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PHASES IN LANTHANUM-NICKEL-ALUMINUM ALLOYS (U)

by

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SAVANNAH RIVER LABORATORY

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May 26, 1987

MEMORANDUM

TO: T. L. CAPELETTI, 773-A

FROM: W. C. MOSLEY, 773-A WC Mosley

PHASES IN LANTHANUM-NICKEL-ALUMINUM ALLOYS

INTRODUCTION

Lanthanum-nickel-aluminum (LANA) alloys will be used to pump, store and separate hydrogen isotopes in the Replacement Tritium Facility (RTF). The aluminum content (y) of the primary $LaNi_{5-y}$ phase is controlled to produce the desired pressure-temperature behavior for adsorption and desorption of hydrogen. However, secondary phases cause decreased capacity and some may cause undesirable retention of tritium. Twenty-three alloys purchased from Ergenics, Inc. for development of RTF processes have been characterized by scanning electron microscopy (SEM) and by electron microprobe analysis (EMPA) to determine the distributions and compositions of constituent phases. This memorandum reports the results of tnese characterization studies. Knowledge of the structural characteristics of these alloys is a useful first step in selecting materials for specific process development tests and in interpreting results of those tests. Once this information is coupled with data on hydrogen plateau pressures, retention and capacity, secondary phase limits for RTF alloys can be specified.

DERIVATIVE CLASSIFIER

SUMMARY

LANA alloys used in development of RTF processes consist of multiple phases. Quantities of some of the secondary phases are controlled by the lanthanum and aluminum contents of the bulk alloy. Deficiency in lanthanum causes formation of Ni_3Al or NiAl depending on the aluminum content. Excess lanthanum causes formation of La_2Ni_7 in $LaNi_5$ and LaNi and La_2Ni_3Al in LANA alloys. $LaNi_2Al$ forms when the aluminum content exceeds the solid solubility limit of the primary phase. Impurities in the lanthanum feed used in LANA alloy preparation are suspected of producing two types of lanthanum-rich inclusions. The influences of secondary phases on LANA alloy behavior during absorption and desorption of hydrogen isotopes are being determined. It is important that alloys used in these absorption/desorption studies be identified by batch number.

DISCUSSION

Phase Distributions

Polished pieces of LANA alloys were examined with the ISI DS130 scanning electron microscope which is equipped with a backscattered electron detector. Images recorded with backscattered electrons (BSE) show atomic number contrast. Phases that have higher (lower) average atomic numbers than the primary phase appear brighter (darker) in the images. This enhanced contrast of BSE images provides better resolution of secondary phases in LANA alloys than can be achieved by secondary electron detection normally used in an SEM or by optical metallography of polished or etched specimens. BSE images of the twenty-three LANA alloys recorded at 200X magnification are shown in Figure 1.

Volume percentages (v/o) of the secondary phases in the LANA alloys were estimated by superimposing a 10 x 10 grid on 50X-500X BSE images and counting the number of grid intersections that coincided with each secondary phase. The estimated volume percentage is the average of determinations made at about twenty different locations. Results for the twenty-three LANA alloys are given in Table 1.

Phase Identification

Phases in the LANA alloys were identified by their chemical compositions as determined by analyses of the characteristic x-rays generated by the electron beams in the SEM and EMPA (Tracor Northern modified ARL Scanning Electron Microprobe Quantometer). The most accurate analyses were achieved with EMPA by energy dispersive spectroscopy (EDS) of x-rays from the samples and standards (LaB_6, Ni, Al, and Si) using ZAF corrections for atomic number (Z), absorption (A), and fluorescence (F). Standardless EDS analyses performed with the SEM yielded aluminum concentrations that were low by a factor of two. Also, a faulty light-element detector on the EMPA prevented accurate analyses using wavelength dispersive spectroscopy (WDS) of the characteristic x-rays.

Figure 2 is a lanthanum-nickel-aluminum ternary diagram showing the compositions of phases in the LANA alloys as determined by EMPA. Silicon, sometimes as high as 2 atomic percent (a/o), was also detected in the alloy phases. Ni_3Al, NiAl, La_2Ni_7, and LaNi were confirmed by x-ray diffractometry when these phases were present at greater than 1 v/o.

Interpretation

The primary $La_xNi_{5-y}Al_y$ phase exists for a narrow range of lanthanum content of x = 1.00 ±0.004. Lanthanum content of the bulk alloy composition outside of this narrow range causes formation of secondary phases. Deficiency in lanthanum causes formation of nickel-aluminum binary phases which appear darker than the primary phase in BSE images (Figure 1). Either Ni_3Al or NiAl forms depending on the aluminum content of the alloy. Ni_3Al was detected in $LaNi_{4.7}Al_{0.3}$ alloy batches 1112, 87075, and 88543 and $LaNi_{4.5}Al_{0.5}$ batch 82099. NiAl was detected in $LaNi_{4.5}Al_{0.5}$ batch 82099 and in lanthanum-deficient alloys for Y = 0.75 and 0.85. The nickel-aluminum inclusions were distributed in the primary $LaNi_{5-y}Al_y$ phase as an interdendritic eutectic that formed during solidification of the molten alloy. These inclusions became somewhat spheroidized by the subsequent heat treatment at about 1100°C used to homogenize the alloy.

