Reaction of Cobalt-Chromium Casting Alloy with Investment

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SYNOPSIS IN INTERLINGUA

REACTION DE ALLIGATO FUSIONAL DE COBALT E CHROMO CON INVESTIMENTO.—Alterationes chimic occurrente intra le investimento ligate a phosphato durante le prisa e le cocer esseva determinate per technicas a diffraction de radios X. Es postulate le occurrentia de certe reactiones durante le processo. Tests del resistentia al compression effectuate a varie temperaturas corroborava ille postulatos.

Esseva trovate al interfacie inter alligato e investimento tres productos de reaction. Immediatemente adjacente al alligato se formava un scalia de color gris sequite de un intimemente adherente scalia de color verde. Esseva etiam trovate intra le investimento areas de un composito de color rubiastre-brun. Le sonda electronic esseva usate pro analysar iste productos.

Cobalt-chromium alloys have been applied in the field of dentistry as investment castings for partial dentures. These alloys are light, strong, and corrosion-resistant, but the metal does not have adequate ductility for adjustment purposes. Previous research work has shown that one means of obtaining this property is to superheat the alloy before casting.[1] However, this procedure causes extensive reaction of the metal with the mold and a close-adhering green scale forms. Removal of this scale requires excessive machining, and loss of dimensional accuracy results. As part of a project to improve cobalt-chromium casting alloys, a study was made to find means of minimizing this scale formation.

To analyze the reaction occurring at high temperature, the nature and chemistry of the investment must be known. Work has been done in the ceramic field on many of the compounds present in the investment. Also, in a general way, dental researchers have discussed reactions that may occur. But, the information is scattered and incomplete.

The phosphate-bonded investment was considered in this investigation, since this investment has favorable high-temperature properties and had been used in the previous investigation.[1] In the phosphate-bonded investments, a soluble phosphate compound

(e.g., $NH_4H_2PO_4$, $Mg(H_2PO_4)_2$, or H_3PO_4), which produces a phosphate ion, and a metallic oxide (such as MgO) form the bond which gives the strength to the investment.

According to Moore and Watts,[2] the basic reaction causing setting at room temperature is $NH_4H_2PO_4 + MgO \rightarrow NH_4MgPO_4 + H_2O$. This is considered a temporary crystalline bond and is expected to decompose upon heating. Gilham-Dayton[3] has postulated that the product formed could be di- or trimagnesium phosphate or $NH_4MgPO_4 \cdot 6H_2O$. Kiehl and Hardt[4] have shown that the compound $NH_4MgPO_4 \cdot 6H_2O$ forms an intermediate hydrate ($NH_4MgPO_4 \cdot H_2O$) at about 50° C. upon heating. Above this temperature, dissociation of the ammonium salt begins, so that by 250° C. $Mg_2P_2O_7$ forms. Earnshaw[5] has found experimentally that on heating expansion slows to the point of shrinkage at 100° C. and attributed this to a loss of water. He also found, "Copious evolution of white fumes occurred in the temperature range 200–260° C.; at the same time ammonia was also given off." A shrinkage also occurred at temperatures above 280° C., in his opinion due to chemical reaction.

The bond that exists at high temperatures is attributed to a silicophosphate bond. Tien and Hummel[6] have formed $SiO_2 \cdot P_2O_5$ quite readily by heating $NH_4H_2PO_4$ and silicic acid together and holding at 700° C. Moore and Watts[2] have felt that the silicophosphate bond is formed at the 280° C. temperature.

Another point considered was the green

TABLE 1

CHEMICAL ANALYSIS OF THE ALLOYS USED

	Cr	W	Fe	C	Si	Co	Ni	Mn	Mo	B	P	S
HS 21.....	27.43	....	1.67	.27	.68	Bal.	2.51	.69	5.45	>.001	....	....
HS 31.....	24.81	7.54	1.65	.48	.72	Bal.	10.47	.78	....	.....	.016	.011

scale formed at the interface during casting. Morral* has pointed out that a reaction can be expected at high temperatures when MgO is used in the investment. Sully[7] has also discussed problems of mold reaction encountered during casting of chromium alloys and has advised using the highest melting refractory mold materials (e.g., zirconia or thoria). Chromium was found to oxidize quite readily during casting. Work has been done by Phalniker, Evans, and Baldwin[8] on the oxidation of Co-Cr alloys. They have found that the alloy was most resistant when 25 per cent chromium was added to the cobalt, and that selective oxidation of chromium protected the alloy. CoO was found immediately adjacent to the alloy. Chromium compounds, rather than those of cobalt, occurred at a further distance from the metal surface, indicating a higher diffusivity of the chromium as compared with cobalt. Felten and Gregg[9] have found the initial oxidation product to be Cr_2O_3. Little work other than oxidation of the alloy has been done, and no results have been reported on interface reaction of Co-Cr alloys with investment.

In this investigation, the compounds present at the various stages of the mixing and casting procedure were analyzed by x-ray-diffraction techniques. To verify the results obtained on the green scale reaction product, samples were also analyzed by the electron probe. By combining the present knowledge with our results from x-ray-diffraction and electron-probe analysis, we propose certain reactions to occur during the investing and casting procedures. Compressive strength tests were then run to test the validity of the reactions.

Materials and Methods

Phosphate-bonded investments have the following approximate composition: quartz

and cristobalite, 90 per cent; MgO, 3 per cent; acid phosphate, 7 per cent. The selected investment† was mixed with liquid‡ and the following stages were selected for analysis: (1) investment powder, (2) set investment, (3) burned-out investment, (4) green scale formed as reaction product with two casting alloys.§

The compositions of the alloys are given in Table 1.

The powder method of x-ray diffraction was used for analysis.[10] The samples were ground and passed through a 300-mesh screen. The powder was mixed with cement,‖ formed into a rod-like shape, and mounted in the camera. The high silica content limited the extent to which analysis could be carried out, and the silica lines possibly obscured lines of minor constituents which could be present. Separation methods were used in stages 2, 3, and 4 and aided in the analysis. However, some lines were not identified.

