On the Reflection of the Ultra-Violet Rays from Metallic Surfaces in Relation to their Micro-Structures

By

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Several papers have been published by Professor Chikashige[1] and his collaborators on the relation between the colours and the micro-structures of the alloys with the visible rays, but no report on this relationship with the ultra-violet rays has hitherto appeared anywhere. The author has, therefore, under the guidance of Professor Chikashige, undertaken the present investigation, by which the following results have been obtained :

1. At the eutectic there is generally a minimum in the intensity curve both for the ultra-violet and the visible rays, but in the Cu–Ag system there is no minimum with the ultra-violet rays.
2. At the compound, a maximum appears.
3. At the solid solution there is a break or a maximum.

Experimental

(1) The Copper and Silver System

In the Cu-Ag system, the following 9 samples were prepared and tested microscopically for their micro-structures :—

An electric-lamp of 1000 watts was used as the light-source for the ultra-violet rays of 3650–3126 Å and Agfa-roll-films for photographing. The arrangement for the experiments was just the same as used hitherto in this laboratory, except that C. Leiss's spectrometer with a quartz-prism was substituted for that of the ordinary visible rays.

1) Zeit. f. anorg. Chemie, **124**, 335 (1922); **154**, 333 (1926)

Table 1

Alloy	I	II	III	IV	V	VI	VII	VIII	IX
%Cu	0	2	10	20	28	45	70	90	100
Structure	Ag	Ag-solid soln.	Ag-solid soln. + slightly eutec.	Ag-solid soln. + eutec.	Pure eutec.	Eutec. + slightly Cu-solid soln.	Cu-solid soln. + eutec.	Cu-solid soln. + slightly eutec.	Cu

The blackening of the film for the 3650 Å line of the Hg spectrum with a certain time of exposure being taken as unit, that for the same wave-length reflected by the 9 samples was compared to it with the time of exposure changed in many ways.

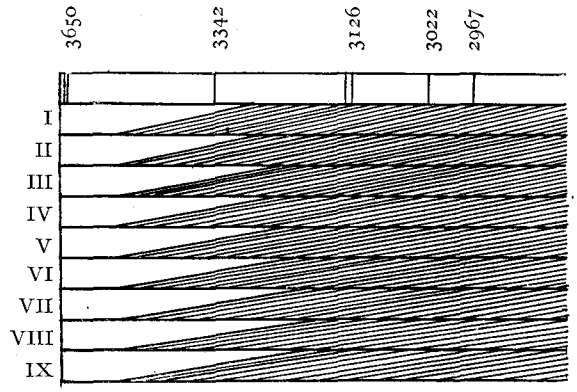
For the same opacity, as determined by means of Hartmann's microphotometer, the corresponding times are recorded; these results are tabulated together with their reciprocals in the following table :—

Table 2

Alloy	Time of exposure for the same blackening in seconds					Intensity of reflection (=1/Time)	Length of spectrum in mm.
	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Mean		
I	16	17	17	17	16.8	59	8.8
II	29	30	30	29	29.5	34	9.1
III	36	36	37	37	36.5	27	9.9
IV	46	48	47	47	47.0	21	10.0
V	55	55	56	56	55.5	18	10.1
VI	74	74	72	72	73.0	14	10.6
VII	94	95	96	95	95.0	11	10.8
VIII	107	107	107	107	107.0	9	11.5
IX	285	290	300	295	292.5	3	11.9

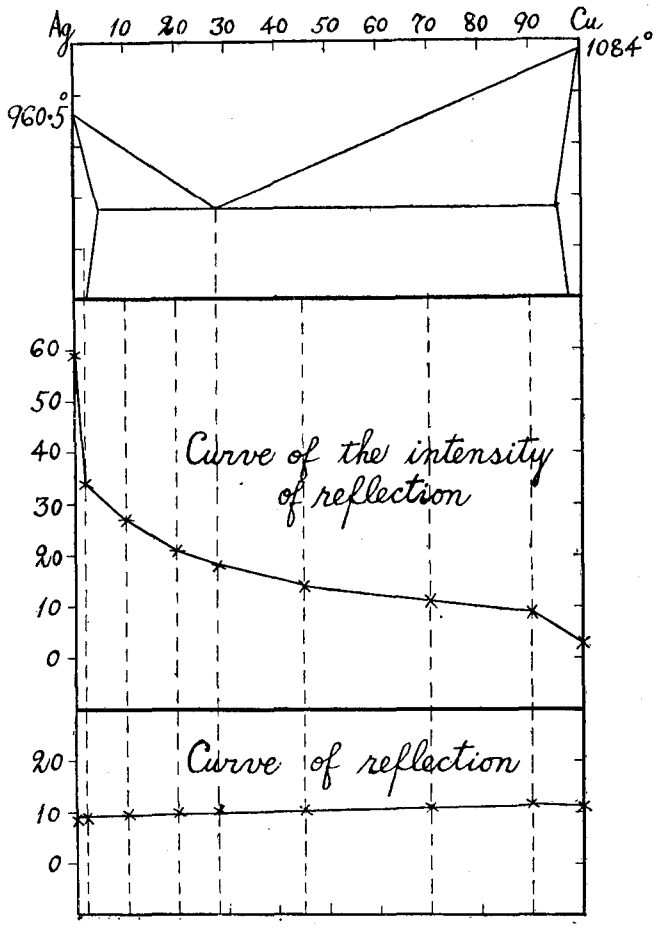
In Fig. 1, Plate I, are reproduced the photograms of the spectra with the same opacity at 3650 Å; from these was measured the blackening with respect to several wave-lengths, and this was then brought into another form as shown in Fig. 2. The lengths of the spectra were then measured from this figure and annexed to Table 2.

