

COBALT AND SIGMA:
PARTICIPANT, SPECTATOR, OR REFEREE?

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Abstract

Starting with the premise that current computer-type methods of predicting the onset of sigma formation in superalloys actually averages the effects of many elements into a linear relationship, a program was undertaken to determine the individual contribution of certain elements. In this paper the non-linear effect of cobalt is explained by its changing role from referee to participant.

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BACKGROUND

There can be little doubt that the requirements of the gas turbine engine continues to pace the development of materials for use up to about 2500°F. Nickel-base alloys, already in service at temperatures in excess of 85 per cent of their incipient melting point, are now being asked to operate for longer design lives than ever before. Over the last 25 years, much has been learned about generating the strength required in the nickel-base system, somewhat less is understood about failure characteristics, and surprisingly little has been determined about corrosion.

One of the early observations in efforts to develop strength in the nickel-base system was that the highest strength properties were the result of instabilities, i. e. the uniformly dispersed precipitation of one or more intermetallic compounds, primarily Ni_3Al and Ni_3Ti . The nature of the Ni_3Al -type compound was such that it afforded instantaneous reversibility to the precipitation process thereby resisting "overaging" and providing fresh precipitates with change in operating temperatures. Thus it can be said that the major strengthening mechanism is an "instantaneously reversible instability." Subsequent trends in alloy development were to add greater amounts of those elements contributing to the precipitation so as to "stabilize the instability" and extend the useful operating temperature. Later efforts centered around additions of elements designed to reside primarily in the matrix, thereby reducing the rate of solid state diffusion primarily between the precipitate and the resulting solid solution. While these efforts led to alloys of increasingly greater stress-rupture strength, they also led to alloys more susceptible to corrosion because chromium, the element contributing most to corrosion resistance, contributes least to the strengthening mechanisms. Generally the chromium was replaced by the heavier refractory elements of larger atomic radii.

The paradox then developed that the alloys were capable strengthwise of operating at higher temperature levels, but the alloying procedures necessary to achieve this level of strength also sensitized them to hot corrosion.

Currently the major alloy development efforts center around compromising strength and corrosion resistance with an anxious eye on "stability." One tool that has developed as the lens through which the "eye on stability" may be focused has been the concept that a great number of the undesirable intermetallic compounds forming in the superalloys are electron compounds, i. e. their structure and existence are based on an electron-atom ratio, and that the likelihood of their formation can be computed if the

composition of the solid solution generating the compound can be determined. Much has already been said and much will continue to be said about the excellent work of Rideout, Beck, Hall, and many others in describing the existence of sigma, Mu, and other intermetallic compounds in ternary systems involving transition elements, and in applying the electron vacancy theories of Pauling to predicting the formation of such compounds from complex solid solutions. Because these were primarily basic phase diagram studies, most of the early work by Rideout and Beck⁽¹⁾ was done at temperatures at or near 1200°C so as to more clearly approach equilibrium conditions.

When an electron compound, notably sigma, became apparent in alloys regularly used in the production of aircraft gas turbine engines, the scope of the investigation took on an applied, rather than a basic outlook and the emphasis changed from establishing a method by which the existence of an electron compound could be determined, to one that would define the onset of such a phase. This was done with the belief that the occurrence of such a phase, particularly in the geometric form of a rod or plate, would suggest unreliability for extended service. This has certainly proved to be true, at least in the marketing and promotional aspects of superalloys.

As is well known, Boesch and Slaney⁽²⁾ very successfully adapted the electron vacancy theories to a production alloy, and many thousands of pounds of Udimet 700 have been made with a resultant matrix, after various precipitation reactions, that is of such composition so as to fall short of the onset of sigma formation. The incorporation of this technique during the melting cycle certainly proves the worth of such an approach as a production tool. Woodyatt et al⁽³⁾ expanded the scope of the electron vacancy approach and attempted to systematize large numbers of superalloys by matching microstructures with matrix electron vacancy numbers. From this came a metallurgically more sophisticated procedure for arriving at the composition of the residual matrix by considering the form and substance of many of the constituents found in the microstructure. Unfortunately, many people interpreted this work as an effort to discover the "universal vacancy number" that would predict electron compounds in all alloy systems prone to their formation. Amid the scurry to apply the new found production tool of PHACOMP to alloys such as Udimet 700 and Rene 100, there arose almost a cult which idolized a vacancy number at or near 2.5. Much emphasis was placed on making the alloys fit the numbers, rather than the numbers fit the alloys. Changes were made in the assignment of vacancy numbers of the individual elements so as to force the matrix, in many cases

regardless of the assumed metallurgical reactions, to conform to a universal number. The antithesis of this position would be that the electron compound, or sigma if you will, which forms would reflect the chemical composition of the ingredients, and that the PHACOMP number predicting the onset of such formation would also be dictated by variations in the elements comprising the compound. It would appear only logical that sigma forming from the Ni-Cr-Mo system would differ from those forming in the Ni-Cr-Co, Co-Cr-Mo, Cr-Co-Ni-Mo, and many others.

ALLOY DEVELOPMENT

Nowhere was, or is, the impact of the "universal vacancy number" concept more in evidence than in alloy development. The early works on PHACOMP were derived utilizing primarily the phase diagrams from Rideout and Beck⁽¹⁾ which represent isotherms at 1200°C, a temperature at which many of the contemporary nickel-base superalloys are on the threshold of incipient melting, and about 400°F above the upper temperature limit associated with sigma in superalloys. The example is often used of combining several ternary phase diagrams into a pyramid so as to approximate a three dimensional space figure of a five compound system. If one selects a "universal vacancy number" of any given value and computes the PHACOMP number across the system, the result is basically a plane (with some degree of mismatch) or stratum across the pyramid. Since such a stratum causes the pyramid to become a frustrum, one can only cannibalize the two words into "frustratum." And this term is apt when one carouses through the results of computerized calculations of commercially available and developmental alloys and finds that many of the results do not agree with the predictions. This suggests that if the PHACOMP system is to be of value, detailed chemical analysis must be made of each of the microconstituents present at the onset of sigma formation so that the composition of the matrix can be determined by subtraction. All of this would be unnecessary if the composition of the matrix could be determined by some direct means. Only under these conditions can the concept of "universal vacancy number" (or range of numbers) be accomplished.

