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AN ELECTRON MICROPROBE DETERMINATION OF MICROSCOPIC ELEMENTAL HOMOGENEITY OF HOT-CROSS-ROLLED AND HIGH-ENERGY-RATE FORGED 21Cr-6Ni-9Mn STEEL

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DISCLAIMER

An Electron Microprobe Determination of Microscopic Elemental Homogeneity of Hot-Cross-Rolled and High-Energy-Rate-Forged 21Cr-6Ni-9Mn Steel

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ABSTRACT

Electron microprobe analysis shows that iron, manganese, and nickel are inhomogeneously distributed in hot-cross-rolled plate and high-energy-rate forgings of 21Cr-6Ni-9Mn steel but that chromium is homogeneously distributed. Increases in iron content correlate with decreases in manganese and nickel. Rolling and forging flow lines occur in regions with high iron and low manganese and nickel. High-energy-rate forging increases inhomogeneity. Inhomogeneities are suspected to exist in the original ingot, where they are given directionality by rolling and are enhanced by high-energy-rate forging.

INTRODUCTION

Austenitic 21Cr-6Ni-9Mn stainless steel is being investigated for high strength applications. High-energy-rate forging (HERF) is used to fabricate complex shapes from hot-cross-rolled plate (HCRP). Metallographic examinations have revealed flow lines in both HCRP and HERF. This paper presents the results of electron microprobe analyses to determine the nature of these flow lines.

EXPERIMENTAL

21-6-9 Stainless Steel Specimens

HCRP was furnished by the Rocky Flats Plant of Rockwell International; this steel was forged by the Precision Forge Company. Table 1 gives the nominal composition of 21-6-9 stainless steel. Figure 1 shows the HCRP and the shapes produced by HERF. Fabrication parameters are summarized in Table 2.

An annealed sample of 21-6-9 stainless steel was used to establish the precision of the electron microprobe analyses.

Methods of Analysis

Two HCRP specimens were prepared for metallographic examination by grinding, polishing, and etching to reveal microstructure. HCRP-A was oriented to display the cross section of the plate. HCRP-B was oriented to display a surface parallel to the roll plane. HERF specimens after forging with Dies 1, 5, and 7 were prepared the same as the HCRP specimens and were oriented to display cross sections of the forgings.

Areas to be analyzed on the HCRP and HERF specimens were marked with indentations on a hardness tester and photographed. Specimens were then repolished to produce smooth surfaces required for electron microprobe analyses. The areas to be analyzed could then be relocated with respect to indentations shown in the reference photographs.

An Applied Research Laboratories Scanning Electron Microprobe Quantometer was used for the electron microprobe analyses. Equally spaced points along lines through the features of interest were automatically analyzed. These lines of analysis points were chosen to be either perpendicular to or parallel to flow lines. Each point was analyzed for Cr, Mn, Fe, Ni, P, S, Al, and Si according to the scheme given in Table 3. X-ray intensities of the four major elements were measured with the same spectrometer to maintain the same takeoff angle (about 52.5°) and, thereby, to minimize effects of surface tilt and roughness. Reference standards were National Bureau of Standards standard reference materials, pure metals, and well-characterized simple compounds. X-ray intensities were converted to elemental concentrations by correcting for atomic number, adsorption, and fluorescence determined with an online version of Magic IV (1). Each analysis required about ten minutes. Therefore, data for each point were normalized to compensate for drift in the electron beam.

Analyzed points on the polished specimens were marked by a spot of carbon formed by reaction of the electron beam with oil vapor from the diffusion pump. Each specimen was photographed after analysis to correlate these spots with the indentations. Specimens were again etched to reveal the microstructure, and photographs were used to correlate the microstructural features with the indentations and the analysis spots.

RESULTS

Flow Line Patterns

Flow lines were observed in HCRP-A (cross section) but not HCRP-B (parallel to roll plane). In the HERF specimens, the flow lines generally followed the surface contours of the forgings.

Elemental Concentration Profiles

The concentrations of Cr, Mn, Fe, Ni, and Si in weight percent were plotted along the analysis lines to show the elemental concentration profiles. Figure 2 shows the inhomogeneities in the Mn, Fe, and Ni concentrations in HCRP-A perpendicular to the flow lines. Gradients in elemental concentrations as high as $\Delta Fe/\Delta x$ = 0.12 wt% per μm, $\Delta Mn/\Delta x$ = 0.06 wt% per μm, and $\Delta Ni/\Delta x$ = 0.05 wt% per μm. Flow lines occurred in areas with above average iron and below average manganese and nickel concentrations. Figure 3 shows that compositional changes were only gradual (<0.03 wt% per μm) in HCRP-B parallel to the roll plane.

