Development of High Quality Ferrochromium Alloy (NKK Super-Chrome)

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A new process of manufacturing high quality ferrochrome (Super-Chrome) to meet demands of superalloy was developed by NKK. This process is composed of three stages, i. e., nitridation of low carbon ferrochrome, acid treatment of chromium nitride and removal of nitrogen from chromium nitride. These stages of this process bring some advantages of high quality control and easy control in shape of product.

An example of chemical composition is as follows ; (wt. %)

Cr	C	Si	P	S	Co	Ni	N	O	Fe
90. 3	0. 01	0. 09	0. 007	0. 003	0. 007	0. 04	0. 004	0. 08	9. 2

Super-Chrome is also suitable for special steel, welding rod of stainless steel or powder metallurgical product.

Introdaction

Chromium is widely used for improving the corrosion resistance and high temperature properties of special alloy and stainless steels. The sources of chromium are chosen for these applications range from economical high and low carbon ferrochromes to costly degassed metallic chromium. However, an economical chromium resource was not available that had a high chromium content and a low level of detrimental elements [1] such as S, P, O and N.

A new process for making the high quality ferrochrome, called Super-Chrome , was developed by NKK. The new process and the characteristics of Super-Chrome are briefly introduced in this paper .

Manufacturing process

A flow diagram of the manufacturing process is shown in Figure 1. The process has three stages : nitridation of low carbon ferrochrome , acid treatment of chromium nitride and removal of nitrogen from chromium nitride.

Choice of adequate raw material
↓
Nitridation in the vacuum furnace (at 1, 100℃)
↓
Hydrochloric acid treatment (extraction)
↓
Degassing in the vacuum furnace (1, 250℃, 7Pa)
↓
Finishing , milling , packing (Products)

Fig. 1. Manufacturing process of Super-Chrome

Nitridation

First, low carbon granular ferrochrome is nitrided in a vacuum furnace at 1, 100℃ under an atmosphere of nitrogen. The rate to nitriding is sensitive to the size distribution of raw material and treatment temperature .

During nitridation at low carbon granular (1 - 5 mm) ferrochrome , the nitrogen content increases parabolically and Cr_2N is formed above 1, 000℃ showed in Figure 2.

In this reaction , the activation energys of nitridation change from 105 to 272 KJ/mol [2] by the raw material sizes and Fe contents.

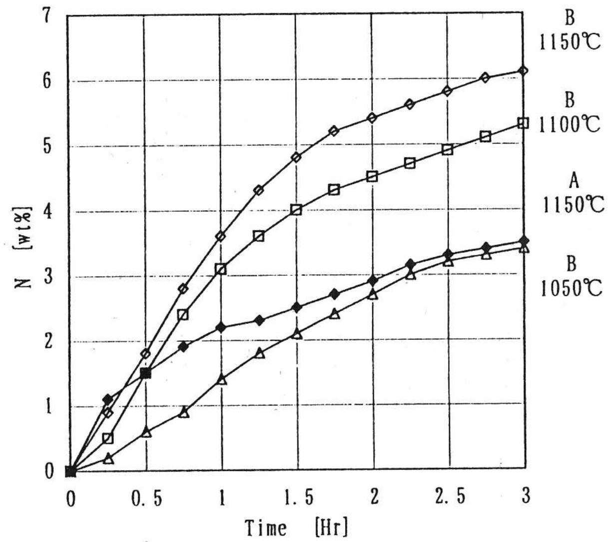


Fig. 2. Rates of nitridation of granular chromium (A) and ferrochrome (B).

Figure 3. shows size effect on reaction rate constant A in the nitridation at 1,000℃. This reaction rate constant is inverse proportion to the particle diameter and changes for Fe contents of the raw material [2]

$$X=\Sigma\{1-(1-At/Rn)^3\}\alpha n \quad (1)$$

X	;	reaction ratio	[−]
t	;	Time	[Hr]
Rn	;	radius of division n	[mm]
A	;	reaction rate constant	[mm/Hr]
αn	;	weight proportion of division n	[−]

The reaction rate should be dicided by nitrogen diffusion speed through nitride layer to reaction site. In the case of economical manufacturing, the size of raw material is most important in the nitridation.

