#### EFFECTS OF A RARE EARTH ADDITION ON UNITEMP\* 901

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#### ABSTRACT

This investigation demonstrates the use of a rare earth to achieve extremely low oxygen and sulfur levels in a vacuum induction melted (VIM) superalloy. Since both the quality of rare earth elements available and VIM technology have increased over the last decade, exacting techniques can be used to achieve consistent results. With the use of current thermodynamic data, the theoretical amount of lanthanum required to react with the remaining oxygen and sulfur in a molten bath of an iron-nickel ba 2 superalloy was determined. Through a judicious addition of lanthanum, the levels of both oxygen and sulfur were reduced to less than 10 ppm with a minimum of retained rare earth. As a consequence, stress rupture ductility was increased, creep rate was lowered and hot workability was improved. In addition, no undesirable structural features were produced. The potential of rare earth elements to counteract arsenic, tin, antimony, selenium and other tramp elements is also discussed.

\*Unitemp is a registered trademark of Universal-Cyclops

#### INTRODUCTION

For several years, it has been recognized that sulfur is markedly deleterious to nickel-base superalloys, in that it impairs elevated temperature ductility (1-2), decreases hot strength (3), and reduces weldability (4-5). It has been shown that ductility over a broad temperature range increases progressively as sulfur is reduced from 78 ppm to 5 ppm (6). Although high quality raw materials and improved melting technology have permitted sulfur levels in superalloys to be lowered to the range of 10 to 100 ppm, it has been suspected that additional property improvements could be realized by further sulfur reduction. The high affinity of rare earth elements for sulfur offers a means of attaining these low sulfur levels. The objective of this study was to improve certain mechanical properties in an iron-nickel base superalloy, Unitemp 901, via ultra-desulfurization.

## PROCEDURE

A Unitemp 901 heat was VIM without a slag, using a charge consisting of low sulfur revert materials in a crucible lined with magnesia-based refractory. After all alloying additions were made to the molten metal bath, a preliminary chemical analysis was performed on a dip sample, a final addition of 300 ppm lanthanum was added and the heat was tapped at  $2715^{\circ}F$  ( $1490^{\circ}C$ ).

An electrode from this heat was subsequently vacuum arc remelted (VAR), forged to billet and sections of this billet were upset to pilot test pieces 3/4 inch (19 mm) thick. Specimens were stress rupture tested per PWA 1003 and AMS 5661 specifications. Both gleeble and creep tests were conducted on this material along with current production material of relatively low sulfur content (12 ppm). Extensive metallographic and scanning electron microscopy examinations were performed on the lanthanum-bearing heat.

All sulfur analyses were conducted with a Leco CS-44 determinator. This instrument, which operates by the infrared method, analyses sulfur levels as low as 5 ppm with a sensitivity of 1 ppm. The accuracy at these low levels is limited only by lack of suitable standards. All ppm values reported herein represent weight percent as opposed to atomic percent.

## RESULTS AND DISCUSSION

#### Background

To provide a better basis for discussing the theory and results of this study, a brief summation of pertinent rare earth properties, relative to micro-alloying in superalloys follows. Three properties of interest are density, melting temperature and vapor pressure. The densities and melting points of the more common rare earth metals are compared with those of nickel, cobalt and iron in Table I. The vapor pressures of lanthanum, cerium, calcium and magnesium at superalloy melt temperatures are depicted in Fig. 1. Because their melting points and vapor pressures are low, rare earth elements will readily melt and be retained in the bath.

The densities and melting points of relevant rare earth oxygen and sulfur compounds are presented in Table II and the free energy of formation of such compounds are shown in Fig. 2. This data indicates that at superalloy melting temperatures, the following order of rare earth compound formation prevails: oxides, oxysulfides, sulfides and nitrides.