To avoid any possible fluorescence, Cu radiation was chosen as most suitable for analysis of the investment. A Ni filter was used. Since any of the metal could be present in the scale in stage 4, the use of a Cu target was questioned. However, very little scatter was found in the results, which would indicate that very little or no Co was present in the green scale.

Microscopic examination has shown three different reaction products occur. The green scale is predominant. A reddish-brown compound also occurs occasionally as discreet nonadhering crystals. The other scale is a gray reaction product, which occurs in a very thin layer (actually, between the green scale and the metal) immediately adjacent

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* F. R. Morral, Cobalt Information Center, personal communication.

† Ceramigold Investment, Whip-Mix Corporation, Louisville, Ky.

‡ Ceramigold Liquid, Whip-Mix Corporation, Louisville, Ky.

§ Haynes Stellite 31 and 21 alloys, Kokomo, Ind.

‖ Duco-cement, DuPont, Wilmington, Del.

TABLE 2

COMPOUNDS FOUND DURING X-RAY DIFFRACTION ANALYSIS

1. *Investment powder:*
    α-Quartz MgO
    α-Cristobalite $NH_4H_2PO_4$
2. *Set investment:*
    α-Quartz $NH_4H_2PO_4$
    α-Cristobalite $NH_4MgPO_4 \cdot H_2O$
    MgO $Mg_3(PO_4)_2 \cdot 4H_2O$
3. *Burned-out investment:*
    α-Quartz $Mg_2P_2O_7$
    α-Cristobalite SiP_2O_7
    MgO $Mg_3(PO_4)_2$
4. *Formed as reaction product:*[*]
    α-Quartz
    α-Cristobalite $MgCr_2O_4$ ($MgO \cdot Cr_2O_3$) (most probable)
    $Mg_3(PO_4)_2$ Cr_3O_4 ($CrO \cdot Cr_2O_3$) (possible)

[*]No differences were found in the scales formed by the two different alloys.

to the cast metal surface and is intermingled with the investment.

Investment samples containing the reaction products were embedded in methyl methacrylate.[*] These samples were then polished petrographically until a flat surface of the desired area was obtained. Two different probes were used for the electron probe analysis. One sample analyzed[†] (Fig. 1) contained the green scale (*A*) and the reddish-brown compound (*B*). Scans were run on these two areas and on the investment immediately adjacent to these areas. The other sample analyzed[‡] (Fig. 2) was of the gray reaction product. These results were obtained as elemental readout.

In order to test whether the silicophosphate bond does indeed form at 280° C. as proposed by Moore and Watts, the crushing strength was determined. Three samples were prepared for each temperature. Temperatures were chosen in a step-wise fashion to coincide with possible reaction points, and samples were heated to each of these temperatures and kept at that temperature for 3 hours before they were tested. By this means, the breakdown of the room-temperature bonds also could be followed.

Results

The compounds that were identified in the various stages are listed in Table 2. Typical *d*-spacing values are shown in

[*] Castolite, Castolite Company, Woodstock, Ill.
[†] Norelco AMR/3 Electron Probe Microanalyzer, Philips Electronic Instruments, Mt. Vernon, N.Y.
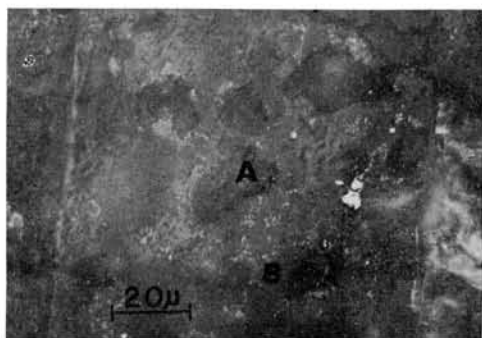[‡] AMX, Applied Research Laboratories, Glendale, Calif.

FIG. 1.—Microstructure of areas in the investment analyzed by microprobe: *A*, green scale; *B*, reddish-brown scale.
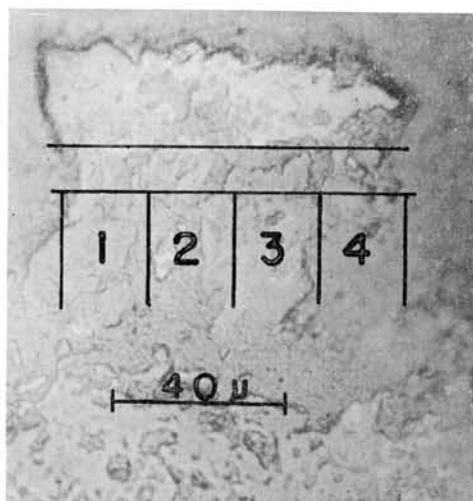

FIG. 2.—Photomicrograph of the investment containing the gray scale. Analysis was made along the area between the two parallel lines.

TABLE 3

TYPICAL D-SPACING RESULTS
(RUN 1—INVESTMENT POWDER)

