Structure of Chromium-Rich Cr-Ni, Cr-Fe, Cr-Co, and Cr-Ni-Fe Alloy Particles Made by Evaporation in Argon

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Structural analyses were performed on alloy particles of chromium-rich Cr-Ni, Cr-Fe, Cr-Co, and Cr-Ni-Fe systems. Fine alloy particles (100 to 1000Å in diameter) were prepared by evaporation of parent alloys in argon at 20 torr. In addition, alloy structures of bulk specimens of the Cr-Ni system were investigated using X-ray diffraction techniques to confirm the results obtained from the particulate alloys. In these binary systems, δ phase with W_3O structure (A-15) and σ phase with β-uranium structure (D^8_b) were identified in addition to the α (bcc) and γ (fcc) terminal solid solutions. The compositional ranges for the σ phase in the Cr-Ni, Cr-Fe, and Cr-Co systems are from low chromium to 68, 63.4, and 62.1 wt pct Cr, respectively. The δ phase exists in the range from pure chromium to 68, 58, and 54 wt pct Cr in the respective Cr-Ni, Cr-Fe, and Cr-Co alloy systems. Similarly, in the Cr-Ni-Fe system, it was found that δ phase occurs in the chromium corner while σ phase exists in the region bridging the two binary σ phases of the Cr-Ni and Cr-Fe systems. Possible modification of phase diagrams of these systems is discussed in view of these results.

CHROMIUM, an indispensable alloy additive to various heat-resisting alloys and stainless steels, has been the subject of dispute for many investigators as to whether or not it possesses an elevated-temperature allotropic phase. As a result, for example, two different versions of the phase-equilibrium diagram for the binary Cr-Ni system are available today, *i.e.*,

1) A simple eutectic diagram[1-7]

Liq. $\rightleftharpoons$ α-Cr (bcc) and γ-Ni (fcc)

2) A diagram consisting of a eutectic and a eutectoid[8-10]

Liq. $\rightleftharpoons$ β-Cr (fcc) and γ-Ni (fcc)

β-Cr (fcc) $\rightleftharpoons$ α-Cr (bcc) + γ-Ni (fcc)

The latter version, reported first by Stein and Grant,[9] indicates the existence of the allotropic β-chromium phase (fcc, a = 3.68Å) above 1840°C and the presence of a eutectoid reaction at 68 wt pct Cr and at 1215°C. Wyder *et al.*[11] and Bare,[12] who later conducted high-temperature X-ray diffraction studies on high-chromium alloys in the Cr-Ni system did not confirm the existence of the β-Cr phase proposed by Stein and Grant. They both concluded that a simple eutectic diagram was valid for the Cr-Ni binary system. More recently, however, Kimoto and Nishida[13] prepared fine-particle specimens of chromium by vaporizing it in a low-pressure argon atmosphere and conducted the structural analysis using both electron and X-ray diffraction techniques. They reported that a new allotropic δ-Cr phase (bcc) was isostructural with W_3O.

If this phase actually exists in chromium, it should be present also in alloy systems such as Cr-Ni. With this assumption the authors investigated the Cr-Ni, Cr-Fe, Cr-Co, and Cr-Ni-Fe systems by duplicating the experimental methods employed by Kimoto and Nishida.

Kimoto and Nishida found that the fine chromium particles obtained by vaporization in a mixture of 6 torr of argon and 0.1 torr of air were α-Cr (bcc; a_0 = 2.88Å). On the other hand those metal particles produced in pure argon were found to possess a new crystal structure. The structure of the new modification of chromium, designated δ phase, was determined to be of a simple cubic lattice with a = 4.588Å. This structure has the disordered atomic arrangement derivable from the A-15 type (or W_3O type) structure, Fig. 1. Table I shows the X-ray diffraction results for the δ-Cr phase which were reported by Kimoto and Nishida. The reflections designated by (s) in the table are those caused by the A-15 type structure while other reflections are those produced by the aforementioned disordered structure. These investigators reported also that the new modification transformed to the ordinary bcc form (α-Cr phase) above 400°C.

Although the data obtained in the Cr-Ni,[14,15] Cr-Fe,[15] and Cr-Co[15] binary systems were published previously in Japan, it was considered pertinent to redescribe the results in this paper along with the data on the Cr-Ni-Fe system.

EXPERIMENTAL

Starting Materials and Alloy Ingots

High-purity chromium (99.999 pct, supplied by Johnson Matthey and Co.), nickel (99.98 pct purity), cobalt (99.8 pct purity), and electrolytic iron which was annealed in dry hydrogen were used in the study. Alloy additions to chromium were made at 5 to 10 wt pct or at. pct increments. Button ingots ranging from 5 to 20

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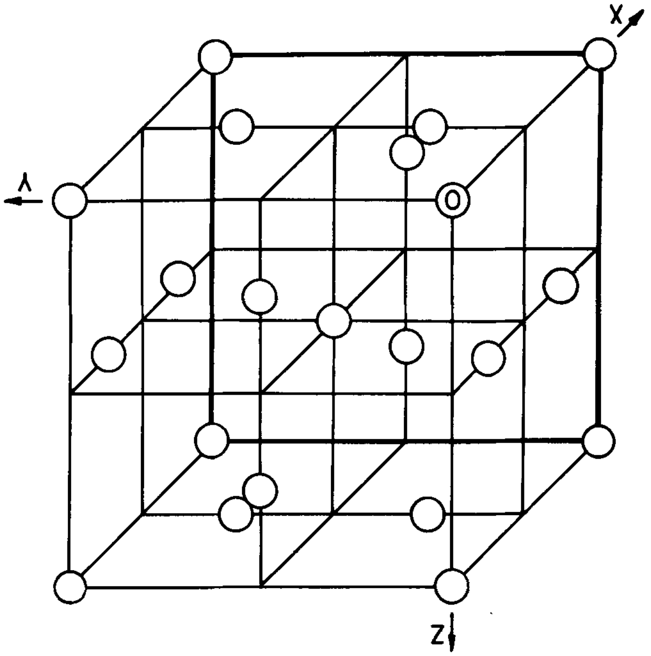

Fig. 1—*A*-15 type structure.