A small lanthanum excess in the bulk alloy causes formation of binary lanthanum-nickel phases. La_2Ni_7 was present as an interdendritic phase and isolated islands in $LaNi_5$ alloy batch 87659. LaNi along with the primary $LaNi_{5-y}Al_y$ phase formed an interdendritic eutectic in $LaNi_{4.25}Al_{0.75}$ alloy batch 1294 and $La_{1.09}Ni_{4.25}Al_{0.75}$ batch 1303. These observations indicate that addition of aluminum to the alloy may prevent formation of La_2Ni_7 in favor of LaNi. A larger lanthanum excess in $La_{1.18}Ni_{4.25}Al_{0.75}$ alloy batch 1302 caused La_2Ni_3Al to form along with LaNi in the interdendritic eutectic.

A series of $La_xNi_{4.25}Al_{0.75}$ alloys with x = 0.82, 0.91, 1.00, 1.08, and 1.19 revealed the effect of lanthanum content on volume percentages of secondary phase. BSE images of these alloys are shown in Figure 1 m through q. The volume percentages of NiAl, LaNi, and La_2Ni_3Al as functions of the lanthanum content (x) are depicted graphically in Figure 3.

In LANA alloys containing high concentrations of aluminum near the limit of solid solubility in the $LaNi_{5-y}Al_y$ primary phase, complex mixtures of secondary phases occurred in interdendritic regions. Dark NiAl inclusions were present along with $LaNi_2Al$, La_2Ni_3Al, and LaNi which appear with increasing brightness levels relative to the $LaNi_{5-y}Al_y$ primary phase in BSE images of $LaNi_4Al$ alloy batches 87656 and 89174 (Figure 1 v and w). $LaNi_2Al$ was the most abundant secondary phase in the interdendritic regions. In $LaNi_4Al$ alloy batch 89174, NiAl was present as large spheroids up to ~100 µm in diameter. The "Chinese script" morphology of the lanthanum-bearing secondary phases suggest that they solidify at higher temperatures and are changed less by homogenization heat treatment than the rounded Ni_3AL and NiAl inclusions. Such behavior explains the presence of small quantities of $LaNi_2Al$ and La_2Ni_3Al in $LaNi_{4.15}Al_{0.85}$ alloy batches 1252 and 1253.

Two types of inclusions containing very high concentrations of lanthanum have been detected in the LANA alloys. One type appears as bright rounded inclusions less than 10 µm in diameter that are sparsely distributed in the $LaNi_{5-y}Al_y$ primary phase (Figure 1e) or associated with the Ni_3Al or NiAl inclusions (Figure 1r). The high brightness suggests that these La-rich inclusions are metallic. After sample preparation by grinding and polishing, these La-rich inclusions react slowly with the atmosphere to crack the $LaNi_{5-y}Al_y$ primary phase and exude material above the polished specimen surface as a function of exposure time. A second type of La-rich inclusion has a needle-like morphology and appears darker than the $LaNi_{5-y}Al_y$ primary phase in BSE images (Figure 1 v and w). The dark intensity suggests that the needles are nonmetallic. Material in the needles extends above the polished surface of freshly prepared specimens. This behavior suggests that the La-rich material in the needles is highly reactive on exposure to the atmosphere. It is thought that both types of La-rich inclusions are caused by impurities in the lanthanum feed used in LANA alloy production.

OTHER STUDIES

Several other characterization studies of LANA alloys are in progress and will be the subjects of subsequent memoranda:

1) X-ray diffractrometry of LANA alloys.

2) Hydrogen determinations on LANA alloys cycled in hydrogen.

3) Characterization of LANA alloys exposed to tritium.