Fig. 2



On the basis of these data are obtained the curves of reflection and its intensity as shown in Fig. 3 :—

Fig. 3



The curve of reflection shows us that the lengths of the spectra vary regularly almost in a straight line from silver to copper in their alloys.

With respect to the curve of intensity, however, we see on the silver side that the addition of copper to silver causes a considerable reduction of the intensity till it reaches the saturation point for silver, and that any further addition tends, though very slowly, to make the intensity still fall. On the contrary, the intensity of reflection by copper is constantly augmented by the addition of silver till it shows a break at about 10% Ag. It is very remarkable that no minimum in the intensity curve is observed at the eutectic point with the ultra-violet rays. This discrepancy from the general law may however be explained in the following manner :—Since the reflective power of pure copper is very much reduced even with the visible rays from the yellow, that of the alloys, which contain primary copper-rich grains in their structures, would be quite independent of the presence of copper, were it not that the quantity of silver varies with that of the admixed copper.

Summary

1. The length of the spectrum decreases gradually from Ag to Cu in their mixtures.

2. The saturated solid solution (2% Cu) on the Ag-side shows a break in the intensity curve.

3. A solid solution of Ag in Cu induces an increase in the intensity, till it shows a break at about 10% Ag.

4. No minimum exists at the eutectic, a great contrast between the visible and the invisible rays.

(2) The Cadmium and Bismuth System

The following samples were selected according to Guertler's diagram :[1]—

Table 3

Alloy	I	II	III	IV	V	VI	VII
%Bi	0	20	40	61	75	90	100
Structure	Cd	Cd + eutec.	Eutec. + Cd	Eutec.	Eutec. + Bi	Bi + eutec.	Bi

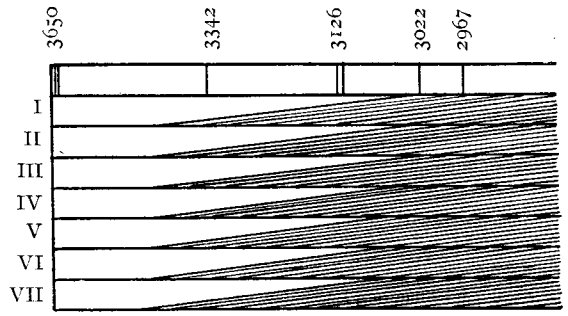
1) Guertler, Metallographic I, 555 (1912)

The comparison of the intensity of reflection was made at the 3650 Å line, the time of exposure required for the same blackening of the photographic film (Fig. 4, Plate I) being thus sought. These results and also the lengths of the spectra, which were measured from Fig. 5, are brought together in the following table :—

Table 4

Alloy	Time of exposure for the same blackening in seconds							Intensity of reflection	Length of spectrum in mm.
	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Mean		
I	250	260	260	240	250	260	253.3	40	17.4
II	270	290	290	280	290	290	285.0	35	17.2
III	410	410	400	390	380	380	395.0	25	17.1
IV	510	510	500	510	510	510	508.3	20	16.3
V	500	500	500	510	510	510	505.0	20	15.8
VI	540	540	540	600	600	720	590.0	17	15.6
VII	480	480	480	480	480	480	480.0	21	15.3

Fig. 5



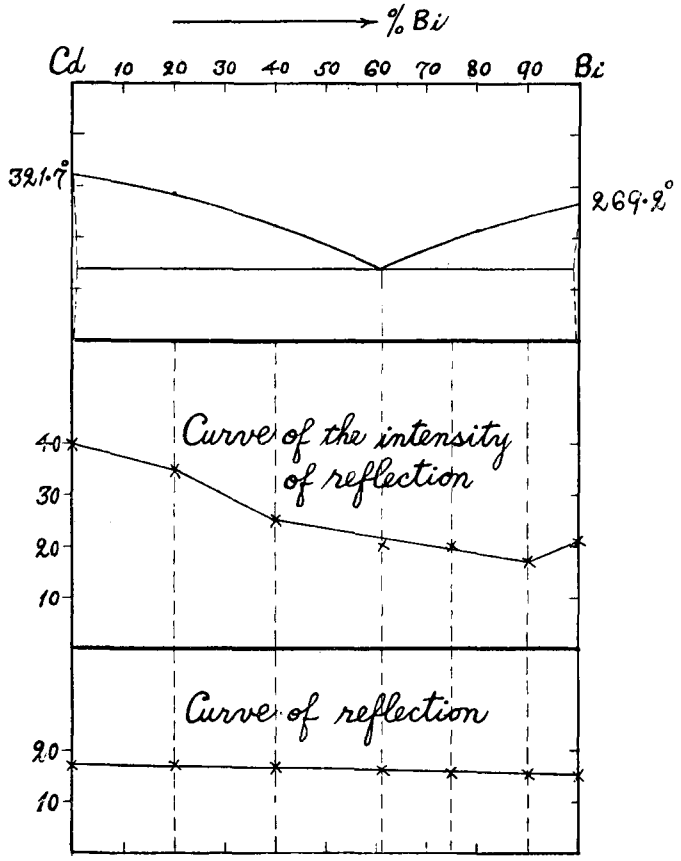
On the basis of these data, the following diagram was drawn :—