Intensity	d-Value	α-SiO$_2$	α-Cristobalite	NH$_4$H$_2$PO$_4$	MgO
Scat M	5.324	....	....	5.32 (100)	....
Scat MS	4.264	4.26 (35)	....	....	....
Wide VS	4.044	....	4.05 (100)	....	....
Scat M	3.786	....	....	3.75 (64)	....
Scat W	3.703	....	....	....	....
VVW	3.447	....	3.515 (3)	....	....
Wide VS	3.357	3.343 (100)	....	....	....
M	3.143	....	3.135 (11)	....	....
Scat M	3.102	....	....	3.075 (89)	....
Scat M	3.065	....	....	3.065 (75)	....
M	2.849	....	2.841 (13)	....	....
Scat M	2.661	....	....	2.659 (18)	....
Scat M	2.641	....	....	2.651 (15)	....
Scat MS	2.491	....	2.485 (20)	....	....
Scat W	2.478	....	....	....	....
Scat MS	2.463	2.458 (12)	2.465 (5)	....	....
W	2.439	....	....	....	2.431 (10)
W	2.380	....	....	2.373 (8)	....
VW	2.337	....	2.340 (1)	....	....
M	2.285	2.282 (12)	....	....	....
M	2.244	2.237 (6)	....	....	....
Scat M	2.130	2.128 (9)	....	....	....
W	2.122	....	2.118 (5)	....	....
MS	2.110	....	....	....	2.106 (100)
Scat M	2.013	....	2.019 (3)	2.009 (29)	....
	.....	....	....	2.004 (22)	....
M	1.982	1.980 (6)	....	....	....
W	1.935	....	1.929 (5)	....	....
W	1.876	....	1.870 (7)	....	....
MS	1.825	1.817 (17)	....	....	....
MS	1.815	....	....	....	....
VW	1.778	....	....	1.773 (5)	....
VW	1.695	....	1.690 (3)	....	....
Scat M	1.677	....	....	1.685 (5)	....
Scat M	1.676	....	....	1.677 (4)	....
Scat M	1.673	1.672 (7)	....	....	....
Scat W	1.661	1.659 (3)	....	....	....
M	1.541	1.541 (15)	....	....	....
VVW	1.533	....	1.533 (3)	1.537 (4)	....
Scat M	1.493	....	1.494 (5)	....	....
Scat W	1.491	....	....	....	1.489 (52)
VVW	1.474	....	....	1.473 (4)	....
	.....	....	....	1.470 (5)	....
W	1.455	1.435 (3)	....	....	....
Se- W	1.271	....	....	....	1.270 (4)
lect-	1.217	....	....	....	1.216 (12)
ed	1.050	....	....	....	1.053 (5)
for W	.9421	....	....	....	.9419 (73)
MgO W	.8591	....	....	....	.8600 (15)
	.8107	....	....	....	.8109 (3)

Table 3 for the run of the investment powder. Figures 3 and 4 show the probe results obtained on the green area (A) and on the investment adjacent. Figures 5 and 6 show the results for the reddish area (B) and the adjacent investment. A scan was made across the line marked in Figure 7 for each of the elements which could be present in the area shown in Figure 2. These are presented graphically in Figures 8 and 9. Since each run was set for maximum intensity, the height of each reading relates the quantity of that element present. Manganese is not included in the results, since it did not register anywhere in this sample.
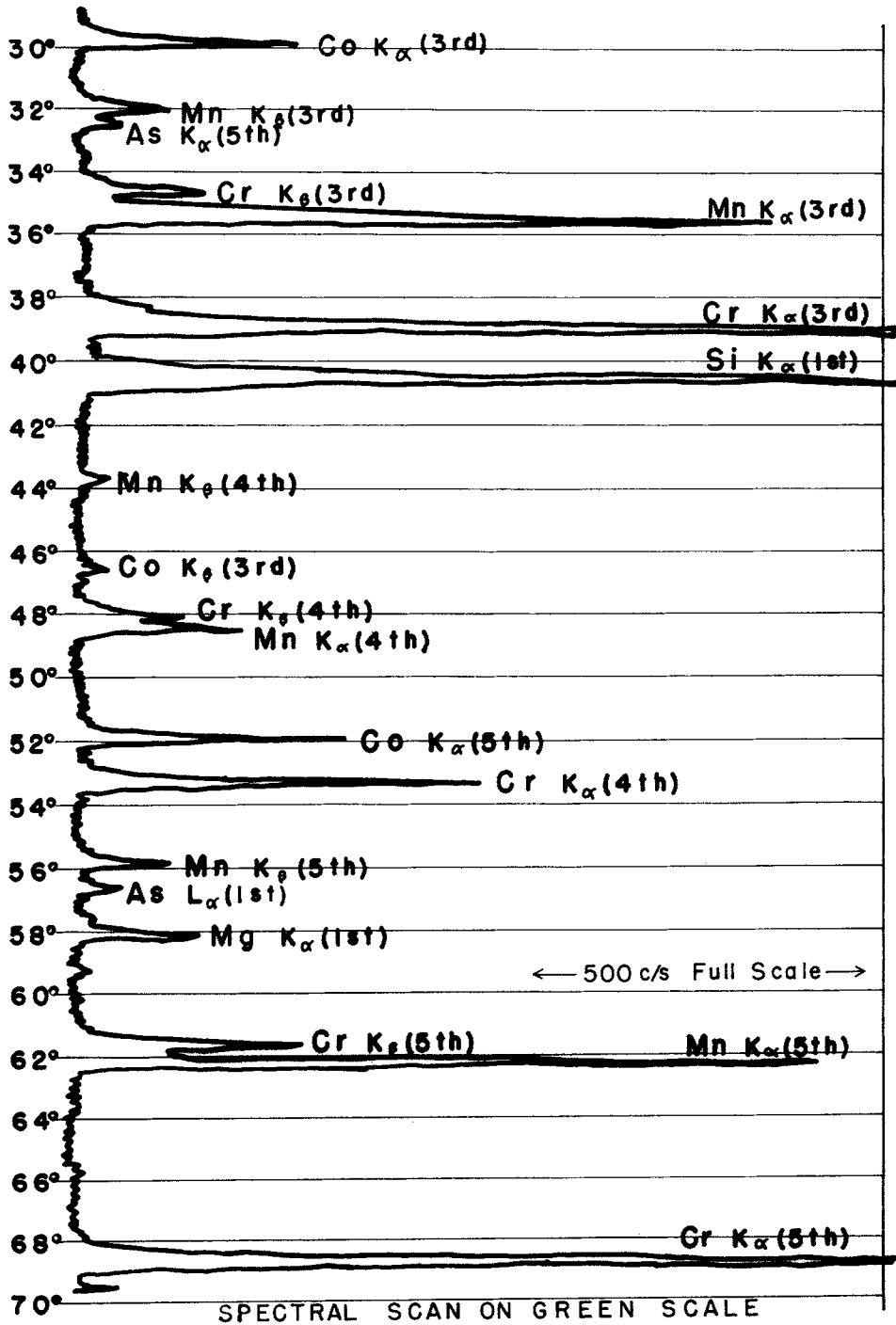
The results for the crushing strength tests

