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Scanning Auger Analysis of Surface Segregation in 21-6-9 and JBK-75

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SCANNING AUGER ANALYSIS OF SURFACE SEGREGATION *
IN 21-6-9 AND JBK-75

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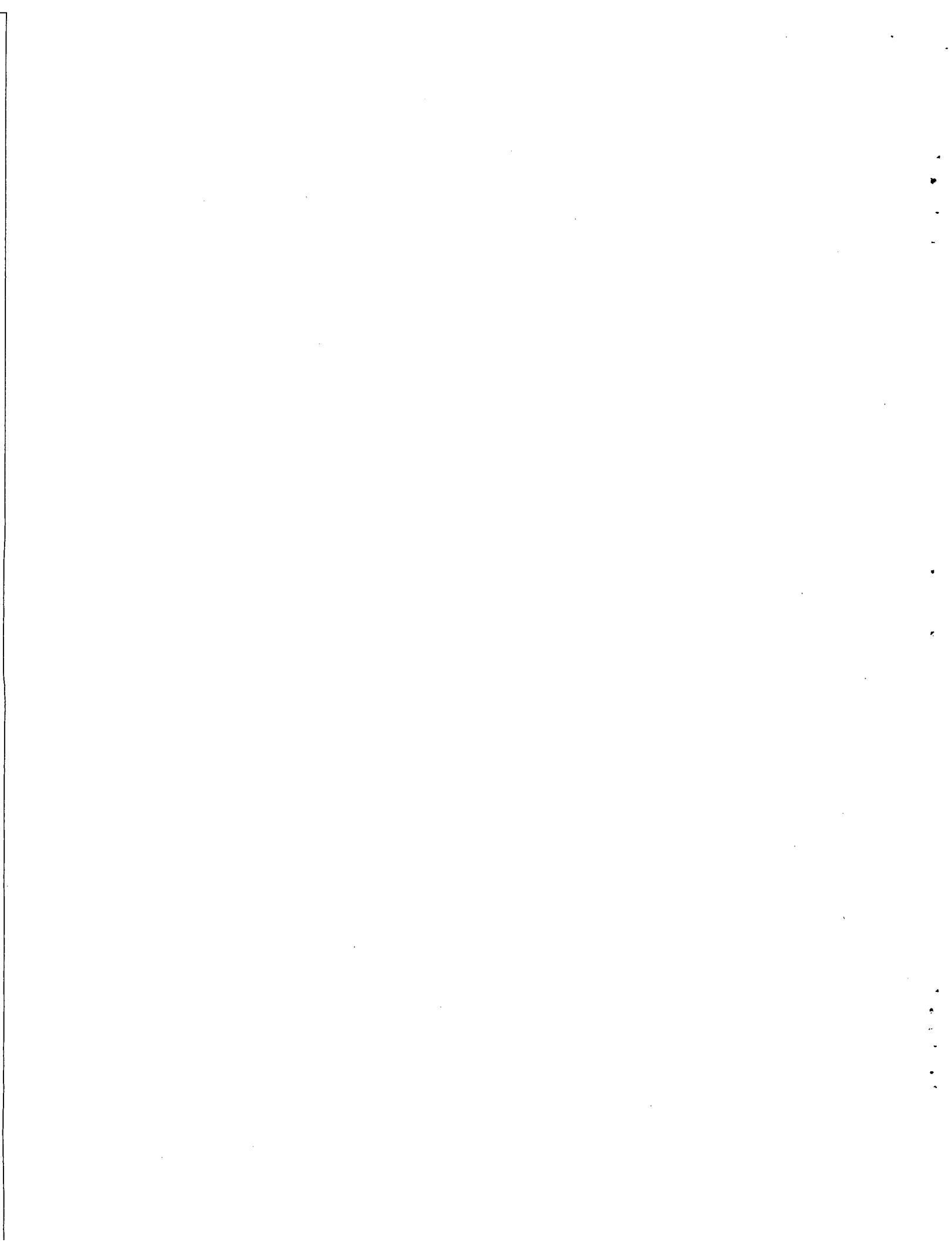
ABSTRACT

