Constitution of the Ni-Cr-Fe System From 0 to 40 Pct Fe Including Some Effects of Ti, Al, Si, and Nb

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The positions of the $\gamma/\gamma + \alpha'$ solvus for nickel-rich Ni-Cr-Fe alloys containing 0 to 40 pct Fe have been determined from 816° to 1260°C (1500° to 2300°F) to within 2 wt pct Cr. In addition, the individual effects of Ti, Al, Si, and Nb on the position of the $\gamma/\gamma + \alpha'$ solvus have been determined.

THE nickel-rich region of the Ni-Cr-Fe phase diagram is of particular importance because it forms the basis for many heat- and corrosion-resistant alloys. Current commercial alloys rarely contain more than 20 to 25 pct Cr. However, the recent discovery of superplasticity in nickel-base alloys,[1] which must contain about 35 to 45 pct Cr to allow the development of fine-grained, two-phased $\gamma + \alpha'$ structures, generated new interest in a rather poorly defined portion of the phase diagram, the region of the $\gamma/\gamma + \alpha'$ solvus. The location of this solvus needed to be accurately defined in order to manipulate the structures to initiate and control superplasticity, as well as to control other mechanical properties of these alloys.[1,2] Since the superplastic alloys are very sensitive to the amount of chromium-rich α' present, the precise location of the $\gamma/\gamma + \alpha'$ solvus in the Ni-Cr-Fe system as well as the influence of other elements commonly found in commercial alloys warranted detailed investigation.

In the present work the position of the $\gamma/\gamma + \alpha'$ solvus has been determined from 816° to 1260°C (1500° to 2300°F). In addition, the effects of small and separate additions of Ti, Al, Si, and Nb on the $\gamma/\gamma + \alpha'$ solvus position have been determined. For the case of titanium, alloys containing 0, 10, and 20 pct Fe were investigated. The effects of Al, Si, and Nb were examined only in alloys containing 20 pct Fe.

EXPERIMENTAL PROCEDURE

Alloy Preparation

Ten-gram heats were double inert-gas arc-melted into buttons using the following materials:

Melt Stock	Purity
Iodide Chromium	99.99+
Nickel 270	99.97+
Electrolytic Iron	99.95+
Sponge Titanium	99.9+
Aluminum	99.99+
Niobium	99.+
Silicon	99.+

Each charge was weighed to an accuracy of 10^{-4} g. The total metal losses on melting were approximately 1 pct of the initial weight, thus indicating essentially complete recovery. Spot checks showed that the actual compositions were the same as the nominal compositions. Because of the high-purity starting materials, the residual elements in each heat were quite low. Several buttons analyzed for carbon were found to contain less than 0.01 pct. A summary of the alloy compositional ranges is presented in Table I. Individual alloys were examined at increments of 2 pct Cr.

For homogenization, the buttons were solution treated for 1 h at 1260°C (2300°F) and water quenched. They were then cold-worked by flattening with a hammer forge. The following heat treatments were then applied to determine the corresponding isotherm.

Temperature	Time, Hours
1260°C (2300°F)	1
1204°C (2200°F)	100
1093°C (2000°F)	170
982°C (1800°F)	400
899°C (1650°F)	1000
816°C (1500°F)	1000

All specimens were water quenched after heat treatment.

Metallography

The $\gamma/\gamma + \alpha'$ solvus was located by metallographic examination for the presence of the α' phase. An aqueous 10 pct HCl solution, used electrolytically, clearly revealed the slightest traces of the chromium-

Table I. Compositional Ranges of Alloys Studied, Wt Pct

Ni	Cr	Fe	Ti	Al	Si	Nb
Bal.	30 to 46	0	–	–	–	–
Bal.	31 to 45	10	–	–	–	–
Bal.	26 to 42	20	–	–	–	–
Bal.	29 to 39	30	–	–	–	–
Bal.	21 to 35	40	–	–	–	–
Bal.	33 to 43	0	0.5	–	–	–
Bal.	30 to 44	0	1.5	–	–	–
Bal.	30 to 40	10	0.5	–	–	–
Bal.	26 to 40	10	1.5	–	–	–
Bal.	28 to 40	20	0.5	–	–	–
Bal.	20 to 36	20	1.5	–	–	–
Bal.	24 to 40	20	–	2.0	–	–
Bal.	26 to 40	20	–	–	1.0	–
Bal.	28 to 40	20	–	–	–	1.0