Summary

1. The curve of reflection runs regularly almost in a straight line.

2. A minimum does not occur at the eutectic but deviates much to the bismuth side having the lower intensity.

Fig.6



(3) The Zinc and Cadmium System

We chose the following 6 samples for the experiments according to Hindrichs' diagram for Zn-Cd[1] :—

Table 5

Alloy	I	II	III	IV	V	VI
%Cd	0	20	50	82.6	95	100
Structure	Zn	Zn + eutec.	Zn + eutec.	Eutec.	Cd + eutec.	Cd

1) Zeit. f. anorg. Chemie, **55**, 415 (1907)

The times of exposure for the same opacity and their reciprocals were found from the results as shown in Table 6.

From the photogram, Fig. 7. Plate II, the blackening with respect to several wave-lengths was found. From these results was drawn the following figure, Fig. 8, and from it were measured the lengths of the spectra, as given in Table 6. The hardness was also determined and recorded in the same table for comparison.

Fig.8

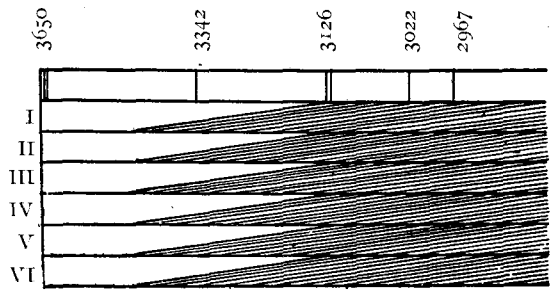


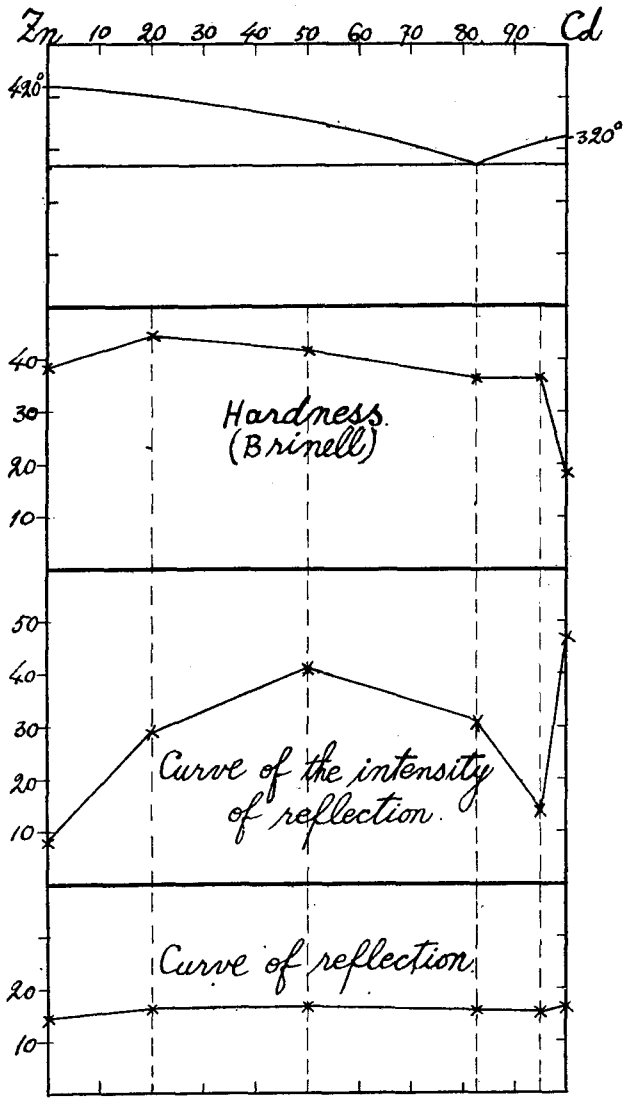
Table 6

Alloy	Time of exposure for the same blackening in seconds						Intensity of reflection	Length of spectrum in mm.	Brinell hardness
	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Mean			
I	1200	1260	1260	1320	1330	1274	8	14.5	38.2
II	350	350	355	355	350	352	29	16.1	44.2
III	250	240	240	240	240	242	41	16.3	41.7
IV	305	320	315	320	330	318	31	15.9	36.3
V	660	660	720	720	720	696	14	15.6	36.3
VI	210	200	215	230	220	215	47	16.4	18.2

On the basis of these results we get the curves of reflection and its intensity as shown in Fig. 9 :—

The intensity curve rapidly rises on mixing cadmium with zinc, and shows the maximum at 50% Cd. From there the intensity curve falls down to 95% Cd, where it reaches the minimum; from there the curve steeply rises up to the pure cadmium. The hardness does not seem to have much influence upon the intensity of reflection, since their maxima appear quite independently.

