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Evaluating Alloy Composition Using The Gibbs Triangle

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Ingot quality is characterized by SPC evaluations; meaning Structure (S), Property (P), and Composition (C). Structure-property studies are classified as "sensitive" attributes while composition is considered to be an "insensitive" parameter. For example, it is common to hear the phrase that global composition is "insensitive" to structure and property values. For superalloys, structural analyses are applied using the scanning electron microscope (SEM) to determine both size, shape and distribution effects for the gamma prime phase. Examination of properties requires mechanical tests for strength, hardness, toughness and, so forth. However, for investigations on composition, the scientific community still depends on optical emission spectroscopy (OES) for measurements of global results using arc burns to represent bulk volume. This leads to the obvious question…. What needs to be done to better quantify the OES results? Further…. How can the controlling microconstituents of a superalloy be better related to the overall composition results for an improved qualification of ingots? This article addresses these needs and priorities. And, the said article is offered as a contribution to the sum of total knowledge.

Keywords carbide formers, gamma formers, gamma prime formers, Ingot-cast 738 and statistical tests, isocompositus (isocomps) lines, optical emission spectroscopy (OES), the Gibbs Triangle

1. Introduction

Historically, Inconel 738 alloy was discovered by Clarence G. Bieber and J. J. Galka with a legal assignment to the International Nickel Company for a US Patent in about 1970 (Ref 1). Since that time, work on Alloy 738 has been described by several authors (Ref 2-7). Here, publications have been primarily concerned about structure, properties, or performance.

A thorough search of the open literature databases revealed no publications on composition per se or compositional effects, and no articles were found that involved optical emission spectroscopy (OES) vs. 738 or phase formers, or the Gibbs Triangle. However, numerous articles have been referenced about the subject of OES…. Thanks to the excellent textbook by Henderson and Imbusch (Ref 8). Another valuable source concerning the history of OES is the excellent article by Volker Thomsen on the pioneering work by Walther Gerlach (Ref 9). In its current form, optical spectroscopy of inorganic solids is a mixture of these study fields: quantum mechanics, group theory, experimental innovation, and spectroscopical measurements.

2. Materials

In general, alloy development practice for Alloy 738 has become somewhat standard over the last 30-something years. But, a rare opportunity to make *wrought* turbine blades for the power generating industry left little margin for error so, leading edge technology was dutifully imposed. Ingots were melted and refined by the {VIM + EBCHR} process. Here, VIM refers to vacuum induction melting and EBCHR means electron beam cold hearth refining. Prior to a refined melt cycle, a unique material specification (HMEC 408021) was compiled and diligently enforced. This Specification was atypical in this respect…. Eight different heats from eight different Producer Mills for Inconel 738 were merged into this new material specification. Accordingly, these critical levels were carefully stipulated…. Ni, Co, Cr, Al, Ti, Ta, Cb, C, Fe, W, Mo, O, N, and H.

Select scrap containing no chips, powder, dust, or contaminations of any type was used for recycling purposes…. Only cleaned portions of old turbine blades were acceptable. And, this select scrap was analyzed on a statistical basis prior to actual melting. After melting, 7 ingots (8-in diam.) and 14 samples (top and bottom) were analyzed by OES at the Producer Mill site (TIMET-CA), and by the coauthors of this article. These results by OES were carefully scrutinized for a study of ingot quality as a basis for product integrity and customer acceptance. For this specific research study, BTEC Turbines served as the Materials Sponsor, but HMEC paid for all laboratory testing including, among others, the associated chemical analyses using the OES method and the phase former approach. Table 1 reveals the complete information on these seven ingots and their compositions, at both top and bottom locations.

3. Discussion

One of America's greatest scientists was Josiah Willard Gibbs (1839-1903) who gave us the Gibbs Phase Rule and the Gibbs Triangle. For more details on his phase rule or triangle, consult any standard textbook on physical metallurgy…. One excellent choice would be the classic metallurgy text by Fred Rhines (Ref 10).