Table I. Diffraction Lines of δ-Cr (Kimoto *et al.*)

N $(h^2+k^2+l^2)$	$h\,k\,l$	d_{obs}, Å (Mo-Kα)	d_{cal}, Å
1	100	–	4.588
2	110	–	3.244
3	111	–	2.649
4	200(*s*)	2.300	2.294
5	210(*s*)	2.049	2.052
6	211(*s*)	1.873	1.873
8	220	1.611	1.622
9	300	–	–
10	310	1.441	1.451
11	311	1.387	1.383
12	222(*s*)	1.327	1.324
13	320(*s*)	1.274	1.272
14	321(*s*)	1.226	1.226
16	400(*s*)	1.145	1.147
17	410	–	1.113

g in size were prepared by either arc melting or plasma jet in high-purity argon (99.9 pct purity) atmosphere.

Preparation of Fine Alloy Particles

The apparatus constructed for preparation of alloy particles consisted of a pyrex bell jar, a tungsten-wire heater (in conical basket shape), a copper mesh backed by carbon film (commonly used in electron microscopy) and the necessary vacuum system and electric power source as shown in Fig. 2. Each alloy weighing from 0.2 to 0.5 g was placed in the tungsten basket. The system was first evacuated down to about 2 × 10^{-5} torr and back-filled with argon to a pressure of about 20 torr. The alloy charge was then heated to melting for evaporation. The current requirement was around 20 amp.

Vapor was condensed onto the inner wall of the bell jar or caught by the carbon mesh. The wall temperature did not exceed 100°C. The condensate was scraped off the wall using a clean rubber scraper for X-ray diffraction analysis. The fine soot-like sample was mixed with collodion-ether solution, coated onto a thin silk thread, and dried. Thin needle-like specimens were approximately 0.5 mm in diameter. The alloy particles caught by the carbon mesh specimen receiver were subjected to electron microscopic examination.

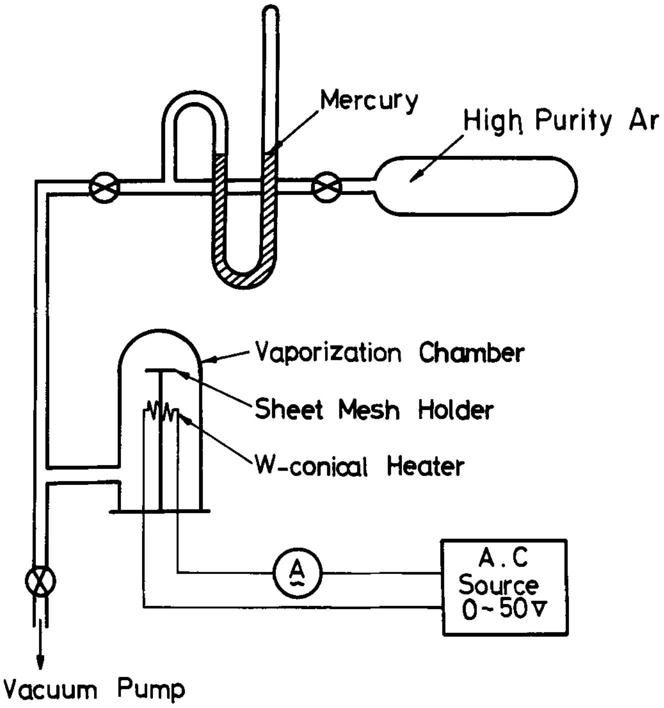

Fig. 2—Schematic diagram of apparatus for evaporating fine particles.

Structural Analysis

In X-ray diffraction analysis the alloy specimens were exposed to CrK$_\alpha$ radiation either in a 114.6 or 57.3 mm Debye-Scherrer camera. The exposure time ranged from 12 to 24 hr at 40 kv and 10 ma. In addition, an electron microscope (HU-11D Model) was employed for transmission electron microscopic examination and selected-area electron diffraction. Some of Cr-Ni alloys in bulk form were also subjected to high-temperature X-ray diffraction analysis.

RESULTS AND DISCUSSION

As a preliminary check, several samples of Cr-Ni alloy particles were analyzed by X-ray microanalysis. The results are as follows:

Chromium, Wt Pct	
Charged	Analyzed
75	75.9
68	68.1
60	58.4
40	40.2
35	35.5

No preferential evaporation of chromium was evident in these alloys. Furthermore, tungsten contamination from the heater was not detected.

