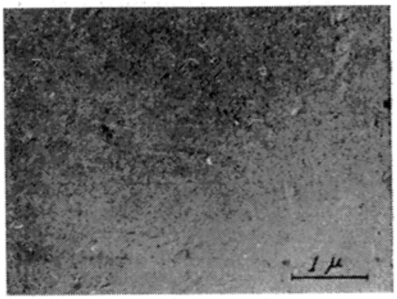
From the above-mentioned results, it will be suggested that the tendency of the oxidation-resistance declines with the increasing roughness of the surface film, because of the crystal-growth of Cr_2O_3 crystallites. To study this problem, the micro-structural change of surface must be observed sufficiently.

III. Observation of the Microstructure of the Surface

The microstructure of each surface film treated at various conditions were illustrated in Photo. V. It was proved from these figures

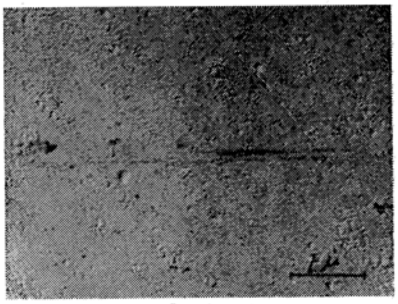
Photo. V. The electron-microscopic structure of each surfaces of "CR" in various stages in oxidation.

(1)



at 300°C for 1 hr.

(2)



at 500°C for 1 hr.

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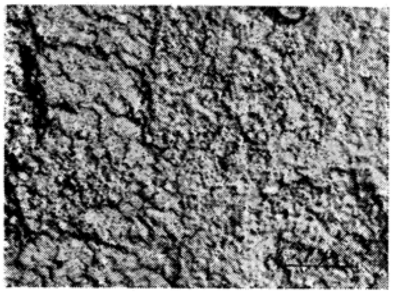
[4] G.P. Thomson and W. Cochrane, "Theory and Practice of electron diffraction", (1939) p. 185.

[5] J. Iidaka and S. Miyake, *Nature* **137**, 457 (1935).

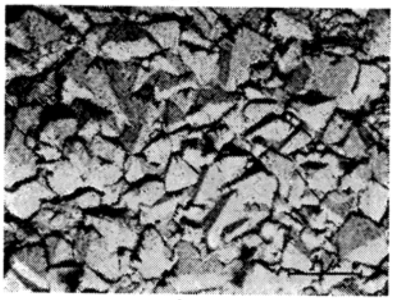
[6] A. Gulbransen and W. R. McMillan, *Ind. Eng. Chem.*, **45**, 1734 (1953).

(3)



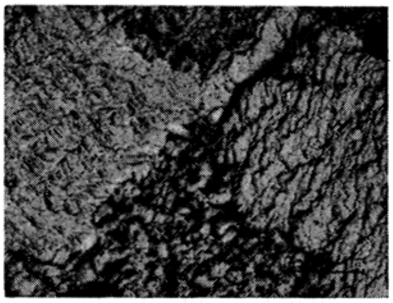
at 800°C for 1 hr.

(4)



at 1000°C for 1 hr.

(5)



Previously heated at 250°C for 1 hr. and again at 1000°C for 1 hr.

that the appearance of the surface up to 500°C was very flat, and the grain size was too small to be measurable as already suggested. However, the oxidized surface above 800°C, became more rouge consequently, and, in this film, the coarse chromic oxide crystals were observed as showed in Photo. V (4).

Moreover, in the oxidized film at 1000°C, the grains became so coarse that their diffraction pattern rings were spotty as shown in Photo IV, (7). Sometimes, as appeared in Photo. V (4), piramid-like large grains of one micron order were observed and the surface began to break out into small cracks.

From such a result, it will be confirmed that the increasing roughness of the surface may be caused by the coarsening of the minute chromic oxide crystals.

It is a valuable new result to discover that the stability of protective film may be more responsible for the structure of film, than the kinds of oxide.

IV. The Inner Structure of "CR" Tip

Lastly, it must be studied why the oxidized film below 800°C consisted of one kind of the chromic oxide, Cr_2O_3, though the nickel binder metal was oxidized already into NiO at 500°C.

Concerning this problem, though it was recently suggested by J. Hinnüber that the binder phase would exist in the alloying state, yet it has not been confirmed experimentally.

Therefore, the inner structure was examined by X-ray and magnetic balance. The method of the X-ray diffraction of "CR" tip was outlined in Fig. 3 and its photographs were illustrated in Photo. VI in which were observed the ortho rhombic structure, Cr_3C_2, and a face centered cubic structure.

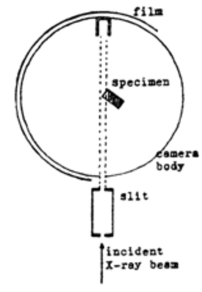


Fig. 3. The method of mounting specimen in this X-ray diffraction.

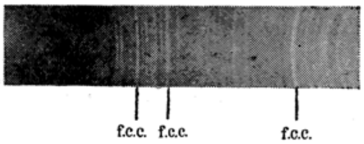


Photo. VI. The X-ray diffraction pattern of "CR" showing some f.c.c. structure.

Though the difference between the lattice constants of this f. c. c. and Ni was almost never observed, it seemed that this f. c. c. was perhaps not the pure Ni. This f. c. c. did not appear in the specimen sintered at such a lower temperature as 500°C, but appeared first clearly at the higher temperature at which the reaction between Cr_3C_2 and Ni occurred. However, the reason was not yet clear that the pure Ni was not observed by X-ray diffraction patterns in the specimen sintered at the lower temperature.