The fact that lanthanum and other rare earths possess high negative standard free energies of formation for their oxides, oxysulfides and sulfides at typical melt temperatures coupled with their high chemical activities favors formation of these compounds. According to Venal and Geiger (12), titanium, aluminum, molybdenum, chromium and iron in molten nickel increase the activity coefficient of sulfur and thereby facilitate sulfur removal. Consequently, it

TABLE I: PHYSICAL PROPERTY DATA OF PERTINENT COMMON RARE EARTH METALS

COMPARED WITH NICKEL, COBALT AND IRON

Element	Atomic No.	Atomic Wt.	Density Lb./in. <sup>3</sup> (g/cc)	Melting Point OF (OC)
Lanthanum	57	138.92	0.22 (6.17)	1688 (920)
Cerium	58	140.13	0.24 (6.77)	1468 (798)
Nickel	28	58.69	0.32 (8.90)	2651 (1455)
Cobalt	27	58.94	0.32 (8.85)	2723 (1495)
Iron	26	55.85	0.28 (7.88)	2802 (1539)

TABLE II: DENSITIES AND MELTING POINTS OF VARIOUS LANTHANUM AND CERIUM OXIDES, OXYSULFIDES AND SULFIDES IN RELATION TO UNITEMP 901

	Density	Melting Point
	Lb./in. <sup>3</sup> (g/cc)	of (oc)
Unitemp 901	0.297 (8.22)	2246-2579 (1230-1415)
La <sub>2</sub> 0 <sub>3</sub>	0.234 (6.51)	4181 (2305)
Ce <sub>2</sub> 03 Ca0	0.247 (6.86) 0.121 (3.35)	3078 (1692) 4676 (2580)
MgO	0.121 (3.33)	5072 (2800)
La <sub>2</sub> 0 <sub>2</sub> S	0.208 (5.77)	3524 (1940)
Ce 202S	0.216 (5.99)	3542 (1950)
$Ce_{2}^{2}O_{2}^{2}S$ $La_{2}^{2}S_{3}$	0.177 (4.93)	3902 (2150)
Ce <sub>2</sub> S <sub>3</sub>	0.186 (5.18)	3434 (1890)
CaS 3	0.078 (2.18)	
MgS	0.101 (2.82)	3632 (2000)
Temperature ,°F 2000 2400 2800	3200 3400 0 0	Temperature,*F 1000 1500 2000 2500 3000
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Fig. 1: COMPARISON OF VAPOR PRESSURES OF COMMON RARE EARTH ELEMENTS WITH Mg, Ca, Ni, Co AND Fo AT SUPERALLOY MELTING TEMPERATURES (Vapor pressures tobare from Lao Brown, Report for the Manhetten Project, MDDC-438C, 1946).

Fig. 2: RELATIVE FREE ENERGY OF FORMATION OF RARE EARTH COMPOUNDS COMPARED WITH CALCIUM AND MAGNESIUM COMPOUNDS. (Ref. 7-10)

is advantageous to desulfurize with rare earths when these other elements are present in the bath as is the case in Unitemp 901. In addition, the large atomic sizes of the rare earth elements make their solid solubility in iron, nickel or cobalt base superalloys negligible. Furthermore, the low vapor pressure of the rare earths as compared to calcium or magnesium constitutes a significant advantage because it renders them easier to control during VIM. This is particularly true in VAR, since the highly volatile calcium and magnesium elements tend to concentrate on the ingot surface, thereby causing initial hot workability impairment due to localized enrichment. Finally, the lower densities and non-wetting characteristics of the rare earth oxides, oxysulfides, and sulfides with respect to superalloys make them amenable to

removal by flotation during teeming.

Of the lanthanide rare earth group, cerium and lanthanum are the most abundant. Lanthanum was chosen over cerium due to its a) lower vapor pressure, b) slightly lower compound densities, and c) lower tendency to form intermetallic compounds with iron. The fact that cerium can exist in both the tetravalent and normal trivalent state explains why cerium behaves differently from other light lanthanides with respect to compound formation. For example, cerium forms intermetallic compounds with iron in which cerium is tetravalent, while lanthanum does not (9). This accounts for the fact that in some cases when mischmetal is added to steel for sulfur control, cerium concentration in the sulfides is quite low compared to the lanthanum, neodymium and praseodymium concentrations. The cerium expected in the sulfides is instead observed as a cerium-iron intermetallic phase located at grain boundaries. This characteristic of cerium is a disadvantage compared with lanthanum because the chance of forming undesirable phases with iron is greater. Mischmetal, which is a mixture of cerium, lanthanum, praseodymium and neodymium, was not used because individual element effects would be difficult to discern and the major component is cerium not lanthanum. Incidentally, rare earth elements do not form intermetallic phases with chromium, molybdenum or titanium (9).