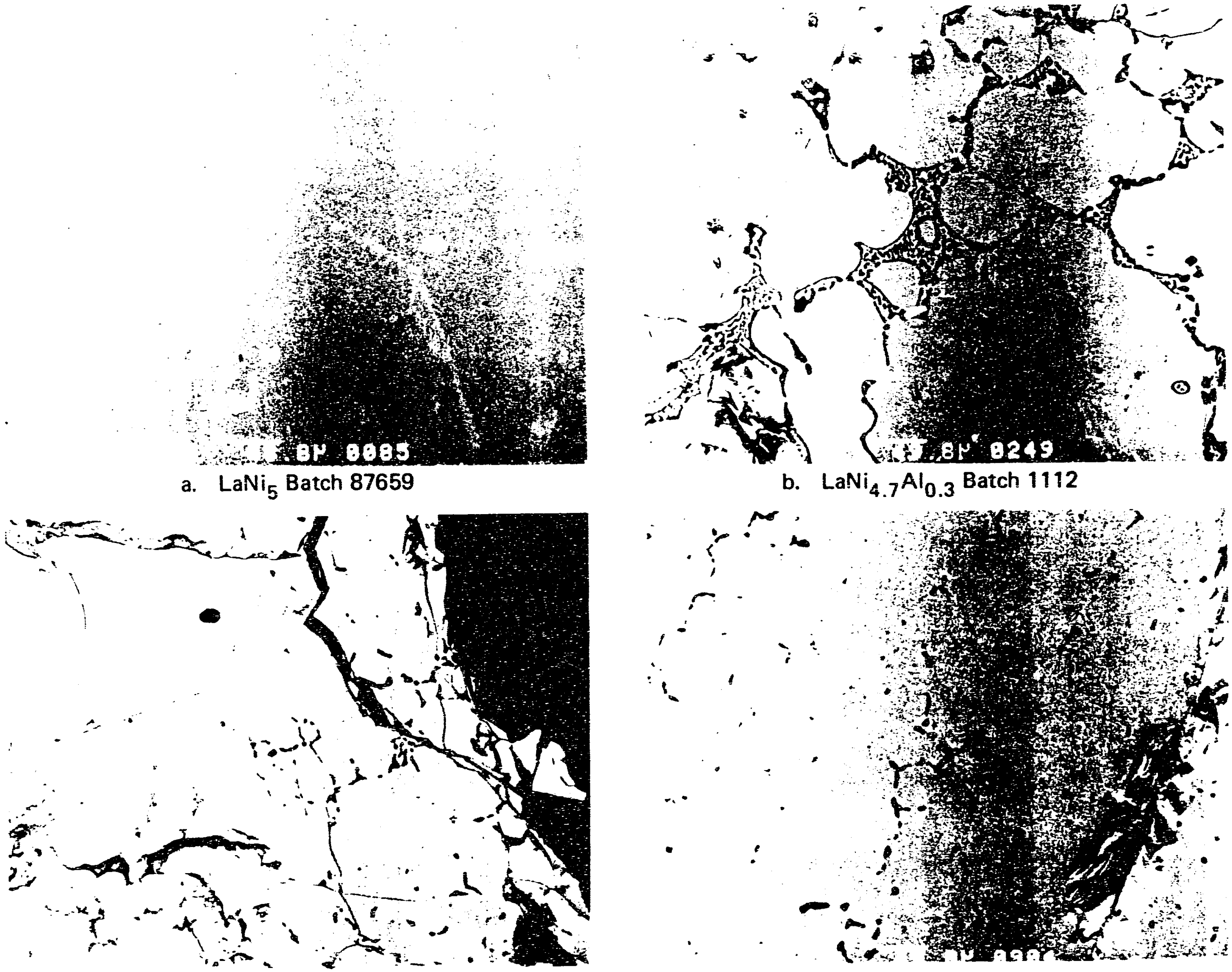
The early stages of decrepitation of LANA alloys has been discussed in DPST-87-446.

TABLE 1

VOLUME PERCENTAGES OF SECONDARY PHASES in La-Ni-Al ALLOYS

Alloy	Batch	Secondary Phases							
		Ni_3Al	NiAl	La_2Ni_7	LaNi	La_2Ni_3Al	$LaNi_2Al$	La-Rich Inclusion	La-Rich Needle
$LaNi_5$	87659	0	0	10	0	0	0	0	0
$LaNi_{4.7}Al_{0.3}$	1112	8	0	0	0	0	0	<<1	0
	87075	3	0	0	0	0	0	<1	0
	88543	4	0	0	0	0	0	<<1	0
$LaNi_{4.5}Al_{0.5}$	1126	0	0	0	0	0	0	<1	0
	82099	4	<<1	0	0	0	0	<<1	0
$LaNi_{4.25}Al_{0.75}$	1158	0	~1	0	0	0	0	<<1	0
	1286	0	19	0	0	0	0	<<1	0
	1287	0	9	0	0	0	0	<<1	0
	1288	0	~1	0	0	0	0	<<1	0
	1294	0	0	0	3	0	0	0	<<1
	1295	0	10	0	0	0	0	<<1	0
$La_{1.18}Ni_{4.25}Al_{0.75}$	1302	0	0	0	9	2	0	0	0
$La_{1.09}Ni_{4.25}Al_{0.75}$	1303	0	0	0	5	0	0	<<1	0
$La_{1.00}Ni_{4.25}Al_{0.75}$	1304	0	<<1	0	0	0	0	<<1	0
$La_{0.91}Ni_{4.25}Al_{0.75}$	1305	0	4	0	0	0	0	<<1	0
$La_{0.82}Ni_{4.25}Al_{0.75}$	1306	0	12	0	0	0	0	<<1	0
$LaNi_{4.15}Al_{0.85}$	1138	0	<1	0	0	0	0	<<1	0
	1251	0	~1	0	0	0	0	<<1	0
	1252	0	<<1	0	0	<<1	<<1	<<1	<<1
	1253	0	<<1	0	0	<<1	<<1	<<1	<<1
$LaNi_4Al$	87656	0	<<1	0	<1	2	6	<<1	<1
	89174	0	8	0	~1	3	12	<<1	~1

