

A STUDY OF INTERGRANULAR CORROSION AND POWDER FORMATION OF 18/8 STAINLESS STEEL

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The heat treatment of stainless steel, the carbide precipitation in the grain boundaries and the influence of heat treatment on the powder formation has been studied. The most suitable bath for the electrochemical disintegration of heat treated stainless steel has been evolved and electrolytic conditions determined.

Much attention has been focussed on the production of stainless steel powder since the second decade of this century, because of its utility for the preparation of permeable parts, namely air or liquid-cooled porous stainless steel inlet nozzles, blades, gas turbine components and acid-resistant porous bearings, discs and filters.

Various processes have been evolved including both mechanical and electrochemical, to produce stress-free, oxide-free, mouldable powder. From the metallurgical standpoint the powder obtained by mechanical means is far inferior.¹

Before disintegrating the as-cast or rolled stainless steel by mechanical or electrochemical methods, a prior heat treatment is essential in order to make the metal susceptible to attack in corrosive media and to reduce the ductility of the steel.² It has been established that when 18/8 steel is heated, chromium and carbon diffuse to the grain boundaries forming brittle chromium carbide. Its precipitation is maximum at about 550-750°C. This treatment is, therefore, responsible for reducing the ductility of the material and leaving the zones depleted in chromium content, thus depriving the material of the originally corrosion-resistant properties.³ On prolonged heating at low temperature or heating beyond 1000°C for shorter period the diffusion of chromium continues even after the precipitation of carbide, and thus creates the uniformity of chromium concentration throughout the mass. This heat treatment, however, controls the grain-size, but cannot obliterate the step of carbide precipitation treatment as has been mentioned earlier and that too within a definite range of temperature.

The conventional disintegration assembly consists of two sets of stainless steel bars, with alternate switching in arrangement so that only one set is in circuit at one time, while the other is cut out. The cathode is made of a lead cylinder.

Since the setting up of a fairly steep chromium concentration gradient in the area of the grain

boundaries depends upon the carbon content and the extent of carbide-forming elements, it is imperative to select a temperature for heat treatment which ensures the optimum yield. Secondly, the corrosive media and the effect of each component of the electrolyte on the yield has to be investigated.

Experimental

The average composition of the 18/8 stainless steel taken for this study is: chromium 18.23, nickel 8.06 and carbon 0.10%.

The stainless steel strips (8" × 4½") were heat treated at 700°C, 750°C and 800°C for different periods with a view to determine the optimum conditions. Small pieces were then cut, polished, etched and studied under the microscope. Electrolytic etching in 10% oxalic acid was employed. The etching time given was from 15 to 30 sec in each case.

The strips heat treated at 700°C for 4 hr were, however, selected for electrochemical disintegration, as the carbide precipitation is complete only under these conditions. This was proved by the comparatively efficient rate of powder formation.

The strips of the above dimensions after being heat treated were mechanically polished to remove the oxide layer formed during heating. Four sets of two sheets each were then arranged in parallel in the bath. A reversing key was provided to interchange the anode and the cathode.

Another experiment was conducted by using a spiral of heat-treated stainless steel strip, which was made the anode and was placed inside the cylindrical lead cathode. The object in view was to increase the surface area. This arrangement did not work as the corrosion was restricted only to that part of the spiral which was directly exposed to the cathode and no disintegration was observed in the internal rings.

Further investigation was, therefore, conducted by using the alternate anode-cathode assembly. The bath was maintained throughout at 10 amp and 25°C. The water used in each was 10 l. The duration of each experiment was 30 min, the reversal time being 2 min.

Results and Discussion

Carbide precipitation is of vital importance for the study of intergranular corrosion and has a direct bearing on the formation and yield of the powder. The temperature range generally recommended for the heat treatment of a wide variety of stainless steels is 550–750°C. Besides temperature, the time allowed for this process is of considerable significance.

The photomicrographs of 18/8 stainless steel pieces (Fig. 1–6), heat treated at different temperatures for varying periods, revealed the different stages of carbide precipitation in the grain boundaries. The precipitation was incomplete after 2 hr at 700°C but was complete after 4 hr treatment at 700°C. The structure of steel remained nearly the same when it was heat treated at 750°C for 4 hr.

The photomicrographs of steel heat treated at 700°C revealed a strained structure because of twinning. This matrix encourages rapid dissolution in a corrosion media. On the contrary the photomicrograph of steel heat treated at 750°C for 3 hr showed carbide precipitation in the grain boundaries and strain-free matrix.

In the present study the lead cathode was replaced by the stainless steel strip and the assembly was provided with a reverse key to alternate the current flow. This obviated the necessity of covering the cathode in a sack of appropriate fabric. This arrangement eliminated the possibility of contamination of the stainless steel by the oxides of the lead, which are formed during the process.