Analyses of specimens forged with Dies 1 and 7 revealed similar inhomogeneities. The concentration profiles for HERF-7A perpendicular to the flow lines (Figure 4) revealed concentration gradients as high as $\Delta Fe/\Delta x$ = 0.36 wt% per μm, $\Delta Mn/\Delta x$ = 0.16 wt% per μm, and $\Delta Ni/\Delta x$ = 0.21 wt% per μm.

As observed for HCRP-A, the flow lines in HERF specimens occurred in areas with above average iron concentrations and below average manganese and nickel concentrations. As shown in Figure 5, the analysis line for HERF-7B did not exactly parallel the flow lines but intersected two flow lines near 40 and 180 micrometers. However, the largest compositional gradients of $\Delta Fe/\Delta x$ = 0.16 Wt % per μm, $\Delta Mn/\Delta x$ = 0.06 wt% per μm, and $\Delta Ni/\Delta x$ = 0.15 wt% per μm were much less than those in HERF-7A.

Correlations Between Elemental Concentrations

In Figure 6, the concentrations of Cr, Mn, and Ni are plotted versus the Fe concentration for each analysis point along the line perpendicular to the flow lines in HERF-7A. The chromium concentrations show essentially no correlation with the iron concentration. Both manganese and nickel concentrations decrease with increasing iron concentration:

$$\text{Mn (wt\%)} = 34.52 - 0.386 \times \text{Fe (wt\%)}$$

and

$$\text{Ni (wt\%)} = 41.31 - 0.530 \times \text{Fe (wt\%)}$$

for 62.5 $\leq$66.5

Homogeneity

Table 4 summarizes the average concentrations and standard deviations (σ) for data along lines perpendicular to the flow lines in HCRP-A and HERF specimens forged with Dies 1, 5, and 7. Results for multiple analyses of a single point on an annealed specimen of 21-6-9 stainless steel are also listed. The standard deviations for the annealed specimen show the precision in the individual elemental analyses.

Inhomogeneity is described better in terms of variances (σ^2) rather than by the standard deviations themselves. Hence, the inhomogeneity for each element in HCRP is given by

$$\sigma_{HCRP} = \quad \sigma_R{}^2 - \sigma_A{}^2$$

where σ_R and σ_A are the elemental standard deviations for HCRP-A and the annealed specimen, respectively. Likewise, the inhomogeneity for each element introduced into the 21-6-9 stainless steel by HERF is given by

$$\sigma_{HERF} = \quad \sigma_n{}^2 - \sigma_R{}^2$$

where $\sigma_n$is the elemental standard deviation for the specimen forged with the nth die (1, 5, or 7).

As shown in Table 5, inhomogeneities in HCRP and HERF specimens are primarily associated with the manganese, iron, and nickel concentrations. The standard deviations for chromium are about the same as measured on the annealed specimen. Thus, the chromium is essentially homogeneous. The HERF step increased inhomogeneity, but no significant changes occurred in subsequent forging steps.

Histograms showing details of the variations of Mn, Fe, and Ni in HCRP-A and HERF-7A are shown in Figures 7 and 8. These were constructed by grouping data and plotting group size versus group number. The size of each group was equal to the precision ($^{\sigma}A$) for analysis for that element. For HCRP-A, the elemental concentrations are grouped symetrically about the averages. However, for HERF-7A, results are skewed, and the iron concentrations appear to have a bimodal distribution.

INTERPRETATION OF RESULTS

The microscopic inhomogeneities in HCRP and HERF are thought to be caused by inhomogeneities in the parent ingot that are given directionality by rolling and forging. Flow lines probably occur in regions high in iron and low in alloying elements because these are regions of low strength. The increase in inhomogeneity during HERF is an example of a physical process causing a chemical change. This increase in inhomogeneity could be caused by elemental diffusion along microscopic temperature gradients created for an instant during forging. The bimodal distribution of iron concentrations in HERF-7A suggests the beginning of phase separation. The reason for chromium being homogeneous while manganese, iron and nickel are inhomogeneous is unknown.

USES OF RESULTS

These results may be useful in interpreting any dependence of physical properties of 21-6-9 stainless steel on flow line orientation. Also, these results suggest that flow lines could be reduced or eliminated by improving homogeneity in the ingot. Because elemental variations in steel will change the size of the face-centered-cubic unit cell of the austenite, knowledge of specimen inhomogeneity will be useful in interpreting results of an x-ray diffraction line profile analyses of HERF 21-6-9 stainless steel presently in progress (2).

FUTURE WORK

Microprobe analyses will be performed on other forms of 21-6-9 stainless steel such as castings, rolled bar, and HCRP subjected to the same heat treatments used in HERF. These studies should reveal more information on how fabrication affects inhomogeneity in 21-6-9 stainless steel.

