

Cerium in Aluminium Alloys^{1,2}

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WORK OF BARTH

IN 1912, Barth,⁵ working under Borchers at Aachen, studied the addition of cerium to aluminium. He used aluminium with 0.11 per cent silicon, 0.27 per cent iron, and metallic cerium of 98.34 per cent cerium, containing some silicon and carbon, as well as other rare earth metals, especially didymium. He melted the aluminium in a graphite crucible in a gas furnace, added the cerium, wrapped in aluminium foil, and poured the alloy into an iron mold, casting rods 20 mm. diameter by 300 mm. long which were made into test bars with a breaking section of 15 mm. diameter by 150 mm. long. He gives the following data:

TABLE I—BARTH'S RESULTS

Ce Added %	Ce Found %	Per cent Si	Tensile Strength Kg./Sq. Mm.	Tensile Strength Lbs./Sq. In.	Elonga- tion %	Reduction of Area %
0	0	0.11	2.86	4080	1.3	3.3
0.05	0.05	0.02	4.00	5700	3.7	3.3
0.10	0.10	0.02	4.87	6950	6.7	6.7
0.20	0.20	0.03	5.52	7850	8.9	10.7
0.40	0.35	0.10	3.86	5500	1.3	2.0
0.60	0.63	0.03	3.71	5270	0.3	2.7
0.80	0.89	0.05	2.67	3800	0.2	2.0
1.00	1.16	0.03	3.29	4680	0.2	3.3
..	8.72	0.06	7.00	9960	0.2	1.3

Notwithstanding the fact that pure chill cast aluminium should give⁶ 12,000 to 14,000 lbs./sq. in. tensile strength with at least 15 to 25 per cent elongation, Barth concluded that small amounts of cerium increased the strength and ductility of aluminium. He states that trials in a large aluminium works of an alloy with 0.2 per cent cerium showed no special improvement in tensile strength, but gave 23.6 per cent improvement in ductility. He admits that his test bars were poured too hot.

From his silicon analyses he argues that cerium removes silicon, and postulates that a cerium silicide is formed which is then oxidized, and the cerium oxide is again reduced by aluminium. Just why silicon should be oxidized in preference to aluminium, or should not be reduced when cerium is, is unexplained.

He claims to find, in alloys high in both cerium and silicon, lamellae of some cerium silicide in his micrographs.

Barth does not base his alleged improvements in ductility so much on the removal of silicon as on the removal of gas. He says that his cast pure aluminium rod was solid from top to bottom, while the alloys with cerium were solid at the bottom but had many gas holes in the upper part, which would seem to be an argument against rather than for cerium.

He finds increased corrosion of his cerium alloys in nitric acid as cerium increases, and ascribes this to the presence of a readily soluble silicide. However, he finds a solid solution of cerium in aluminium up to 11 per cent, and, in alloys below 11 per cent cerium, nothing in his micrographs that is due to cerium.

Barth's work and conclusions appear to be of extremely doubtful value.

SCHULTE'S INVESTIGATIONS

In 1921, Schulte,⁷ also working under Borchers at Aachen, went into the matter again, stating that subsequent work had thrown doubt on Barth's conclusions. Schulte failed to find a decrease of silicon in the aluminium alloys with cerium, and discards that hypothesis. He found a solid solution and cerium in aluminium up to 13 per cent cerium. He tested rolled material, his results being given in Table II. He does not give the analysis of the cerium used, the analysis of his castings, the size of test bar used, nor the annealing temperatures.