Fig.9



The minimum deviates strikingly to the cadmium side having the higher intensity. The greater intensity at 50% Cd may probably produce such a phenomenon quite abnormally.

The curve of reflection runs not straight, but roughly parallel to the curve of intensity.

Summary

1. The curves of the intensity of reflection and the length of the spectrum, together with the hardness curve, were drawn.

2. The intensity curve shows a maximum at 50% Cd and a minimum at 95% Cd. That this minimum deviates to the cadmium side having the higher intensity, is quite abnormal.

3. The curve of reflection runs not straight, but roughly parallel to the curve of intensity.

(4) The Copper and Nickel System

The following 6 alloys were prepared in accordance with W. Guertler and G. Tammann's diagram[1] for the Cu–Ni system, and annealed for two hours at 700°C.

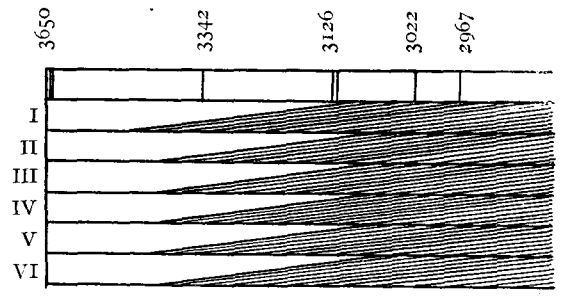
Table 7

Alloy	I	II	III	IV	V	VI
Atom.–%Ni	0	20	40	60	80	100
Wt.–%Ni	0	18.75	38.10	58.05	78.68	100
Structure	Cu	homogeneous				Ni

The times of exposure for the same opacity and their reciprocals were found from the results as shown in Table 8.

From the photogram, Fig. 10, Plate II, the blackening with respect to several wave-lengths was found, and on the basis of these results was drawn the following figure, Fig. 11, from which were measured the lengths of the spectra as given in Table 8. The Brinell hardness is there also mentioned.

Fig. 11



1) Zeit. f. anorg. Chemie, **52**, 25 (1907)

Table 8

Alloy	Time of exposure for the same blackening in seconds									Intensity of reflection	Length of spectrum in mm.	Brinell hardness
	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8	Mean			
I	370	370	430	420	540	530	490	440	448.7	10	13.8	44.2
II	170	180	200	230	250	250	270	220	221.2	20	14.0	57.8
III	65	70	100	100	130	130	130	80	100.6	45	14.1	67.1
IV	95	95	150	145	160	160	160	110	134.3	34	14.1	80.5
V	110	110	165	160	180	180	180	120	150.6	30	14.2	83.3
VI	150	150	190	200	250	240	240	180	200.0	23	13.8	78.3

From these data we get the curves of reflection and its intensity as shown in Fig. 12 :—

Thus, the curve of the intensity rapidly rises on mixing 20 atomic per cent. nickel with copper, and reaches the maximum at 40 atomic % Ni. From there the curve falls down to the pure nickel. The curve of reflection is almost parallel to the concentration axis.

The hardness curve rises very rapidly on mixing nickel with copper and reaches the maximum at 80 atomic % Ni; from here the curve falls down to the pure nickel. There seems to be no relation between this and the curve of intensity.

Further, an investigation was made with the visible rays according to Prof. Chikashige's method, because such an experiment seems still to be lacking.

At the place of the C-line were sought the times of exposure for the same blackening (Fig. 13, Plate III), from which the intensities of reflection were measured. These results with the lengths of the spectra, which were measured from Fig. 14, are brought together in the following table.

Table 9

Alloy	Time of exposure for the same blackening in seconds										Colour, i.e. Length of spectrum in mm.	Intensity of reflection
	I	II	III	IV	V	VI	VII	VIII	IX	Mean		
I	10	10	12	11	11	12	9	11	10	10.6	4.1	47
II	15	14	14	13	13	15	14	14	13	13.8	9.8	36
III	17	15	14	14	14	15	14	15	13	14.5	12.6	34
IV	21	21	21	20	20	22	21	22	19	20.7	12.9	24
V	21	21	21	20	20	21	21	22	20	20.7	13.0	24
VI	20	18	20	20	20	19	20	20	19	19.5	12.9	25