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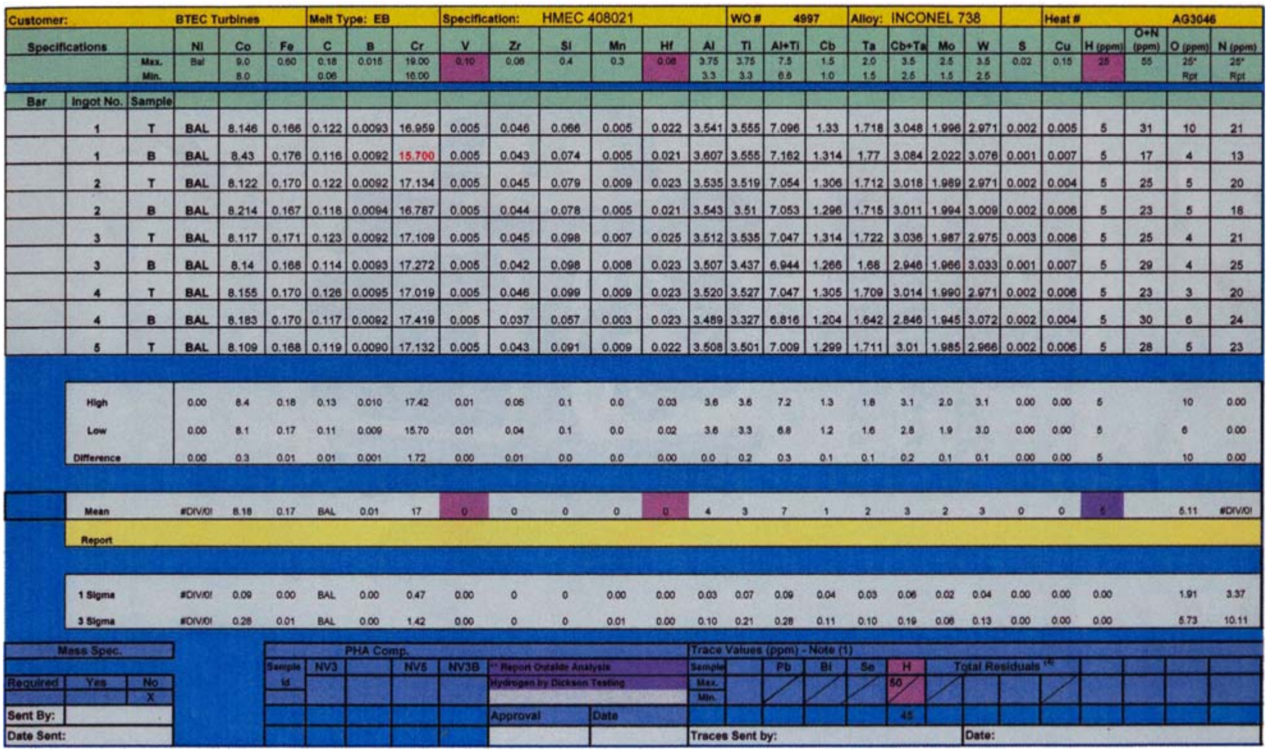
Table 1 Material control laboratory heat analysis. EB heat analysis—qualifiers



Customer: BTEC Turbines | Melt Type: EB | Specification: HMEC 408021 | WO # 4997 | Alloy: INCONEL 738 | Heat # AG3046