If PHACOMP is attempted in any other manner, e. g. assuming various semi-quantitative metallurgical reactions across the board blanketing several alloy systems, it can only result in the determination of a separate vacancy number cutoff for each individual alloy system. Alloys forming only $M_{23}C_6$ would differ from those forming M_6C or mixtures of carbides, and those containing additions of elements participating heavily in gamma prime compounds would differ from those remaining closer to the classical

Ni_3Al or $\text{Ni}_3(\text{Al-Ti})$ compound. Cobalt-base alloy systems would differ from nickel-base. Within each individual alloy system there would be chemical variations that would trigger sigma formation, and the matrix at that particular time should have a PHACOMP number regardless of the method used to calculate it; the accuracy of the actual number would increase with the preciseness of the knowledge of the chemical composition of phases existing at that time. Obviously, the rate of change of the matrix composition will affect the susceptibility of the system to sigma formation.

EFFECTS OF COBALT

With an eye toward alloy development, a program was started to evaluate the effects of various elements on the precipitation of sigma using a Martin Metals alloy, MAR-M alloy 421, as the individual alloy system base. The nominal composition is given in Table 1. We chose to evaluate the effects of cobalt first. This choice was based on several reasons including:

1. INCO 713 with no cobalt formed sigma at very low PHACOMP values; whereas, experimental alloys with very high cobalt contents do not form sigma.
2. Cobalt participates in many of the compounds existing in superalloys, both electron compounds and gamma prime-types.
3. Cobalt has recognized effects on the solubility and particle sizes of carbides and gamma prime precipitates.
4. Cobalt-base alloys form sigma at higher PHACOMP numbers than do nickel-base alloys.

To illustrate the effects of cobalt, the computerized PHACOMP system utilizing the reactions set forth in N_{V5} was used as recommended by the planning committee for the International Symposium of Phase Stability.

DETERMINATION OF N_{V5} CUTOFF FOR MAR-M ALLOY 421

Keeping the cobalt contents constant at 10 per cent, the N_{V5} cutoff for MAR-M alloy 421 was established by additions of various active sigma inducing elements such as the BCC chromium, tungsten, molybdenum, etc., and various inactive or indirect elements such as aluminum and titanium.

Unstressed specimens were exposed at 1500°F and 1650°F for times out to 3000 hours with samples taken periodically to establish the onset of sigma formation as determined by optical microscopy with X-ray verification. Linear regression analysis showed that sigma should never form with an N_{v5} of 2.445 or less, and the equation to predict the onset of sigma for any given time would be:

$$N_{v5} = \frac{K_1}{t} + K_2 \quad (1)$$

$$\begin{aligned} \text{where } K_1 &= 37.96 \\ K_2 &= 2.445 \end{aligned}$$

Representative N_{v5} numbers would be 2.48 at 1000 hours, and 2.46 at both 2000 and 3000 hours. These data are shown in Figure 1.

A series of heats were made at constant cobalt levels of 0, 20, and 30 per cent to determine the effect of cobalt when added to the base composition. Observations obtained in a manner similar to that of the 10 per cent series indicates that no sigma was formed even when the cobalt was raised to 30 per cent, the N_{v5} PHACOMP number being 2.63, well above the cutoff of 2.445. This says that the basic substitution of cobalt for nickel raised the PHACOMP number but lowered the susceptibility to sigma phase, a fact inconsistent with the PHACOMP equation. Also contrary to the equation was that at 0 per cent cobalt, the alloy formed considerable amounts of sigma at a PHACOMP number of 2.2, well below the calculated "universal vacancy number" of 2.50, plus or minus a reasonable amount. These data are shown in Table 2.

At the 20 per cent cobalt level, additions similar to those carried out at the 10 per cent level, followed by exposure, observation, and linear regression analysis developed that in the basic equation (1)

$$\begin{aligned} K_1 &= 40.33 \\ K_2 &= 2.513 \end{aligned}$$

$$\text{thus: } N_{v5} = \frac{40.33}{t} + 2.513 \quad (2)$$

Comparison of the curves for the 10 and 20 per cent levels, Figure 1, shows that increasing cobalt raises the cutoff PHACOMP number for the onset of sigma formation.

Linear regression analysis of all of the available data led to the master equation representing the effect of cobalt on the onset or threshold of sigma formation. Because the mathematical analysis assumes a random distribution of all other elements, the equation should be valid for all systems forming sigma of the same general type as the alloys studied. The approximate composition of these compounds are given in the next section. The master equation is as follows:

$$\log N_{v5} = (.0389 + \frac{.8012}{t}) \log Co + .3553 \quad (3)$$

Figure 2. plots three curves, two based on equation (3) and one representing the normal linear relationship of Cobalt and N_{v5} . If zero cobalt is assumed, equation (3) yields an $N_{v5} = 2.09$. The lower curve represents the normal linear relationship of N_{v5} if cobalt is substituted for nickel. The upper two curves represent equation (3) calculated at times of 100 hours and 1500 hours, with cobalt contents to about 30 per cent.

Several interesting observations are apparent from these graphs. One important item is that small additions of cobalt have a dramatic effect in raising the sigma threshold of nickel-base superalloys, while larger amounts are relatively impotent. Using the 1500 hour curve as a guideline, additions of up to about 5 per cent cobalt have a positive slope relative to the linear N_{v5} line; whereas, additions over about 5 per cent are negative. Near 5 per cent cobalt the instantaneous slope of the 1500 hour line is equal to that of the standard N_{v5} line but about .23 vacancy numbers above it. At about 23 per cent cobalt the standard N_{v5} line and the 1500 hour line from equation (3) intersect; the 100 hour intercept is extended to about 28 per cent.

Thus it appears that from the standpoint of stability, one advantage that can be gained is represented by the area between the curves in Figure 2. Additions of cobalt delay the onset of sigma formation well beyond that predicted from PHACOMP calculations based on a generalized series of metallurgical assumptions.

