FTD-HT-23-403-70

FOREIGN TECHNOLOGY DIVISION

PREPARATION OF THE CHROMIUM CARBIDES Cr_7C_3 and $Cr_{23}C_6$

by

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EDITED TRANSLATION

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English pages: 6

Source: Izvestiya Vysshikh Uchebnykh Zavedeniy. Khimiya i Khimicheskaya Tekhnologiya (News of Institutions of Higher Learning. Chemistry and Chemical Technology), Vol. 12, No. 2, 1969, pp. 224-227.

Translated by: L. Thompson/TDBRS-3

PREPARATION OF THE CHROMIUM CARBIDES Cr_7C_3 and $Cr_{23}C_6$

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Chromium carbides are high-melting, hard, and noncorroding substances [1-3] whose presence and distribution in chrome-nickel steels is connected in a group of works [4-7] to the onset of a tendency to intercrystalline corrosion.

To study the electrochemical and corrosion properties of the carbide phases of chromium it is necessary to prepare them in a single-phase condition; this process was studied in detail in works [8-10].

This work presents a refinement of the technological processes for preparing chromium carbides by reducing chromium oxides with carbon and the direct synthesis of chromium and carbon in industrial hydrogen furnaces.

Experimental Part

Chromium carbide Cr_7C_3 was produced according to the reaction

$$7Cr_2O_3 + 27C \rightarrow 2Cr_7C_3 + 21CO.$$

Chromium oxide (GOST [All-Union State Standard] 2012-54) and lamp black (GOST 7885-50), first roasted at 800° and 400°C respectively for

two hours, were screened to a fraction not larger than 25 μm. An adjustment to the composition of the charge was inserted according to data in [11]. The charge was mixed in mechanical rollers with addition of a solution of dextrin calculated as 5 g to 100 g of the charge. The charge was dried at 110°C for six hours and was pressed into briquettes 25 × 20 mm in size at a pressure of 300 kg/cm^2; the charge was again dried for two hours at 110°C and was subjected to carbidization. The results are presented in Table 1. The briquettes were heated in TsEP-356 industrial hydrogen furnaces in a stream of purified and dried hydrogen and were maintained at a given temperature for one hour and then were cooled to room temperature in the furnace cooler. The obtained product was ground and subjected to a second roasting for 15 minutes at a given temperature. The prepared product was analyzed for the total content of carbon [11] and for free carbon [12]. Bound carbon was determined by the formula

$$C_{bou} = \frac{C_{tot} - C_{free}}{100 - C_{free}} 100\%.$$

The chromium content was determined by the persulfate-silver method [11]. Through X-ray structural analysis (Table 4) it was established that of the four groups of carbides, only the third consists of single-phase structures. The carbides obtained at temperatures higher than the optimum (1300°C) contain Cr_3C_2 carbides as admixtures, and carbides obtained at lower temperatures contain the lower carbide $Cr_{23}C_6$ and underreduced chromium oxide. Table 1 presents the ratio of the product weight after reaction A to the calculated weight of the carbide B, by which it is possible to judge the completeness of the reaction.

For carbide groups 3 and 4, for which the ratio A/B is close to the theoretical, the content of C_{free} is insignificant and the amount of C_{bou} is close to the stoichiometric composition. The optimum values of these indicators appear in carbides of the third group.

The carbide $Cr_{23}C_6$ is derived according to the reaction

Table 1. Results of experiments on producing the chromium carbide Cr_7C_3.

Group No.	Temperature, °C	Briquette wt, g: before heating	Briquette wt, g: after heating A	Calculated wt of carbide B, g	A/B	Content, % by weight: C_{total}	Cr	C_{free}	C_{bound}	Cr + C_{total}	Detected phases
		Calculated composition				9,01	90,99	—	9,01	100	
1	1100	230,60	133,34	106,0	1,26	14,09	74,55	10,04	4,50	88,64	$Cr_7C_3 + Cr_2O_3 + Cr_{23}C_6$
2	1160	107,00	71,00	62,0	1,14	12,90	78,20	8,20	5,12	91,10	$Cr_7C_3 + Cr_2O_3 + Cr_{23}C_6$
3	1300	86,29	49,23	49,9	0,99	9,05	90,50	0,05	9,00	99,55	Cr_7C_3
4	1400	171,60	98,00	99,0	0,99	9,91	90,15	0,21	9,89	100,06	$Cr_7C_3 + Cr_3C_2$

Table 2. Results of experiments on producing the chromium carbide $Cr_{23}C_6$.