Specifications			Ni	Co	Fe	C	B	Cr	V	Zr	Si	Mn	Hf	Al	Ti	Al+Ti	Cb	Ta	Cb+Ta	Mo	W	S	Cu	H (ppm)	O+N (ppm)	O (ppm)	N (ppm)
		Max.	Bal	9.0	0.60	0.18	0.015	19.00	0.10	0.08	0.4	0.3	0.08	3.75	3.75	7.5	1.5	2.0	3.5	2.5	3.5	0.02	0.15	25	55	25*	25*
		Min.		8.0		0.06		16.00						3.3	3.3	6.6	1.0	1.5	2.5	1.5	2.5					Rpt	Rpt
Bar	Ingot No.	Sample																									
	1	T	BAL	8.146	0.166	0.122	0.0093	16.959	0.005	0.046	0.066	0.005	0.022	3.541	3.555	7.096	1.33	1.718	3.048	1.996	2.971	0.002	0.005	5	31	10	21
	1	B	BAL	8.43	0.176	0.116	0.0092	15.700	0.005	0.043	0.074	0.005	0.021	3.607	3.555	7.162	1.314	1.77	3.084	2.022	3.076	0.001	0.007	5	17	4	13
	2	T	BAL	8.122	0.170	0.122	0.0092	17.134	0.005	0.045	0.079	0.009	0.023	3.535	3.519	7.054	1.306	1.712	3.018	1.989	2.971	0.002	0.004	5	25	5	20
	2	B	BAL	8.214	0.167	0.118	0.0094	16.787	0.005	0.044	0.078	0.005	0.021	3.543	3.51	7.053	1.296	1.715	3.011	1.994	3.009	0.002	0.006	5	23	5	16
	3	T	BAL	8.117	0.171	0.123	0.0092	17.109	0.005	0.045	0.098	0.007	0.025	3.512	3.535	7.047	1.314	1.722	3.036	1.987	2.975	0.003	0.006	5	25	4	21
	3	B	BAL	8.14	0.168	0.114	0.0093	17.272	0.005	0.042	0.098	0.008	0.023	3.507	3.437	6.944	1.266	1.68	2.946	1.966	3.033	0.001	0.007	5	29	4	25
	4	T	BAL	8.155	0.170	0.126	0.0095	17.019	0.005	0.046	0.099	0.009	0.023	3.520	3.527	7.047	1.305	1.709	3.014	1.990	2.971	0.002	0.006	5	23	3	20
	4	B	BAL	8.183	0.170	0.117	0.0092	17.419	0.005	0.037	0.057	0.003	0.023	3.489	3.327	6.816	1.204	1.642	2.846	1.945	3.072	0.002	0.004	5	30	6	24
	5	T	BAL	8.109	0.168	0.119	0.0090	17.132	0.005	0.043	0.091	0.009	0.022	3.508	3.501	7.009	1.299	1.711	3.01	1.985	2.966	0.002	0.006	5	28	5	23
	High		0.00	8.4	0.18	0.13	0.010	17.42	0.01	0.05	0.1	0.0	0.03	3.6	3.6	7.2	1.3	1.8	3.1	2.0	3.1	0.00	0.00	5		10	0.00
	Low		0.00	8.1	0.17	0.11	0.009	15.70	0.01	0.04	0.1	0.0	0.02	3.6	3.3	6.8	1.2	1.6	2.8	1.9	3.0	0.00	0.00	5		6	0.00
	Difference		0.00	0.3	0.01	0.01	0.001	1.72	0.00	0.01	0.0	0.0	0.00	0.0	0.2	0.3	0.1	0.1	0.2	0.1	0.1	0.00	0.00	5		10	0.00
	Mean		#DIV/0!	8.18	0.17	BAL	0.01	17	0	0	0	0	0	4	3	7	1	2	3	2	3	0	0	5		5.11	#DIV/0!
	Report																										
	1 Sigma		#DIV/0!	0.09	0.00	BAL	0.00	0.47	0.00	0	0	0.00	0.00	0.03	0.07	0.09	0.04	0.03	0.06	0.02	0.04	0.00	0.00	0.00		1.91	3.37
	3 Sigma		#DIV/0!	0.28	0.01	BAL	0.00	1.42	0.00	0	0	0.01	0.00	0.10	0.21	0.28	0.11	0.10	0.19	0.06	0.13	0.00	0.00	0.00		5.73	10.11

Mass Spec.

Required	Yes	No
		X

Sent By:
Date Sent:

PHA Comp.