Microprobe analyses of 304L stainless steel HCRP and HERF are in progress.

ACKNOWLEDGEMENT

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References

(1) Hamilton, W. J., et al., "Automated electron microprobe analysis: A system for the ARL-SEMQ based on mass storage and speed capabilities of the flexible-magnetic disk," Proc. 12th MAS Conf., 1977: 52A (August, 1977).

(2) Sturcken, E. F., et al., "Materials Evaluation Studies of High-Energy-Rate Forged (HERF) 21-6-9 Steel," DAMSUL COMMITTEE REPORTS, November 1980.

Table 1

Nominal Composition of 21-6-9 Stainless Steel, wt%

Cr	19 - 21.5
Mn	8 - 10
Ni	5.1 - 7.0
N	0.2 - 0.3
C	0.02 - 0.04
Al	0.017
Si	0.3 - 0.7
P	0.20
O	(70 ppm)
S	0.015 max

Table 2

High-Energy-Rate Forging of 21Cr-6Ni-9Mn Stainless Steel

Starting Material:

1-3/4-inch-thick hot-cross-rolled plate

High-energy-rate forging (eight steps)

Die Number	Temperature, °F
1	2000
2	2100
2	1800
3	1750
4	1700
5	1650
6	1600
7	1550

- Heated 15 to 30 minutes before each forging step
- 1 forging blow at each step
- Water quench for 30 minutes after each forging step
- Final thickness: about 1/2 inch

Table 3

Microprobe Analysis Scheme

Element	Spectrometer	Crystal	Standard
Cr	1	LiF	NBS SRM 479
Mn	1	LiF	Mn Metal
Fe	1	LiF	NBS SRM 479
Ni	1	LiF	NBS SRM 479
Al	3	RbAP	Al Metal
Si	3	RbAP	NBS SRM 483
P	2	ADP	GaP
S	2	ADP	FeS

25-kV Beam Voltage
10-nA Beam Current
10-Second Counting Time

Data Reduction by Magic IV
Results normalized

LiF - Lithium Fluoride (200)
RbAP - Rubidium Acid Phthlate (100)
ADP - Ammonium Dihydrogen Phosphate (101)

Table 4

Elemental Concentrations and Standard Deviations in Weight Percent for Annealed, HCRP and HERF 21-6-9 Stainless Steel

Element	Annealed		HCRP		HERF					
					Die 1		Die 5		Die 7	
	Avg	σ_A	Avg	σ_R	Avg	σ_1	Avg	σ_5	Avg	σ_7
Cr	18.82	0.15	18.05	0.17	18.36	0.24	18.39	0.18	18.41	0.20
Mn	9.26	0.06	9.63	0.21	9.44	0.38	9.37	0.40	9.49	0.35
Fe	64.03	0.16	65.18	0.55	64.94	0.93	65.07	0.85	64.76	0.85
Ni	7.05	0.10	6.94	0.29	6.98	0.49	6.90	0.44	7.02	0.49
Si	0.65	0.03	0.18	0.01	0.19	0.03	0.23	0.02	0.19	0.02

Table 5

Inhomogeneity in HCRP and HERF 21Cr-6Ni-9Mn Stainless Steel

	HCRP	HERF		
	$\sigma_R^2 - \sigma_A^2$, wt%	$n^{\sigma 2} - \sigma_R^2$, wt%		
Element		Die 1	Die 5	Die 7
Cr	0.08	0.17	0.06	0.11
Mn	0.20	0.32	0.34	0.28
Fe	0.53	0.75	0.65	0.65
Ni	0.27	0.39	0.33	0.39
Si	<0.01	0.03	0.02	0.02

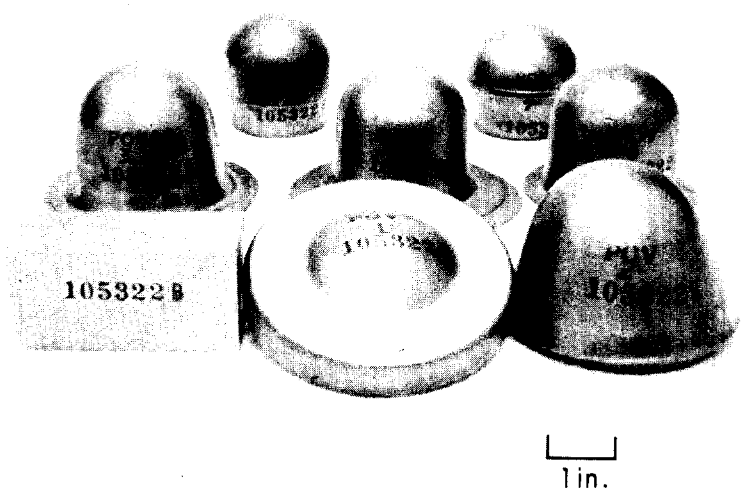


Figure 1 21Cr-6-Ni-9Mn Stainless Steel Hot-Cross-Rolled Plate (HCRP) and Specimens After Each Step of High-Energy-Rate Forging (HERF)