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rich α' phase. Representative photomicrographs are shown in Fig. 1 to illustrate the sensitivity of these observations. Since the compositions varied in increments of 2 pct Cr, the technique was sensitive enough to define the locations of the various solvus curves to within 2 wt pct Cr. The 10 pct HCl solution also outlined chromium-rich σ phase, but did not allow one to distinguish between it and α'. According to Hattersley and Hume-Rothery[3] it is possible to accomplish this by stain etching with a 10 Normal KOH solution. However, it was found that even with this solution an unambiguous distinction between α' and σ was not possible. This left some doubt, as will be described, as to the locations of the regions where σ and α' coexist in the middle portion of the phase diagram.

Microprobe Analysis

In addition to a metallographic analysis, an electron microprobe analysis was conducted to establish the $\alpha'/\gamma + \alpha'$ solvus and the tie-lines between the α'/α'

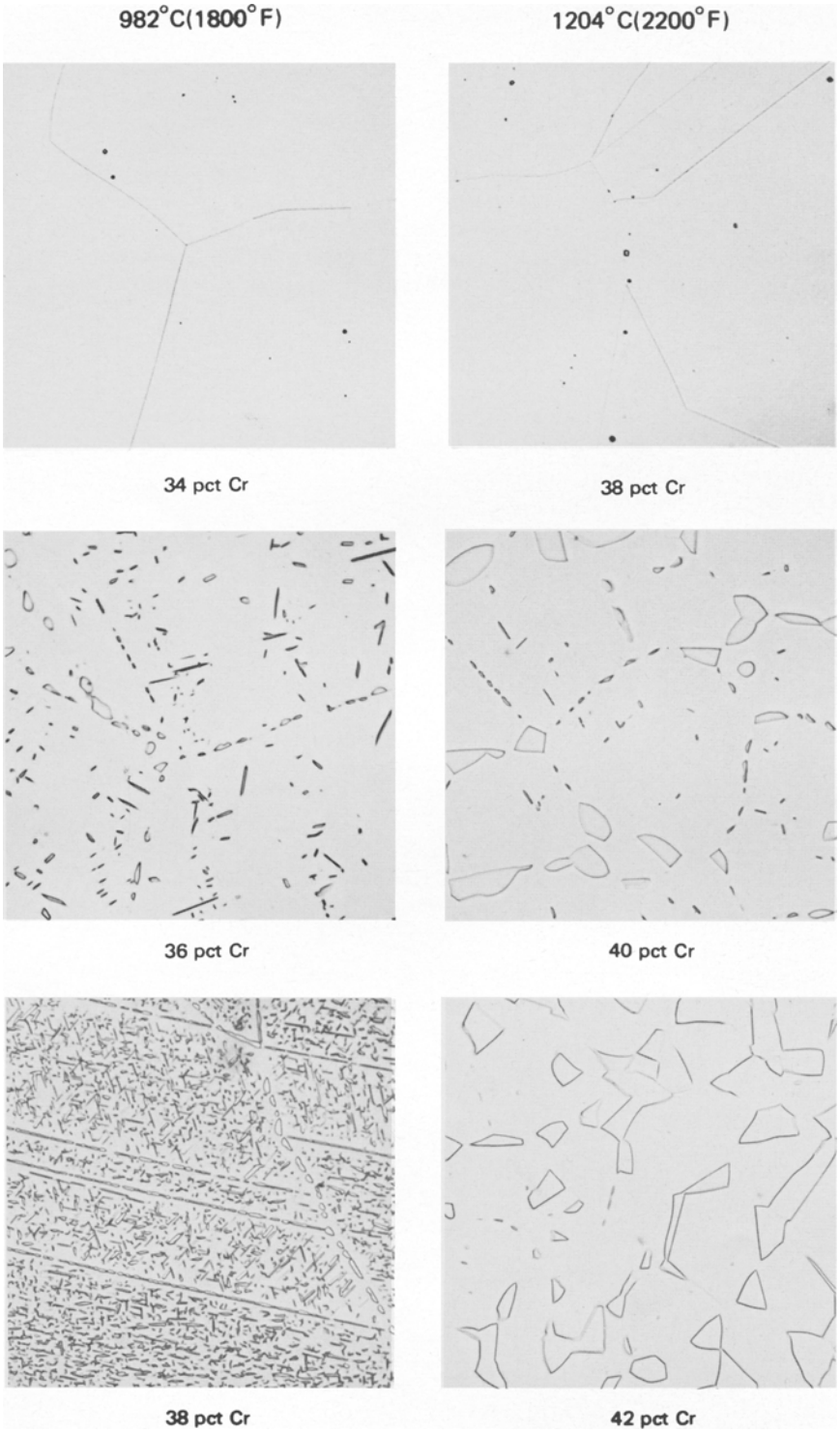

Fig. 1—Photomicrographs illustrating the appearance of α' in ternary Ni-Cr-Fe alloys at 982° and 1204°C (1800° and 2200°F).

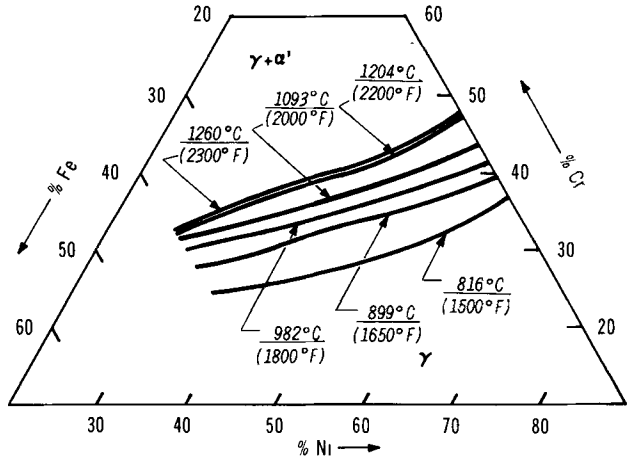

Fig. 2—Isothermal sections of the Ni-Cr-Fe phase diagram showing the location of the $\gamma/\gamma + \alpha'$ solvus from 816° to 1260°C (1500° to 2300°F) determined metallographically.

Table II. The $\gamma/\gamma + \alpha'$ Solvus Coordinates for Ni-Cr-Fe Alloys, Wt Pct

	Solvus Temperature, °C					
	816	899	982	1093	1204	1260
Fe	Cr	Cr	Cr	Cr	Cr	Cr
0	37.0	39.2	41.1	43.8	47.0	47.7
10	31.8	35.8	38.0	39.9	42.2	42.8
20	28.5	33.0	35.0	36.5	39.0	39.5
30	26.0	30.0	32.0	33.8	35.7	36.2
40	24.0	27.5	30.0	31.3	32.0	32.4

+ γ solvus and the $\gamma/\gamma + \alpha'$ solvus. The fineness of the α' phase precipitated below 1204°C (2200°F) precluded extensive use of this technique, however, because the α' could not be analyzed without matrix interference. The analysis was therefore restricted to the 1204° and 1260°C (2200° and 2300°F) isotherms.