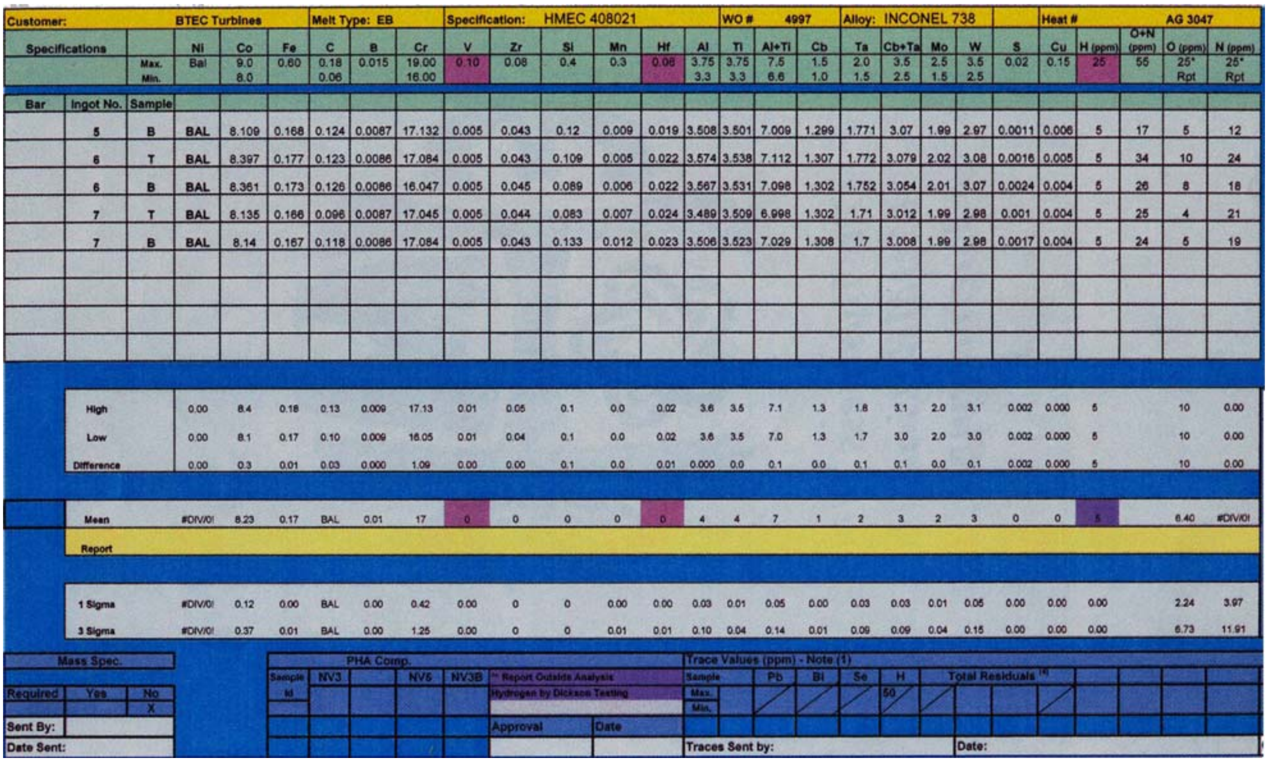
Sample Id	NV3		NV5	NV3B

** Report Outside Analysis
Hydrogen by Dickson Testing
Approval | Date

Trace Values (ppm) - Note (1)

Sample		Pb	Bi	Se	H	Total Residuals (4)
Max.					50	
Min.						
					45	

Traces Sent by: | Date:



Customer: BTEC Turbines | Melt Type: EB | Specification: HMEC 408021 | WO # 4997 | Alloy: INCONEL 738 | Heat # AG 3047

Specifications			Ni	Co	Fe	C	B	Cr	V	Zr	Si	Mn	Hf	Al	Ti	Al+Ti	Cb	Ta	Cb+Ta	Mo	W	S	Cu	H (ppm)	O+N (ppm)	O (ppm)	N (ppm)
		Max.	Bal	9.0	0.60	0.18	0.015	19.00	0.10	0.08	0.4	0.3	0.08	3.75	3.75	7.5	1.5	2.0	3.5	2.5	3.5	0.02	0.15	25	55	25*	25*
		Min.		8.0		0.06		16.00						3.3	3.3	6.6	1.0	1.5	2.5	1.5	2.5					Rpt	Rpt
Bar	Ingot No.	Sample																									
	5	B	BAL	8.109	0.168	0.124	0.0087	17.132	0.005	0.043	0.12	0.009	0.019	3.508	3.501	7.009	1.299	1.771	3.07	1.99	2.97	0.0011	0.006	5	17	5	12
	6	T	BAL	8.397	0.177	0.123	0.0086	17.084	0.005	0.043	0.109	0.005	0.022	3.574	3.538	7.112	1.307	1.772	3.079	2.02	3.08	0.0016	0.005	5	34	10	24
	6	B	BAL	8.361	0.173	0.126	0.0086	16.047	0.005	0.045	0.089	0.006	0.022	3.567	3.531	7.098	1.302	1.752	3.054	2.01	3.07	0.0024	0.004	5	26	8	18
	7	T	BAL	8.135	0.166	0.096	0.0087	17.045	0.005	0.044	0.083	0.007	0.024	3.489	3.509	6.998	1.302	1.71	3.012	1.99	2.98	0.001	0.004	5	25	4	21
	7	B	BAL	8.14	0.167	0.118	0.0086	17.084	0.005	0.043	0.133	0.012	0.023	3.506	3.523	7.029	1.308	1.7	3.008	1.99	2.98	0.0017	0.004	5	24	5	19
	High		0.00	8.4	0.18	0.13	0.009	17.13	0.01	0.05	0.1	0.0	0.02	3.6	3.5	7.1	1.3	1.8	3.1	2.0	3.1	0.002	0.000	5		10	0.00
	Low		0.00	8.1	0.17	0.10	0.009	16.05	0.01	0.04	0.1	0.0	0.02	3.6	3.5	7.0	1.3	1.7	3.0	2.0	3.0	0.002	0.000	5		10	0.00
	Difference		0.00	0.3	0.01	0.03	0.000	1.09	0.00	0.00	0.1	0.0	0.01	0.000	0.0	0.1	0.0	0.1	0.1	0.0	0.1	0.002	0.000	5		10	0.00
	Mean		#DIV/0!	8.23	0.17	BAL	0.01	17	0	0	0	0	0	4	4	7	1	2	3	2	3	0	0	5		6.40	#DIV/0!
	Report																										
	1 Sigma		#DIV/0!	0.12	0.00	BAL	0.00	0.42	0.00	0	0	0.00	0.00	0.03	0.01	0.05	0.00	0.03	0.03	0.01	0.05	0.00	0.00	0.00		2.24	3.97
	3 Sigma		#DIV/0!	0.37	0.01	BAL	0.00	1.25	0.00	0	0	0.01	0.01	0.10	0.04	0.14	0.01	0.09	0.09	0.04	0.15	0.00	0.00	0.00		6.73	11.91

Mass Spec.