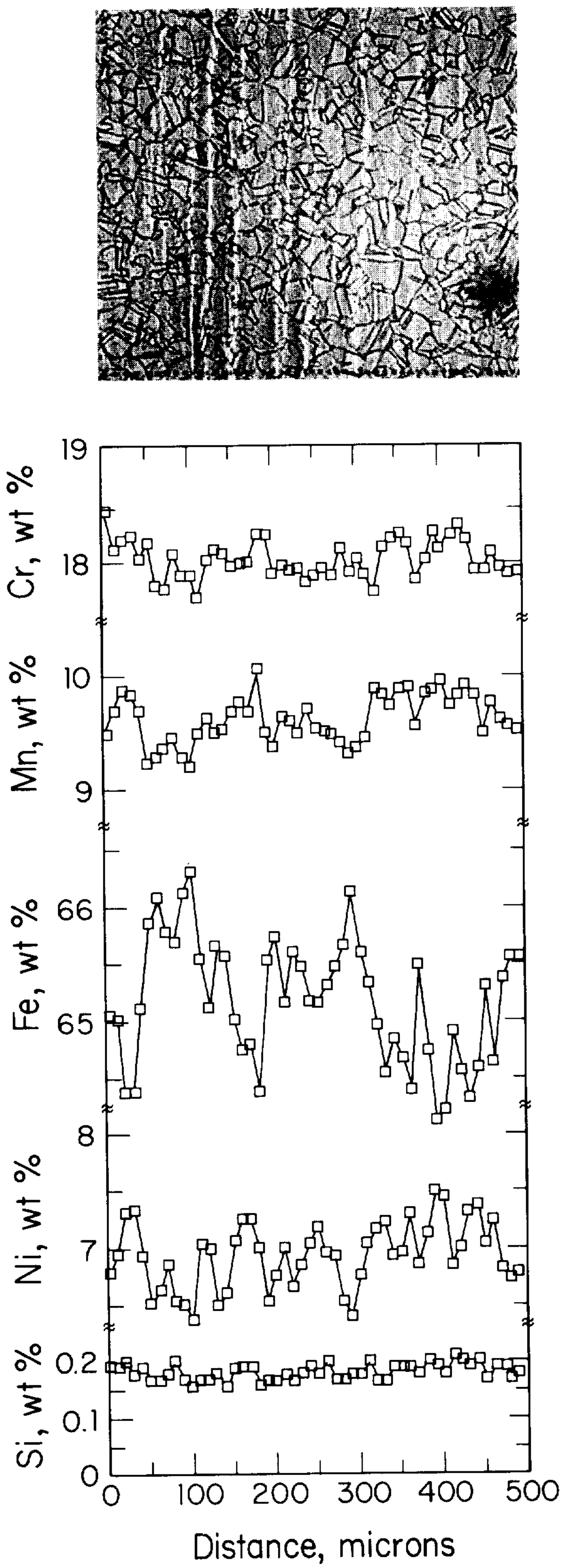


Figure 2 Elemental Distribution in HCRP-A Perpendicular to Flow Lines

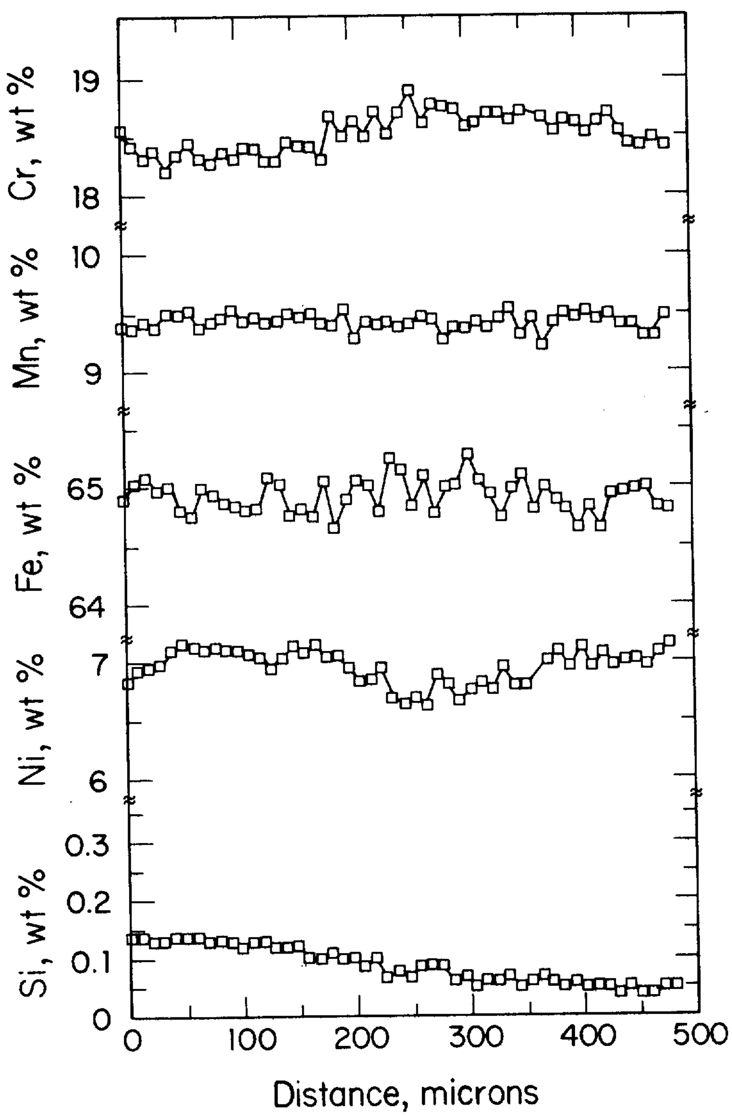