Measurements of surface segregation have been carried out on two austenitic stainless steels: Fe-21Cr-6Ni-9Mn and JBK-75. Highly polished polycrystalline samples of each material have been heated *in-situ* in an ultra-high vacuum system to temperatures ranging from 400° to 800°C and examined at temperature using scanning Auger spectroscopy. The results for 21-6-9 show that segregation is strongly heterogeneous with isolated regions enriched in either nitrogen, sulfur or tin. Above approximately 700°C the surface composition becomes strongly enhanced in both nitrogen and boron. For JBK-75 the surface is seen to be enriched in both titanium and nickel. Cosegregation effects and the relationship between surface and bulk composition resulting from exposure to elevated temperature are presented.

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Impurity segregation in alloys has, over the past few years, come to be acknowledged as a major controlling factor in the behavior of materials in a variety of applications [1-7]. In general, this phenomenon has been associated with a degradation in material properties as is observed, for example, in temper embrittlement, hydrogen embrittlement, and stress corrosion cracking to name but a few. Segregation can also strongly affect surface properties important to areas such as catalysis, permeation, and tribology.

Interaction between impurities can strongly modify their segregation to grain boundaries. In this paper results of surface segregation on two austenitic stainless steels, 21Cr-6Ni-9Mn (21-6-9) and JBK-75 measured using scanning Auger spectroscopy are presented which directly show the nature of the interaction between various impurities during segregation. These results also show that such measurements carried out with conventional Auger apparatus (electron beam diameter = 0.2 mm) can be misleading.

EXPERIMENT

All measurements were carried out in an ultra-high vacuum (UHV) system with a base pressure of 1×10^{-10} torr (1.3×10^{-8} Pa) using a Physical Electronics model 545 scanning Auger system (nominal beam diameter ≈ 3 microns). Specimens of 21-6-9 and JBK-75 were machined into 1 mm thick discs approximately 6 mm in diameter and mounted onto standard Varian heater assemblies. The composition of both 21-6-9 and JBK-75 is shown in Table I.

After sputter-cleaning, specimens were heated for periods up to approximately one hour. Surface compositions were monitored at temperature. All Auger spectra were taken in the derivative mode with modulation amplitudes less than or equal to 2 volts peak-to-peak in order to minimize spectral distortion.

RESULTS

I. 21-6-9

Overall, the dominant surface-active species observed segregating at elevated temperatures were sulfur and nitrogen. Nitrogen is intentionally added to the alloy as a solid solution strengthener whereas sulfur exists merely as a tramp impurity. An example of this segregation is shown in Figure 1 which illustrates typical surface conditions resulting from heating to 500 C for 1 hour. Figures 1a, 1b, and 1c show Auger maps for sulfur, nitrogen and tin respectively, each taken for the same surface region. Figure 1d illustrates schematically an overlay of these three maps and serves to illustrate both the heterogeneity of the segregation as well as the lack of co-segregation of these species.

This lack of co-segregation is further shown in Figures 2a, 2b, and 2c which give the full Auger spectra for each of the three regions in Figure 1. In each case the composition of the segregated layer is dominated by a single species: either nitrogen, sulfur, or tin. The spectrum shown in Figure 2d is characteristic of the clean surface and was taken after prolonged 1 keV argon sputtering. Whereas these spectra show the repulsive nature of the interaction between nitrogen, sulfur, and tin they also, in each case, illustrate co-segregation effects involving other elements. For example, in the nitrogen rich region there is an enhancement in the chromium signal, in the sulfur rich region there is an enhancement in the manganese signal and in the tin rich region there is a slight enhancement in the nickel signal.