Co Kα (3rd)

Mn Kβ(3rd)
As Kα(5th)

Cr Kβ(3rd)

Mn Kα(3rd)

Cr Kα(3rd)

Si Kα(1st)

Mn Kβ(4th)

Co Kβ(3rd)

Cr Kβ(4th)
Mn Kα(4th)

Co Kα(5th)

Cr Kα(4th)

Mn Kβ(5th)
As Lα(1st)

Mg Kα(1st)

← 500 c/s Full Scale →

Cr Kβ(5th)

Mn Kα(5th)

Cr Kα(5th)

SPECTRAL SCAN ON GREEN SCALE

FIG. 3.—Microprobe results for analysis of green scale.
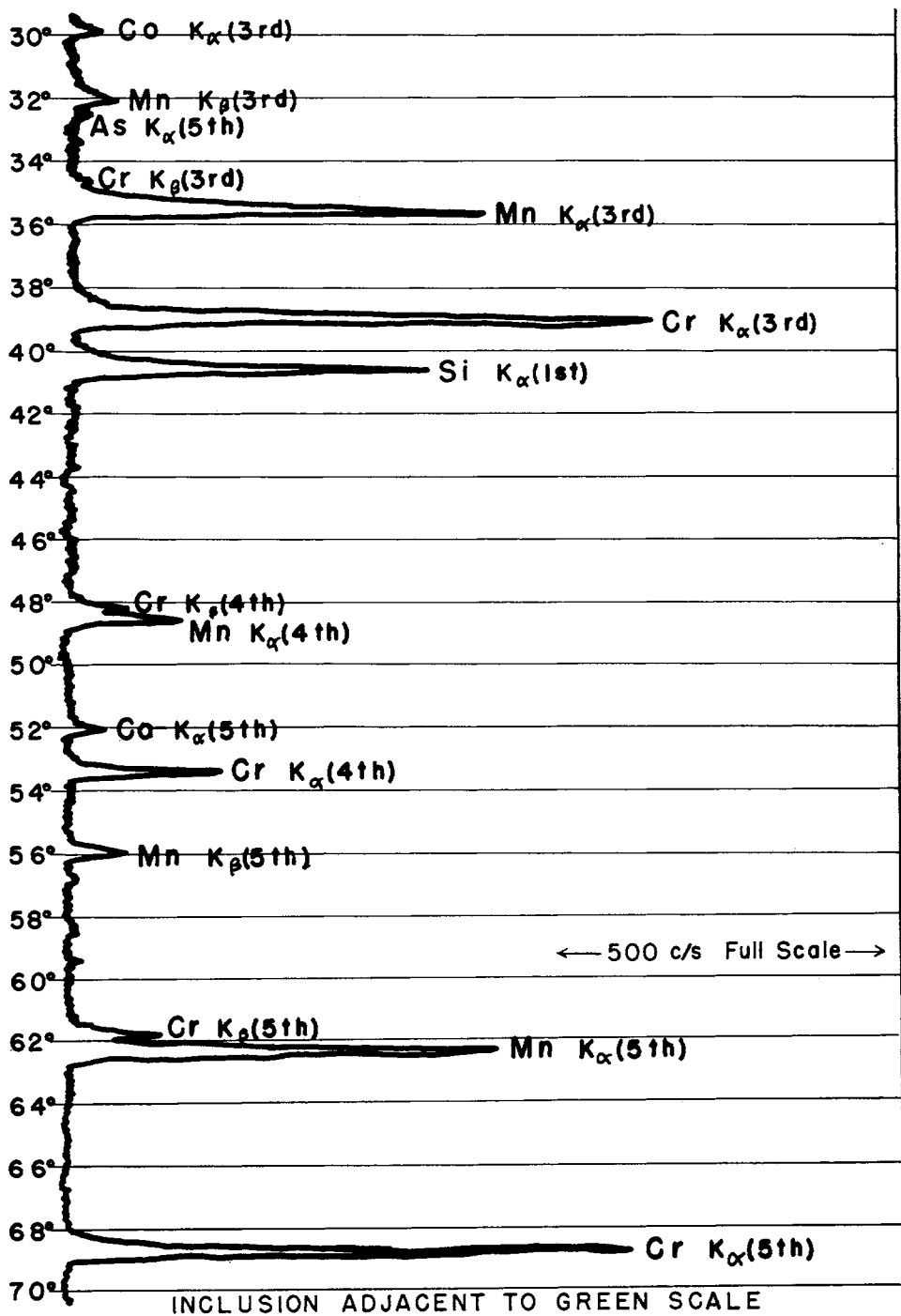
FIG. 4.—Microprobe results for analysis of area adjacent to green scale.