~ = approximately equal to
< = less than
<< = much less than



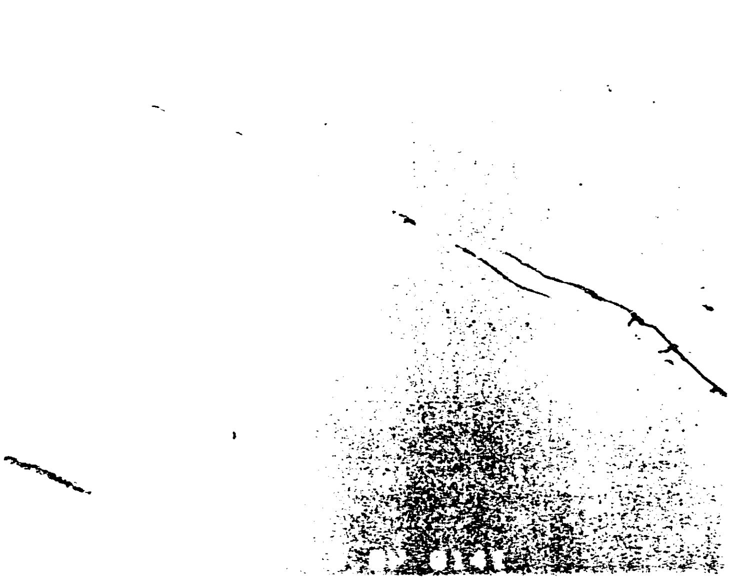
a. $LaNi_5$ Batch 87659

b. $LaNi_{4.7}Al_{0.3}$ Batch 1112

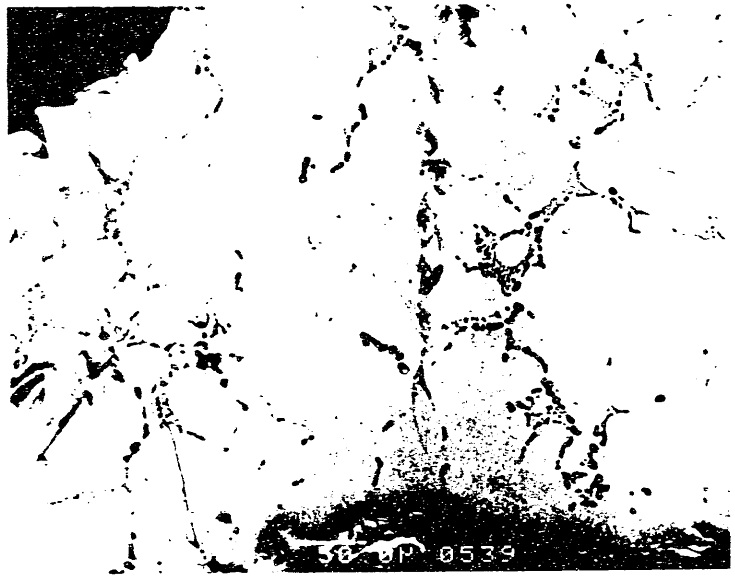
c. $LaNi_{4.7}Al_{0.3}$ Batch 87075

d. $LaNi_{4.7}Al_{0.3}$ Batch 88543

FIGURE 1: Microstructures of La-Ni-Al Alloys



e. $LaNi_{4.5}Al_{0.5}$ Batch 1126

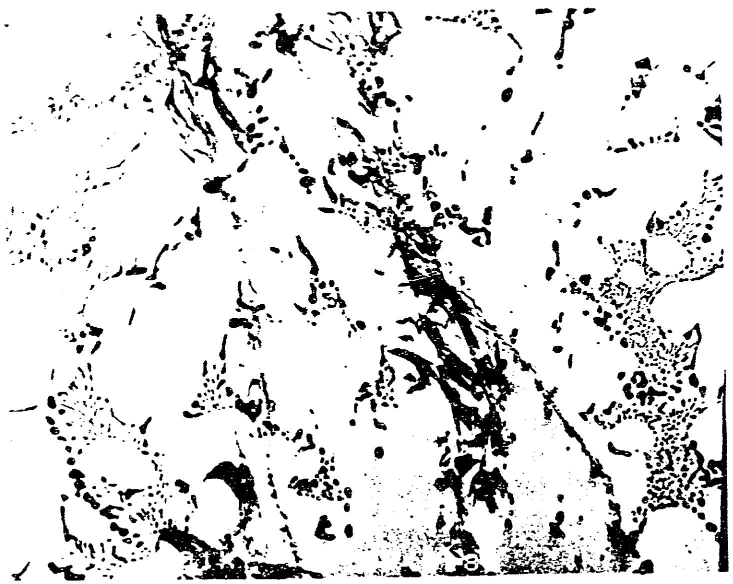


f. $LaNi_{4.5}Al_{0.5}$ Batch 82099

g. $LaNi_{4.5}Al_{0.5}$ Batch 1158

h. $LaNi_{4.25}Al_{0.75}$ Batch 1286

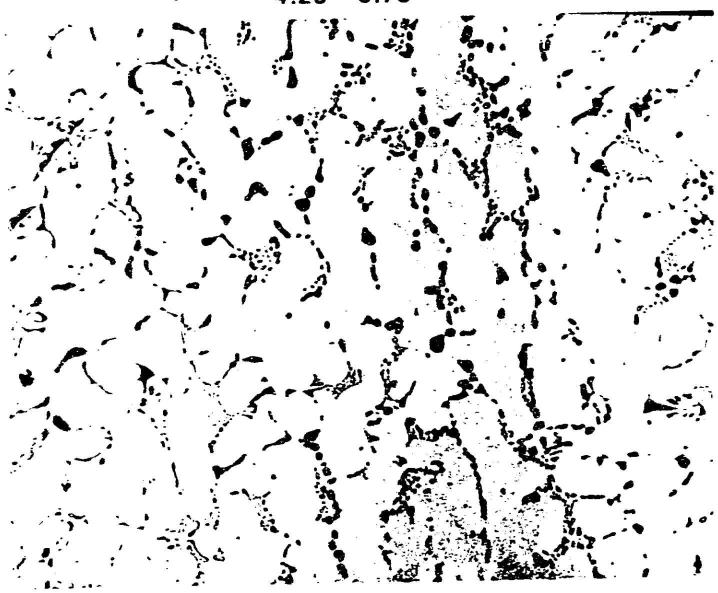
FIGURE 1 (Contd): Microstructures of La-Ni-Al Alloys