Required	Yes	No
		X

Sent By:
Date Sent:

PHA Comp.

Sample Id	NV3		NV5	NV3B

** Report Outside Analysis
Hydrogen by Dickson Testing
Approval | Date

Trace Values (ppm) - Note (1)

Sample		Pb	Bi	Se	H	Total Residuals (4)
Max.					50	
Min.						

Traces Sent by: | Date:

Usage of the Gibbs Triangle for this article on the effect of phase formers requires that each of all components are defined by the sum total of 100%. If that be the case, then, what applies to phase mixtures ABC according to Rhines can also apply to other applications; viz. phase formers, if the analysis is correctly executed. In this manner, isocompositus (isocomps) boundary lines can be generated for important phase formers.

When using the phase former approach, it is assumed that certain elements are driving the end result. For example, it is known that solutes of (Co + Cr) contribute to the gamma matrix formation, along with the host solvent (Ni). It is also accepted that solutes of (Ti + Al) control the gamma prime reaction in a nickel-rich alloy. Finally, solute elements of (C + Ta + Cb + Fe + W) govern the carbides that form in this nickel-base Alloy 738.

For ingot (1) top, the GF term is derived in this manner:

$$\mathrm{GF} = (\mathrm{Co} + \mathrm{Cr}) \div (\mathrm{Ni})$$

$$\begin{aligned}\mathrm{GF} &= (8.43\% + 16.959\%) \div (59.32\%)\\ &= 42.32\%\end{aligned}$$

which makes the argument that 42.32% of the alloy goes to form the matrix phase, gamma (γ).

Similarly,

$$\mathrm{GPF} = (\mathrm{Al} + \mathrm{Ti}) \div (\mathrm{Ni})$$

$$\begin{aligned}\mathrm{GPF} &= (3.541\% + 3.555\%) \div (59.32\%)\\ &= 11.96\%\end{aligned}$$

which makes the statement that 11.96% of the alloy goes to form the gamma prime phase (γ').

In like manner,

$$\begin{aligned}\mathrm{CF} &= (\mathrm{C} + \mathrm{Ta} + \mathrm{Cb} + \mathrm{Fe} + \mathrm{W}) \div (\mathrm{Ni})\\ \mathrm{CF} &= (0.122\% + 1.718\% + 1.33\% + 0.166\%\\ &\quad + 2.971\%) \div (59.32\%)\\ \mathrm{CF} &= 10.66\%\end{aligned}$$

which says that 10.66% of the alloy goes toward the formation of complex carbides in this alloy.

Therefore, the grand total for these phase former elements and their associated values for ingot 1 (top) are as follows:

$$42.3\% + 11.96\% + 10.66\% = 64.92\%(\mathrm{Total}).$$

If one assumes the cardinal position that we care less about the trace elements in this alloy than we do about the critical phase former elements…. Then, we have a new method by which we can evaluate the effects of these *more* critical phase fields of GF, GPF, and CF. All that remains is to normalize these specific results so that, together, they must equal 100%…. Recalling that the lengths *a*, *b*, and *c* or GF, GPF, and CF must equal 100% according to Rhines. This is to say that if the values of 42.3%, 11.96%, and 10.66% are normalized to a 100% summation (using pie chart software), then these three constituents are resolved as GF = 65.2%, GPF = 18.4%, and CF = 16.4% such that, together, all three constituents are summed to a total of 100%…. See Fig. 1 and 2.

At the top location of ingot 1:

42.3%	11.96%	10.66%	64.92%
65.2%	18.4%	16.4%	100%

At the bottom location of ingot 1:

40.17%	11.92%	10.74%	62.83%
63.9%	19.0%	17.1%	100%

If this be done for all 7 ingots at all 14 test locations, then, Fig. 3 is the end result…. a common loci that is approximately 65.0% (GF), 17.5% (GPF), and 17.5% (CF). From this observation, it follows that these seven ingots are very uniform, indicative of high quality and representative of excellent workmanship.