Fig. 12

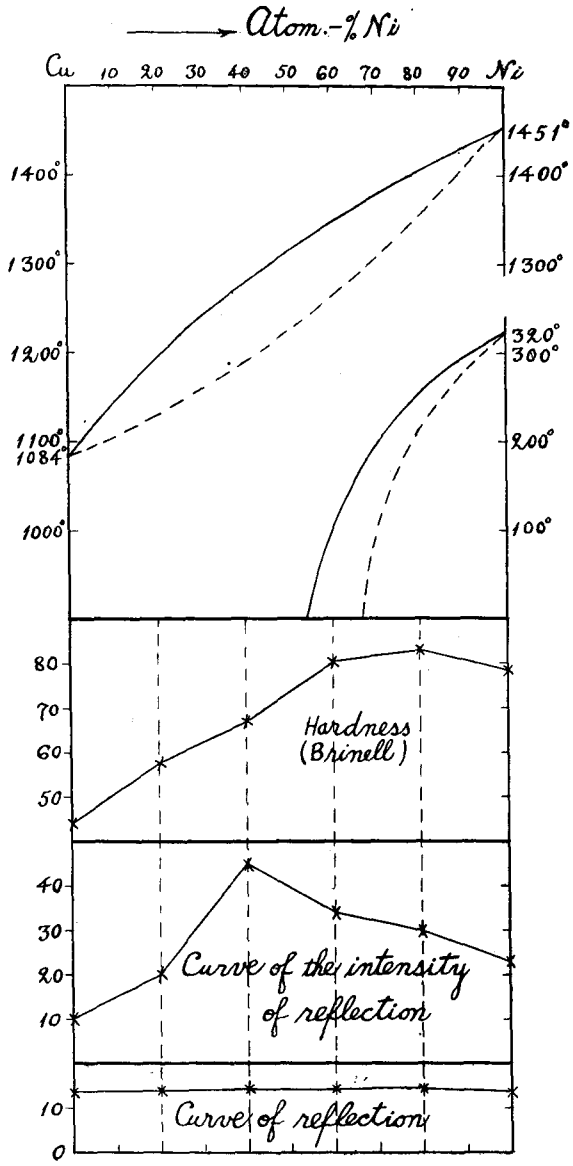
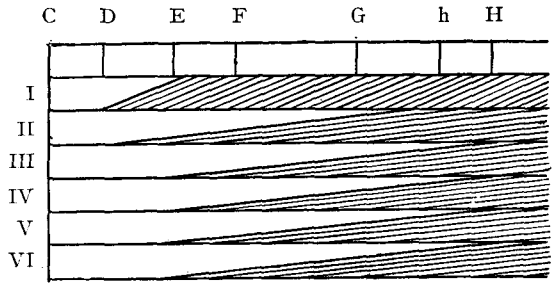
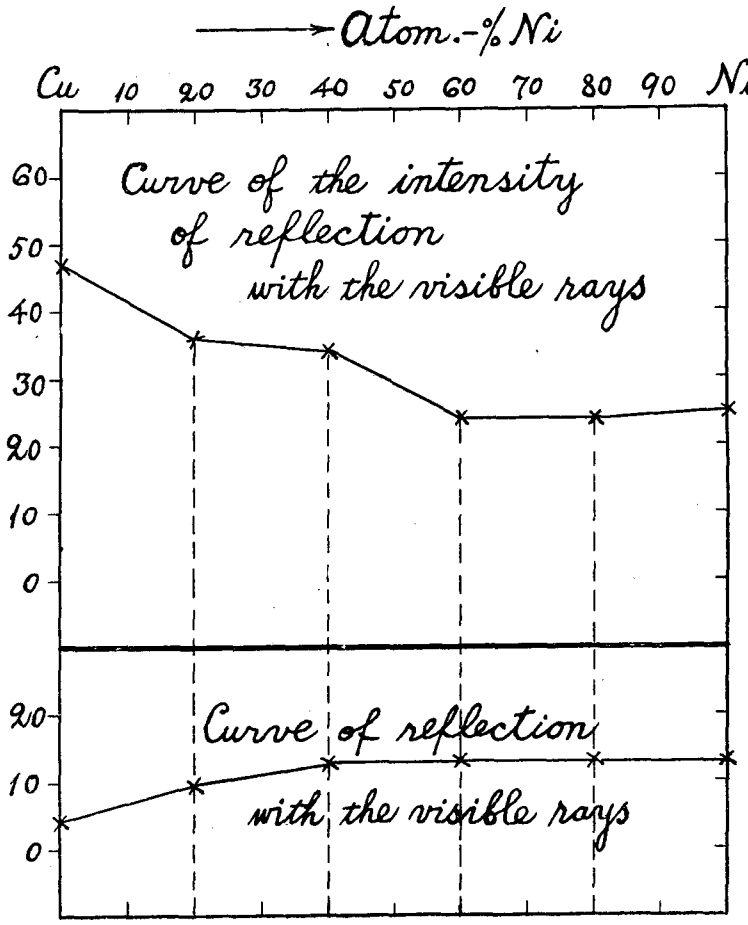

Atom.-% Ni
Cu 10 20 30 40 50 60 70 80 90 Ni
1400°
1300°
1200°
1100°
1084°
1000°
1451°
1400°
1300°
320°
300°
200°
100°
80
70
60
50
Hardness (Brinell)
40
30
20
10
Curve of the intensity of reflection
10
0
Curve of reflection

Fig.14



From these results the following diagram was drawn :—

Fig.15



The curve of the intensity falls here on adding nickel to copper, till it shows a break at 40 atomic % Ni; from this point the curve suddenly falls, reaches a slight minimum between 60 and 80 atomic % Ni, and then again rises very gradually up to the pure nickel. Besides, it is evident from the curve of reflection that the copper loses its colour with an increasing amount of nickel till it becomes white at 40 atomic % Ni.