As a test of the validity of the equation derived here, a series of heats were made at 0, 1, 2, 4, and 6 per cent cobalt levels with the remaining chemistry balanced so as to be above the electron vacancy number predicted by the N_{v5} calculation (assuming 2.09 as the threshold point for zero cobalt) but below the 2.4-2.5 value most often suggested as the universal vacancy number. Only the 0 per cent cobalt alloy formed sigma, the sigma

forming within 250 hours (1500°F) at a N_{V5} vacancy number of 2.23. The remaining alloys, having cobalt contents of 1 to 6 per cent, and N_{V5} vacancy numbers of 2.24 to 2.32 did not show sigma at 1500 hours. Of additional interest was the fact that the 0 per cent cobalt alloy also formed profuse amounts of body-centered-cubic phase very similar to that found by Radavich⁽⁴⁾ and others in some heats of INCO 713C and Inconel 718. With increasing exposure time at 1500°F, the amount of sigma decreased relative to that of the body-centered-cubic phase. None of the cobalt containing samples formed this phase, at least as was detectable by X-ray diffraction of extracted residues. Specimens were exposed at 1400°F in hopes that the body-centered-cubic phase would act as a lower temperature pre-precipitate but none was found to times of 1500 hours.

These studies have shown that the effect of cobalt on the onset of sigma formation deviates from the linear function described by the PHACOMP equation. Obviously other elements present in relatively small amounts (less than 15 per cent) can be similarly related, that is, non-linear, some probably being positive and others negative to the linear slope. Thus PHACOMP may, by averaging the individual contributions, predict a number representing the threshold of sigma formation, but the number will vary with the amount and type of alloying elements included.

Microstructural studies have shown that an empirically derived formula for the effect of cobalt on sigma formation can be used to aid in the prediction of the onset of sigma formation. The formula provides some explanation for some of the outstanding exceptions to current methods of phase prediction where sigma can form at very low vacancy numbers. Use of the formula on a cobalt-base alloy such as MAR-M alloy 509 predicts a sigma cutoff point of 2.63 which is in agreement with other work.

STRUCTURAL ANALYSIS

For about the last five years, the literature has been virtually overcome with references to sigma and other undesirable intermetallics in superalloys. More effort has been expended on the detection and appearance of these compounds than on the determination of their physical make-up and their effects on mechanical properties. Figures 3. and 4. are representative of the type of sigma found in this study. The replica micrographs (6000X) show the microstructures following a 3000 hour exposure at 1550°F of a 10 per cent cobalt alloy having an N_{V5} of 2.6. Both figures clearly show the platelike geometry of the sigma and the slightly rounded nature of the gamma prime particles. Figure 3.

shows the breakdown of the MC carbide with the subsequent re-precipitation of a lower carbide, in this case $M_{23}C_6$. Figure 4. shows a typical grain boundary area with a discontinuous precipitate of $M_{23}C_6$ and the start of a gamma prime envelope of both grain boundary and sigma particles. It is interesting to note that several of the sigma platelets are attached to carbide particles, thereby complicating chemical analysis of extracted residues.

Figure 5. depicts a typical microstructure of sigma prone 10 and 20 per cent cobalt alloys following 2750 hour exposure at 1550°F. Figure 6. represents the microstructure of a 0 per cent cobalt alloy showing sigma along with particles of the body-centered-cubic phase, sometimes referred to as "J-phase" that often precedes sigma formation, particularly in alloys free of cobalt and/or containing iron. In this study, "J-phase" was found only in the cobalt-free samples, i. e. less than .2 per cent; none of which contained over .10 iron. Attempts were made to induce the BCC "J-phase" in the 1, 2, 4, and 6 per cent cobalt alloys by 1500 hours exposures at 1400°F and 1500°F. None was found. The smaller particles in Figure 5. are believe to be "J-phase" and the larger ones are sigma.

Electron microprobe analyses and X-ray fluorescence on extracted residues were performed on a series of samples to give an indication of the degree of participation by cobalt in sigma formation. The results are summarized in Table 3. All of the results must be taken in a semi-quantitative spirit as contamination is unavoidable in either method of analysis; the particle size being so small that matrix excitation is present in the microprobe analysis, and complete separation of particles is a practical impossibility in residue analysis.

Assuming a clear separation of particles, sigma platelets in the 0 per cent cobalt alloy as obtained by microprobe analysis would be about 60 Ni - 20 Cr - 5 Al - 5 W - 4 Mo - 1.5 Ti - 1 Cb. Assuming severe matrix but no carbide contamination, one can rationalize the subtraction of the matrix from the sigma particle analyses and arrive at a fabricated sigma composition of about 45 Ni - 40 Cr - 15 Mo, well within the $\alpha + \sigma$ boundaries described by Rideout and Beck at 1200°C.

X-ray fluorescence of powders extracted from the 0 per cent cobalt alloy gave strong patterns for the BCC "J-phase" and the tetragonal sigma, plus weak patterns for the carbides. Assuming the Ti and Cb in the residue is primarily the contribution of the carbides, we again have a Ni-Cr-Mo composition, but with about 30 Ni - 65 Cr - 5 Mo. The BCC "J-phase" is similar to the BCC

phase designated epsilon by Rideout and Beck⁽¹⁾ and Alpha Chromium by Raudebaugh⁽⁵⁾ et al; the residue analyses falls very close to the $\alpha + \epsilon + \sigma$ shown by Rideout and Beck at 1200°C. Continued exposure at 1550°F for 3000 hours developed stronger intensity for the J-phase (or epsilon) and a weaker intensity for sigma, thereby permitting a more complete separation. Residue analyses at very strong BCC intensities gave a compound of about 20 Ni - 75 Cr - 5 Mo, definitely within the epsilon area of Rideout and Beck⁽¹⁾.

Of the 10 per cent cobalt specimens, sample 4N-4 gave the greatest amount of clear sigma residue. Despite the fact that sigma was induced by increasing amounts of the BCC columbium, very little columbium was found in the sigma, but the platelets were about 35 per cent cobalt. The nickel content remained nearly constant with that at the zero cobalt sample, thereby indicating that the cobalt replaced the chromium. The molybdenum also remained constant.

At the 20 per cent cobalt level, the specimen yielding the cleanest sigma extraction was that with the sigma induced by progressive additions of chromium to the base composition. The pattern was the same as the 10 per cent level, i. e. cobalt comprised about 35 per cent of the compound at the expense of chromium; molybdenum was again unchanged.