RESULTS AND DISCUSSION

Ternary Ni-Cr-Fe Alloys

The positions of the $\gamma/\gamma + \alpha'$ solvus from 816° to 1260°C (1500° to 2300°F) for alloys containing 0 to 40 pct Fe are shown in Fig. 2 and the corresponding coordinates are tabulated in Table II. These boundaries were constructed from the metallographic observations. At the 0 pct Fe level the data correlate well with the data given in Hansen[4] for the solubility of α' in γ. At the highest iron level of 40 pct, very reasonable agreement was obtained with the data of Hattersley and Hume-Rothery.[3] The exact location of the ternary $\gamma + \alpha' + \sigma$ phase field in the center portion of the diagram is uncertain. Although Hattersley and Hume-Rothery were able to utilize a 10 Normal KOH electrolytic staining etch in addition to X-ray analysis to distinguish α' from σ, their limited number of alloys did not enable them to determine accurately the position of this region. In the present work, the use of the 10 Normal KOH solution was found not to be sufficiently definitive to deduce the exact location of the $\gamma + \alpha' + \sigma$ phase field because of the inability to distinguish clearly between the σ and α' in a given metallographic sample. It should be emphasized, however, that there

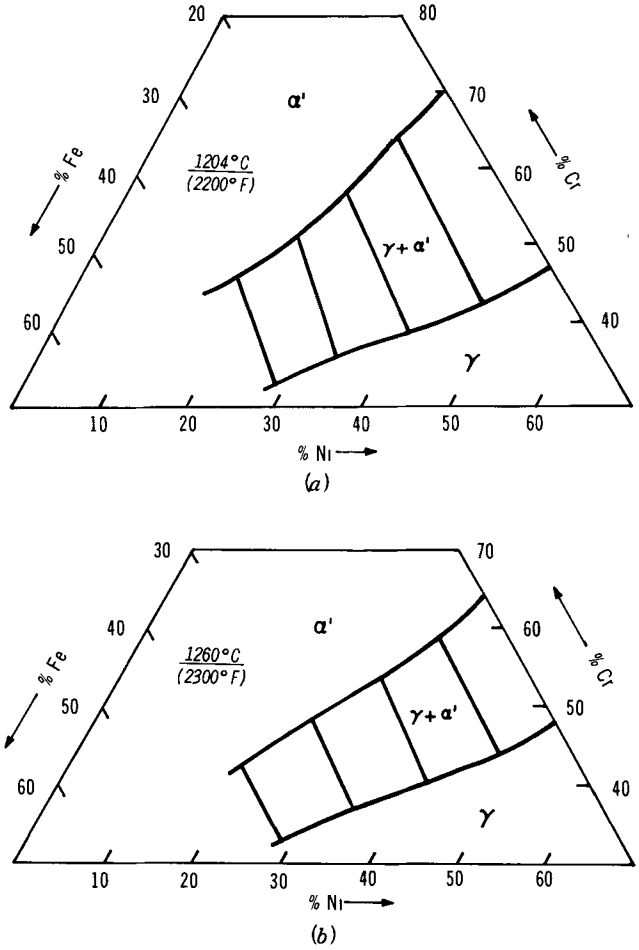

Fig. 3—Isothermal sections of the Ni-Cr-Fe phase diagram at 1204°C (2200°F) and 1260°C (2300°F) showing tie lines determined by microprobe analysis.

was no difficulty in determining the position of the phase boundary in the center portion of the diagram by the appearance of a second phase, be it α' or σ. Because of the difficulty in distinguishing between α' and σ when they appeared simultaneously, it was not possible to locate the corner of the $\gamma + \alpha' + \sigma$ triangle touching the $\gamma/\gamma + \alpha'$ solvus. It is obvious that a very careful and intensive study will have to be made of this portion of the phase diagram to define clearly the location of the three-phase triangle between the two two-phase fields.