i. $LaNi_{4.25}Al_{0.75}$ Batch 1287

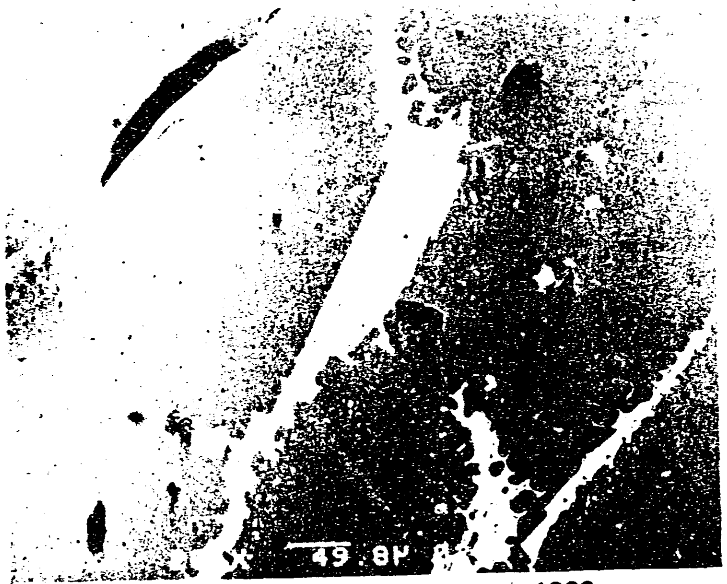
j. $LaNi_{4.25}Al_{0.75}$ Batch 1288

k. $LaNi_{4.25}Al_{0.75}$ Batch 1294



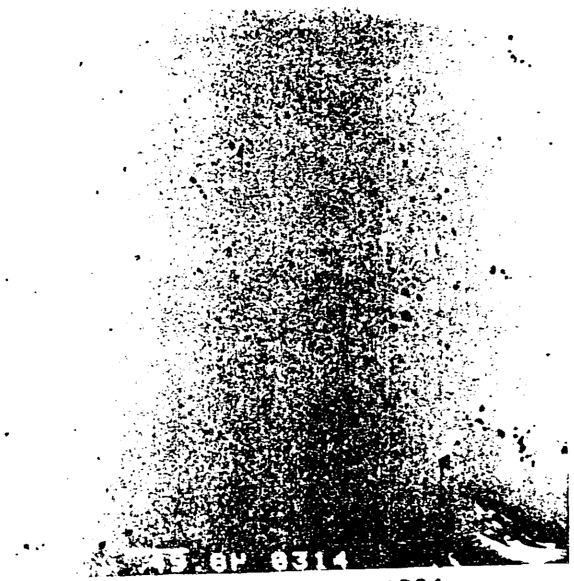
l. $LaNi_{4.25}Al_{0.75}$ Batch 1295

FIGURE 1 (Contd): Microstructures of La-Ni-Al Alloys

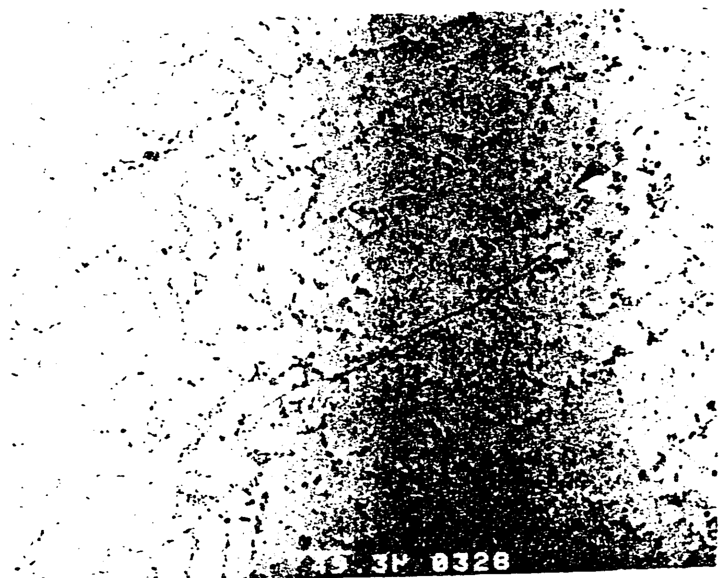


m. $La_{1.18}Ni_{4.25}Al_{0.75}$ Batch 1302

n. $La_{1.09}Ni_{4.25}Al_{0.75}$ Batch 1303

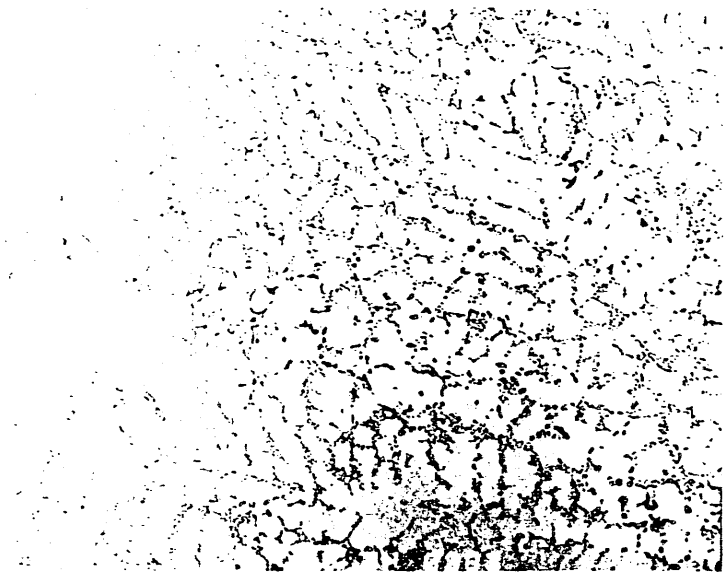


o. $La_{1.00}Ni_{4.25}Al_{0.75}$ Batch 1304



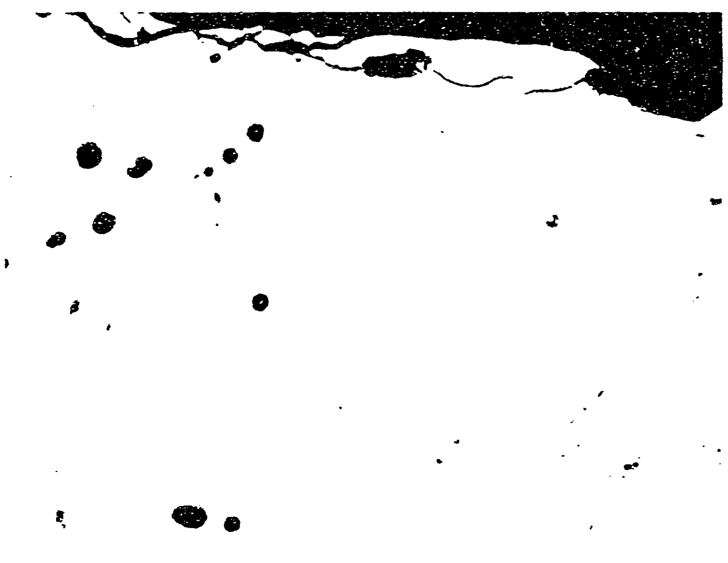
p. $La_{0.91}Ni_{4.25}Al_{0.75}$ Batch 1305