TABLE II—SCHULTE'S RESULTS

<i>Al-Ce Alloys</i> Annealed ^a							
Per cent Ce.....	0	0.05	0.11	0.19	0.33	0.45	0.77
Tensile strength:							
Kg./sq. mm....	8.63	8.85	8.93	9.1	9.1	9.1	9.15
Lbs./sq. in....	12,250	12,650	12,700	12,900	12,900	12,900	13,050
Elongation, per cent.....	28.6	30.5	32.4	34.1	34.1	32.6	32.3
Cold worked—Reduction ratio, 70 per cent							
Tensile strength:							
Kg./sq. mm....	15.25	15.4	15.1	14.8	15.0	15.9	16.0
Lbs./sq. in....	21,700	22,000	21,500	20,500	21,500	22,600	22,800
Elongation, per cent.....	4.6	5.7	6.0	6.4	6.5	6.2	5.1
Cold worked—Reduction ratio, 90 per cent							
Tensile strength:							
Kg./sq. mm....	18.3	..	18.3	18.3	..	18.3	..
Lbs./sq. in....	26,050	..	26,050	26,050	..	26,050	..
Elongation, per cent.....	1.8	..	3.4	3.7	..	2.9	..
<i>Al-Cu-Ce Alloys—Cu about 3 per cent</i> Annealed ^a							
Per cent Ce.....	0	0.09	0.19	0.31	0.46		
Tensile strength:							
Kg./sq. mm....	17.7	18.0	17.5	17.0	17.0		
Lbs./sq. in....	25,200	25,600	24,500	24,200	24,200		
Elongation, per cent.....	24.0	25.0	25.6	22.6	22.0		
Cold worked—Reduction ratio 60 per cent							
Tensile strength:							
Kg./sq. mm....	23.0	23.0	23.7	23.9	24.0		
Lbs./sq. in....	32,700	32,700	33,700	33,900	34,100		
Elongation, per cent.....	4.0	4.5	5.0	4.0	4.0		
<i>Al-Mg-Ce Alloys—Mg about 4 per cent</i> Annealed ^a							
Per cent Ce.....	0	0.10	0.13	0.16	0.22		
Tensile strength:							
Kg./sq. mm....	18.0	19.7	19.9	19.9	..		
Lbs./sq. in....	25,500	28,000	28,300	28,300	..		
Elongation, per cent.....	20.0	23.6	22.0	24.0	..		
Cold worked—Reduction ratio 60 per cent							
Tensile strength:							
Kg./sq. mm....	37.5	38.8	40.0	40.0	38.4		
Lbs./sq. in....	53,000	55,000	57,000	57,000	54,500		
Elongation, per cent.....	2.3	2.3	2.5	3.0	2.3		

^a Control experiments on cast pieces are said to have checked the tensile and elongation figures for these annealed specimens, but no figures are given.
^b Cast Al-Cu-Ce alloys were not tested.

Schulte claims that the conductivity of aluminium is not decreased by the presence of cerium up to 0.77 per cent. He considers that the alleged improvement in ductility is real, and ascribes it to the elimination of aluminium nitride, stating that his pure aluminium contained 0.028 per cent aluminium nitride, the alloy with 0.2 per cent cerium, 0.014 per cent aluminium nitride, and that with 0.77 per cent cerium, 0.0094 per cent aluminium nitride, but states that "the favorable influence of cerium appears to be strongly encroached upon by the presence of small amounts of other metals." It would have been more convincing if Schulte had given the details of the analytical method for nitrogen, with the data to show how well duplicate samples agreed. On a sample of aluminium that had been overheated and in which the presence of nitrogen was considered possible, one laboratory reported 0.16 per cent and 0.109 per cent aluminium nitride on duplicate samples, while a very careful analyst in another laboratory found in the same samples from 0.02 per cent to 0.012 per cent aluminium nitride.

OTHER PREVIOUS WORK

The curves of Carpenter and Tavernar⁸ show that pure aluminium, cold worked and fully annealed, gives 13,000 lbs./sq. in. tensile strength, 36 per cent elongation, while the figures of the Aluminum Company of America⁹ show that it gives 13,000 lbs. tensile and 14 to 35 per cent elongation, depending on the gage, and that at a 70 per cent reduction the tensile strength should be 21,000 lbs. and the elongation 2 to 7 per cent, according to gage. At 90 per cent reduction the figures are 30,000 lbs. and up to 2 per cent elongation.

According to the curves of Carpenter and Edwards,⁸ a 3 per cent copper alloy, cold rolled, reduction ratio 60 per cent, gives

⁸ Authors quoted in *Bur. Standards, Circ. 76* (1919), 36, 39, 42. Also recent data from Aluminum Company of America.

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⁵ *Metallurgie*, 8 (1912), 261.

⁶ *Bur. Standards, Circ. 76* (1919), 22.

⁷ *Metal u. Ers.*, 18 (1921), 236. Translation with comments by "R. E. Search" in *Metal Ind.*, 20 (1922), 142.

40,000 lbs. tensile strength, with about 4 per cent elongation. Hence, while Schulte's alloys containing cerium show, by comparison with his similar alloys free from cerium, a slight increase in ductility, his best figures for the cerium-containing alloys are no better than those given by other authorities for the same alloys free from cerium.