There can be little doubt that cobalt, when present in the alloy in amounts above about 5-6 per cent, takes an active participants role in the formation of sigma. Below about 5-6 per cent, cobalt plays the more passive role as referee, helping to determine if the BCC "J" (or epsilon) phase will form, or if the tetragonal lattice of sigma is the more stable. In the case of a cobalt-free commercial alloy, INCO 713C, iron has been known to play a similar though opposite function. It has been well established that iron actively participates in the formation of gamma-prime, and Radavich,⁽⁴⁾ Barker and Ross⁽⁶⁾ have shown that increasing iron content lowers the solution temperature of the gamma-prime. This process, with the accompanying release of Chromium to the immediate solid solution, has been suggested as a source of BCC "J" phase and sigma in alloys containing iron. Iron, when present in amounts of only a few per cent tend to hasten the precipitation of "J" phase and sigma, whereas cobalt inhibits their formation. An equation derived for the effect of cobalt on sigma formation predicts that superalloys containing no cobalt will be on the threshold of compound formation at an N_{v5} number of about 2.10. If cobalt is present in amounts up to about 5-6 per cent, the precipitation of the tetragonal sigma and the

BCC "J" or epsilon phase is inhibited. In amounts over about 5-6 per cent, cobalt participates actively in the sigma compound at the expense of chromium. As the cobalt content within the compound increases, the lattice parameter of the sigma decreases. As the cobalt in the alloy increases, the threshold of compound formation increases as signified by an increasing vacancy number.

DISCUSSION

All of these data suggest that the instantaneous composition of the gamma prime plays a very significant role in the precipitation of the undesirable electron compounds in superalloys. It has been long established that the gamma prime precipitation mechanism has instantaneous reversibility, and that the composition changes with time and temperature. It is only reasonable to expect that small changes in the content of those elements participating in gamma prime formation will have a profound effect on the matrix composition, particularly in the region immediately surrounding a gamma prime particle of whatever type, i. e. primary, eutectic, secondary, etc..

Microprobe analysis on the 0 per cent, 10 per cent, and 20 per cent cobalt alloys has shown that as cobalt is added to the system, it enters both the matrix and the gamma prime. In doing so, it displaces chromium from the gamma prime to enter the matrix, and Ni, Ti and Al from the matrix to the gamma prime. (Table 4.)

This presumably stabilizes the face-centered structure of the gamma prime and decreases the tendency for formation of body centered intermetallic and electron phases.

It has been shown that from a starting nominal composition, additions of various BCC elements can in fact promote the formation of sigma. It can be postulated that these elements, such as columbium, tungsten, etc. contribute to sigma formation, not primarily by direct participation in the sigma compound, but by substitution in the gamma prime, thereby releasing chromium to the solid solution within the immediate surrounding area. Once nucleated, the compound grows, drawing on a matrix of similar composition from the nearby gamma prime particles.

Cobalt acts in a different manner than iron with regard to stability/instability. Although both contribute directly in the sigma compound, their primary role, particularly when present in small amounts, is quite different. Cobalt stabilizes the gamma prime compound and iron contributes to its instability. Cobalt, by

raising the solvus temperature of the gamma prime thereby inhibits, or referees the formation of undesirable compounds such as sigma and the BCC phase. On the other hand, the literature shows that iron reduces the solvus temperature, thereby contributing to the formation of undesirable compounds within the immediate area. Again as a referee rather than as a participant.

That cobalt enters into the formation of gamma prime is a well established fact. Many equations for electron vacancy calculations acknowledge the fact and incorporate some amount of cobalt into the gamma prime precipitation reaction. As illustrations of the effect of cobalt on gamma prime, Figures 7., 8., and 9. represent the microstructure of 10, 20, and 30 per cent cobalt additions to the nominal MAR-M alloy 421 type of composition after 3000 hours exposure at 1550°F. The decrease in gamma prime particle size is obvious, and this substitution of cobalt for nickel can be made without increasing the susceptibility of the alloys toward sigma formation.

CONCLUSION

1. Small additions of those elements entering into the gamma prime formation can have a profound effect upon the formation of undesirable electron compounds.
2. When added in small amounts, elements such as cobalt and iron act primarily in a referee's role in the precipitation of sigma, rather than as direct participants. When present in amounts below about 5 per cent, cobalt and iron enter into the gamma prime compound, presumably releasing chromium to the surrounding matrix, thereby increasing the concentration of chromium in that immediate area.
3. When present in amounts above about 5 per cent, cobalt plays an increasingly active role as a direct participant in the sigma compound at the expense of chromium.
4. An equation predicting the threshold of sigma formation as a function of cobalt content has been derived by means of linear regression analysis of data points generated by empirical observations. Increasing cobalt content increases the threshold of sigma formation as depicted by the vacancy number calculated by the N_{v5} PHACOMP method.
5. A body-centered-cubic Ni-Cr-Mo compound previously referred to as J-phase (similar to the α chromium phase in iron containing alloys) can be formed in iron-free alloys (less than

.10 per cent). Small amounts of cobalt suppress the formation of the BCC phase whereas iron promotes it.

6. Judgement based on a "universal vacancy number" of any given value can be misleading in determining the relative "stability" of superalloys. Solid state diffusion phenomena pertaining to the decomposition of eutectic gamma-prime particles, and to the dynamic nature of the instantaneously reversible general gamma-prime precipitate dictate that the matrix composition immediately adjacent to the particles, the area serving as the source of sigma.

7. Service operational conditions rarely duplicate the stress/thermal conditions of an isothermal stress-rupture or static exposure. Because many of the electron compounds exist within the rather narrow temperature range of about 1300°F to 1750°F, it is conceivable that precipitation of undesirable compounds occurring under isothermal-isostress conditions would not appear in environmental profiles of rapidly changing temperature and stress. Not only is the existence of the compounds threatened by variable thermal conditions, the actual formation of said compounds is complicated by the dynamic nature of the instantaneously reversible gamma-prime interface.