FIGURE 1 (Contd): Microstructures of La-Ni-Al Alloys



q. $La_{0.82}Ni_{4.25}Al_{0.75}$ Batch 1306

r. $LaNi_{4.15}Al_{0.85}$ Batch 1138



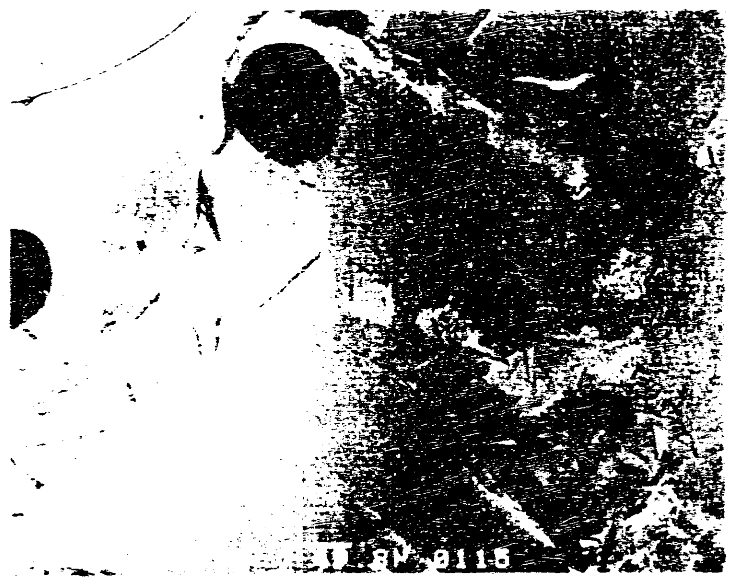
s. $LaNi_{4.15}Al_{0.85}$ Batch 1251

t. $LaNi_{4.15}Al_{0.75}$ Batch 1252

FIGURE 1 (Contd): Microstructures of La-Ni-Al Alloys

u. $LaNi_{4.15}Al_{0.75}$ Batch 1253

v. $LaNi_4Al$ Batch 87656

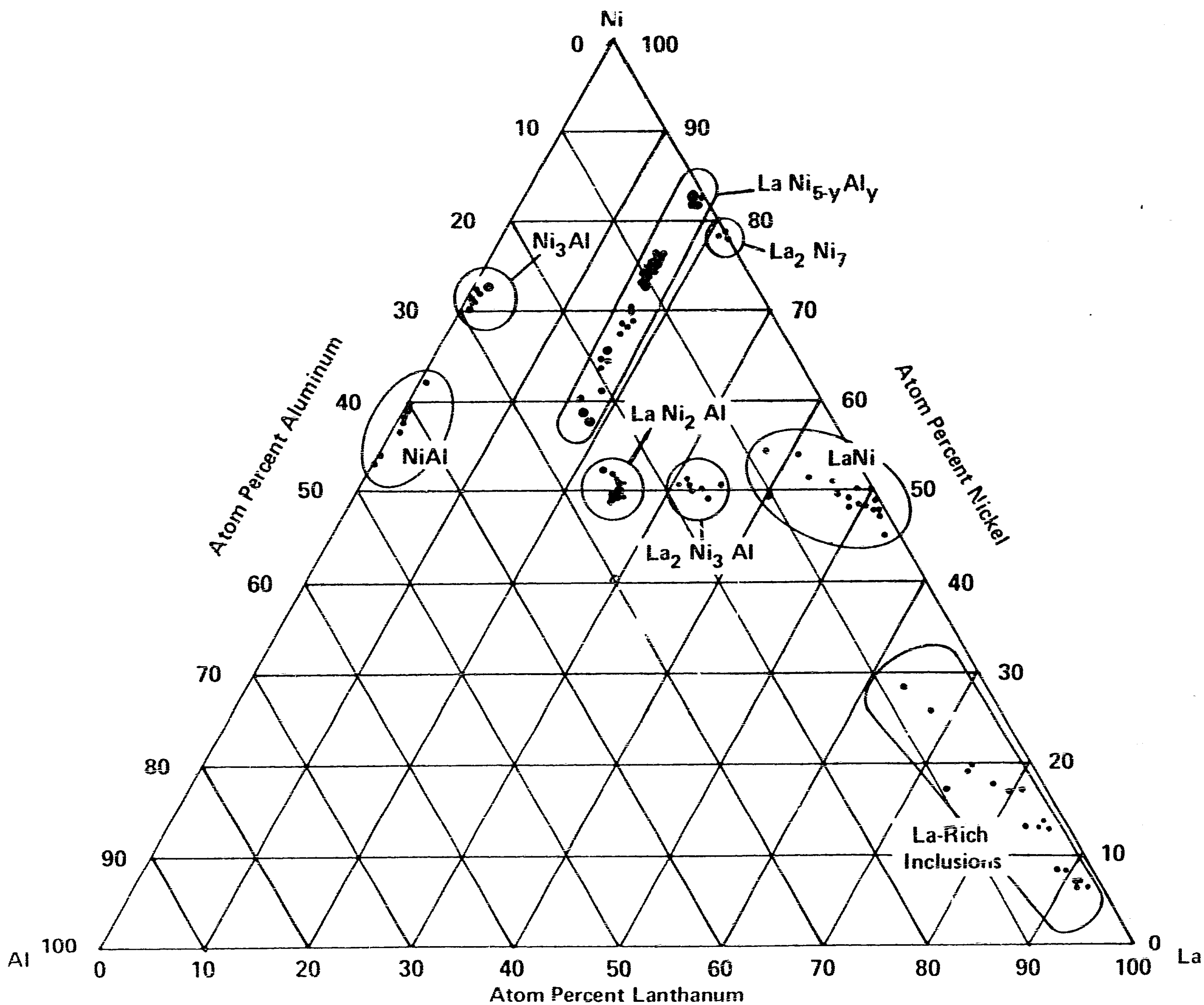


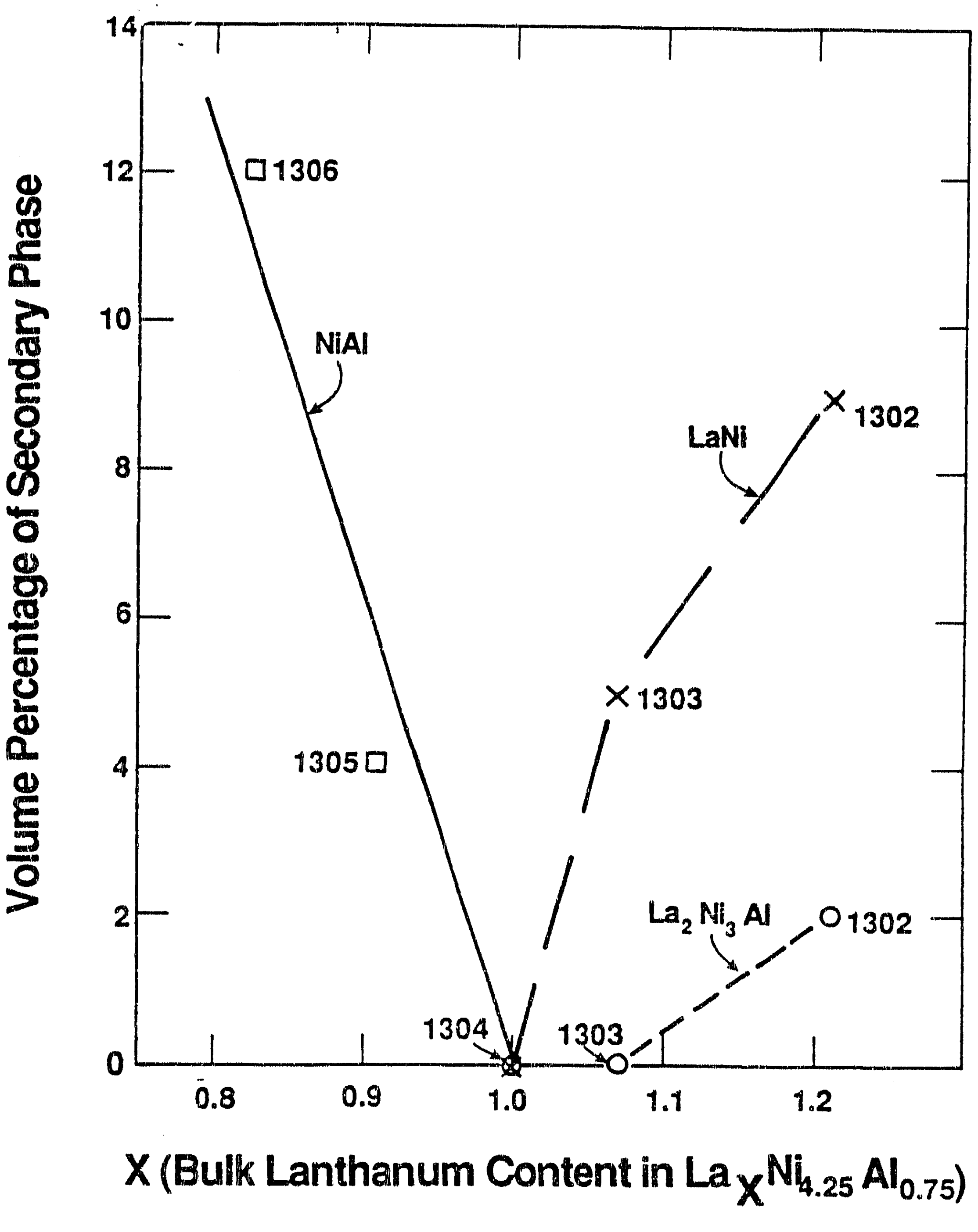
w. $LaNi_4Al$ Batch 89174

FIGURE 1 (Contd): **Microstructures of La-Ni-Al Alloys**

FIGURE 2

Phases in La-Ni-Al Alloys by SEMQ-EDS-ZAF





14
12
10
8
6
4
2
0
Volume Percentage of Secondary Phase
1306
NiAl
LaNi
1302
1303
1305
$La_2 Ni_3 Al$
1302
1304
1303
0.8
0.9
1.0
1.1
1.2
X (Bulk Lanthanum Content in $La_X Ni_{4.25} Al_{0.75}$)

OSR 3-4A-W (Rev 1-89)

WESTINGHOUSE SAVANNAH RIVER COMPANY

INTER-OFFICE MEMORANDUM

April 27, 1992 ASD-MIS-920031

TO: All MIS Employees

SUBJECT: PROCESS ACTION PLAN

In the month since our All Hands Meeting, I have seen significant efforts to implement our action plans. Significant efforts are underway in each of the process areas, but we need to maintain a strong personal commitment to these goals—not only because they will help our customers, but because they also will help us.