From these considerations it is evident that the 40 atomic % Ni alloy shows very marked characteristics, having a maximum in the intensity curve for the ultra-violet rays, a break for the visible rays and becoming white in colour. It is perhaps because this alloy is, though not the hardest, the most suited for polishing, that it shows these peculiarities. The alloys between 60 and 80 atomic % Ni are too hard to be better polished than pure nickel, so that the intensity curve acquires a minimum in the visible rays. For the ultra-violet rays, however, the intensity curve does not show such a minimum. This must be due to the great decrease in the reflective power of pure nickel.

Summary

1. The curves of reflection and intensity both for the ultra-violet and visible rays were obtained; the hardness curve being also established.

2. The intensity curve for the ultra-violet rays shows a maximum at 40 atomic % Ni, while the curve of reflection is practically horizontal.

3. The intensity curve for the visible rays shows a break at 40 atomic % Ni, having a slight minimum between 60 and 80 atomic % Ni.

4. The copper loses its colour with an increasing amount of nickel, becoming at last white at 40 atomic % Ni.

(5) The Magnesium and Zinc System

The following samples were selected for the experiments in accordance with Grube's diagram[1]:—

Table 10

Alloy	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
%Zn	0	15	30	40	51.7	60	70	84.32	93	96.8	99	100
Structure	Mg	Eut. B + Mg	Eut. B + Mg	Eut. B + Mg	Eut. B	Eut. B + $MgZn_2$	Eut. B + $MgZn_2$	$MgZn_2$	Eut. D + $MgZn_2$	Eut. D	Eut. D + Zn	Zn

1) Zeit. f. anorg. Chemie, **49**, 72 (1906)

The comparison of the intensity of reflection was made at the 3650 Å line, and the times of exposure corresponding to the same blackening of the photographic film (Fig. 16, Plate III) were sought in exactly the same manner as in the former system. These results and also the lengths of the spectra, which were measured from Fig. 17, are brought together in the following table :—

Fig. 17

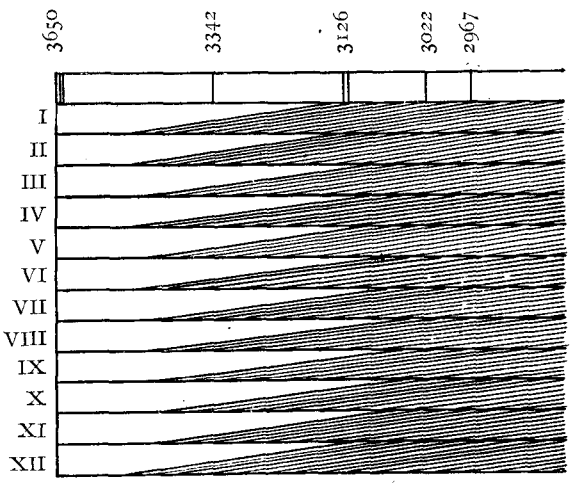
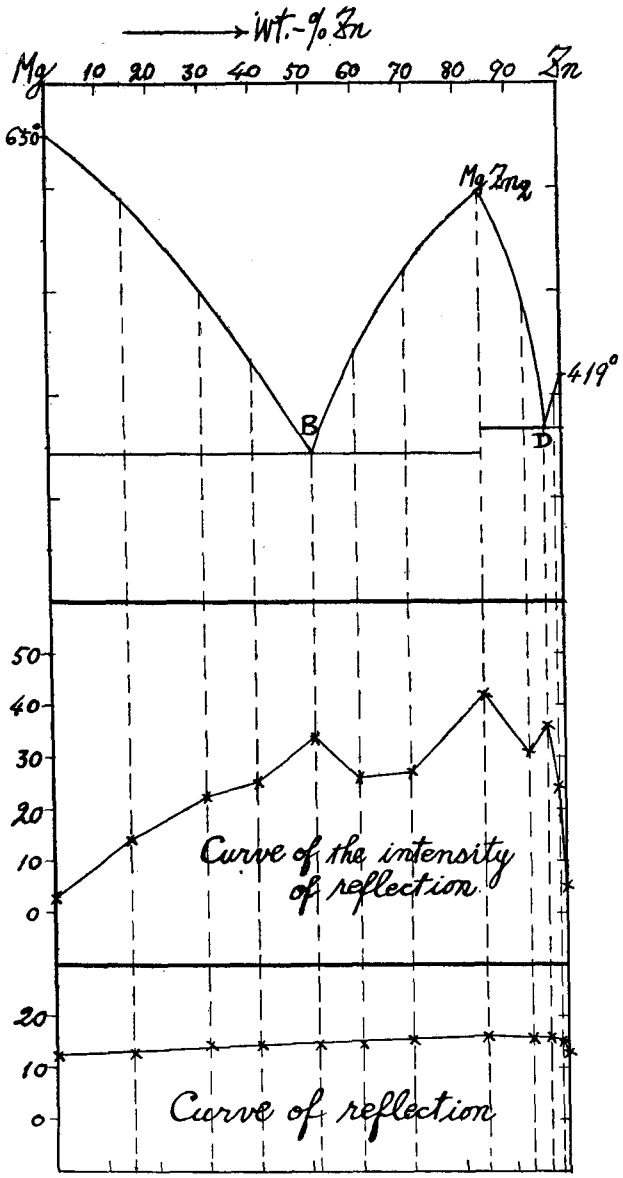