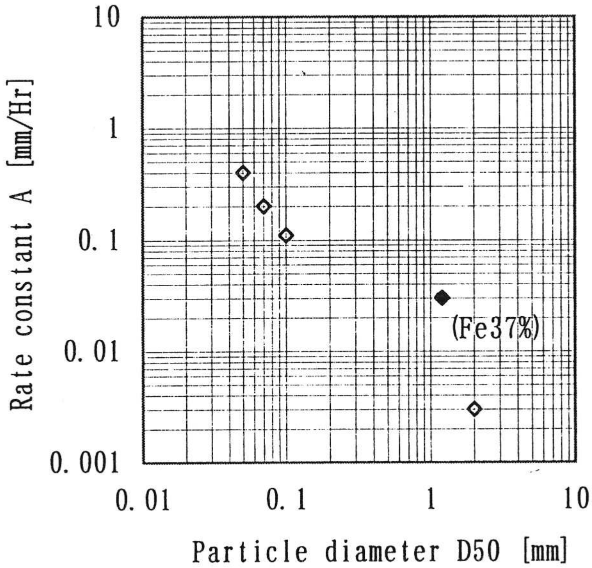
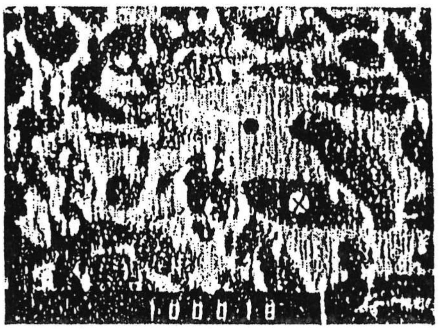


Fig. 3. Size effect between reaction constant A and particle diameter D_{50} at 1,000℃
(◇ ; Chromium, ◆ ; Ferrochrome−Fe 37%)



Spot analysis
●Cr 19%, Fe 81%, N 0%
⊗Cr 83%, Fe 8.5%, N8.5%
10μm

Fig. 4. SEM images of ferrochromium nitride (nitrided B) at 1,150℃ for 3 hrs.

Nitrided ferrochrome has two microscopic phases Cr_2N and metal as shown in Figure 4. This metallic phase contains 81% Fe, 19% Cr and small amount of Si, P, Co, Ni.

Under lower temperature conditions, CrN phase is additionally formed at the case of powdered chromium sources, this CrN phase has less content of Fe than Cr_2N.

Acid treatment

Secondly, nitrided and milled ferrochrome is immersed in a hydrochloric acid bath to remove the phase that contains mainly Fe. Chromium nitride is then condensed by filtering, water washing and drying. In this process, the material is purified by removal of the Fe phase, which contains Si, P, Ni and Co.

Figure 5. shows content of detrimental elements change, that means the change is affected by chromium content proportional to acid addition. In this reaction, the content of some detrimental elements are removed calculably to the addition of acid under the appropriate mixing condition.

The reaction vessel is equipped with up-flow paddles to obtain strong stirring in due to the high density of nitrided chromium. In this treatment, the size of nitride changes finer and desireable for the next treatment.