30° — Co Kα(3rd)

32° — Mn Kβ(3rd)
As Kα(5th)

34° — Cr Kβ(3rd)
Mn Kα(3rd)

36°

38°
Cr Kα(3rd)

40° — Si Kα(1st)

42°

44°

46°

48° — Cr Kβ(4th)
Mn Kα(4th)

50°

52° — Co Kα(5th)
Cr Kα(4th)

54°

56° — Mn Kβ(5th)

58°
←— 500 c/s Full Scale —→

60°

62° — Cr Kβ(5th)
Mn Kα(5th)

64°

66°

68° — Cr Kα(5th)

70° — INCLUSION ADJACENT TO GREEN SCALE
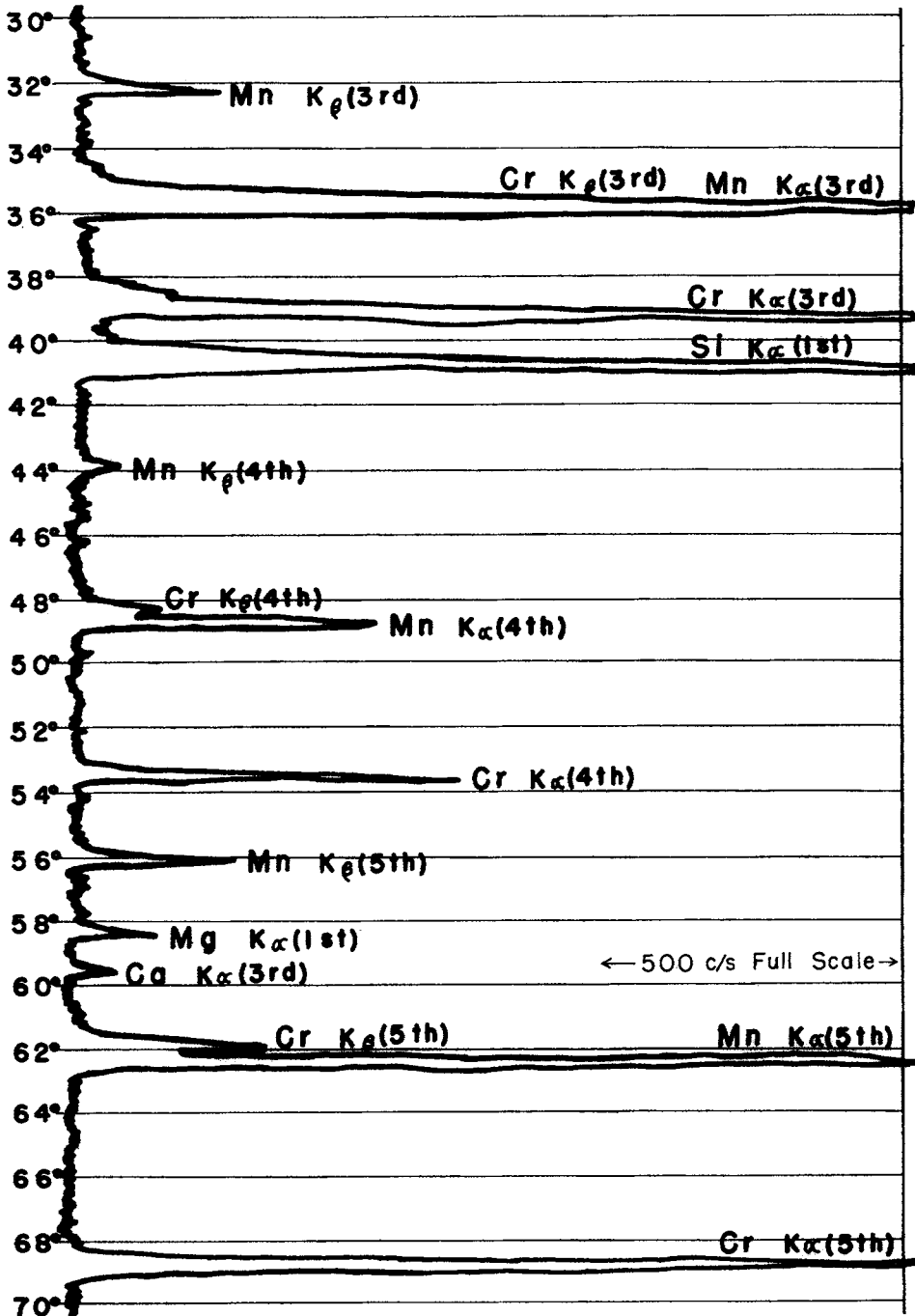
FIG. 5.—Microprobe results for analysis of reddish-brown scale.
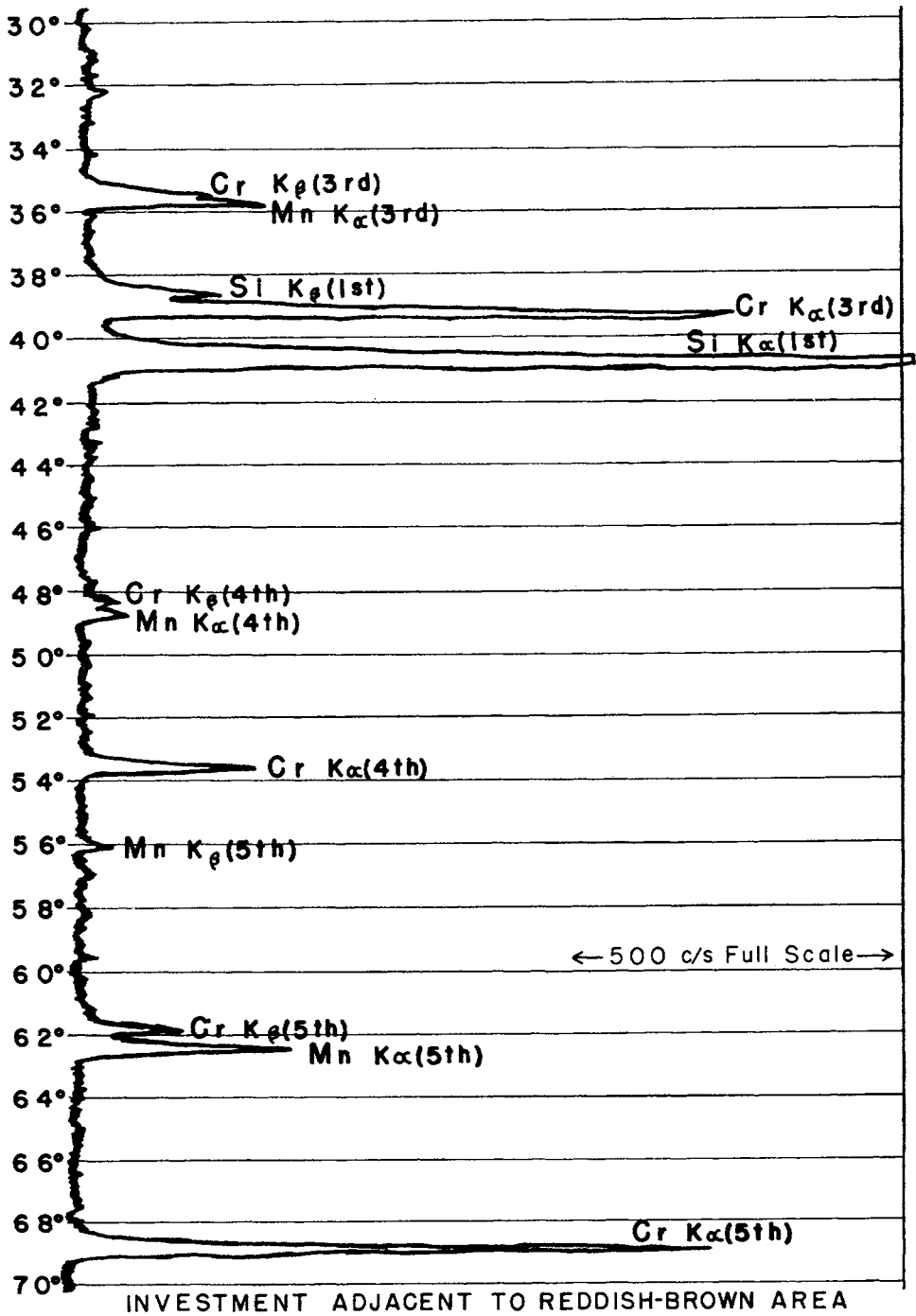
FIG. 6.—Microprobe results for analysis of area adjacent to reddish-brown scale.