Figure 3 Elemental Distributions in HCRP-B Parallel to Roll Plane

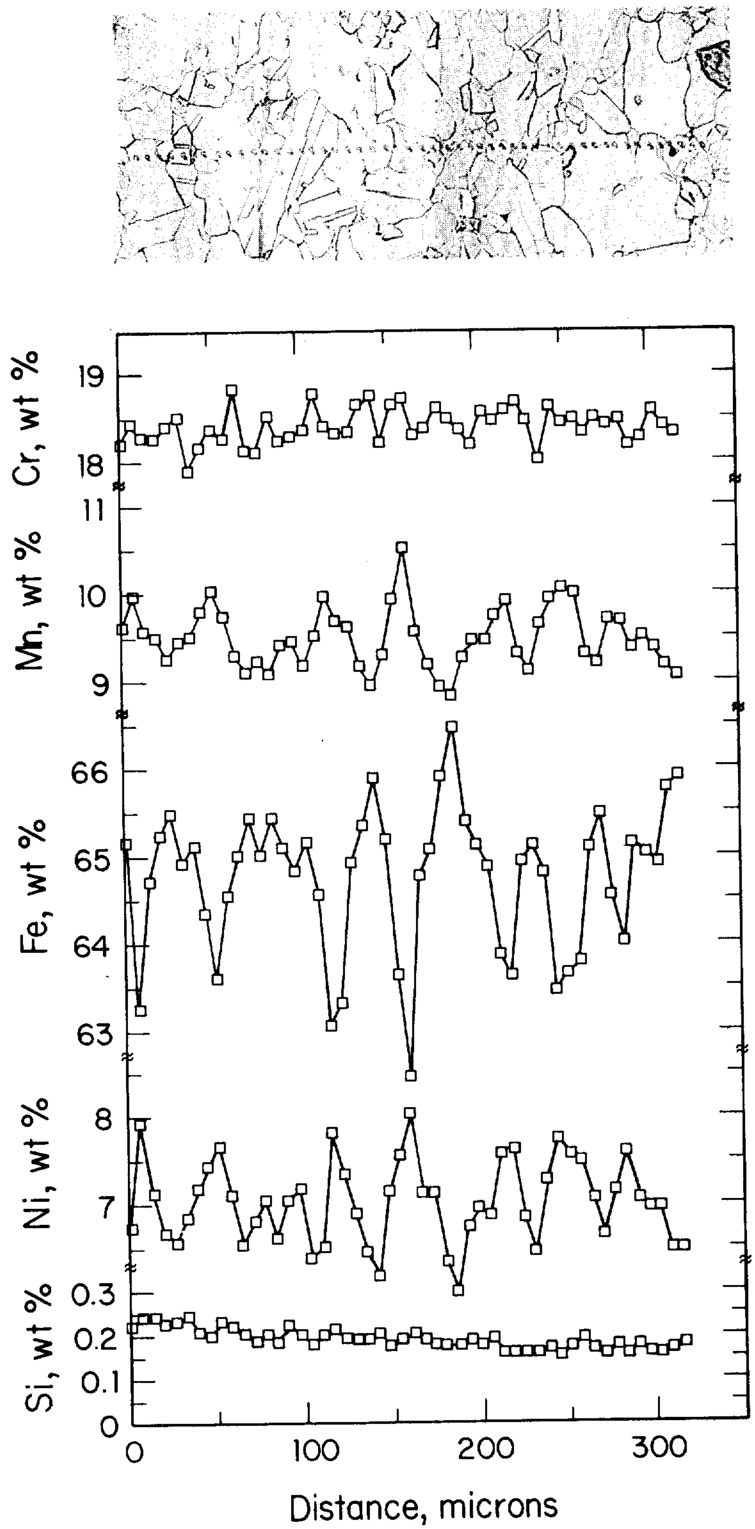
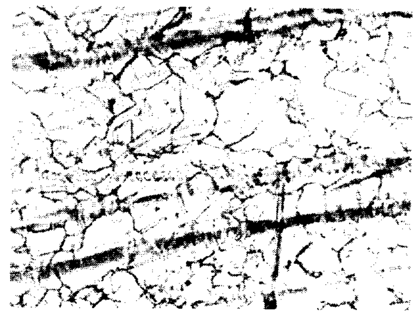