## Theoretical Calculation of Controlled Rare Earth Addition

The objective was to add a total amount of lanthanum sufficient to react with all the oxygen and sulfur present leaving only a minimal excess to compensate for any losses. Based on the work of Lu and McLean (13) plus the thermodynamic data in Fig. 2, the following ordered sequence of liquid metal reactions was assumed to occur as oxygen and sulfur decreased:

(1) 2 La + 3 [0] = La
$$_2$$
0 $_3$  where: [ ] indicate a component in (2) 2 La + 2 [0] + [S]  $\stackrel{3}{=}$  La $_2$ 0 $_2$ S liquid metal solution (3) 2 La + 3 [S] = La $_2$ S $_3$ 

These reactions are depicted graphically, in Fig. 3. The starred point in Fig. 3 represents the starting oxygen and sulfur levels (35 ppm and 20 ppm respectively) in the Unitemp 901 heat prior to the lanthanum addition.

When the lanthanum addition is made, it is believed that  $\text{La}_2 0_3$  forms initially until the dissolved oxygen drops to the level coincident with the  $\text{La}_2 0_3/\text{La}_2 0_2 \text{S}$  boundary. At this point, the reaction probably follows this boundary forming  $\text{La}_2 0_2 \text{S}$  on  $\text{La}_2 0_3$  particles until the latter are isolated from the bath, after which the reaction traverses the  $\text{La}_2 0_2 \text{S}$  field with the formation of fresh  $\text{La}_2 0_2 \text{S}$  particles until the  $\text{La}_2 0_2 \text{S}/\text{La}_2 0_3$  boundary is reached. Then  $\text{La}_2 S_3$  would be expected to form. Based on these reactions, the theoretical minimum amount of lanthanum required to react with all the oxygen and sulfur present is calculated as follows:

$$\frac{\text{PPM La Required}}{\text{Atomic Wt. La}} = \frac{2}{3} \quad \frac{\left( \begin{array}{c} \text{PPM Oxygen Prior} \\ \text{to Lanthanum Addition} \\ \text{Atomic Wt. of Oxygen} \end{array} \right)}{\text{Atomic Wt. of Oxygen at}} \\ + \quad \left( \begin{array}{c} \text{PPM Oxygen At} \\ \text{La}_2 0_3 / \text{La}_2 0_2 \text{S Boundary} \\ \text{Atomic Wt. of Oxygen} \end{array} \right)}{\text{Atomic Wt. of Oxygen}} \\ + \frac{2}{3} \quad \left( \begin{array}{c} \text{PPM Sulfur at La}_2 0_2 \text{S/La}_2 \text{S}_3 \text{ Boundary}} \\ \text{Atomic Wt. of Sulfur} \end{array} \right)}{\text{Atomic Wt. of Sulfur}}$$

For the low starting levels of oxygen and sulfur present in the Unitemp 901 heat, the minimum lanthanum addition required was:

PPM La Required = 138.9 
$$\left[\frac{2}{3} \left(\frac{35-2}{16}\right) + \left(\frac{2-0}{16}\right) + \frac{2}{3} \left(\frac{18-0}{32}\right)\right] = 260 \text{ ppm}$$

A 300 ppm lanthanum addition represented only a 40 ppm excess. This addition was made in the form of a master alloy, whose impurity levels and pertinent physical properties are shown in Table III. The density and liquidus temperature indicate that it readily mixes with nickel, cobalt and iron base superalloy melts. Furthermore, this is a high quality material superior to the rare earth mixtures commonly available several years ago.

Although it should be noted that the excess lanthanum necessary will vary with the particular melting vessels, attainable chamber pressures, refractory stability, i.e., on availability of oxygen from any source, it is believed that the typical excess required would be on the order of 25 to 150 ppm for VIM.