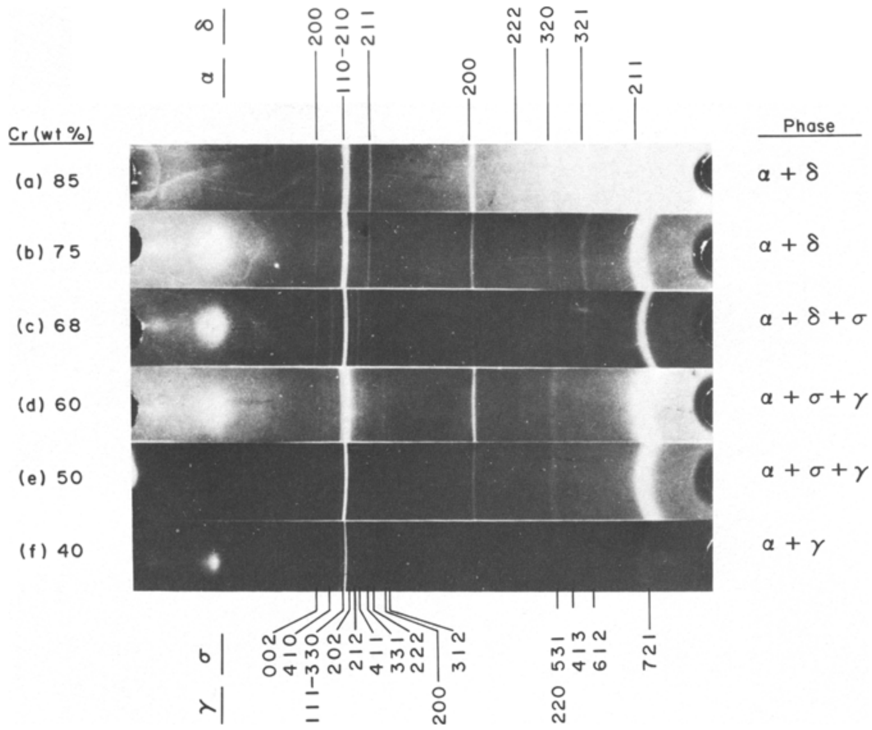

Fig. 3—X-ray Debye-Scherrer patterns of Cr-Ni alloy particles.

It was observed that each particle showed faint extinction contours and was assumed to consist of a single crystal. The morphology of the alloy particles obtained in this study was similar to that of pure chromium particles reported by Kimoto *et al.*[13]

X-Ray Diffraction Data

1) THE Cr-Ni SYSTEM

Six alloys were prepared and studied in the Cr-Ni system in the compositional range from 85 to 40 wt pct Cr. X-ray films obtained for these alloys are compared in Fig. 3 in which phases and *hkl* indices are identified.

Tables II through V tabulate the X-ray data obtained for 85, 68, 50, and 40 wt pct Cr-Ni alloys. As can be seen, the observed $\sin^2\theta$ values are in agreement with the calculated ones. The identified phases, their lattice type and lattice parameters in the Cr-Ni alloys are summarized in Table VI.

In addition to the α and γ terminal solid solutions, the existence of the δ phase (W_3O-type structure) and the σ phase (β-U-type structure) was established. The fcc β phase reported first by Grant and his coworkers was not found in any of these alloys investigated. The δ phase presented in Table II was determined in the alloy containing 85 wt pct Cr. The diffraction lines for this phase coincided with only those strong lines of the δ-Cr phase reported by Kimoto and Nishida[13] (designated with *s* in Table I). These lines matched very well with those of the normal *A*-15 structure. It is considered therefore that the addition of nickel provides restraint on disordering of the δ-Cr phase from the *A*-15 type structure. The same reasoning can be applied to the Cr-Fe and Cr-Co systems, as will be discussed later. The lattice parameters of the δ-Cr phase continuously decrease with increasing nickel contents, see Table VI.

The σ phase was found to exist in the alloys contain-

Table II. X-ray Diffraction Data for 85 Wt Pct Cr-Ni Alloy

		α	δ			
$d_{obs.}$	I_{obs}	Index	$\sin^2\theta_{obs}$	$\sin^2\theta_{cal}$	Index	Note
2.290	w		0.250	0.249	200	
2.235	vw					K_{β}, $d = 2.034$ (110)
2.044	w		0.314	0.312	210	
2.031	vs	110				
1.870	m		0.375	0.374	211	
1.439	s	200				
1.320	vw		0.752	0.748	222	
1.290	vw					K_{β}, $d = 1.175$ (211)
1.272	vw		0.810	0.811	320	
1.226	w		0.872	0.873	321	
1.176	vs	211				
Lattice Parameter, Å			$a = 2.88_1$	$a = 4.58_8$		

Table III. X-ray Diffraction Data for 68 Wt Pct Cr-Ni Alloy

		α	δ	σ		
$d_{obs.}$	$I_{obs.}$	Index	Index	$\sin^2\theta_{obs.}$	$\sin^2\theta_{cal}$	Index
2.290	w		200	0.250	0.240	002
2.152	w			0.283	0.288	410
2.090	vw			0.300	0 305	330
2.047	w		210			
2.037	s	110		0.317	0.308	202
1.984	vw			0.330	0.325	212
1.945	vw			0.346	0.348	411
1.897	vw			0 364	0.365	331
1.870	vw		211	0 375	0.376	222
1.774	vvw			0 416		
1.437	w	200		0.635	0 636	531
1.268	vvw		320			
1.241	vvw			0.839	0.829	413
1.223	vvw		321	0.876	0.867	612
1.171	s	211		0.956	0 957	721
Lattice parameter, Å			$a = 2.87_7$	$a = 4\ 58_4$	$a = 8.82_5$ $c = 4.59_8$	$c/a =$ 0.52_1

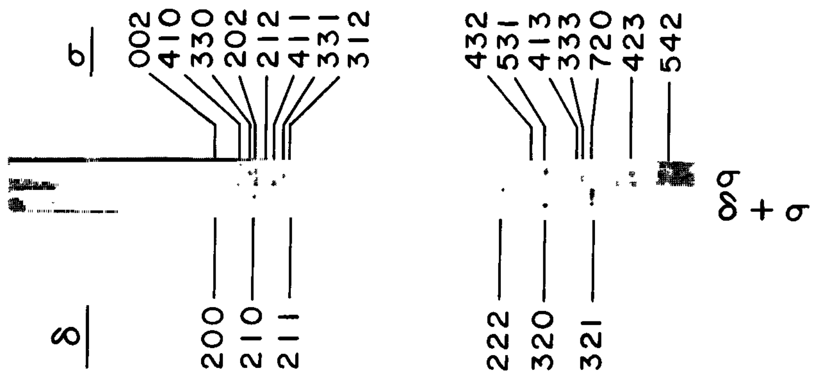

Fig. 4—High temperature Debye-Scherrer patterns of 68 wt pct Cr-Ni alloy. (*a*) At about 1250°C; (*b*) at room temperature after cooling from 1250°C.