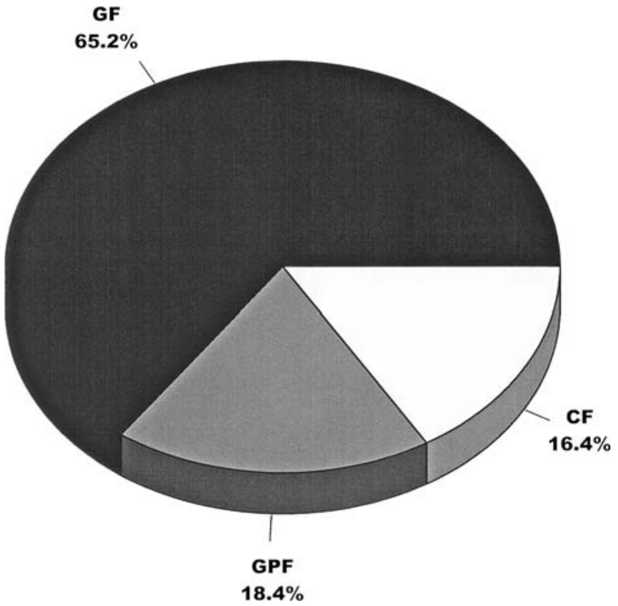


Fig. 1 Variation of phase formers for data on ingot one at the top location

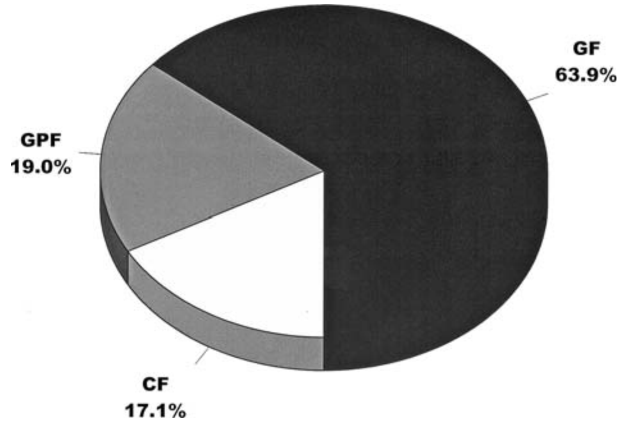


Fig. 2 Variation of phase formers for data on ingot one at the bottom location

Data of this type can also be used to evaluate the degree of segregation for any given ingot. Consider the data for two important scenarios…. Ideal (ingot 5) and worst case (ingot 6). Phase former parameters do represent compositional trends at a specific location, and end users have been more than concerned with the differences that exist for composition at the top and bottom location of a given ingot. Today, ingots are trimmed and OES examinations are made at these two locations to provide the primary means for either acceptance or rejection of the as-cast ingot. If concentration factors (C') are plotted against the multiplier factors (M') that are used for normalization to 100%, then alloy segregations at top and bottom can be better examined by this new compositional methodology…. Consider the following:

At the top location of ingot 5:

42.57%	11.82%	10.60%	64.99%
2.35	8.46	9.43	1.54

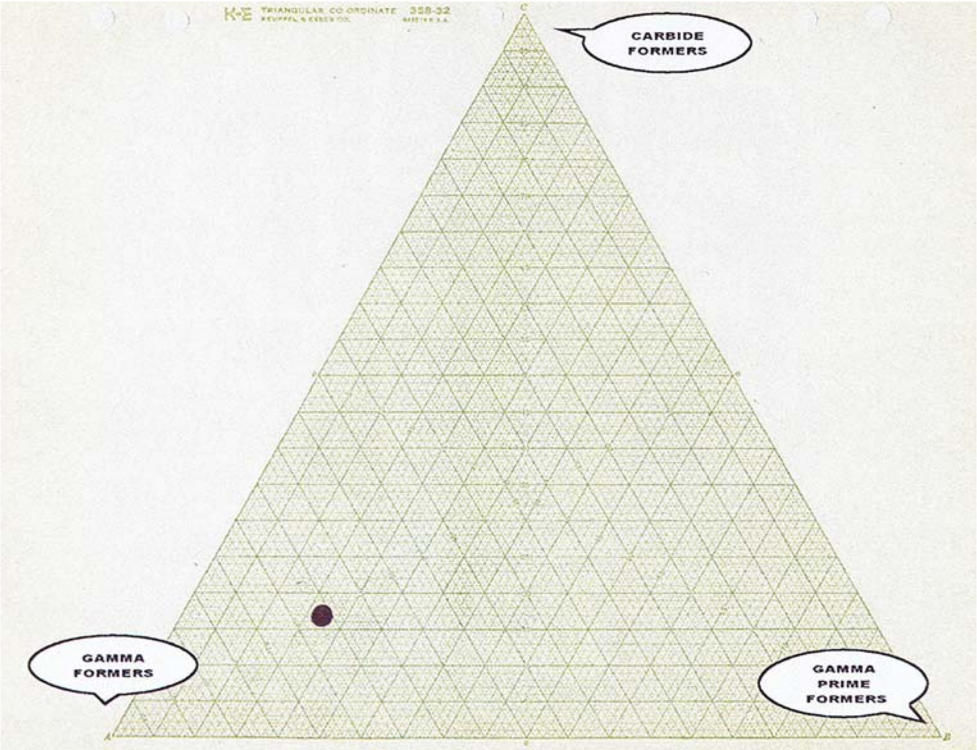


Fig. 3 A Gibbs solution for the three phase formers

At the bottom of ingot 5:

42.62%	11.84%	10.69%	65.15%
2.35	8.45	9.35	1.54

where, for 5T, the following applies….

$$\begin{aligned}\text{Total} &= 100\% \div 64.99\% = 1.54\\ \text{GF} &= 100\% \div 42.57\% = 2.35\\ \text{GPF} &= 100\% \div 11.82\% = 8.46\\ \text{CF} &= 100\% \div 10.60\% = 9.43\end{aligned}$$

If (C') is plotted on the y-axis and (M') is plotted on the x-axis of a trend curve, segregation effects are evident…. See Fig. 4 where both top and bottom curves are superimposed. The same response does not apply for ingot 6…. A worse case scenario.

At the top of ingot 6:

43.28%	12.08%	10.97%	66.33%
2.31	8.28	9.12	1.51

At the bottom of ingot 6:

40.76%	11.85%	10.74%	63.35%
2.45	8.44	9.31	1.58

Note Fig. 5. These two curves are not superimposed.

Data of this type can also be used to estimate the most likely composition that exists at the midlength location of a given ingot…. Based on a combination of probability theory and the phase former approach. Traditionally, ingot composition is checked at the top and bottom location only. OES determinations at the midlength region would require the ingot to be sectioned into two parts and that is illogical. This new statistical