The anode-cathode alternating arrangement is necessary as the intergranular corrosion at the anode gets progressively inhibited due to polarization.

The bath was made up by adding the specific volumes of H_2SO_4 , HF and H_2O_2 to one litre of water.

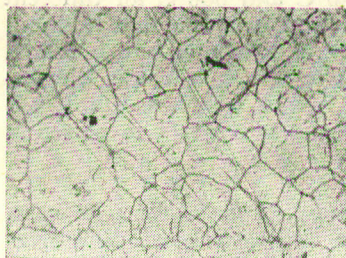


Fig. 1.—Stainless steel heat treated at 700°C for 2 hr $\times 100$.

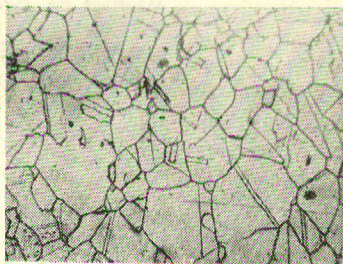


Fig. 2.—Stainless steel heat treated at 700°C for 4 hr $\times 100$.

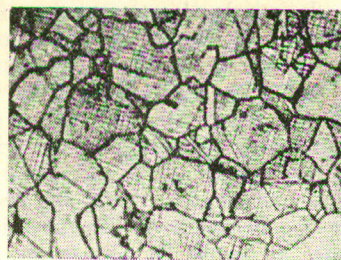


Fig. 3.—Stainless steel heat treated at 750°C for 2 hr $\times 100$.

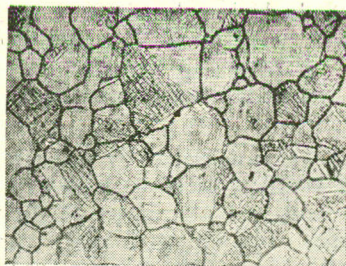


Fig. 4.—Stainless Steel heat treated at 750°C for 3 hr $\times 100$.

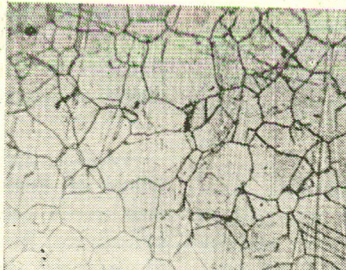


Fig. 5.—Stainless steel heat treated at 750°C for 4 hr $\times 100$.

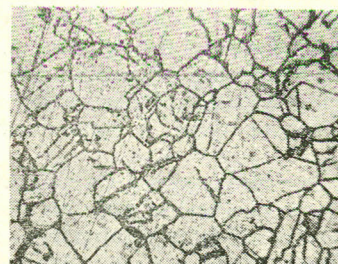


Fig. 6.—Stainless steel heat treated at 800°C for 4 hr $\times 100$.

Single component effect was studied by varying one component at a time. When the volume of H_2SO_4 is increased from 5 ml to 10 ml, there is a corresponding rise in the yield, i.e., 100%, and a slight decrease in the voltage, i.e., 0.5 volts (Table 1). This bath, however, accelerates the oxide formation mainly of chromium and nickel. When H_2O_2 is used along with H_2SO_4 , the yield becomes quite low, and oxides of nickel with traces of chromium and iron are formed.

The incorporation of HF increases the yield, while the voltage remains more or less static.

On varying the proportion of H_2O_2 , while keeping the volume of H_2SO_4 constant, the yield was not affected and the voltage declined from 8 to 5.5 volts.

On varying the proportion of HF and keeping the volume of H_2SO_4 and H_2O_2 constant, the powder produced was free of oxides and the yield ranged from 6 to 9 g.

On varying the proportion of H_2O_2 and HF while keeping the volume of H_2SO_4 constant, the voltage recorded was the lowest in the series of experiments. The yield initially increased but then decreased as the volume of H_2O_2 was increased from 5 ml to 15 ml. It further diminished when 20 ml of HF and 5 ml of H_2O_2 were employed. This composition, however, did yield the best results, as 30 g of stainless steel powder, free of oxides was obtained.

From these experiments some useful conclusions have been drawn.

1. The voltage always drops with the increase of the ions in the system.
2. In the absence of H_2O_2 , oxidation occurs and the powder formation is adversely affected.
3. With the use of two components the voltage consumption is generally higher and the yield is quite low.

Another important aspect which requires careful study is the effect of the interval for replenishing the reagents of the bath and the duration of lapses in the efficiency and the yield/hr. A series of experiments, as represented in Table 2, were carried out to develop the optimum conditions for powder formation. The composition which gave the maximum yield (H_2SO_4 , 30 ml; HF, 15 ml; H_2O_2 , 10 ml) was selected for further study.