Table 11

Alloy	Time of exposure for the same blackening in seconds					Intensity of reflection	Length of spectrum in mm.
	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Mean		
I	780	900	840	840	840.0	3	12.4
II	175	180	175	175	176.3	14	13.0
III	110	120	105	110	111.3	22	14.5
IV	100	105	95	95	98.8	25	14.4
V	70	80	70	70	72.5	34	14.4
VI	95	95	100	95	96.3	26	14.8
VII	90	90	95	90	91.3	27	15.7
VIII	55	65	60	60	60.0	42	16.3
IX	75	90	80	75	80.0	31	15.9
X	70	70	70	65	68.8	36	16.0
XI	105	100	110	100	103.8	24	15.5
XII	540	540	510	490	520.0	5	13.3

From the results stated above, we get the curves of reflection and its intensity as shown in Fig. 18 :—

Fig. 18



In the curve of the intensity the compound shows a maximum. For the eutectic region from Mg to the compound $MgZn_2$, the alloys containing primary magnesium-rich grains produce good textures on adding Zn to Mg, while those containing primary compound-rich grains induce bad ones, so that the intensity of reflection increases at first and the minimum does not occur at the eutectic B but deviates to the compound side having the higher intensity. Similarly, for the eutectic region from Zn to the compound $MgZn_2$, the intensity of reflection rapidly increases at first and the minimum does not occur at the eutectic D but deviates to the compound side having the greater intensity.

In the curve of reflection the change is regular except that it is curved by a slight addition of magnesium to zinc.

Summary

1. The compound shows a maximum in the intensity curve. With regard to both eutectics, B and D, the positions of the minima always deviate to the side of the compound $MgZn_2$ having the higher intensity.

2. The curve of reflection changes regularly except that it is curved by a slight addition of magnesium to zinc.

In conclusion, the author wishes to express his heartiest thanks to Prof. Dr. M. Chikashige for his kind guidance during the progress of this investigation, and also to Dr. G. Nakamura for his kind advice in the spectroscopic procedure. His thanks are also due to Prof. Dr. M. Kimura for his valuable suggestions with respect to some optical questions.