Therefore, when the magnetic properties of these specimens were measured, the intensity of saturation magnetization of the specimen sintered at the temperature which the f. c. c. appeared, was more remarkably small than that of the sintered one at the lower temperature. On the other hand, the Curie temperature of the specimen was measured by magnetic balance. One of these results was shown in Fig. 4.

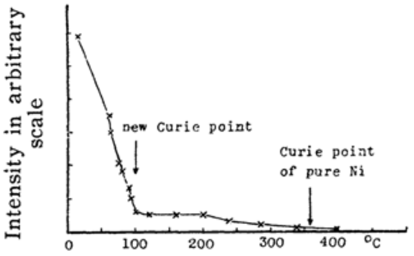


Fig. 4. Magnetization curve of " CR ".

This indicated a Curie temperature of 100°C differing from the usual one, 358°C of the pure Ni. Curie points lay below 150°C, and the amount of these materials which have these Curie points are more numerous than pure Ni, as they can be estimated from Fig. 4.

If this alloy is assumed to be Ni-Cr solid solution, it will be expected that the quantity of Cr dissolved in Nickel binder phase is 5 per cent or more by weight. Therefore, it can be confirmed that the binder phase no longer exists as pure Ni, but as some Ni-Cr alloy or some intermetallic compound of double carbide of Cr_3C_2-NiC. If this assumption is true, then the appearing of nickel chrome spinel at 1000°C coincides with the previous works.

General Discussion

From these experimental results, two subjects to be discussed more sufficiently were as follows.

a) The oxidation of " CR " was nothing but the complicated process combined with the following to processes: the decarburization and oxidation of the Cr_3C_2 grain, and the oxidation of some Ni-Cr alloy in the part of binder.

b) The dense and flat oxidized film composed of the chromic oxide crystallites very suitable for oxidation-resistance. In such film, these minute crystallites tend to have a orientation.

With the coarsening of these crystallities, the surface became rough gradually, and broke out into small cracks. Such film was not sutiable to prevent oxidation. Generally speaking, it was confirmed that the tendency of oxidation-resistance depended not only on the kind of oxide but on the chracteristic structure of the surface film.

Firstly, from the above mentioned experimental confirmation that " CR " consisted of both Cr_3C_2 and some Ni-Cr alloy, the consideration in the item a) was concluded.

From the previous experimental results, the reason was easily understood why the formation of the spinel oxide, $NiO \cdot Cr_2O_3$, was observed in the oxidized film at 1000°C or up. However, to our regret, the reason of the nickel oxide not being found in the oxidized film below 800°C has not yet been revealed.

According to the information of the oxidation process of Ni-Cr alloy by J. Gulbransen, the nickel mono-oxide was observed at such a low temperature at 500°C, and its tendency depended considerably on the composition of such alloy.

Though this difference between our result and Gulbransen's might have been due to small amounts of Ni-Cr alloy in " CR ", further studies were necessary.

Secondly, as described in the item b), the oxidation-resistance depended also on the structural change of the surface film. Therefore, it was necessary to understand a mechanism of the decarburization and oxidation of Cr_3C_2, during which process the structure of the oxide film changed with rise of temperature. To understand it easily, some models of oxidation process were sketched schematically in Fig. 5. This film consisted of small bricks, which were the chromic oxide crystallites, and the noted arrow in the bricks was the direction of C-axis. The brick pictured with the broken line was the imperfect crystal. The shaded one was the spinel-type oxide. As shown in these figures (a) (b) (c), the surface film was the aggregation of the chromic oxide crystallites. With the rise of temperature, these changed in size as well as in the crystal structure. In the figure (c), the oxide film composed of these oriented crystals carried out the effective role in preventing the oxidation. These models were devised from the above-mentioned experimental results by the electron diffraction. In the figures (d, e), the surface became more rough corresponding to the crystal growth of these crystallites. In this stage, these crystals grew remarkably at random and the rate of oxidation increased rapidly. This model was devised from the

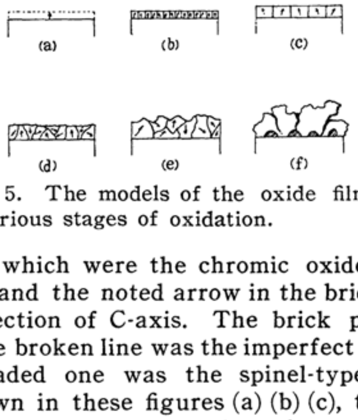


Fig. 5. The models of the oxide film at various stages of oxidation.

experimental results concerning the surface micro-structural change of "CR" and the shape-change of Cr_3C_2 powder in oxidation. During the oxidation of the chrome carbide (Cr_3C_2) powder at various temperatures the irregularities were formed on the surface of powder, and increased with the rise of temperature. This result was shown in Photo. II (2).

Lastly, a little more description of the oriented film was added.

When the specimen already heated to have the oriented film was heated again at higher temperature with the virgin one, the latter tended to be more remarkable in the crystal growth and the increasing roughness of surface than the former. Such tendency was observed from the comparison in Photo. V (4, 5).

From this experimental result, it was confirmed that the oriented film was more suitable for oxidation-resistance than the non-oriented one, yet much remained to be investigated.

The authors wish to express their great indebtedness to Professor Keizo Iwase for helpfull advice, and Professor Ryoji Uyeda for useful discussions in the part of the electron diffraction pattern. Thanks are due to Mr. Kazuichi Sugiura for aid in the electron microscope work, and also Tungaloy Products Co. which kindly offered them the specimens.

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Tungaloy Products Co.