Table IV. X-ray Diffraction Data for 50 Wt Pct Cr-Ni Alloy

d_{obs}	I_{obs}	α Index	σ Index	γ Index
2.282	vvw		002	
2.111	vvw		410	
2 068	m		330	111
2.033	vs	110	202	
1.971	vvw		212	
1.932	vvw		411	
1.888	vvw		331	
1.829	vvw		222	
1.789	vw		312	200
1.436	m	200	531	
1.266	m			220
1.171	vs	211	721	
Lattice parameter, Å		$a = 2.87_3$	$a = 8\ 81_8$ $c = 4\ 57_8$ $c/a = 0\ 51_9$	$a = 3.59_1$

Table V. X-ray Diffraction Data for 40 Wt Pct Cr-Ni Alloy

d_{obs}	I_{obs}	α Index	γ Index	Note
2.201	vvw			unknown
2 072	s		111	
2.032	vs	110		
1.897	vw			unknown
1.803	w		200	
1.435	vw	200		
1.264	w		220	
1.170	s	211		
Lattice parameter, Å		$a = 2\ 87_1$	$a = 3.59_0$	

Table VI. Lattice Parameters of Various Phases in Cr-Ni Alloys (a and c in Å)

Phase	Lattice Type	Chromium, Wt Pct 85	75	68	60	50	40
α	*A*2	$a = 2.88_1$	$a \approx 2.87_9$	$a = 2.87_7$	$a = 2.87_2$	$a = 2.87_3$	$a = 2.87_1$
δ	*A*15	$a = 4\ 58_8$	$a \approx 4.58_7$	$a = 4.58_4$	–	–	–
σ	$D^8{}_b$	–	–	$a = 8.82_5$ $c = 4\ 59_8$ $c/a =$ 0.52_1	$a = 8.82_0$ $c = 4\ 56_7$ $c/a =$ 0.51_8	$a = 8.81_8$ $c = 4.57_8$ $c/a =$ 0.51_9	–
γ	*A*1	–	–	–	$a = 3.59_1$	$a = 3.58_9$	$a = 3.59_0$

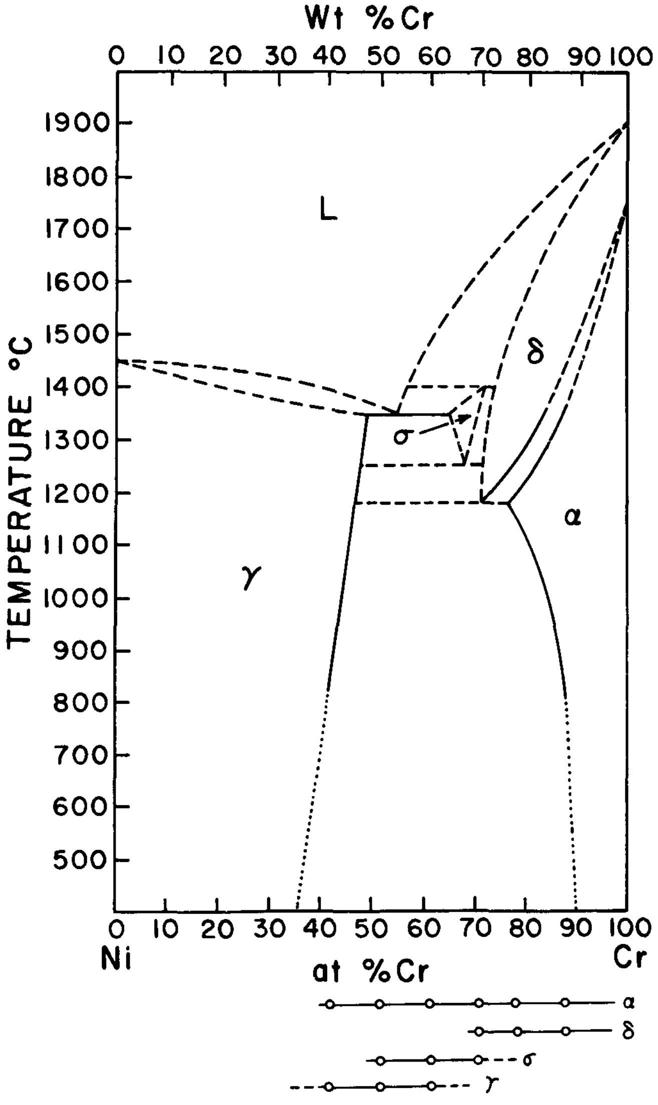

Fig. 5—Tentative phase diagram for Cr-Ni system, constructed on the basis of the determined compositional ranges for phase occurring.

ing 68, 60, and 50 wt pct Cr though it was most predominant in the 68 wt pct Cr alloy. This phase is tetragonal and its axial ratios, determined from several high-angle reflections, were approximately 0.52.

The σ phase, commonly found in alloys of the transition metals of the first long period, was first discovered in Cr-Fe alloys.[16] The formation of this phase has since been confirmed in many other alloy systems. However, σ formation in the Cr-Ni system has not been ascertained. Beck *et al.*[17] suggested after conclusion of their investigation of the Cr-Ni-Mo system that the σ phase might be found at approximately 70 at. pct Cr in the Cr-Ni binary system. Sully[18] predicted also the