Fig. 3 shows the results of the microprobe study to determine the location of the $\alpha'/\alpha' + \gamma$ solvus and the tie-lines between that solvus and the $\gamma/\gamma + \alpha'$ solvus at 1204° and 1260°C (2200° and 2300°F). The tie-line intercepts are tabulated in Table III. Attempts to locate the $\alpha'/\alpha' + \gamma$ solvus at lower temperatures were unsuccessful owing to the fineness of the α' phase. The data obtained at 1204° and 1260°C (2200° and 2300°F), however, appear to be reasonable and although the iron levels determined by this means were consistently slightly lower, particularly at 1260°C (2300°F), than the nominal values, good correlation with the $\gamma/\gamma + \alpha'$ solvus position determined metallographically was obtained. It is felt, therefore, that the present determination of the $\alpha'/\alpha' + \gamma$ solvus is reasonably accurate. The results at 0 pct Fe agree well with the determinations of Bechtoldt and Vacher[5]

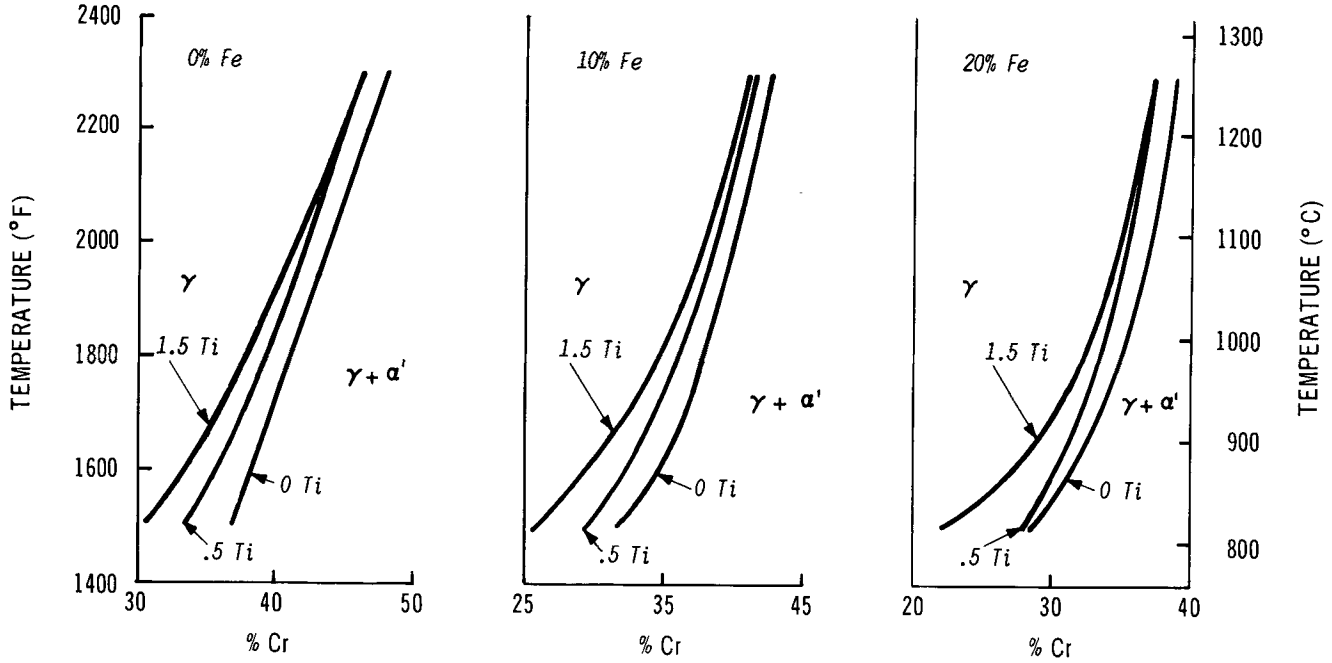

Fig. 4—Effect of titanium on the $\gamma/\gamma + \alpha'$ solvus for alloys containing 0, 10, and 20 pct Fe.