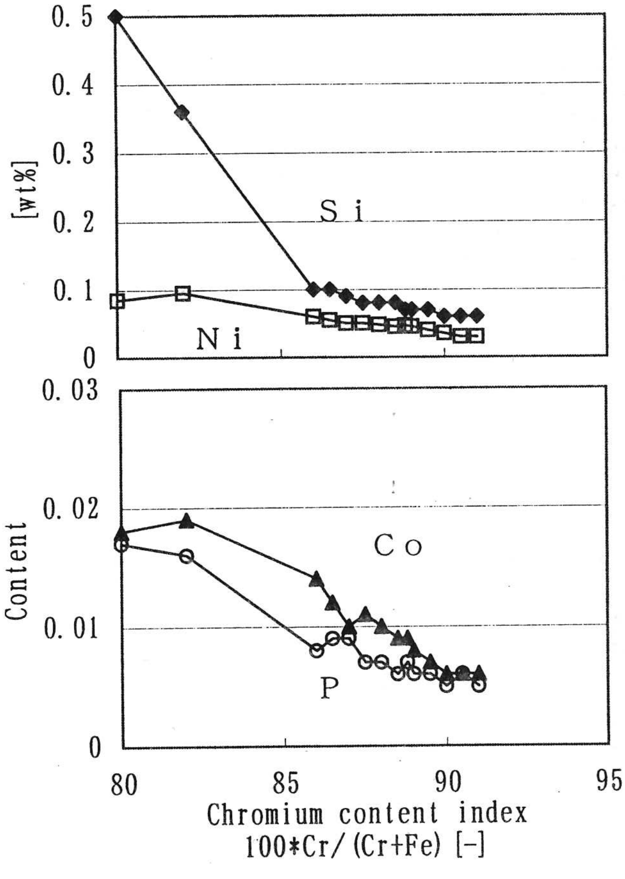


Fig. 5. Content of detrimental elements.

Degassing

Finally, chromium nitride containing solid solute Fe is heated and degassed at pressures below the equilibrium conditions [3] for nitride formation.

The reaction rate is relatively fast because the raw material size is very fine about 5 μm. Table 1. shows that nitrogen contents of some raw materials under the same degassing conditions change with the diameter of several ferrochrome sources. As nitrogen content of lumpy material cannot removed in the limited time, their diffusion speed and reaction ratio were mainly controlled by the size of raw materials.

Table 1. Degassing behavior of some ferrochromes

raw material	diameter [mm]	N before Treatment [wt%]	N after Treatment [wt%]
Low carbon ferrochrome	40	0.052	0.032
Low carbon ferrochrome	10	0.048	0.025
Low carbon ferrochrome	2	0.038	0.012
nitrided ferrochrome (P)	0.1	7.2	0.007
this case	0.005	10.1	0.004

at 1,250℃, 24 Hrs under vacuum

The N content of the product is stably controlled to 40 ppm at 1,250℃. Also, C and O are also removed during this degassing by adding carbonaceous material. Figure 6. shows relationship between carbon and oxygen content controllably change in degassing treatment.

Figure 7. shows a typical pressure patern of degassing process. In this stage, the productivity of endothermic degassing treatement should be changed with the capacity and precision of vacuum and heating conditions.