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Table 1. Chemical Composition of Base Composition
(MAR-M alloy 421)

<u>Element</u>	<u>Wt. %</u>	<u>Atomic %</u>
C	.15	0.70
Cr	15.5	16.78
Co	10.0	9.55
Cb	1.8	1.09
Mo	1.8	1.06
W	3.5	1.07
Al	4.3	8.97
Ti	1.8	2.12
B	.015	0.08
Zr	.05	0.03
Ni	Bal.	58.56

Table 2. Chemical Composition of Various Alloys

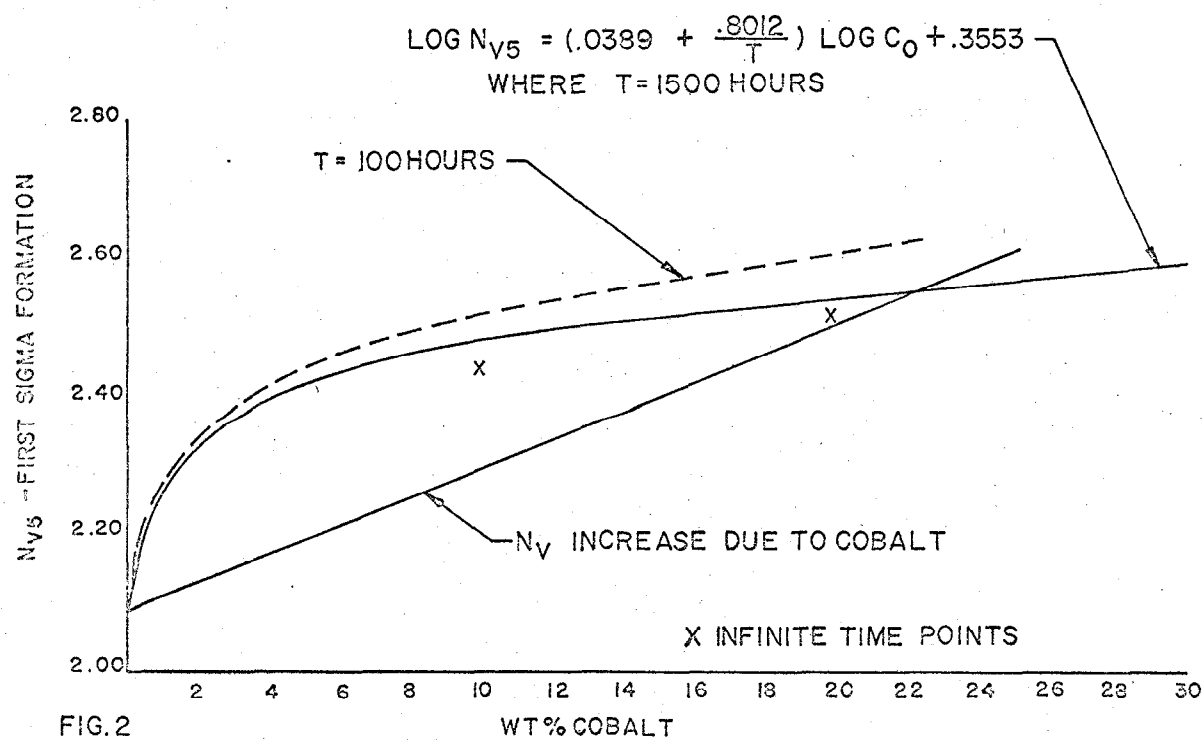
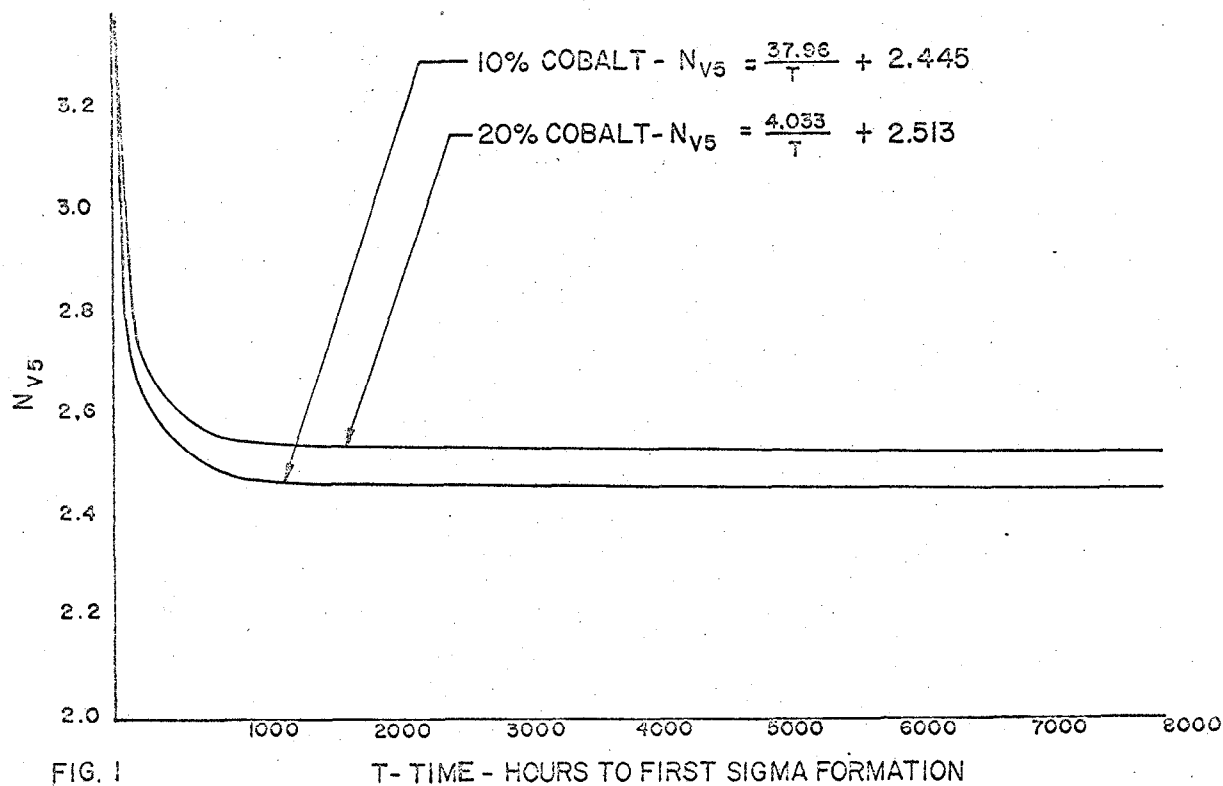
<u>Alloy</u>	<u>N_{v5}</u>	<u>Sigma</u>	<u>Co</u>	<u>Cr</u>	<u>Al+Ti</u>	<u>W</u>	<u>Mo</u>	<u>Ta</u>	<u>Cb</u>
INCO 713	2.08	yes	--	12.5	6.9	--	4.2	--	2.0
INCO 700	2.22	no	29	15	5.3	--	3.7	--	---
MM 421	2.28	no	10	15.5	6.1	3.5	1.8	--	1.8
INCO 738	2.36	no	9	16	7.0	2.0	1.8	1.8	1.0
4K	2.23	<250	--	15	6.4	4.1	2.1	--	2.2
4L	2.24	no	10	15	5.8	3.4	1.8	--	2.0
4N	2.50	no	20	15	6.0	3.5	1.8	--	1.8
4P	2.67	no	30	15	6.0	3.5	1.8	--	1.8
410	2.34	no	10	15.6	6.4	3.5	1.8	--	1.8
439	2.38	no	10	15.8	6.0	4.0	2.2	--	2.2
455	2.47	1500	10	16.0	6.3	4.1	2.0	--	2.2
408	2.52	500	10	15.1	6.6	4.0	2.2	--	2.2
4N-4	2.59	<250	20	15	5.7	3.3	1.7	--	3.3
4N-7	2.56	500	20	15	5.9	6.5	1.6	--	1.5
4N-14	2.67	2000	20	15	7.0	3.2	1.6	--	1.7
4N-20	2.80	<250	20	17	7.2	3.0	2.1	--	2.0
4AN	2.24	no	1.0	15	6.2	4.1	2.0	--	2.0
4AO	2.26	no	2.0	15	6.4	4.1	2.0	--	2.1
4AP	2.27	no	4.2	15	6.2	4.0	2.0	--	2.1
4AQ	2.32	no	6.1	15	6.3	4.0	2.0	--	2.1