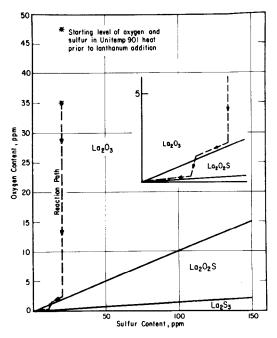


Fig. 3: POSTULATED REACTION PATH FOR DEOXIDATION-DESULFURIZATION REACTIONS IN UT901 LAN-THANUM BEARING MATERIAL. L'Postulated reactions adapted from theory proposed by LU and McLEAN (ref. 13)]

TABLE III: TYPICAL IMPURITY LEVELS (WEIGHT PERCENT) AND PERTINENT PHYSICAL PROPERTIES OF THE LANTHANUM MASTER ALLOY

C	P	S	0	Liquidus Temperature °F (°C)	Density Lb./in. <sup>3</sup> (g/cc)
0.02	0.001	0.002	0.089	1240 (671)	0.25 (6.97)

The concept presented in Fig. 3 was developed by Lu and McLean using solution thermodynamics with liquid iron as the solvent. Owing to the similarities between iron and nickel the diagram would not be expected to change substantially for nickel base alloys. There is not sufficient data to establish an exact diagram; however, this diagram provides a logical system for analyzing the chemical behavior of a rare earth addition to an iron or nickel melt.

## Chemical Analysis of Unitemp 901 With Controlled Lanthanum Addition

The chemical analysis of the lanthanum bearing Unitemp 901 heat is presented in Table IV, while pertinent oxygen, sulfur and lanthanum analyses are presented in Table V.

TABLE IV: CHEMICAL COMPOSITION (WEIGHT PERCENT) OF UNITEMP 901 HEAT

<u>C</u>	Mn	<u>Si</u>	<u>P</u>	<u>Cr</u>	Ni	Мо	Co	<u>A1</u>	Ti	<u>B</u>	Fe
. 03	.10	. 03	. 009	12 2	12 6	5 5	. 01	. 24	2.8	. 015	Ra1

TABLE V: LANTHANUM, OXYGEN AND SULFUR ANALYSES IN UNITEMP 901 HEAT AT VARIOUS MELT STAGES

Sample	S (ppm)	O (ppm)	La (ppm)
Dip from VIM bath Prior to La Add VIM Electrode VAR Ingot	20 1 to 5 1 to 5	35 5 to 10 5 to 10	 30 25 to 30

These oxygen, sulfur and lanthanum levels represent the total amounts of these elements present whether they exist in the form of compounds or in solid solution. It is believed that most of the oxygen has reacted with lanthanum to form  ${\rm La}_2{\rm O}_3$  and  ${\rm La}_2{\rm O}_2{\rm S}$  and the remainder has combined with aluminum as  ${\rm Al}_2{\rm O}_3$  such that the amount in solid solution is negligible.

### Mechanical Property Test Results

To determine the effect of both lower oxygen and sulfur and the microalloy addition of lanthanum, stress rupture and creep tests were conducted. Stress rupture and creep specimens were heat treated [2000°F (1093°C)/2 hrs./WQ +  $1450^{\circ}F$  (788°C)/4 hrs./AC + 1325°F (718°C)/24 hrs./AC]. Stress rupture tests were conducted at  $1200^{\circ}F$  (650°C)/90 ksi (620 MPa). These test results are compared to those of standard production Unitemp 901 tests in Table VI. The data on the lanthanum-bearing Unitemp 901 heat show both increased stress rupture life and ductility as compared with conventional material. However, one observation not apparent from this data is that the lanthanum-bearing heat generally exhibited the combination of both high rupture life and high ductility whereas test results for standard heats possessing high rupture life usually exhibited below average ductility and high ductility test values were accompanied by below average rupture life. Results of creep tests conducted at  $1200^{\circ}$ F  $(650^{\circ}$ C)/85 ksi (586 MPa) are presented in Table VII. The creep rates of both materials were the same up to 50 hours after which the lanthanum bearing heat exhibits a lower creep rate which is consistent with the longer stress rupture life observed.