Table III. Solvus Tie-Line Intercepts for Ni-Cr-Fe Alloys, Wt Pct

Temperature, °C	$\alpha'/\alpha' + \gamma$		$\gamma/\gamma + \alpha'$	
	Fe	Cr	Fe	Cr
1204	0.0	70.0	0.0	47.0
1204	8.5	64.0	10.0	42.5
1204	22.8	57.0	20.0	39.0
1204	26.2	51.6	29.8	36.0
1204	35.6	46.5	38.2	33.0
1260	0.0	64.0	0.0	48.0
1260	7.6	58.8	8.1	44.0
1260	16.6	53.8	18.0	40.0
1260	27.0	48.5	28 0	35.0
1260	38.0	42.4	38.0	33.0

and Svechnikov and Pan.[6] It is most important to emphasize that the results of these authors and the present investigation show that the solubility of γ in α' at 1204° and 1260°C (2200° and 2300°F) is significantly higher (some 12 wt pct) than presently quoted in Hansen.[4]

Effect of Titanium on the $\gamma/\gamma + \alpha'$ Solvus

The effect of 0.5 and 1.5 pct Ti on the $\gamma/\gamma + \alpha'$ solvus at 0, 10, and 20 pct Fe is illustrated with isopleths in Fig. 4. At 0.5 pct, Ti had a general uniform effect of stabilizing the α' or conversely decreasing the solubility of α' in γ over the entire range of temperatures studied, 816° to 1260°C (1500° to 2300°F). Increasing titanium to 1.5 pct tended to further move the $\gamma/\gamma + \alpha'$ solvus to lower chromium contents, particularly below about 1095°C (2000°F). At higher temperatures this level of titanium had little further effect on the solvus than did the 0.5 pct addition. In addition to affecting the position of $\gamma/\gamma + \alpha'$ solvus, 1.5 pct Ti also resulted in the formation of a needle- or plate-like phase, tentatively identified as η-Ni_3Ti, at 816° and 899°C (1500° and 1650°F).

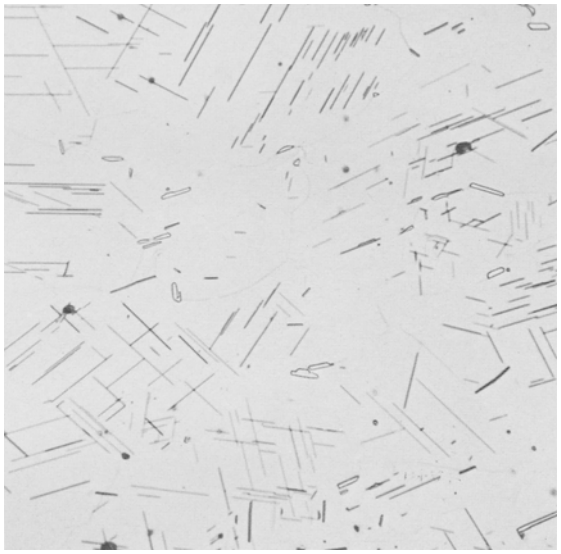

Fig. 5—Micrograph illustrating an acicular phase, probably η-Ni_3Ti, in a Ni-24 pct Cr-20 pct Fe-1.5 pct Ti alloy at 899°C (1650°F).

An example of the precipitation of this phase is given in Fig. 5.

Effect of Al, Si, and Nb on the $\gamma/\gamma + \alpha'$ Solvus

The individual effects of 2 pct Al, 1 pct Si, and 1 pct Nb on the $\gamma/\gamma + \alpha'$ solvus are shown in Fig. 6 for alloys containing 20 pct Fe. All three additions stabilized the α' phase in a manner similar to titanium. It is interesting to note in Fig. 6 that the addition of 2 pct Al was twice as effective as the 1 pct Si or Nb additions. In other words, the effects seemed to be somewhat proportional to the weight percentages of the elements added. No new phases were observed in any of the metallographic samples as a result of the Al, Si, and Nb additions.