BUREAU OF MINES STUDIES

Considering that the previous results from Aachen obtained by Barth have been discredited, and that the improvement due to cerium alleged by Schulte is pretty small at best, it seemed by no means certain that cerium would be of use in aluminium; but, since the Bureau of Mines, in coöperation with the Welsbach Company, was studying the effect of the cerium group of metals in steel, it was decided to try it out in some cast aluminium alloys also.

EXPERIMENTAL—The aluminium used in making up the alloys contained about 0.25 per cent silicon, 0.25 per cent iron. The cerium-group metals were added as "mix metal." This contained about 10 per cent iron, the balance being cerium-group metals, their proportion being roughly as follows: cerium, 45 per cent; lanthanum, 25 per cent; neodymium and praseodymium, 15 per cent; samarium, 10 per cent. (The word "cerium" in the following description of the Bureau of Mines experiments is to be taken as referring to the mixture of cerium-group elements contained in the mix metal.) The aluminium and rich 50 Cu–50 Al alloy were melted in a rocking furnace. Additions of mix metal or magnesium were made just before pouring into the ladle. Comparison heats were made with and without cerium.

Test bars were cast in green sand in lots of four, and all tensile test figures are the average of four closely agreeing tests. The test bars were of the standard S. A. E. form, tested without machining.

In the 4 and 8 per cent copper alloys, with and without 0.25 per cent cerium equivalent to 0.22 per cent cerium-group metals after deducting iron, which is Schulte's optimum amount of cerium, half of the heat was poured and then the other half heated further to see if cerium would exert its alleged effect on aluminium nitride, whose formation should be facilitated by raising the temperature.

With any alloy used, whether it contained cerium or not, the higher the temperature to which it was heated, the greater the number of pinholes.

DISCUSSION OF RESULTS—The 3.8 per cent Cu, 0.60 Mg alloy was included for comparison with the 3.8 per cent Cu, 0.80 and 1.60 Ce alloys, because magnesium silicide is considered⁹ to be in one way or another the active agent in the age-hardening of Duralumin. Merica suggests¹⁰ that it is the removal of free silicon by the formation of the compound magnesium silicide, which is essential. He shows that copper aluminide, which is doubtless the active hardening agent in Duralumin, tends to precipitate about particles of magnesium silicide, which makes it appear that magnesium silicide forms nuclei for the precipitation from solid solution of very finely divided copper aluminide, thus accounting for the necessity for the presence of magnesium in order to secure satisfactory hardening.

If the mere removal of free silicon is the essential point, and if Barth's statement as to the ready formation of cerium silicide is correct—and this is borne out by the statement of Hirsch¹¹ that in the melting of cerium in a porcelain crucible, the crucible is attacked and a layer of silicide formed inside the crucible which protects it from further attack—it seemed possible that cerium might form cerium silicide, which would act in the same way as magnesium silicide.

But the data of Table III show that it did not, and that the alloys containing cerium were not hardened by the regular heat treatment used on Duralumin.

No signs of any silicide were found on microscopic examination, the alloys with cerium looking just like those without it. In passing, it might be remarked that the heat-treated 3.8 Cu–0.60 Mg alloy did not show, even at 1000 diameters, any of the blue magnesium silicide constituent, but from the solubility curve of Hanson and Gayler⁹ no visible magnesium silicide would be expected.

Schulte himself found almost no advantage in the use of cerium in a 3 per cent copper alloy, the elongation on annealed specimens rising from 24.0 to 25.6 per cent and on cold-rolled specimens from 4 to 5 per cent, figures obviously within the variation from bar to bar of such alloys. "R. E. Search," in commenting⁷ on Schulte's work, calls this an "important increase" in ductility, and later says that as the weak point of the light aluminium cast alloys is their meager elongation, the "discovery of the increased ductility must be acclaimed as a distinct gain in the fields of endeavor whether purely scientific or practical."