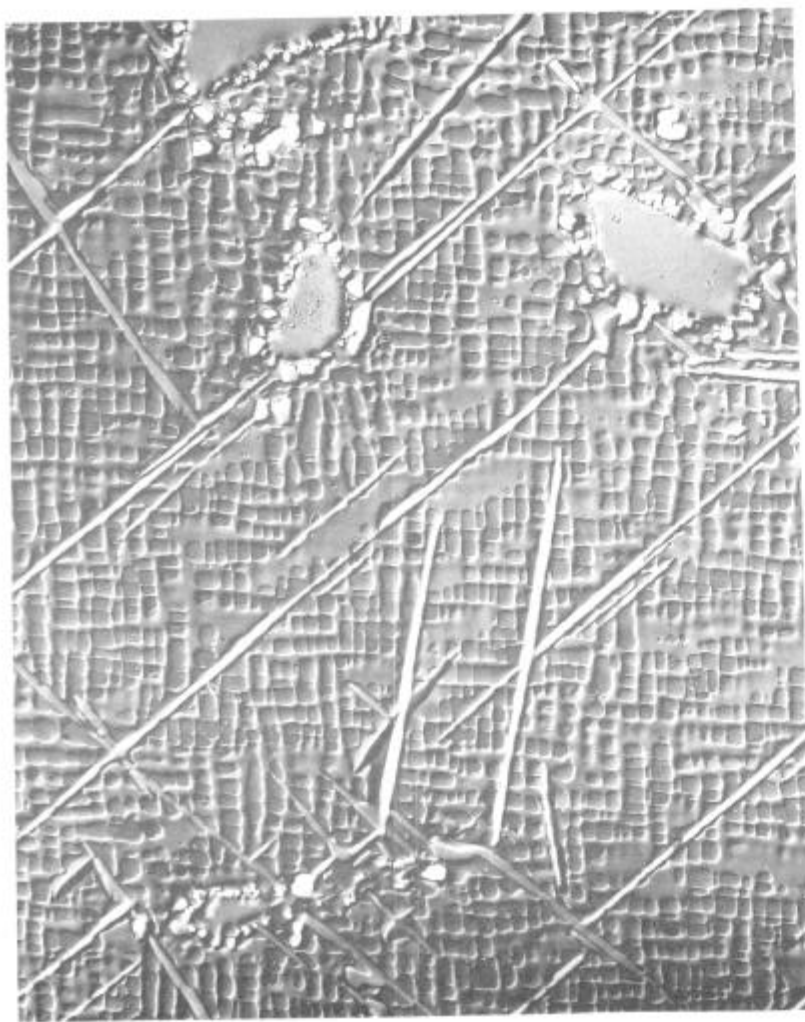
Table 3. Particle Analyses

<u>Source:</u>		<u>W</u>	<u>Cr</u>	<u>Mo</u>	<u>Ni</u>	<u>Co</u>	<u>Ti</u>	<u>Cb</u>
<u>Microprobe</u>								
<u>4K - Sigma Particles - 0% Co</u> (severe matrix excitation)	sample (1)	4.76	21.4	2.32	62.3	----	1.63	1.02
	sample (2)	4.35	19.5	4.13	63.3	----	1.70	1.18
	sample (3)	5.32	21.2	3.05	63.7	----	1.53	.97
<u>Corresponding Matrix</u>								
	sample (1)	4.51	12.4	1.66	72.9	----	1.67	1.13
	sample (2)	3.59	13.0	1.65	71.7	----	1.54	1.10
	sample (3)	4.04	13.8	1.53	71.7	----	1.49	1.00
<u>Residue Analyses</u>								
<u>4K - 0% Co</u>								
(s) + J-phase (s) + M ₂₃ C ₆ (1000 hrs/1550°F)		NA	62.2	2.9	25.6	.2	1.7	6.8
J-phase (vs) + (w) (3000 hrs/1550°F)		NA	74.4	3.4	18.7	.2	1.2	2.5
<u>4N-4 Hi Cb Heat - 10% Co</u>								
(s) + MC (w) (2750 hrs/1500°F)		NA	38.4	2.1	23.1	34.5	.6	1.6
<u>4N-20 Hi Cr Heat - 20% Co</u>								
(vs) + MC (w) (2750 hrs/1500°F)		NA	31.2	1.9	24.9	33.1	2.2	6.6
<u>713 LC</u>								
+ MC		NA	37.6	9.3	38.2	.5	1.9	6.7
<u>U-700</u>								
+ M ₂₃ C ₆		NA	61.0	8.5	16.3	9.2	5.3	----

Table 4 - Atomic Compositions of Matrices and Gamma Primes
With Increasing Cobalt