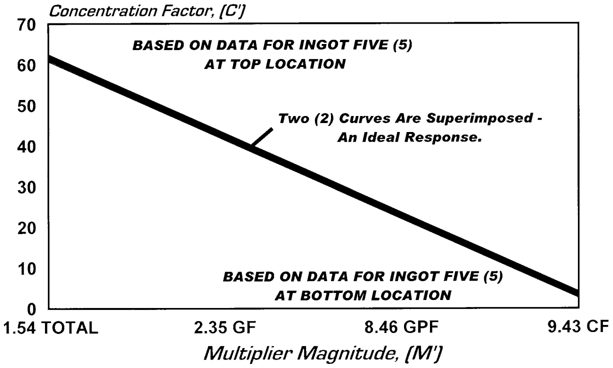


Fig. 4 Phase formers in Alloy 738 gamma vs. gamma prime vs. carbide

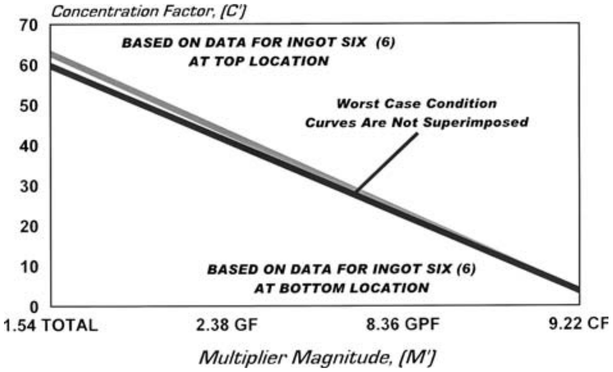


Fig. 5 Phase former in Alloy 738 gamma vs. gamma prime vs. carbide

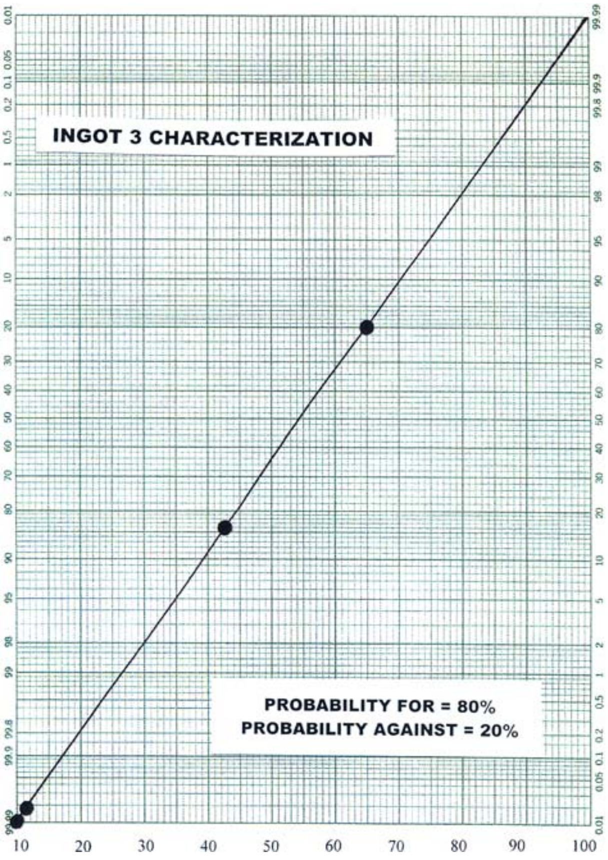


Fig. 6 Ingot 3 characterization

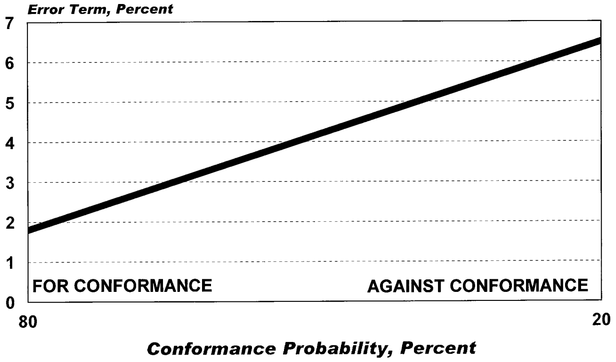


Fig. 7 Ingot 3 characterization: prediction of composition at the mid-length location

technique allows a quality assurance procedure to safely predict what the most likely midlength composition must be…. Based upon top/bottom observations using the phase former approach.

Using only probability type paper, the values for "GF," "GPF," and "CF" are plotted on the *x*-axis for expectancy ranges between 0.01 and 99.99 on the *y*-axis. Then, the probability for or against conformance is read directly. For a demonstration exemplar, see Fig. 6 and 7 and Table 2 and 3.

Table 2 Reference values for phase former *averages* using observations by OES testing (a)

Ingot number	GF	GPF	CF	Total
1	41.235	11.94	10.7	63.875
2	42.415	11.915	10.635	64.965
3	42.74	11.81	10.605	65.155
4	42.81	11.69	10.53	65.03
5	42.595	11.83	10.645	65.07
6	42.02	11.965	10.855	64.84
7	42.48	11.81	10.56	64.85

(a) Using only probability paper, the values for "GF," "GPF," "CF," and "Total" are plotted on the *x*-axis for expectancy ranges between 0.01 and 99.99 on the *y*-axis. Then the probability *for* or *against* conformance is read directly…. See Table 3

Table 3 Reference values for estimation of conformance (a)

Ingot number	Probability for conformance	Probability against conformance
1	76	24
2	78.2	21.8
3	80	20
4	79.8	20.2
5	79.7	20.3
6	78.5	21.5
7	78.3	21.7
Average ± Standard Deviation	78.6 ± 1.4	21.4 ± 1.4
Range, maximum	80	24
Range, minimum	76	20
Median	78	22
Error term	1.8	6.5

(a) The statistical argument is as follows: If one opts *against* conformance, the error term is almost four times larger than if one opts *for* conformance; therefore, the mid-length values should fall on the same distribution curve as does the top and bottom data

4. Conclusions

Most of the salient findings have already been discussed in considerable detail, but supplementary points about this new procedure do merit a proper summation at this time. If a metallurgist knows his alloy system well enough to predict the controlling constituents for a given end result…. Then, the Gibbs Triangle can be used with a phase former approach to determine if the Producer Mill has given the metallurgist what was wanted and needed. In this contract with TIMET-CA, seven ingots were ordered and the precise levels of (Co + Ni), (Ti + Al), and (C + Ta + Cb + Fe + W) were specified to deliver the end results that were expected of Bieber's Alloy 738. This is to say that the Producer Mill (TIMET-CA) delivered exactly what was desired…. Homogeneous products with significant reliability, admirable workmanship, and excellent quality. The melting process of (VIM + EBCHR) is more than justified.

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