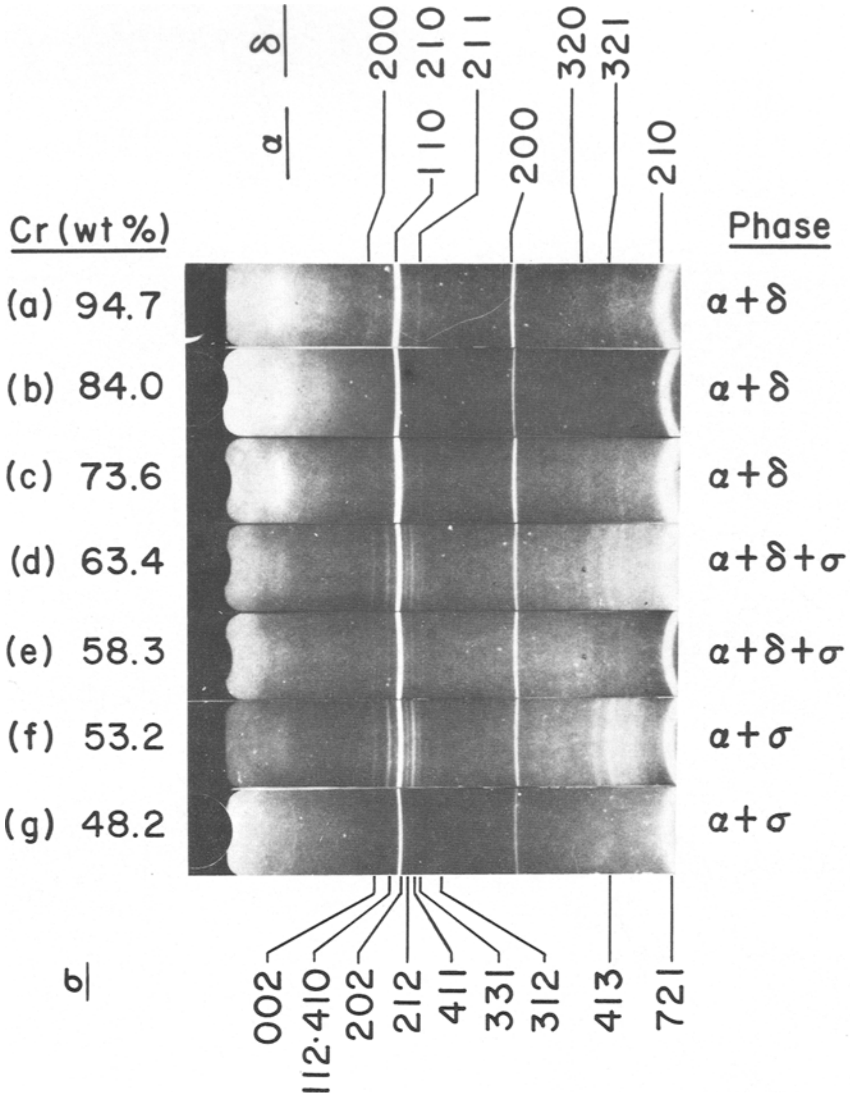

Fig. 6—X-ray Debye-Scherrer patterns of Cr-Fe alloy particles.

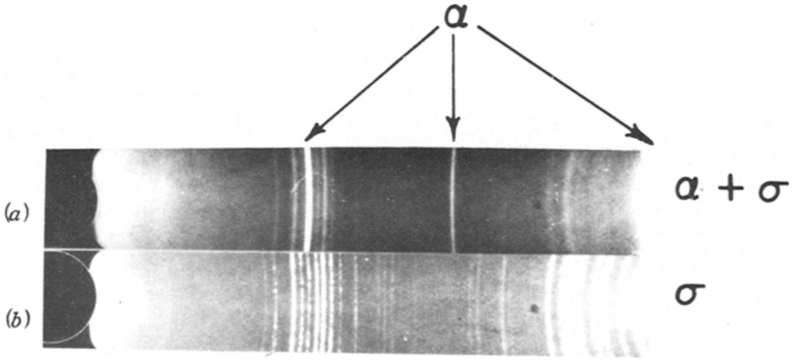

Fig. 7—X-ray Debye-Scherrer patterns of σ phase in 48.2 wt pct Cr-Fe alloy. (*a*) Particles; (*b*) bulk specimen.

σ-phase formation in the 70 at. pct Cr-Ni alloy on the basis of theory of the electronic concentration in the transition metals. Schüller and Schwaab[19] reported the presence of the σ phase in vacuum-deposited Cr-Ni alloy film: it is only the experimentally determined evidence. In their review paper on the σ phase Hall and Algie[20] suspected that the reported σ formation in the Cr-Ni thin film might be due to the presence of impurities. To ascertain whether σ formation in the Cr-Ni alloys would occur only under an extreme condition, such as in vaporized fine alloy particles, bulk specimens were studied also using high-temperature X-ray diffraction technique.

Needle-like specimens were prepared as follows: first, by electric-discharge technique, about 1 mm diam by 10 mm length specimens were removed from button alloy ingots and, second, final dimensions of 0.3 to 0.5 mm diam were obtained by electrolytic polishing. The specimens thus prepared were held in Al_2O_3 tubing and were exposed to X-rays in a high-temperature

Table VII. Lattice Parameters of Various Phases in Cr-Fe Alloys (a and c in Å)

Phase	Lattice Type	Chromium, Wt Pct						
		94.7	84.0	73.6	63.4	58.3	53.2	48.2
α	$A2$	$a = 2.87_8$	$a = 2.87_6$	$a = 2.87_2$	$a = 2.87_2$	$a = 2.87_3$	$a = 2.87_0$	$a = 2.87_0$
δ	$A15$	$a = 4.58_6$	$a = 4.57_3$	$a = 4.56_3$	$a = 4.55_5$	$a = 4.55_7$	–	–
σ	$D^8{}_b$	–	–	–	$a = 8.82$ $c = 4.56$ $c/a = 0.517$	$a = 8.83$ $c = 4.57$ $c/a = 0.517$	$a = 8.80$ $c = 4.55$ $c/a = 0.517$	$a = 8.84$ $c = 4.58$ $c/a = 0.518$