TABLE 4

STRENGTH OF INVESTMENT

Temperature (° C.)	Compressive Strength (p.s.i.)	Standard Deviation		Remarks		
Room temperature (2 hours).	1,700	40			Excess Water	
Room temperature (6 days)..	2,100	72	$NH_4MgPO_4 \cdot 6H_2O$ $\downarrow$ $NH_4MgPO_4 \cdot xH_2O$		$Mg_3(PO_4) \cdot 4H_2O$	
200....................	2,000	85	$\downarrow$			
250....................	1,800	10	$Mg_2P_2O_7(250°)$ $\downarrow$			
300....................	1,700	65	completed			$SiO_2 + P_2O_5$
450....................	2,100	65		$Mg_3(PO_4)_2 \cdot xH_2O$		$\downarrow$ SiP_2O_7
500....................	2,300	50		$Mg_3(PO_4)_2$ completed		breakdown of bond
1,000....................	1,150	128				$\downarrow$
1,300....................	1,600	25				fusing
1,400....................	3,100+	...	fusing	fusing	fusing	extensive fusing

are shown in Table 4. The standard deviations of the compressive-strength values are shown. This table also correlates the reactions, so that compound formation and breakdown can be directly related to the strength at that particular tempera-

ture. The analysis-of-variance results of these strengths at the various testing conditions are shown in Table 5.

Discussion

The presence of MgO throughout is attributed to the fact that the compound as received is impure; the manufacturers adjust the amount added to the investment to have a certain percentage of reactive MgO.* The

FIG. 7.—Back-scatter pattern of same area shown in Figure 2. Line designates path of electron beam during scans for the elements.

TABLE 5

ANALYSIS OF VARIANCE FOR COMPRESSIVE STRENGTH FOR DIFFERENT CONDITIONS

| Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square
Specimens (Columns)...	712.64	9	78.07
Experimental Error (Residual).........	15.28	20	0.764

F of the samples $= 78.07/0.764 = 102.1$. F for 95 per cent confidence at $N_1 = 9$, $N_2 = 20$, is given in tables (3.96). (A. J. Duncan, Quality Control and Industrial Statistics, 1955, p. 620.)

MgO that remains is unreactive at mixing temperatures, although reactivity may change with temperature increase.

By co-ordinating the literature survey with the results from this investigation the following reactions are proposed. At room temperature during mixing of the investment:

$2NH_4H_2PO_4 + 2MgO + 6H_2O$

$\rightarrow NH_4MgPO_4 \cdot 6H_2O + NH_4H_2PO_4$ (excess)