Earlier work by Cremisio, et.al. (14), who studied the effect of cerium additions to Inconel 901 revealed improved transverse tensile ductility but no substantial improvement in stress rupture properties. On the other hand, similar improvements in stress rupture ductility of Inconel 718 have been reported by Muzyka and Whitney (15) with a neodymium addition and Kennedy (16) with an yttrium addition. Svistunova and Estulin studied the effects of rare earth additions on a nickel base superalloy and observed increased stress rupture strength and ductility (17).

With respect to hot workability, gleeble testing revealed that the lanthanum-bearing Unitemp 901 had slightly higher hot ductility over the temperature range  $1450^{\circ}F$  ( $790^{\circ}C$ ) to  $2050^{\circ}F$  ( $1120^{\circ}C$ ). This data is shown graphically in Fig. 4. Both heats exhibited excellent hot workability.

TABLE VI: STRESS RUPTURE<sup>a</sup> TEST RESULTS [1200°F/90 ksi (650°C/620 MPa)]
OF LANTHANUM BEARING AND STANDARD UNITEMP 901

	Life (Hours)		Elongation (%)		Red. of Area	
	Range	Avg.	Range	Avg.	Range	Avg.
La Treated UT 901 <sup>b</sup>	74.0-162.6	115.5	13.2-21.7	17.3	18.7-33.4	24.7
Standard UT 901c	31.3-198.8	87.1	4.2-19.6	10.2	4.2-22.8	12.8

- a) Specimen design contained both smooth and notched sections;
- Average of six tests; c) Data determined by surveying the most recent 25 production heats of UT 901, representing over 100 test values in which normal sulfur levels average 30 ppm.

TABLE VII: CREEP TEST RESULTS OF LANTHANUM BEARING AND STANDARD UNITEMP 901 CONDUCTED AT 1200°F (650°C)/85 ksi (586 MPa)

Material*	Percent	Creep at	Indicated	Hours
	50	100	150	
La Bearing UT 901	.035	.055	.085	
Standard UT 901	.035	.150	.325	
*The grain size of both	specimens v	was ASTM 1	L-3.	

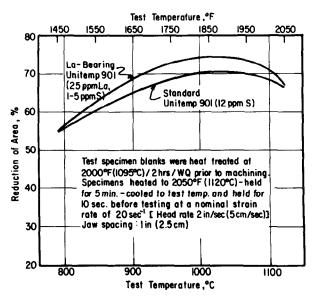


Fig. 4: GLEEBLE DUCTILITY FOR La-BEARING AND STAN-DARD UNITEMP 901 TESTED ON COOLING FROM 2050°F (1120°C). NOTE THE La-BEARING HEAT DISPLAYS SLIGHTLY HIGHER DUCTILITY. I Specimens represent transverse orientation on a nominal 10 inch (25cm) square billet.]

# Microscopy

Longitudinal and transverse micros of the lanthanum bearing Unitemp 901 were examined in the as-worked and heat-treated conditions. Special care was necessary to prevent the rare earth inclusions from being pulled out or dissolved in water during preparation. Bright-field and polarized-light optical microscopy, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS) were utilized to locate and identify rare earth compounds.

Wilson and Wells (18) have shown that in HSLA steels some rare earth oxy-sulfides exhibit specific colors when examined with polarized light. This characteristic was initially used to scan the micros at low ( $\sim$ 100X) and high (>800X) magnifications. A few "pin-point" indications were found only at the higher magnification. These inclusions were observed under polarized light and bright field illumination and then encircled for examination with the SEM and EDXS. All of the inclusions observed were yellowish-orange, randomly dispersed, globular and less than 5  $\mu$ m in diameter. Wilson and Wells have indicated that the orange color is typical of rare earth oxysulfide (RE<sub>2</sub>0<sub>2</sub>S) and the size is of the same order as they reported. EDXS confirmed the presence of lanthanum and sulfur in proportions which would indicate La<sub>2</sub>0<sub>2</sub>S. X-ray distribution photographs are shown in Fig. 5 for one such typical inclusion.