As just one measure of how we are helping ourselves, I'd like to tell you of a recent development involving MIS and the Internal Audit Department (IAD). As a consequence of the Consolidated Business Systems Review—a concentrated DOE-HQ assessment of WSRC administrative systems, one area that was to be reviewed was printing and publications. When I met with IAD, I gave them an overview of our improvement program, a copy of our report, and a copy of my All Hands Meeting presentation. The result was that IAD determined they would not do our audit, but monitor our success in implementing our action plan. The difference is one of us taking charge of our destiny, or having others set the path for us.

Yet, creating the plan and implementing the plan are not the same. That is why I am reiterating some of our major goals:

1. Each of us has to make a personal commitment. Personnel assigned actions need to complete them thoroughly and in a timely manner. This includes working together, keeping co-workers and supervisors informed and involved, and sharing ideas so that our actions benefit all of MIS.

2. Each of us has to follow the sequence established. Actions called out in the plan are arranged sequentially, with one often leading naturally into the next. We need to be keeping up, reviewing proposed resolutions with the appropriate supervisors and affected personnel, ensuring the solution is accurate and thorough, and then obtaining verification of completion from the appropriate Process Team Leader.

3. Each of us has to want to make things happen. We each have a stake in this venture. You should be contacting people who are working on areas of interest to you, sharing your experience, and bringing your expertise and abilities to our mutual benefit. We now have new avenues to make sure our ideas and suggestions are heard and considered, including opportunity to follow the evolution of our programs, personal involvement, and the Verification of Excellence forms.

4. Each of us has to have pride in our work and reorganization. We need to continue to look for ways to improve our products and operations and to make our customers aware of our talents and abilities.

I am highly encouraged by what I have seen so far, and am gratified by the regular flow of complimentary letters I have seen our people receiving from our customers. We have made a good start, but we must recognize the vision is still in front of us. Let's keep up the solid effort.

Dan

D. L. Plung, Manager
Management Information Services

DLP:ss

DATE
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