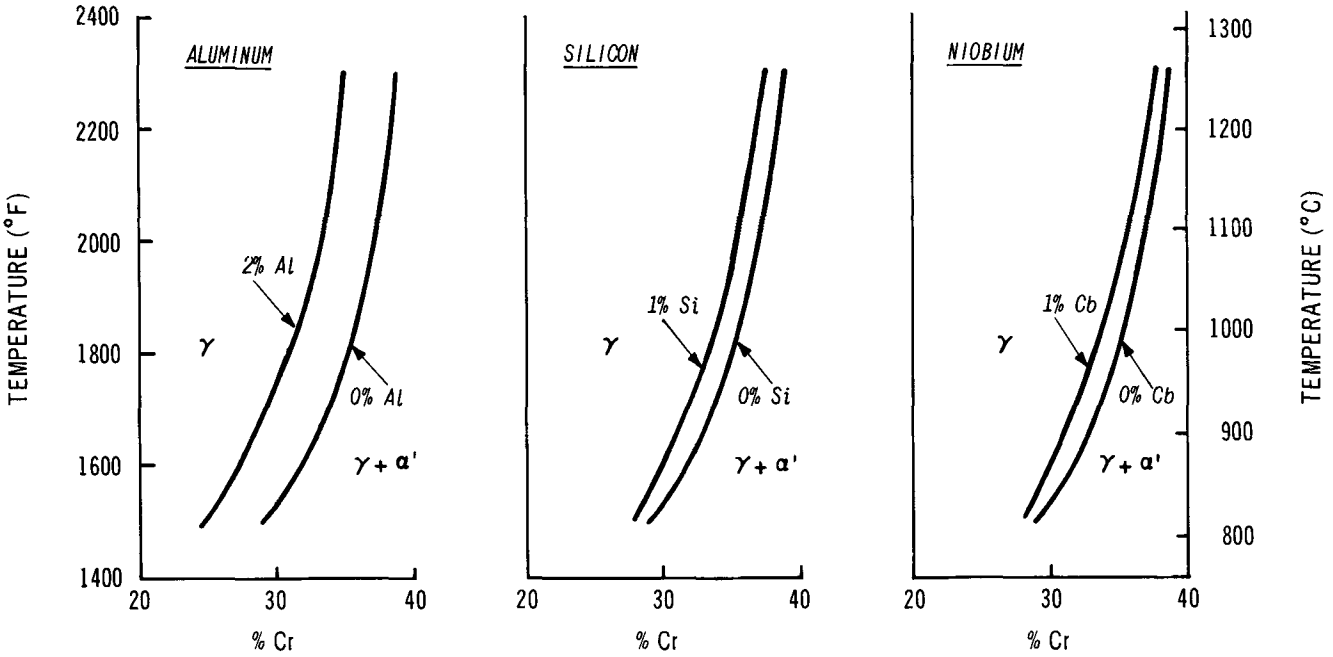

Fig. 6—Effect of Al, Si, and Nb on the $\gamma/\gamma + \alpha'$ solvus for alloys containing 20 pct Fe.

SUMMARY AND CONCLUSIONS

The positions of the $\gamma/\gamma + \alpha'$ solvus for nickel-rich Ni-Cr-Fe alloys containing 0 to 40 pct Fe have been determined from 816° to 1260°C (1500° to 2300°F) to within 2 wt pct Cr. In addition, the individual effects of Ti, Al, Si, and Nb on the position $\gamma/\gamma + \alpha'$ solvus have been determined. The results show that:

1) Ti, Al, Si, and Nb all stabilize the α' phase. The effect of 1.5 pct Ti increases with decreasing temperature while the effect of 0.5 pct Ti does not change with temperature. In all other cases, stabilization of α' was uniform over the entire temperature range studied.

2) In alloys containing 1.5 pct Ti an additional phase, suggested to be η-Ni_3Ti, was detected at 816° and 899°C (1500° to 1650°F).

3) The electron microprobe analysis used to determine the $\alpha'/\alpha' + \gamma$ solvus at 1204° and 1260°C (2200° and 2300°F) indicated that the solubility of γ in α' for iron-free alloys at those temperatures was significantly greater than presently quoted in Hansen.[4]

4) The presence of σ phase could not be determined unambiguously using a selective stain etchant.

ACKNOWLEDGMENT

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