	<u>MATRIX</u>			<u>GAMMA PRIME</u>		
	<u>0% Co</u>	<u>10% Co</u>	<u>20% Co</u>	<u>0% Co</u>	<u>10% Co</u>	<u>20% Co</u>
Al	9.1	7.8	7.6	7.8	7.9	12.7
Cr	14.3	16.8	18.2	16.0	15.6	3.7
Co	-	10.3	19.0	-	9.8	13.5
Cb	0.7	0.6	0.7	1.0	0.9	2.7
Mo	1.0	1.0	1.0	1.0	1.1	1.0
Ni	71.7	60.7	50.4	71.3	61.8	63.0
Ti	1.9	1.6	2.1	1.9	2.1	2.9
W	1.3	1.2	1.0	1.0	0.8	0.5





6166

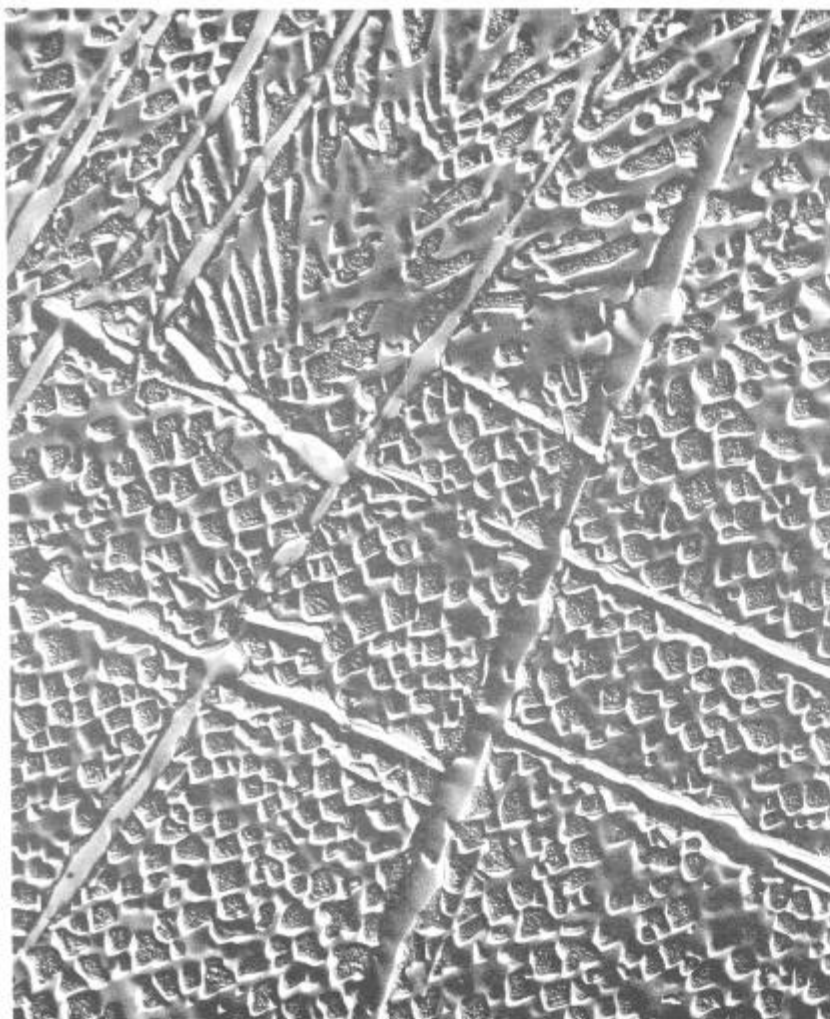
6000X

Fig. 3. Sample 408: Sigma Platelets and Carbide Re-precipitation



6166

Fig. 4. Sample 408: Sigma Platelets and Grain Characteristics



6527

7800X

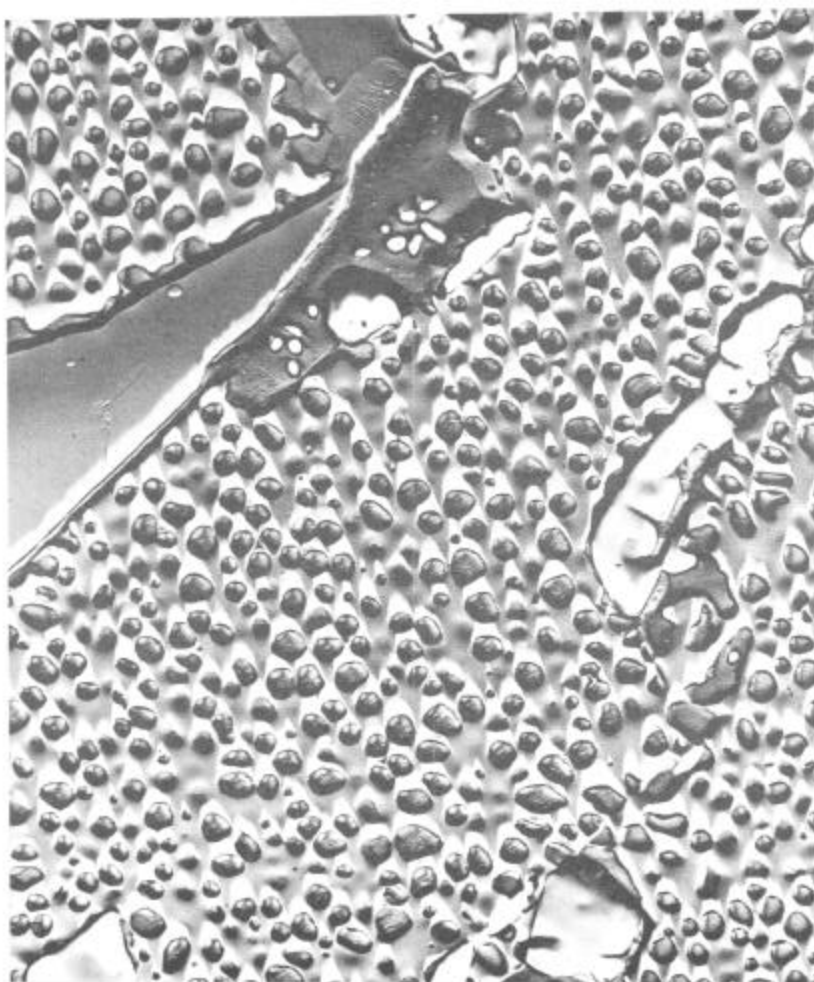
Fig. 5. Sample 4N-4: Sigma Platelets Forming Within 250 Hours
at 1550°F