Figure 4 Elemental Distributions in HERF-7A Perpendicular to Flow Lines



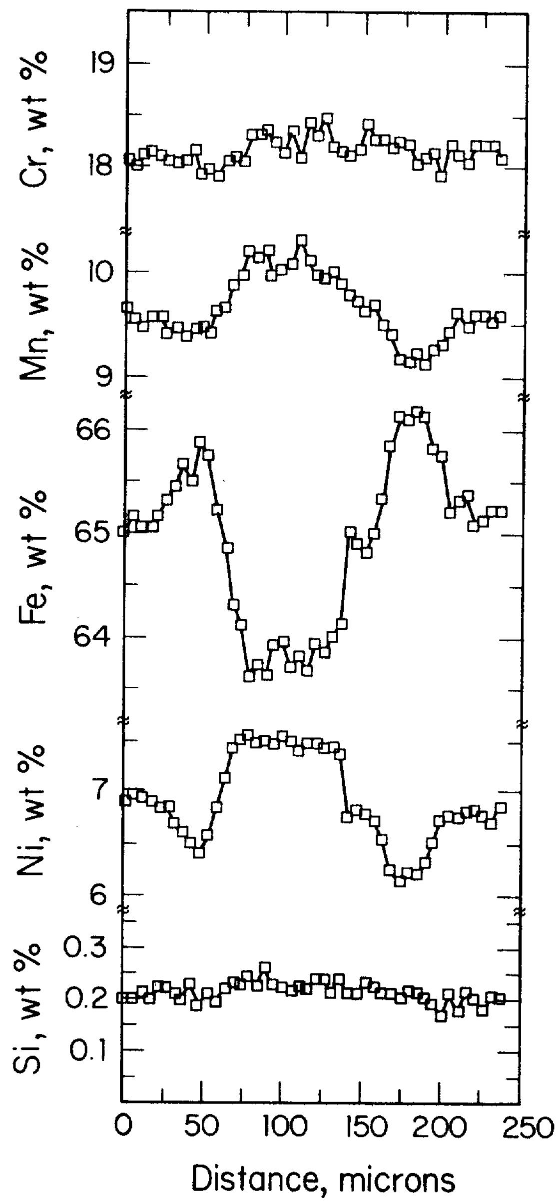


Figure 5 **Elemental Distributions in HERF-7B Nearly Parallel to Flow Lines**

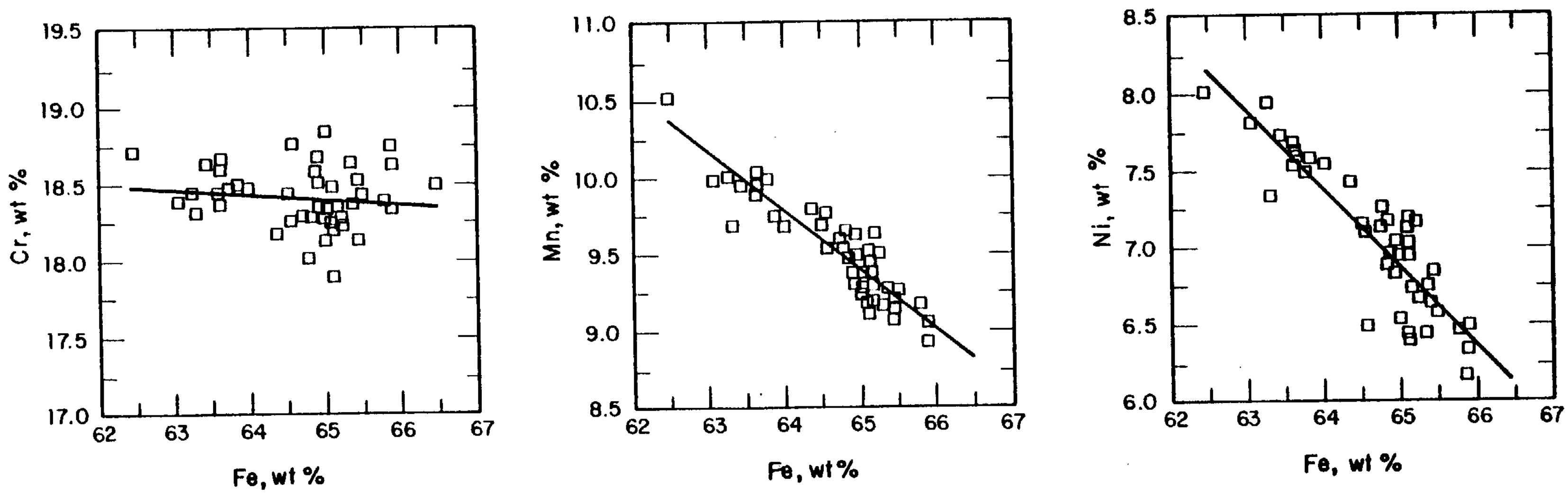