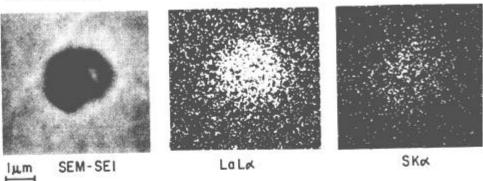


Fig.5: SEM SECONDARY ELECTRON IMAGE AND X-RAY DIS-TRIBUTION PHOTOGRAPHS OF A TYPICAL LANTHANUM OXYSULFIDE OBSERVED IN THIS STUDY.

# Further Advantages of Rare Earth Additions

Currently, three domestic high temperature alloys, Unitemp 188 (nominal .04 La), Air Resist 215 (nominal .1 Y) and Hastelloy S (nominal .02 La) contain a rare earth addition. In these alloys the rare earth has been added strictly for oxidation resistance. The rare earth addition and retention in these alloys are considerably higher than what are advocated in this paper. It is proposed that rare earth elements have potential to improve properties other than oxidation resistance.

Rare earth elements have the ability to neutralize certain deleterious trace elements. Arsenic, tin and antimony cannot be effectively removed by VIM (19) but these elements form high melting point compounds with rare earth elements and can be thereby neutralized as discussed by Luyckx (20). Lead, bismuth and thallium also form high melting point compounds with rare earth elements but these highly volatile elements are readily removed by vacuum melting. Selenium, of course, will react with rare earth elements in a manner similar to sulfur. In contrast, calcium and magnesium do not form intermetallic compounds with these low melting point elements (Pb, Bi, Sb, As, Sn, T1). Therefore, rare earth elements may be used to counteract the harmful effects of tramp elements should these elements reach unacceptable levels. It is conceivable that the time may come when a rare earth addition as a weighted multiple of oxygen, sulfur and certain tramp elements will be essential in superalloy melting practices.

Reducing sulfur to levels below 5 ppm may permit higher levels of strengthening elements in the future while still maintaining adequate stress rupture notch-ductility. To boost transverse tensile ductility and impact resistance in superalloys the trend is to lower the carbon content, which unfortunately fosters higher oxygen levels that oppose sulfur removal. Stress rupture properties can deteriorate as carbon is reduced. The judicious use of a rare earth addition may permit employment of lower carbon levels without simultaneous degradation of stress rupture properties.

## RECOMMENDATIONS AND CONCLUSIONS

#### Recommended Practice

Others who have desulfurized with rare earth additions have reduced sulfur from levels greater than 100 ppm to levels in the 10 to 50 ppm range. The risk of retaining excessive amounts of the rare earth is great under such conditions because rather high levels (>1000 ppm) of the rare earth must be added. When too much rare earth is retained, forgeability, cleanliness, mechanical properties, and weldability may be adversely affected simultaneously or individually. Consequently, rare earth retained in excess of that required to combine with remaining amounts of oxygen, sulfur and low melting impurities will combine with iron and nickel to form undesirable phases. Consequently, it is proposed that a rare earth addition be employed under strictly controlled conditions and retained at low levels. Such was the case in this study, with the result that sulfur was lowered with a beneficial effect on stress rupture ductility, creep rate and hot workability.

Therefore, the recommendation is to employ a small rare earth addition (<1000 ppm) for ultra-desulfurization when the initial oxygen content of the bath is <50 ppm,whereby sulfur is reduced from the 10 to 50 ppm range to <5 ppm. Under such conditions the rare earth retention should be <200 ppm and preferably <50 ppm. In addition, to properly control the rare earth addition, the following vacuum melting practices should be adhered to: a) a magnesia-based crucible refractory system is preferred owing to its high thermodynamic stability; b) the melt and mold chamber pressures should be <100 microns; c) the teeming refractory should be thoroughly dried and stable; and d) the rare earth charge material should be chemically analyzed to insure that it does not contain excessive amounts of impurities.