$+ MgO$ (unreactive) $+ H_2O$.
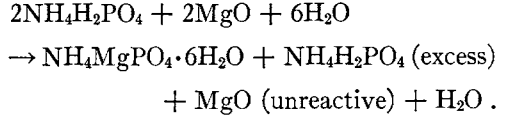
At 100° C. expansion slows to the point of shrinkage, probably due to loss of excess water in the mix. Also water loss, starting
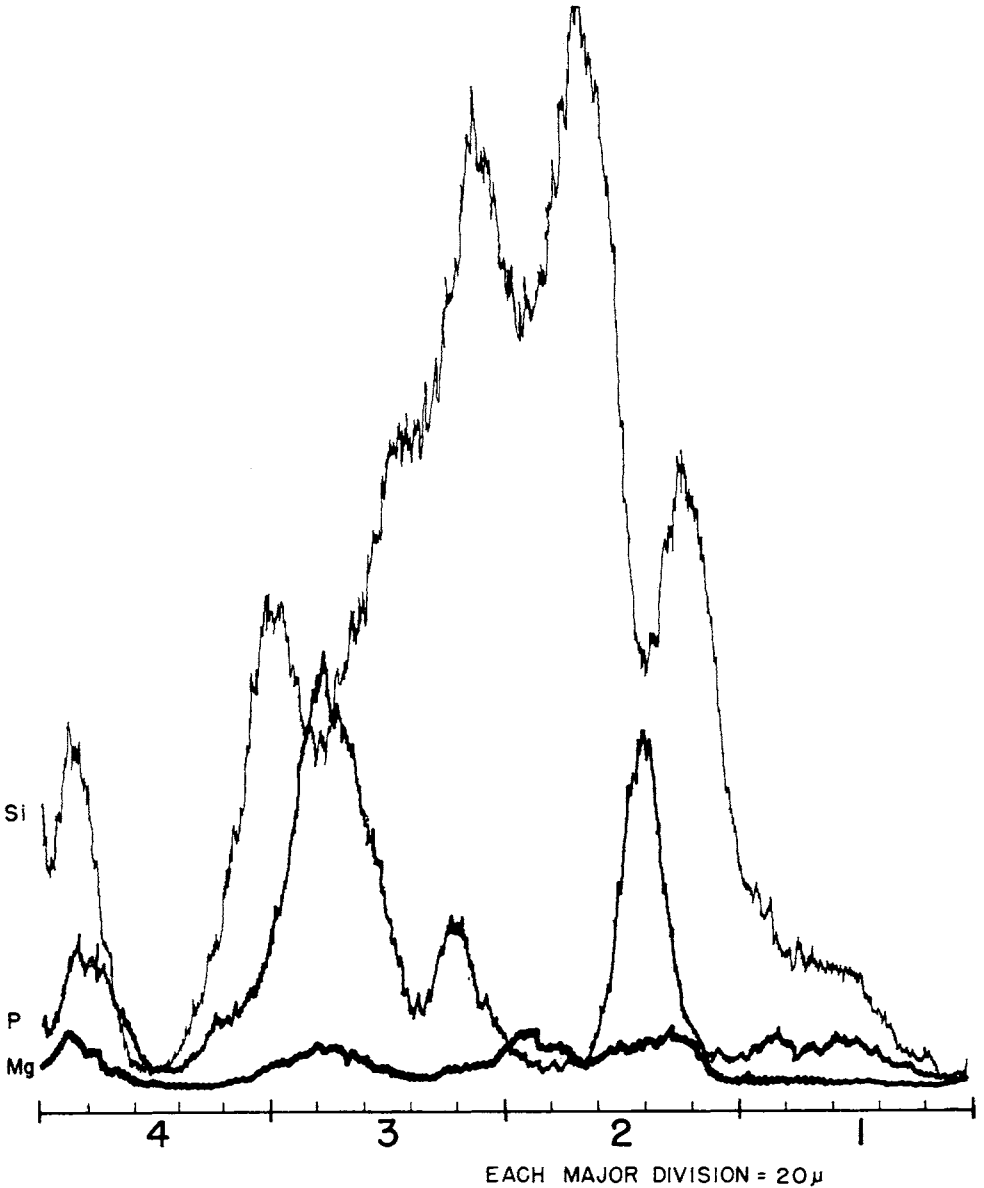

FIG. 8.—Line graphs of investment elements analyzed in Figure 7.

at 50° C., occurs as the hexahydrate is reduced to the monohydrate:[4]

$$NH_4MgPO_4 \cdot 6H_2O \rightarrow NH_4MgPO_4$$
$$\cdot H_2O + 5H_2O \, .$$
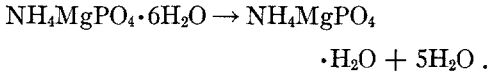
At the same time, ammonia also begins to leave the salt. Under equilibrium conditions, the monohydrate converts as follows by 250° C.:

$$2NH_4MgPO_4 \cdot H_2O \rightarrow Mg_2P_2O_7$$
$$+ 2NH_3\uparrow + 3H_2O\uparrow \, .$$
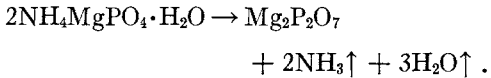
Although not identified in the x-ray-diffraction results, during setting $Mg_3(PO_4)_2 \cdot 4H_2O$ should also form. Upon heating, this compound also loses water:

$$Mg_3(PO_4)_2 \cdot 4H_2O \rightarrow Mg_3(PO_4)_2 + 4H_2O \, .$$
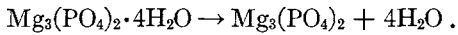
Hydrated magnesium phosphate decomposes below 500° C., which would result in a decrease in bond strength in this range.[3]

At the 200–260° C. range

$$2NH_4H_2PO_4 \rightarrow P_2O_5 + 2NH_3\uparrow + 3H_2O\uparrow \, .$$
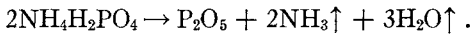
The results of the crushing strength tests are shown in Table 4.

The results in Table 5 confirm the validity of the compressive-strength values. Analysis of variance is one of the most powerful tools of statistical analysis. This procedure determines whether the variations in compressive strength were due to actual differences in the specimens or to experimental error. As shown in Table 5, the calculated ratio for means square (102.1) is much larger than the value from the table (3.96); therefore, the differences in compressive strengths of the investment at the various conditions actually occur.