TABLE III—BUREAU OF MINES RESULTS

Cast Cu-Al Alloys									
—ALLOY—		Tem- perature in Ladle °C.	Tem- perature Poured into Mold	Proportional Limit ^b Lbs./ Sq. In.	Tensile Strength Lbs./ Sq. In.	Elong- ation Per cent in 2 In.	Days after Casting be- fore Brinell Test		
Cu Per cent	Ce ^a Per cent								
4	0	700	680	5500	20,000	6			
4	0	760	680	5500	19,200	6			
4	0.25	665	665	5500	19,900	5			
4	0.25	760	680	5500	19,000	4			
8	0	710	680	8500	18,500	1.5			
8	0	810	680	8500	21,000	1.5			
8	0.25	760	680	8500	20,000	1.5			
8	0.25	880	680	8500	19,600	1			
							Brinell (500 Kg.)		
3.8	0	760	670	Not determined	21,000	6.5	43.5	9	
3.8	0.80	780	680		17,500	4	42.5	9	
3.8	1.60	750	680		17,600	4	41.5	8	
3.8	{ 0.60 mg.	685	680		21,700	2.5	72	7	
6		0	730		680	19,300	3	53.5	8
6		0.80	730		680	19,550	3.5	55.5	8
8		0	740		680	21,700	2.5	65	7
8	0.80	720	680		21,500	2.5	61	7	
<i>Heat-Treated Alloys—1 hr. at 495° C. in NaNO₃-KNO₃ Quenched in Oil, Heated in Oil 1 Hr. at 145° C.</i>									
3.8	0	760	670	5200	23,100	6.5	45		
3.8	0.80	780	680	5200	19,700	5	40		
3.8	1.60	750	680	5800	22,000	6.5	45		
3.8	{ 0.60 mg.	685	680	19,000	31,300	2	76		
6		0	730	680	6600	22,850	2.5	53.5	
6		0.80	730	680	6000	23,800	3	50	
8		0	740	680	6100	22,900	2.5	62	
8	0.80	740	680	6100	21,700	2	55		

^a "Ce" stands for mix metal, figures not corrected for iron in mix metal.

^b By Berry strain gage—figure given is point at which slope of stress-strain curve becomes twice that of the elastic portion of the curve.

The results in Table III show, instead, a somewhat decreased ductility, but within the variation to be expected from bar to bar of the alloys without cerium. It should be remembered that the cerium used contained some iron, which increased the iron content of the alloys to which cerium was added so that the iron varied from about 0.25 to about 0.41 per cent and, while no very great effect is likely to be due to this increase in iron, its action would be in the direction of a decrease in ductility.

In the light cast aluminium-copper alloys, whether used in Schulte's optimum amount of about 0.20 per cent or in higher amounts, cerium appears to be without useful effect—in fact, without any marked effect one way or the other.

The possibility still exists that pure cerium, free from the other cerium-group metals, might be of value, but the cost of separation makes that possibility very remote from the commercial point of view, and the chemical similarity of that group of metals makes it rather unlikely that one of them will

⁹ Hanson and Gayler, *J. Brit. Inst. Metals*, **27** (1921), 321.

¹⁰ Merica, Waltenberg and Scott, *Bur. Standards, Sci. Paper* **347** (1919), 311.

¹¹ Hirsch, *Trans. Am. Electrochem. Soc.*, **20** (1911), 57.

nullify any benefit caused by another, especially as Schulte's claim is on the basis of scavenging effect on the nitrogen rather than on the basis of true alloying action.

The aluminium used in the Bureau of Mines experiments was of good quality and probably not contaminated with aluminium nitride. If we accept the unproved assumption that reclaimed boring ingot, for example, does contain aluminium nitride, the possibility remains that a very small "dose" of cerium might help, but it seems certain that in the usual run of good metal used for casting alloys, the use of cerium would be an expense not attended by any benefit.

The test pieces of the Bureau of Mines experiments have not been analyzed. The charges were carefully weighed and

there was no sign of loss of cerium. Only cursory microscopic examination of the pieces has been made. In view of the discouraging results of the physical tests it was felt that analytical and micrographic work would be time wasted.

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Contributions to Chemistry of Wood Cellulose II—Nature of Wood Cellulose¹

By Louis E. Wise

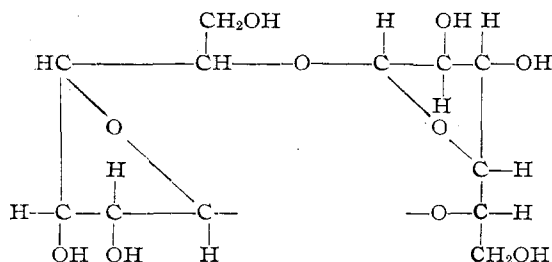
NEW YORK STATE COLLEGE OF FORESTRY, SYRACUSE, N. Y.