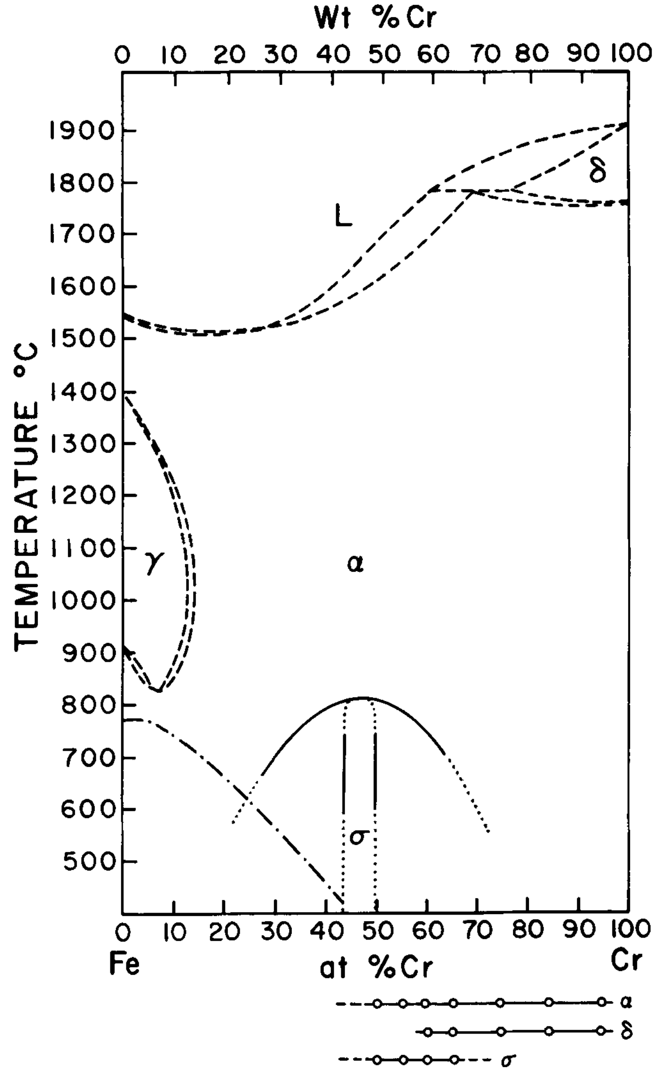

Fig. 8—Tentative phase diagram for Cr-Fe system, constructed on the basis of the determined compositional ranges for phases occurring.

camera with a molybdenum heater. The flow of high-purity H_2 gas was maintained at about 150 cu cm per min during the experiment. The camera temperature was held above 1250°C and the temperature measurement was conducted by optical pyrometry.

A high-temperature X-ray film of a 68 wt pct Cr-Ni alloy as well as a room-temperature X-ray film of the same specimen, which was cooled to room temperature in the H_2 stream before exposure, are shown in Figs. 4(a) and 4(b), respectively. The elevated temperature X-ray photograph exhibits a tetragonal pattern with lattice parameters $a = 8.80$Å, $c = 4.55$Å, and $c/a = 0.52$, indicating that the phase is σ. On the other hand, the room temperature diffraction pattern consists of two phases, δ ($a = 4.55$Å) and a small amount of σ. It is therefore concluded that there exists a high-temperature stable region for the σ phase in the Cr-Ni system. Its retention at room temperature is due to a rapid quenching of the specimen in the H_2 stream.

Fig. 5 illustrates the modified Cr-Ni phase diagram proposed on the basis of the experimental data obtained thus far. Included in the diagram are the phase regions determined for each phase occurring in the system.

2) THE Cr-Fe SYSTEM

Seven Cr-Fe binary alloys containing from 94.7 to 48.2 wt pct Cr were prepared for the study of this system. Fig. 6 is included for comparative viewing of the diffraction patterns of these alloys. In Fig. 7 the σ phase (single phase) obtained from a bulk 48.2 wt pct Cr-Fe alloy is compared with that from the particulate alloy. The diffraction patterns for the σ phase in both specimens are in good agreement. Therefore no difference in the lattice parameters and the composition of the σ phase is discernible between the bulk specimen and the particulate alloy specimen.

The phases and their lattice parameters, identified in these seven Cr-Fe alloys, are tabulated in Table VII. A modified phase diagram for the Cr-Fe system is presented in Fig. 8, in which the phase regions determined for various phases are shown also. The Cr-Fe system has a continuous solid solution (α phase) over the entire composition. The δ phase is formed in the composition range greater than 58.3 wt pct Cr. Its lattice parameters are found to decrease with increase in iron content.

The σ phase observed to occur in alloys containing less than 63.4 wt pct Cr is considered to be the precipitates from the α phase during cooling of the particulate alloys. The lattice parameters obtained for the α phase are in accord with those reported by Preston.[21]

3) THE Cr-Co SYSTEM

In the Cr-Co system seven alloys whose chromium contents ranged from 83.3 to 37.0 wt pct were investigated. X-ray films obtained from these alloys can be viewed in Fig. 9 while the lattice-parameter data are summarized in Table VIII. A tentative Cr-Co binary phase diagram constructed on the basis of the experimental data is shown in Fig. 10.

In the Cr-Co system, similar to the Cr-Ni system, four phases were observed: α, δ, σ, and γ. Elsea and colleagues[22] proposed the existence of δ phase, an ele-

Fig. 9—X-ray Debye-Scherrer patterns of Cr-Co alloy particles.