Group No.	Temperature, °C	Briquette wt, g: before heating	Briquette wt, g: after heating A	Calculated wt of carbide B, g	A/B	Content, % by weight: C_{total}	Cr	C_{free}	C_{bound}	Cr + C_{total}	Discovered phases
		Calculated composition				5,68	94,32	—	5,68	100	
1	1200	115,00	66,90	44,30	1,5	6,68	87,50	0,06	6,62	94,18	$Cr_{23}C_6 + Cr_7C_3$
2	1300	95,90	93,80	95,90	0,975	6,20	88,20	0,08	6,12	94,40	$Cr_{23}C_6 + Cr_7C_3$
3	1310	96,50	95,50	96,50	0,988	5,96	92,63	0,10	5,87	98,59	$Cr_{23}C_6 + Cr_7C_3$
4	1400	190,16	189,07	188,98	1,003	5,52	94,30	0,15	5,38	99,97	$Cr_{23}C_6$
5	1500	96,56	96,23	96,56	0,955	6,33	93,52	0,39	5,96	99,85	$Cr_{23}C_6 + Cr_7C_3 + Cr_3C_2$

Previously prepared electrolytic chromium mixed with lamp black was pressed into 10 × 10 mm briquettes at a pressure of 200 kg/cm^2 and was subjected to carbidization at different temperatures (see Table 2). The rise in temperature from 1000°C to the starting point was accomplished in 15 minutes and at the given temperature aging was accomplished for the same amount of time. From a charge of the same composition containing 20% less carbon than calculated, 5 groups of $Cr_{23}C_6$ carbide were obtained. X-ray structural analysis fixed a single-phase structure in only the fourth group. In the remaining groups several carbide phases were detected. This is explained by the fact that the area where Cr_7C_3 carbides exist is substantially wider than that for $Cr_{23}C_6$. The free energy of formation of Cr_7C_3 is 2.5 times higher than for $Cr_{23}C_6$ carbide (see the figure) [13]; at temperatures lower or higher than the optimum (1400°C), the reaction of Cr_7C_3 formation suppresses the $Cr_{23}C_6$ reaction.

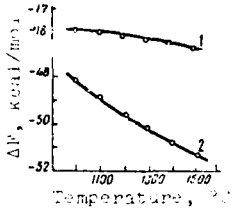

Figure. Change in the free energy of formation ΔF of the carbides $Cr_{23}C_6$ (1) and Cr_7C_3 (2) as a function of carbidization temperature.

The ratio A/B (see Table 2) changes little in the 1200-1500°C range and it approaches unity as the quantity of $Cr_{23}C_6$ carbide in the product increases.

The content of carbon in carbides obtained at 1200-1350°C is greater than the stoichiometric, since the product contains mixtures of carbides which are enriched with carbon as compared to $Cr_{23}C_6$ carbide. As the temperature of carbide synthesis is increased up to the optimum the content of bound carbon decreases and at the optimum temperature (1400°C) reaches its minimum, which corresponds to the stoichiometric composition of the $Cr_{23}C_6$ carbide.

An increase in the sintering temperature leads anew to an increase in the amount of bound carbon, in connection with the formation of higher carbides.

Conclusions

1. A two-stage process is proposed for obtaining the single-phase carbide Cr_7C_3 by reducing chromium oxide with lamp black in a TsEP-356 industrial hydrogen furnace. It consists of heating the charge in an atmosphere of hydrogen to 1300°C for 15 minutes, maintaining it at that temperature for one hour, cooling the product to room temperature with subsequent crushing and supplementary heating in a hydrogen atmosphere for 20 minutes.