Plate I

Fig.1

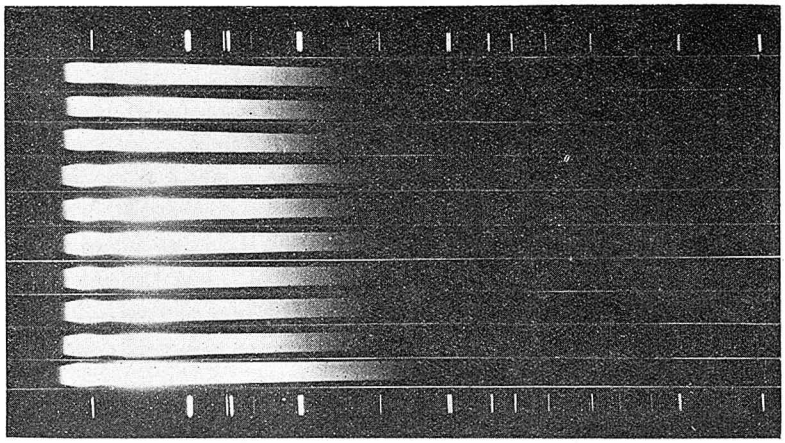


Fig.4

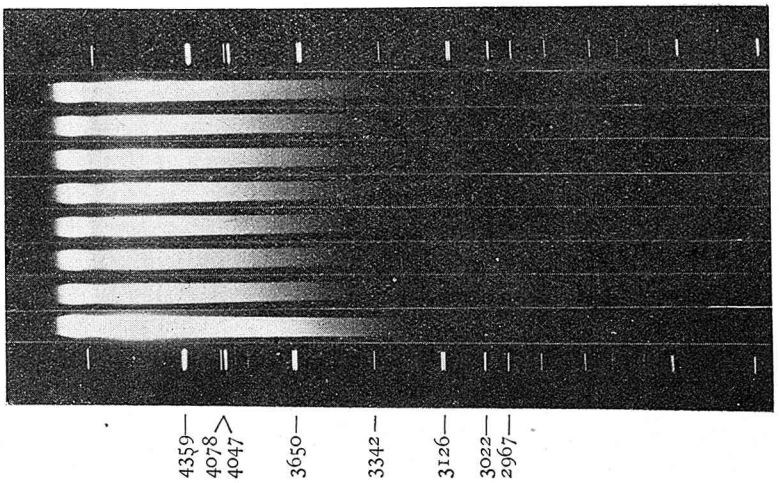


Plate II

Fig.7

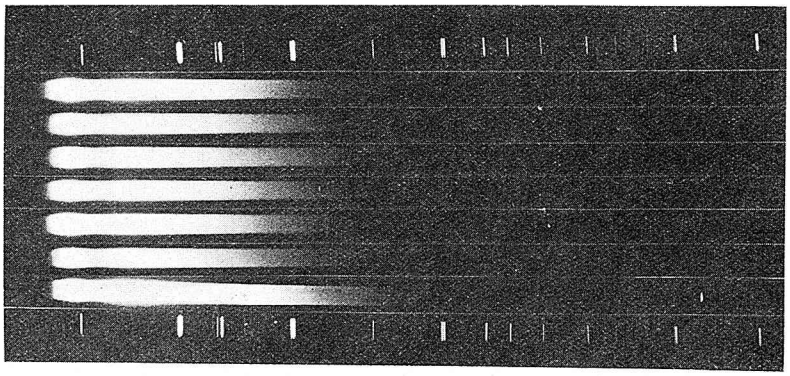


Fig.10

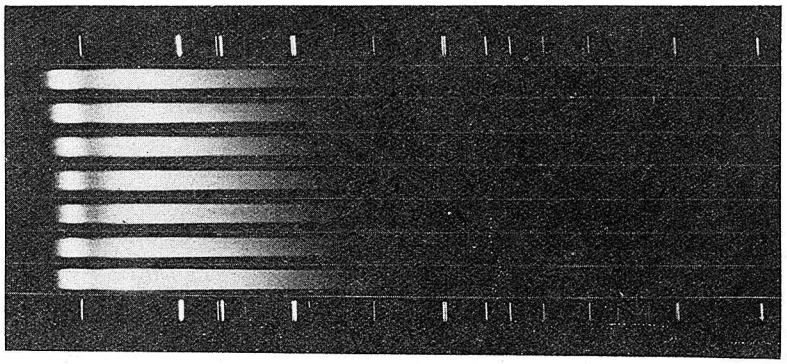


Plate III

Fig.13

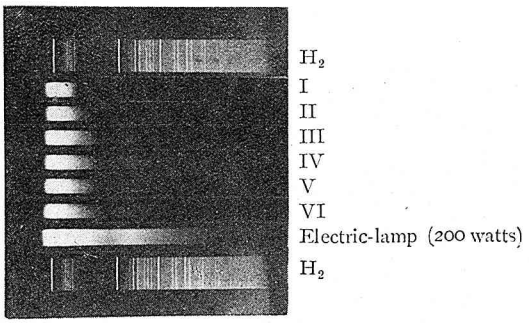
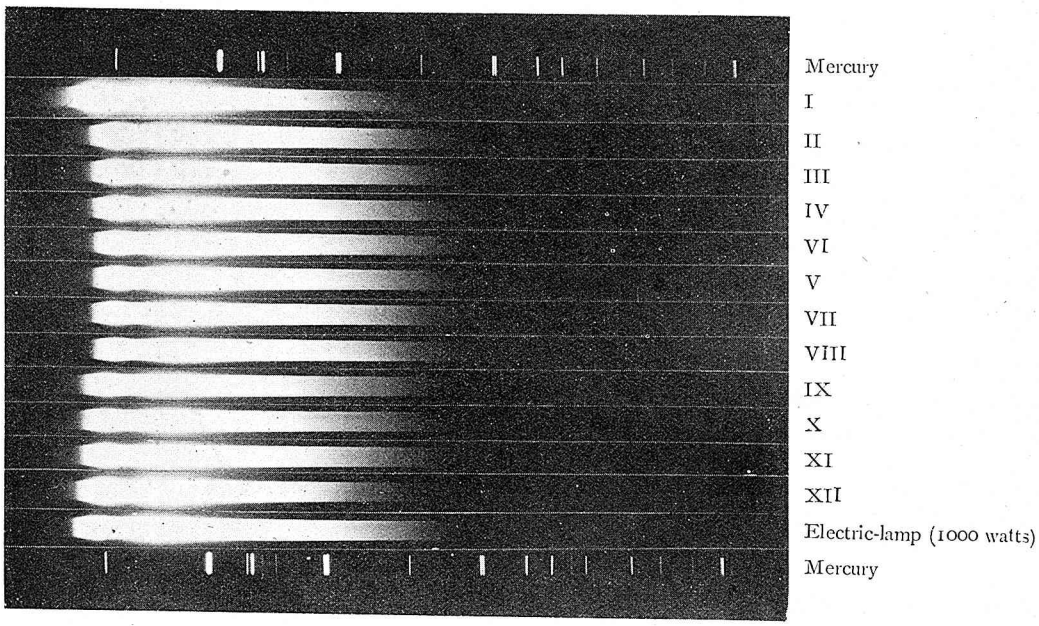



Fig.16