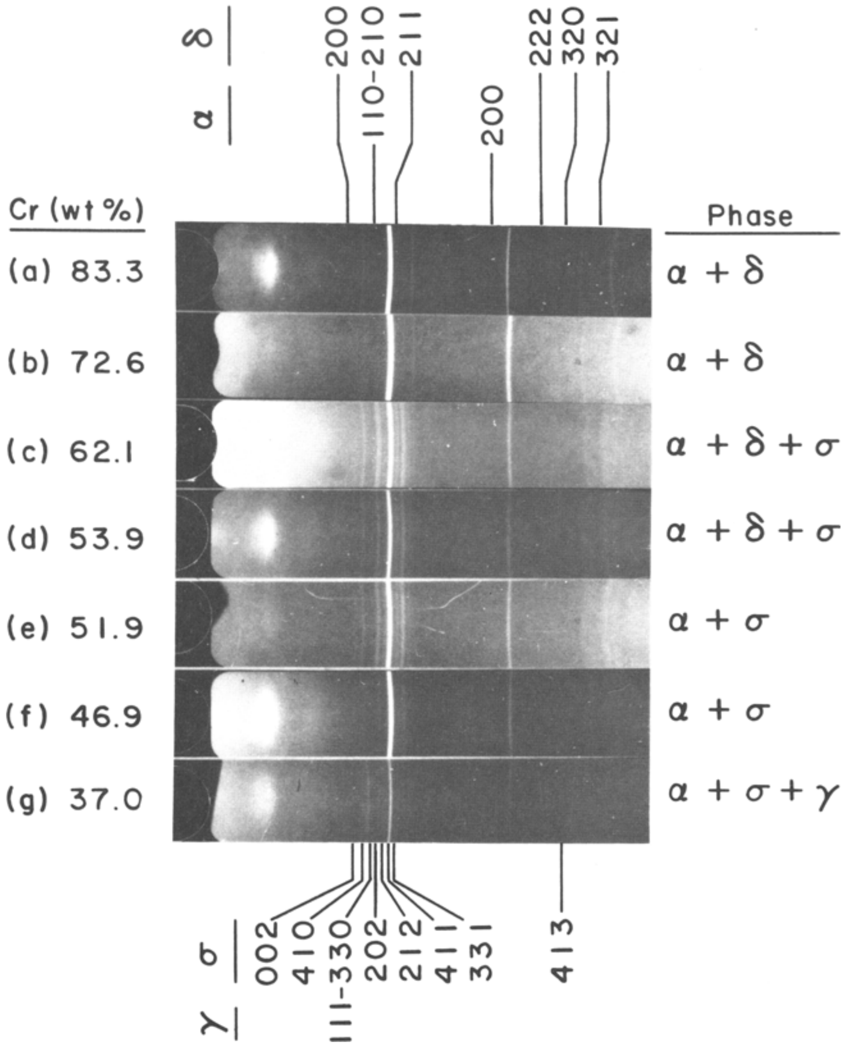

Table VIII. Lattice Parameters of Various Phases in Cr-Co Alloys (a and c in Å)

Phase	Lattice Type	Chromium, Wt Pct 83.3	72.6	62.1	53.9	51.9	46.9	37.0
α	$A2$	$a = 2.87_5$	$a = 2.87_1$	$a = 2.86_8$	$a = 2.86_6$	$a = 2.86_6$	$a = 2.86_1$	$a = 2.85_9$
δ	$A15$	$a = 4.57_6$	$a = 4.56_2$	$a = 4.55_9$	$a = 4.55_8$	–	–	–
σ	$D^8{}_b$	–	–	$a = 8.74$	$a = 8.84$	$a = 8.80$	$a = 8.79$	$a = 8.83$
				$c = 4.55$	$c = 4.56$	$c = 4.57$	$c = 4.56$	$c = 4.57$
				$c/a = 0.520$	$c/a = 0.516$	$c/a = 0.519$	$c/a = 0.519$	$c/a = 0.518$
γ	$A1$	–	–	–	–	–	–	$a = 3.56$

vated-temperature intermediate phase (of unknown structure) which is situated at Co_2Cr_3 (about 57 pct Cr) and stable at temperatures greater than about 1300°C. They did not find the high-temperature modification of chromium proposed by Grant *et al.* This investigation also did not confirm the presence of a phase corresponding to the fcc β phase as described earlier in the Cr-Ni system.

The δ phase of W_3O structure was determined to exist in this system in the composition range greater than 53.9 wt pct Cr. In view of the fact that its lattice parameters change continuously with chromium content, it is deemed feasible that the δ phase in question is the δ-Cr primary solid solution. Judging from the results of the alloy particle experiment in these three binary systems, it appears valid to consider the δ phase as the high-temperature modification of the α-Cr phase. The δ-Cr phase reported by Kimoto and Nishida is now deduced to be the elevated-temperature allotropic form of chromium.

4) THE Cr-Ni-Fe SYSTEM

The same techniques as were used in the binary alloy studies were employed to investigate the Cr-Ni-Fe ternary system. In Fig. 11 the δ- and σ-phase fields are indicated by the shaded areas with a narrow region where overlapping of the two phases occurred. It can be seen that the δ phase is formed in alloys located in the chromium corner while the σ phase is found in

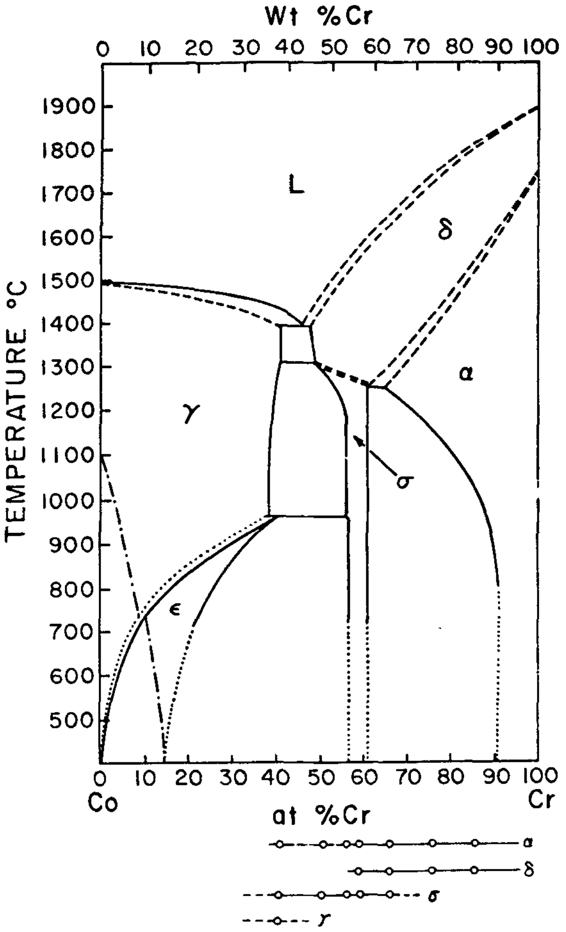

Fig. 10—Tentative phase diagram for Cr-Co system, constructed on the basis of the determined compositional ranges for phases occurring.

alloys which are situated in the phase field bridging the two binary σ phases of the Cr-Ni and Cr-Fe systems.