2. The single-phase carbide $Cr_{23}C_6$, close in stoichiometric composition to the calculated, may be obtained in a stream of hydrogen by synthesis of metallic chromium and lamp black at 1400°C; the time of the temperature rise to 1400°C is 15 minutes and holding at the optimum temperature is for the same length of time.

References

1. Samsonov, G. V. Tugoplavkiye soyedineniya (Refractory compounds). Metallurgizdat, M., 1963.

2. Samsonov, G. V., and K. I. Portioy. Splavy na osnove tugoplavkikh soyedineniy (Alloys based on refractory compounds). Oborongiz, M., 1961.

3. Kiffer, R., and P. Shvartskopf. Tverdyye splavy (Hard alloys). Metallurgizdat, M., 1957.

4. Khimushin, F. F. Nerzhaveyushchiye stali (Stainless steels). Izd. "Metallurgiya," M., 1967.

5. Gudremon, E. Spetsial'nyye stali (Special steels). Vol. 1. Izd. "Metallurgiya," M., 1966.

6. Rocha, H. Z. Schweisstechnick, 52, 3 (1962).

7. Miroshnikova, K. A. Kand. dissertatsiya (Candidate dissertation (Moscow, 1967)).

8. Kosolapova, T. Ya., G. V. Camsonov. Zh. prikl. khimii, 32, 55, 1505 (1959); 33, 1704 (1960).

9. Samsonov, G. V., and T. Ya. Kosolapova. "Poroshkovaya metallurgiya v mashinostroyenii" (In the Collection: "Powder metallurgy in machinery construction"). Mashgiz, 1961.

10. Kosolapova, T. Ya. Avtoreferat dissertatsii (Author's abstract of dissertation (Moscow, 1961)).

11. Analiz tugoplavkikh soyedineniy (pod red. G. V. Samsonova) (Analysis of refractory compounds (edited by G. V. Samsonov)). Metallurgizdat, M., 1962.

12. Kosolapova, T. Ya., and S. V. Radzikovskaya. Zavodsk. laboratoriya, 26, 138 (1960).

13. Uiks, K. Ye., and F. Ye. Blok. Termodinamicheskiye svoystva 65 elementov, ikh okislov, galogenidov, karbidov i nitridov (The thermodynamic properties of 65 elements, their oxides, halides, carbides, and nitrides). Metallurgizdat, M., 1965.

Materials Science Department

Submitted
28 February 1968

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Foreign Technology Division
Air Force Systems Command
U. S. Air Force

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE
PREPARATION OF THE CHROMIUM CARBIDES Cr(SUBSCRIPT 7)C(SUBSCRIPT 3) AND Cr(SUBSCRIPT 23)C(SUBSCRIPT 6)

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Translation

5. AUTHOR(S) (First name, middle initial, last name)
Freyd, M. Kh. and Suprunov, V. A.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
1969	6	13

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 7343	FTD-HT-23-403-70
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Foreign Technology Division Wright-Patterson AFB, Ohio

13. ABSTRACT

The study of preparation techniques of given chromium carbides was needed to obtain single phase carbides for determination of electrochemical and corrosion characteristics. Intercrystalline corrosion in Ni-Cr steel was correlated with the presence of these chromium carbides. The effect of temperature in the 1100-1500 degree centigrade range was studied on the composition of given products. A given single phase was obtained by reaction in two steps: first, heating at 1300 degrees centigrade a briquetted mixture of given chromium carbides and lamp black in a hydrogen stream for 1 hr., then heating the cooled and pulverized charge again for an additional 20 min. under identical conditions. At a temperature lower than the optimum the product contained given chromium carbides; at a higher temperature, it contained given chromium carbides impurity. The single phase nearly stoichiometric chromium carbides given was prepared by on heating at 1400 degrees centigrade a briquetted charge of electrolytic chromium and lamp black in a hydrogen stream for 15 min. Two given mixtures were produced at a temperature below or above 1400 degrees centigrade respectively. Both reactions were carried out in an industrial hydrogen furnace. Orig. art. has: 1 figure, 2 tables, and 3 formulas. [AP9010126]

DD FORM 1 NOV 1473

UNCLASSIFIED

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Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Chromium Carbide Inorganic Synthesis						