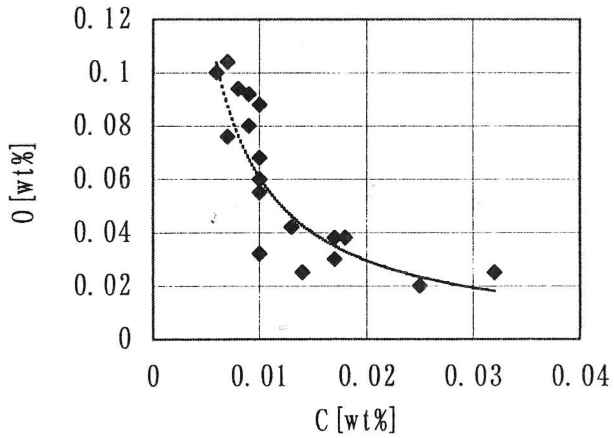


Fig. 6. Relationship between carbon and oxygen concentration of the product

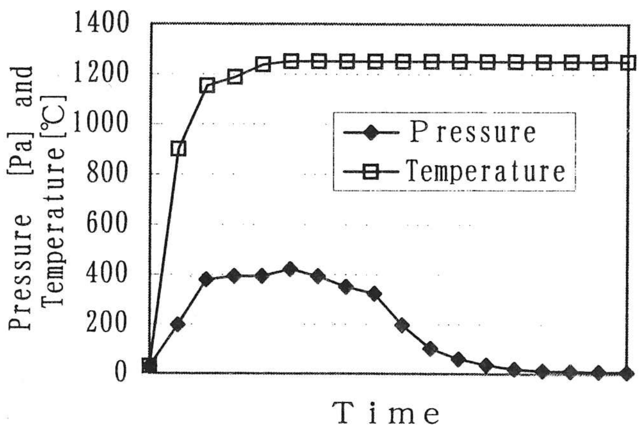


Fig. 7. A typical pressure patern of degassing in the production

Characteristics

Chemical composition

A typical chemical composition of Super-Chrome are shown in Table 2. Super-Chrome are :

(1) N, O and C are low after the degassing. In particular, N is extraordinarilly low (40 ppm).

(2) Fe, Si, P, Ni and Co are low after acid treatment.

(3) the amount of detrimental elements are stably controlled at low levels by the use of selected low carbon ferrochrome and through purification processes such as scid treatment and degassing.

Table 2. An example of chemical composition (Wt%)

Cr	C	Si	P	S	Co	Ni	V	Ti	N	O	Fe
90.3	0.01	0.09	0.007	0.003	0.007	0.04	0.08	0.002	0.004	0.08	9.2

Table 3. shows the controlability of main elements in the each treatements. The care of raw material is most important of all quality control.

Size and Shape

High dense lumps with a specific gravity of about 5 are produced in the degassing process without briquet-making. In addition, this product is easily milled because it has a high chromium content and sintered structure. Standard sizes of lump are 200-10mm, those of powder are -60 Mesh and -150 Mesh. A SEM image of the powder is shown in Figure 8.

Table 3. Quality control of Super-Chrome

Element	Low carbon ferrochrome (raw material)	nitridation	acid treatment	degassing
Cr/Fe	○	–	◎	–
Si	◎	–	○	–
P	○	–	◎	–
S	◎	–	◎	○
C/O	–	–	○	◎
N	–	–	–	◎
Ni/Co	○	–	◎	–
Mn	◎	–	–	○
V/Ti	◎	–	–	–

◎ ; very significant
○ ; significant
– ; negligible

Fig. 8. A SEM image of Super-Chrome powder

Merits of Super-Chrome

These new products are easily applied for ;
(1) chromium source for superalloys or specialty steels those require low levels of gaseous elements -- Super-Chrome can be replaced metallic chromium --
(2) chromium source for stainless welding materials
(3) chromium source for powder metallurgical product

Table 4. shows the comparison of main chromium sources from a view of some elements. Super-Chrome is excellent at gaseous elements, especially the best at nitrogen content which is most important to superalloy for rotating.

Table 4. Comparison of Chromium Alloys

Alloys	Metalic Chromium			EF twostage ferro-chrome	Low carbon ferro-chrome	NKK Super Chrome
	Electrolysis		Thermit			
Element	Vacuum	Standard				
Cr/Fe	◎	◎	◎	○	×	○
Si	◎	◎	○	×	×	○
C	◎	○	○	○	○	◎
P	◎	◎	◎	△	×	○
S	△	×	×	◎	○	◎
N	△	×	×	×	×	◎
O	◎	×	○	○	×	○
Co	◎	◎	◎	△	×	○

◎ ; excellent　△ ; normal
○ ; good　× ; bad

Conclusion

A new and original process was developed by NKK, and the characteristic of Super-Chrome is as follows ; that is excellent as a new chromium source for special steel, welding rod of stainless steel or powder metallurgical product.
Nitride-refining is applied to produce a high quality ferrochrome with low nitrogen content. The features of this new products including its chemical composition and size, would create new demands for many special materials.

References

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