6524

Fig. 6. Sample 4K: (0 Cobalt) After 3000 Hours
Sigma and BCC - Phase

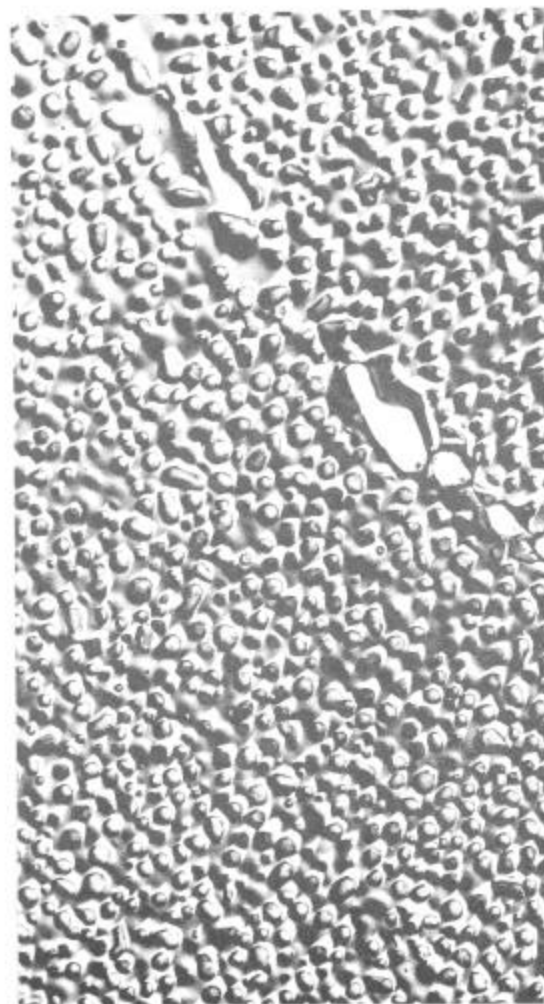
Reduce 30% for publication



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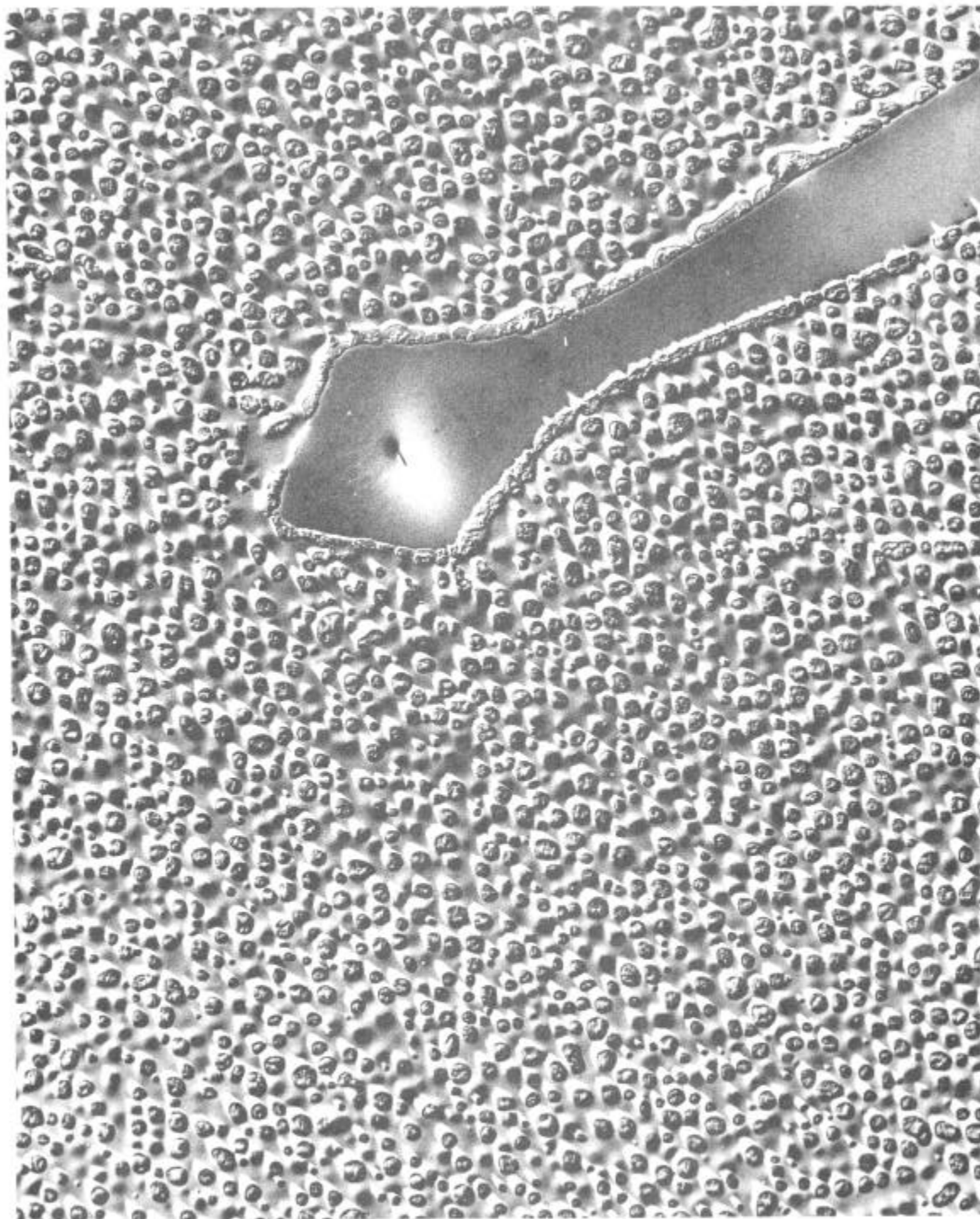
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Fig. 7. Sample 4L: (10% Cobalt) After 3000 Hours at 1550°F
Note Gamma Prime Particle Size



6529

Fig. 8. Sample 4N: (20% Cobalt) After 3000
Note Gamma Prime Part



6531

7800X

Fig. 9. Sample 4P: (30% Cobalt) After 3000 Hours at 1550°F
Note Gamma Prime Particle Size