# Conclusions

It can be concluded from this study that:

- 1) A small rare earth addition can reduce sulfur from 20 ppm to < 5 ppm.
- Stress rupture ductility is enhanced and limited creep data indicated a lower creep rate by ultra-desulfurization via the rare earth addition.
- 3) No concurrent manufacturing difficulties were found.
- 4) Extremely fine ( $<5\,\mu\text{m}$ ), globular La $_20_2\text{S}$  particles were detected. However, these particles were both exceedingly sparse and randomly distributed in the matrix. The presence of La $_20_2\text{S}$  is consistent with the current information on rare earth compound formation.
- 5) A rare earth addition for control of sulfur and possibly other deleterious tramp elements should be made available to superalloy metallurgists.

#### ACKNOWLEDGEMENTS

The authors wish to express their appreciation to the management of Universal-Cyclops for permission to publish this work. Special thanks are extended to A. J. Mirarchi, G. Krishnamurti and M. Somerville for their technical consultation. Also the work of D.: J. Reitmeyer, J. L. Milavec, J. T. Manant and J. Shepos in testing and preparation of the paper are acknowledged. Finally, we express our gratitude to R. G. Wells for his helpful suggestions concerning metallographic preparation.

#### REFERENCES

- P. D. Merica and R. G. Waltneburg, U. S. Nat. Bur. Std. Tech. Paper No. 281, April 2, 1925.
- 2) A. M. Hall, AIME Tech. Pub. No. 1584, Feb. 1943, pp. 1-7.
- 3) E. F. Khimishin, <u>High Temperature Steels and Alloys</u>, Translated Book FTD-HC-23-391-70, Clearinghouse, Dept. of Commerce, p. 403.
- 4) G. R. Pease, Weld. J., July 1957, pp. 330-S to 334-S.
- 5) Effects of Minor Elements on the Weldability of High Nickel Alloys, Proceedings of Symposium Sponsored by the Welding Research Council, 1969.
- J. E. Doherty, A. F. Giamei and B. H. Kear, <u>Can. Metall. Quart.</u>, Vol. 13, No. 1, 1974, pp. 229-36.
- K. A. Gschneidner, N. Kippenhan, and O. D. McMasters, <u>Thermochemistry of the Rare Earths</u>, Rare Earth Information Center, Iowa State University, <u>Ames</u>, Iowa, 1973.
- 8) K. A. Gschneidner and N. Kippenhan, <u>Thermochemistry of the Rare Earth Carbides</u>, <u>Nitrides</u>, <u>and Sulfides for Steelmaking</u>, Rare Earth Information Center, Iowa State University, Ames, Iowa, 1972.
- 9) K. A. Gschneidner, Jr., "Alloy Theory of the Influence of Small Additions of Rare Earth Metals on the Properties of Common Metals", Ames Laboratory, ERDA, Iowa State University, Ames, Iowa, 1976.
- 10) W. G. Wilson, D. A. R. Kay and A. Vahed, J. Met., May 1974, pp. 14-23.
- G. V. Samsonov, <u>High Temperature Compounds of Rare Earth Metals With Non-Metals</u>, 1965, New York Consultants Bureau, pp. 211-80.
- 12) W. V. Venal and G. H. Geiger, Metall. Trans., Nov. 1973, pp. 2567-73.
- W. K. Lu and A. McLean, <u>Ironmaking and Steelmaking (Quart.</u>), No. 4, 1974, pp. 228-33.
- 14) R. S. Cremisio, J. G. Cannon and C. F. Elliott, Proceedings of the Third International Symposium on Electroslag and Other Special Melting Technology, Part III, 1971, pp. 1-30.
- 15) D. R. Muzyka and C. R. Whitney, U. S. Patent 3,575,734, April 20, 1971.
- 16) R. L. Kennedy, U. S. Patent 3,907,552, Sept. 23, 1975.
- 17) T. V. Svistunova and G. V. Estulin, Stal, Sept. 1963, pp. 725-28.
- 18) W. G. Wilson and R. G. Wells, Met. Progr., Dec. 1973, pp. 75-77.
- 19) R. E. Schwer, M. J. Gray and S. F. Morykwas, Proceedings of the Fifth International Symposium on Electroslag and Other Special Melting Technologies, Part II, 1974, pp. 689-706.
- 20) L. Luyckx, "Mechanisms of Rare Earth Action on Steel Structures", 1975 Materials Science Symposium, Oct. 1975, Cincinnati.