Figure 6 Correlations Between Elemental Concentrations for HERF-7A

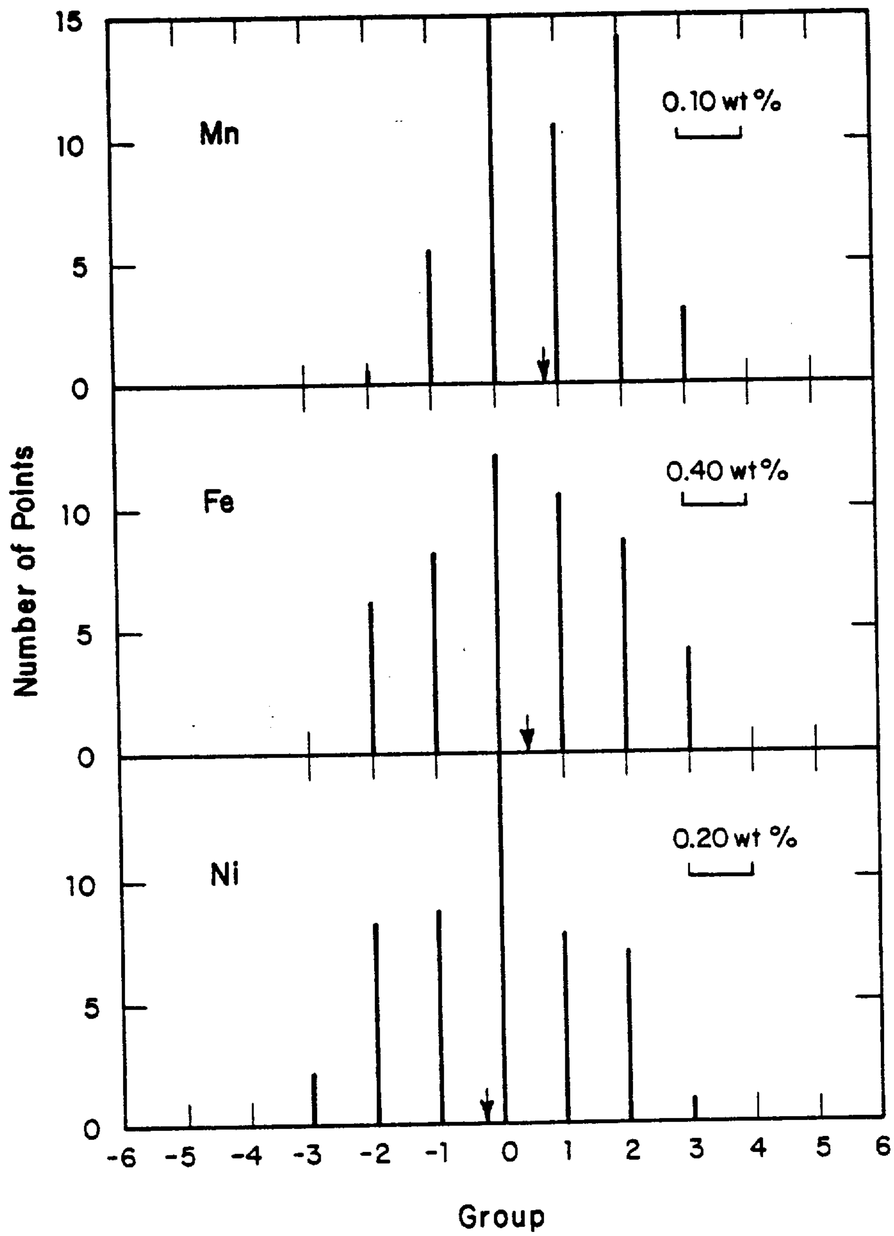


Figure 7 Distribution of Elemental Concentrations Perpendicular to Flow Lines in 21Cr-6Ni-9Mn Hot-Cross-Rolled Plate (HCRP-B). Arrows Indicate Averages.