The values decrease in the range where the compounds which give room-temperature strength begin to break down. This is completed by 500° C. The silicophosphate bond appears to form at a higher temperature than the 280° C. proposed by Moore and Watts. The strength begins to increase at about 300° C. By 1,000° C. the breakdown of this bond is evidenced. By 1,300° C., as fusing of the constituents begins, the strength again increases. Thus
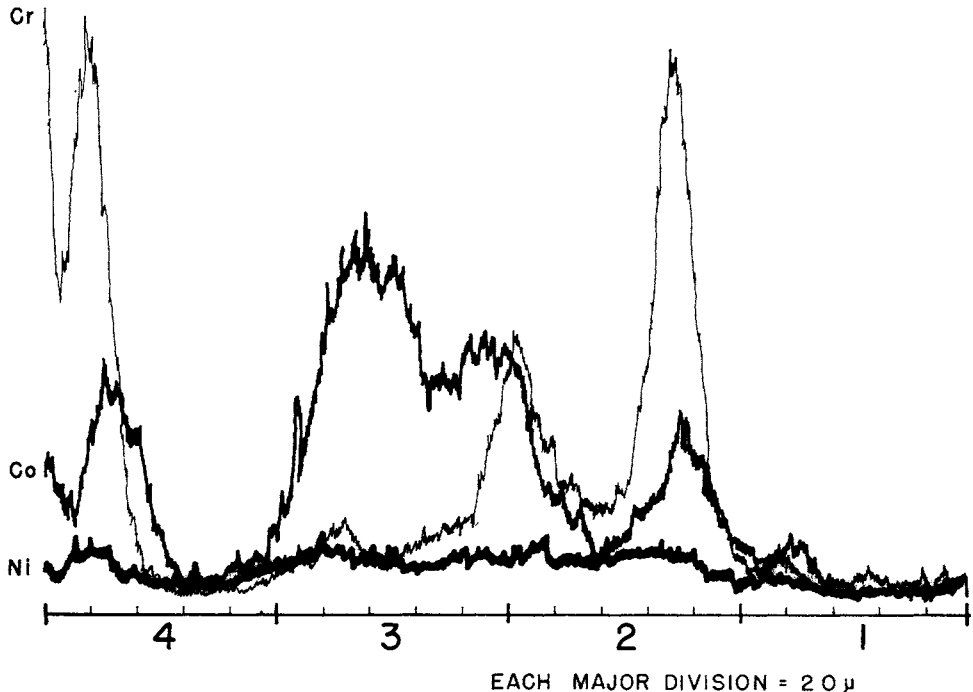

FIG. 9.—Line graphs of alloy elements analyzed in Figure 7.

magnesia- and silicophosphate compounds and unreacted MgO and SiO_2 are present at the casting temperature. The x-ray results indicate that the green scale which forms is $MgCr_2O_4$ ($MgO \cdot Cr_2O_3$) or Cr_3O_4. The $MgCr_2O_4$ more closely correlates with the x-ray-diffraction lines. The results were substantially the same for both casting alloys. Probe analysis substantiates this result. Scans of the green scale and of the investment adjacent to the green scale are shown in Figures 3 and 4. These results are strictly qualitative and give only a general indication of the elements and their amounts present. Since this was a general scan, phosphorus, being a light element, was not determined.

Almost all the elements that exist in the metal and in the investment appear in the green scale analysis. As is shown in Table 1, Cr, Co, and Mn are present in the alloy, whereas Mg and Si are present in the investment. All of these elements are present in the green scale. Mg and Si would be expected to appear in greater quantity in the investment. However, the concentration of both Mg and Si is greater in the green scale than in the investment immediately adjacent to the green scale. Evidently this investment was depleted of these elements when the green scale formed. Although less than in the green scale, Cr, Co, and Mn also appear in the investment in noticeable quantities. Comparison of the occurrence of these metals in Figures 3 and 4 shows that Cr and Mn have a higher rate of diffusion into the investment than has Co.

The scan on the reddish-brown area did not show the presence of any Co. This could be expected, since none of the thin gray scale has been found adjacent to the reddish areas. Cr and Mn were present in large amounts. As occurred in the green scale, Cr had a high diffusivity and therefore showed in a high concentration on the adjacent investment. Mn in this situation does not diffuse as readily as in the green-scale situation. The presence of the small amount of Ca is considered as an impurity in the investment. Since this scale appears so sparsely, no analysis was made by x-ray diffraction.

The scans for the gray scale were run differently. Each element was run separately, and the probe was set at maximum intensity for that position.

This method of analysis, then, shows graphically the composition of the investment and gray scale along the line where the beam passed on the specimen. Lines are numbered correspondingly on Figures 2, 7, 8, and 9. The results showed that the alloy elements are closely approximated in the gray scale and that this scale is a mixture of the cast metal and the investment. However, no Mn was found in either the gray scale or the investment. Therefore, the diffusibility of the Mn must be so great that it passes through the thin gray scale into the green scale. The Co does not appear in too great a quantity considering the high percentage present in the alloy. Cr and Ni coincide with the Mg and must behave in a manner similar to Cr in the green scale. Co does not occur closely with any of the investment materials but tends to decrease when the investment materials increase. This probably is the separate oxide CoO mentioned by Phalniker *et al.*[8] and does not combine readily with the investment.

Jackson, Ford, and White[12] have found that Cr_2O_3 wets MgO quite readily and forms a bond easily. In order to test this conclusion—that oxidation product of the alloy (Cr_2O_3) is reacting with MgO in the investment to form an adherent green scale —alloy was cast into a non-MgO investment (silicate-bonded investment). Although some green scale formed, the quantity was not as great and did not adhere tightly. The surface was much improved.

Summary

A survey was made of the literature to date in this area. Analysis by x-ray diffraction was used in deriving the reactions occurring during setting and burnout. Crushing-strength tests at various temperatures confirmed these reactions. The reaction product of the alloy with the investment was shown to be $MgCr_2O_4$. It was proposed that with investment containing MgO, excessive heating of the alloy accelerates bonding of the Cr_2O_3 to the MgO grains, producing a scale which is very difficult to remove. Use of a non-MgO investment substantiated this conclusion.

The results for the three different reaction products showed that the thin gray scale formed immediately adjacent to the cast metal surface and contained most of the metal elements. Mn entirely and Cr par-

tially diffused rapidly outward and were found in the green scale. To a lesser extent, Co occurred in the same manner, but not in so great a proportion as is found in the original alloy. The reddish-brown areas showed as a reaction of the easily diffusing Cr and Mn with another constituent of the investment.

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