When the bath was not given any rest, progressive polarization occurred and the passive film protecting the grain was destroyed, though the periodic interchange of anode and cathode was employed to minimize these effects. With the fresh solution the yield/hr is 50 g, but after a rest of 2 hr it increases to 61 g. It decreases in the third operation to 45 g. The replenishing, however, did not improve the yield and it registered a continuous decline. In another set of experiments with fresh solution, the rest in between the operations positively improved the yield. However, after four operations, each of 30 min duration, the yield falls off, and replenishing becomes necessary. When the operation was started 2 hr after replenishing, the yield was maximum. It is, therefore, essential to replenish the reagents of the bath after every four operations.

TABLE 1.—EFFECT OF THE COMPOSITION OF THE BATH ON THE POWDER FORMATION.

Current = 10 amp, Temp = 25°C; Volume of water = 10 l., Time = 30 min

H_2SO_4 (ml)	HF (ml)	H_2O_2 (ml)	Voltage	Yield (g)	Remarks
5.0	—	—	8.5	4.00	Oxide formation
7.0	—	—	8.3	4.5	
10.0	—	—	8.1	8.0	
15.0	—	—	8.0	8.0	
10.0	—	5	4.7	3.5	
15.0	—	5	3.8	5.0	
20.0	—	5	3.2	5.5	
20.0	—	10	3.8	3.0	
5.0	2.5	—	8.0	5.0	Oxide formation
10.0	2.0	—	8.0	5.5	
10.0	3.0	—	7.9	6.8	
10.0	4.0	—	7.9	8.5	
10.0	5.0	—	7.8	8.5	
5.0	—	5	8.0	3.0	
5.0	—	10	7.0	3.0	
5.0	—	15	5.5	3.0	
20.0	5.0	5.0	3.7	6.0	
20.0	10.0	5.0	3.6	7.0	
20.0	15.0	5.0	3.5	9.0	
30.0	15.0	5.0	3.0	20.0	Oxide formation
30.0	15.0	10.0	3.0	30.0	
30.0	15.0	15.0	3.0	25.0	
30.0	20.0	5.0	3.0	15.0	

The particle size distribution given in Table 3 indicates that the size ranges from + 100 to -240 B.S.S. mesh. The size of the particle, however, depends upon the grain size of the metal, which in turn depends upon its mechanical working and heat treatment.

TABLE 2.—EFFECT OF THE CONDITIONS OF THE BATH TOGETHER WITH LAPSES ON THE CUMMULATIVE YIELDS/HR.

Composition of bath : H_2SO_4 , 30 ml, HF, 15ml; H_2O_2 , 10 ml.

Conditions of the bath	laps	Cummulative yield /hr(g)			Remarks
		1st $\frac{1}{2}$ hr	2nd $\frac{1}{2}$ hr	Total	
I Fresh solution	—	25	30	55	
Same bath	—	20	10	30	
Same bath	—	20	13	33	
Same bath	Left overnight	60	58	118	Contained much of the oxides of nickel
II Fresh solution	—	31	28	59	
Same bath	2 hr	30	31	61	
Same bath	2 hr	25	20	45	
Fully replenished with H_2SO_4 , 30 ml; HF, 15 ml; H_2O_2 , 10 ml	2 hr	20	15	35	
III Fresh solution	—	15	15	30	
Same bath	2 hr	30	28	58	
Same bath	2 hr	32	29	61	
Same bath	Left overnight	15	11	26	The electrodes were out of the bath as oxidation sets in if left in the bath
Fully replenished with H_2SO_4 , 30 ml; HF, 15 ml; H_2O_2 , 10 ml	—	30	33	63	
The same bath as above (III. 5)	2 hr	29	31	60	
IV Same bath	2 hr	28	30	58	
Same bath	2 hr	12	15	27	
Fully replenished with H_2SO_4 ; 30 ml; HF, 15 ml	2 hr	31	33	64	

TABLE 3.—PARTICLE SIZE DISTRIBUTION OF THE TOTAL YIELD OF SECTION IV IN TABLE 2.

Mesh size	Percentage
+100	2.1
+120	7.32
+140	11.18
+170	22.60
+240	41.00
-240	15.70

References

1. *Symposium on Powder Metallurgy 1954, Special Report No. 58* (The Iron and Steel Institute, 4 Grosvenor Gardens, London, 1956), p. 181.
2. Claus G. Goetzl, *Treatise on Powder Metallurgy* (International Publishers Inc., New York, 1949), vol. I.