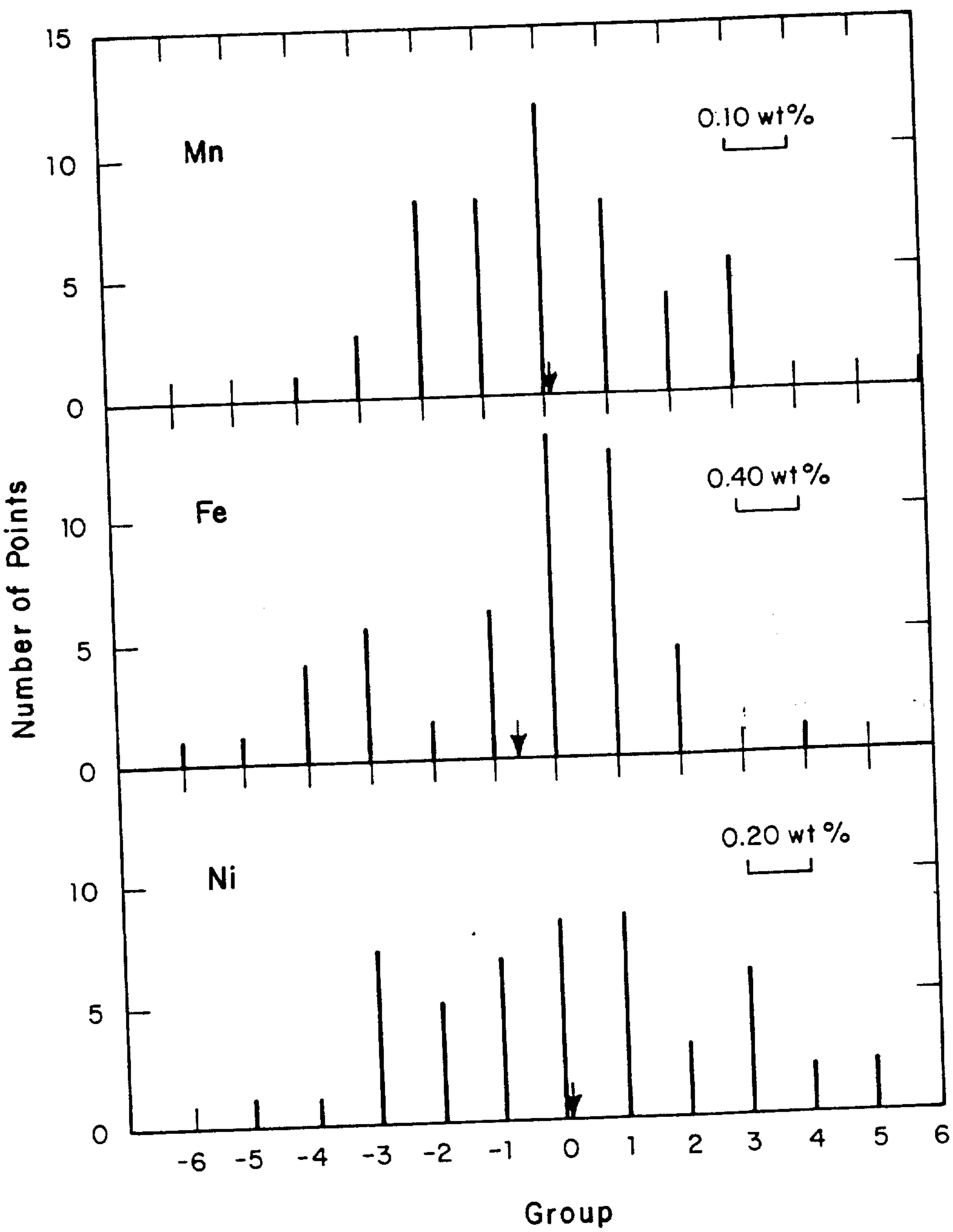


Figure 8 Distribution of Elemental Concentrations Perpendicular to Flow Lines in High-Energy-Rate-Forged Steel (HERF-7A). Arrows Indicate Averages.

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TO DISTRIBUTION

Attached is a copy of the following:

DP-MS-81-7, "An Electron Microprobe Determination of Microscopic Elemental Homogeneity of Hot-Cross-Rolled and High-Energy-Rate Forged 21CR-6Ni-9MN Steel"

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