This implies that the two binary σ phases form a continuous solid solution. Furthermore, the σ phase can precipitate out as primary crystals from the melt in the Cr-Ni binary alloys as well as in the Cr-Ni-Fe alloys containing iron in small quantities, as predicted by the Cr-Ni binary phase diagram proposed earlier.

It is noteworthy to remark here that the σ phase field in the ternary Cr-Ni-Fe system is much wider than is heretofore considered. This finding, pertinent in dealing with iron-base superalloys and stainless steels, necessitates reinvestigation of the Cr-Ni-Fe phase diagram now in use.[23,24]

SUMMARY

Structural analysis was performed on alloy particles of chromium-rich Cr-Ni, Cr-Fe, Cr-Co, and Cr-Ni-Fe systems by X-ray and electron diffraction methods. Structures of bulk specimens of the Cr-Ni system were investigated also using X-ray diffraction techniques to confirm the results obtained from the particulate alloys. In these three binary systems, δ phase with W_3O structure (*A*-15) and σ phase with β-U structure (D_b^8) were identified in addition to the α (bcc) and γ (fcc) terminal solid solutions. The lattice parameter of the δ solid-solution phase was found to nearly coincide with that of pure δ-Cr (4.588Å) which was reported by Kimoto *et al.* in 1967.

As for the Cr-Ni system, both high-temperature X-ray diffraction analysis and ambient-temperature X-ray analysis on samples quenched from elevated temperatures were conducted. The occurrence of the σ phase ($a = 8.80$Å, $c = 4.55$Å, $c/a = 0.52$) at high temperature was confirmed by each method. The formation

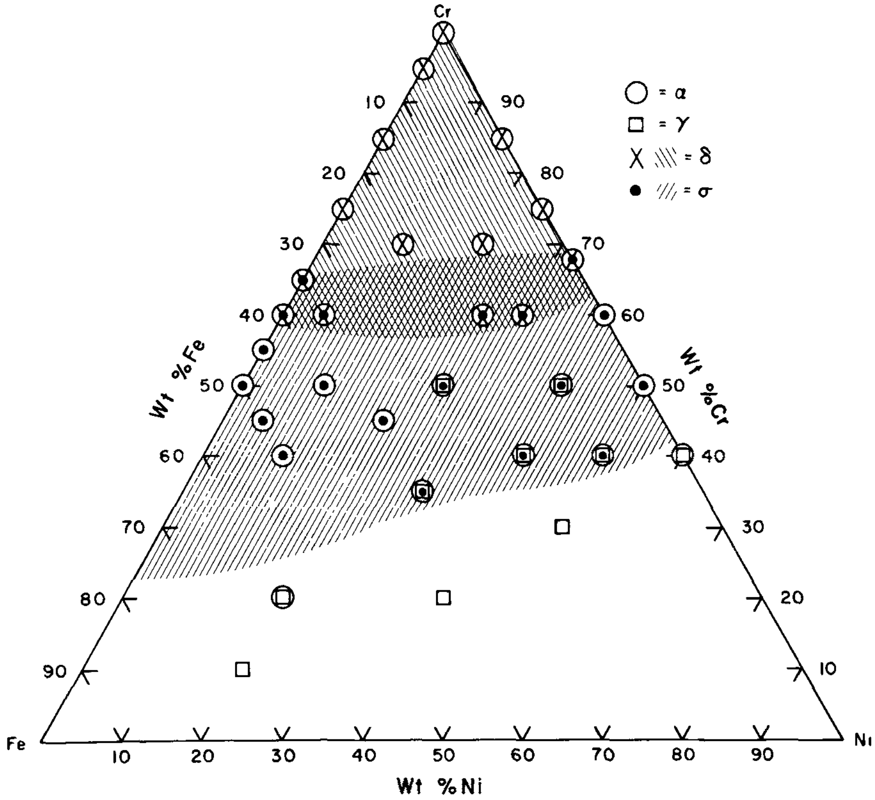

Fig. 11—The δ- and σ-phase field observed in the Cr-Ni-Fe system based on the study of particulate alloys.

of σ phase in the Cr-Ni system, suggested earlier by many investigators, is now verified experimentally. A tentative Cr-Ni phase diagram is proposed by incorporating the high-temperature σ phase and the δ phase which replaces the β-Cr phase reported by Grant *et al.*

A modified binary phase diagram has been constructed for the Cr-Fe alloy system in which the existence of δ phase, the high-temperature allotrope of chromium, is shown in the composition range greater than about 58.3 wt pct.

In the Cr-Co system the δ phase was determined to exist over the composition greater than 53.9 wt pct Cr. This phase as the elevated-temperature modification of chromium replaces the δ phase of unknown structure which was reported earlier by Elsea and coworkers in the proposed Cr-Co binary phase diagram.

As a result of structure analysis of Cr-Ni-Fe alloy particles the phase fields for both δ and σ phases were delineated. The δ phase occurs in the chromium corner while σ phase exists in the region bridging the two binary σ phases of the Cr-Ni and Cr-Fe systems. The results indicate that it is necessary to restudy the Cr-Ni-Fe phase diagram which is currently in use.

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