During the World War the dearth of cotton in Germany and Austria stimulated research which had for its object the industrial substitution of wood cellulose for cotton cellulose. It also encouraged comparative studies on the chemical constitution of cotton cellulose on the one hand, and of wood cellulose on the other. The value of such studies is naturally of more than passing academic interest. Their industrial importance may be gaged from a number of articles that have appeared within the past eight years in American and foreign journals of applied chemistry,² and the ultimate results of these investigations must have a decided bearing on those industries which require the use of a highly purified cellulose in their manufacturing processes.

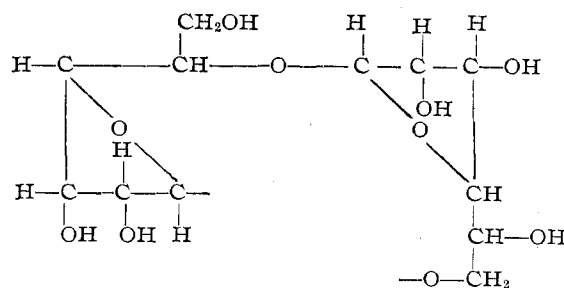
The accumulation of data, however, gives the industrialist little more than a labyrinth of isolated facts, unless these data are subjected to a thorough critical analysis. Not infrequently such data may be interpreted in a variety of ways, and the danger then arises of accepting an interpretation which will limit or cripple further advance in this particular branch of cellulose chemistry. This article has for its object the brief recapitulation of the experimental work of a number of investigators, the results of which may perhaps be welded into a constructive working hypothesis on the nature of wood cellulose.

CONSTITUTION OF COTTON CELLULOSE

A GENERAL agreement now exists regarding the presence of the cellobiose linkage or residue, or more correctly the anhydrocellobiose linkage, which may be represented by either Formula I³ or II:⁴



FORMULA I



FORMULA II

There is at present, however, no definite agreement regarding the limiting yield of cellobiose^{4,5} that may be obtained from cotton cellulose. Investigators are by no means in accord when called upon to decide whether or not the cellulose molecule is made up entirely of cellobiose residues.

Different hypotheses regarding the size of the cellulose molecule have also appeared in the cellulose literature. Views on this subject may be briefly summarized as follows: (a) a relatively enormous molecule made up of a great number of anhydrodextrose residues,^{3,6} many of which go to make up the anhydrocellobiose linkages⁷ referred to above; (b) a large

¹ Presented before the Division of Cellulose Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922, in connection with the symposium on "The Nature of Wood Cellulose."

² Articles on comparison of wood and cotton cellulose include those by Heuser and Boedeker, *Z. angew. Chem.*, **34** (1921), 461; Lenze, Pleus, and Mueller, *J. prakt. Chem.*, **101** (1920), 213; Wise and Russell, *THIS JOURNAL*, **14** (1922), 285; Mahood and Cable, *Ibid.*, **14** (1922), 727. Articles on nitration of wood cellulose include those by Schwalbe, *Z. angew. Chem.*, **27** (1914), 662; Wells and Edwards, *Paper*, **23** (1919), 180; Woodbridge, *THIS JOURNAL*, **12** (1920), 380. A modern research on acetylation of wood cellulose is that by Hägglund, Löfman, and Färber, *Cellulosechemie*, **3** (1922), 13.

³ Hibbert, *THIS JOURNAL*, **13** (1921), 256; Irvine, *J. Chem. Soc.*, **123** (1923), 525.

⁴ Karrer, *Helvetica Chim. Acta*, **5** (1922), 187.

⁵ Ost, *Ann.*, **398** (1913), 337; Madsen, Dissertation, Hannover, **1917**. Hess and Wittelsbach, *Z. Elektrochem.*, **26** (1920), 232; Freudenberg, *Ber.*, **54** (1921), 767; Irvine, *loc. cit.*

⁶ von Euler, *Chem. Ztg.*, **45** (1921), 977, 998.

⁷ The older hypotheses, which did not take the cellobiose grouping into consideration, include those of Tollens, "Handbuch der Kohlenhydrate," p. 252; Green and Perkin, *J. Chem. Soc.*, **81** (1906), 811; Cross and Bevan "Cellulose," p. 75; Vignon, *Bull. soc. chim.*, **21** (1899), 599.