After sputtering and subsequent heating, the pattern of surface enrichment is always the same for a given surface region. This is interpreted, in the case of sulfur, as being due to the existence of near-surface manganese sulfide precipitates. It was found that the emergence of sulfur-enriched

islands upon heating could be prevented by exposing a freshly sputtered surface to oxygen at approximately 100 C. This procedure is illustrated in Figure 3. After repeated heating-sputter cycles (Figure 3a-3c) the surface is oxidized and re-sputtered so that no oxygen is observed on the surface but does presumably remain in the grain boundary regions (Figure 3d and 3e). The oxygen in the grain boundary cannot be detected since the boundary width, typically ≤ 20 angstroms, is vastly smaller than the size of the Auger electron beam. When this sample is again heated, areas which previously showed sulfur islands no longer occur (Figure 3f). Figures 4a and 4b show sulfur maps observed during the first and ninth heating cycles (between heating cycles the surface was sputter-cleaned). Note that even after nine cycles the same regions appear enriched in sulfur. Figure 4c shows the surface composition observed after heating subsequent to oxygen exposure and sputter-cleaning. The regions previously enriched in sulfur no longer appear, so that the grain boundary oxides have effectively blocked diffusion. Even after extensive sputtering (removal of $> 1000 \text{ \AA}$) and subsequent heating, the observed surface enrichment (Figure 4d) does not return to its initial configuration.

II. JBK-75

In contrast to 21-6-9, JBK-75 is a precipitate strengthened stainless steel which gains its strength due to the formation of various titanium precipitates upon aging at elevated temperature, typically in the range of 625 to 725 C. The ultimate strength is determined by both the aging temperature and time.

Figures 5a and 5b show respectively the Auger spectra for a sputter-cleaned surface and for the same surface after heating to 720 C for approximately 4

hours. For these conditions the material has not yet reached peak strength. The segregated surface layer contains a variety of elements not present on the clean surface, namely phosphorus, sulfur, and oxygen. In addition there is a strong enhancement in both the titanium and carbon signals.

Figure 6 shows the Auger maps for sulfur, titanium and carbon. A comparison of Figures 6c and 6d illustrates that titanium and carbon show the same surface enrichment pattern indicating their tendency for co-segregation: no such correlations could be made for any of the other segregating species.

CONCLUSIONS

These results show that through a study of surface enrichment produced by high temperature treatment one is able both to identify surface active constituents and to determine qualitatively the nature of the interaction between the segregating species. A summary is presented in Table II.

In addition, since the observed surface enrichment is strongly heterogeneous, measurements of surface composition need to be made with probe beam diameters that are small compared to the dimensions associated with variations in composition. As a general rule in order to avoid misleading results, the incident electron beam should be kept smaller than the grain size.

In general these results show quite simply that elements which readily form naturally occurring compounds are observed to co-segregate. As a first approximation one would expect that this would not be the case for species which interact repulsively. Unfortunately this does not strictly hold true for all cases, so that the strength of the relative interactions (i.e. heats of formation) is important. A more complete analysis of this data within the frame work of the Guttman-McLean segregation theory [8] is now underway.

Figure Captions

- Figure 1: Scanning Auger maps for a) nitrogen b) sulfur and c) tin for the same surface region after heating to 500°C for 1 hour. A composite of these maps is shown schematically in d).
- Figure 2: Auger spectra for the three regions in Figure 1: a) nitrogen rich region b) sulfur rich region c) tin rich region. The characteristic Auger spectrum for a sputter-cleaned surface is shown in d) for comparison.
- Figure 3: Sequence of sputter-heating cycles is shown in a) through c) where surface enrichment in sulfur always occurs at the same position. Figures d) through f) show oxidation and subsequent heating of surface. See text for details.
- Figure 4: Experimental results for measurement sequence depicted in Figure 3. Figures a) and b) are sulfur Auger maps for the first and ninth heating cycles respectively. Figure c) is sulfur map after intermediate oxidation: note absence of previously sulfur rich regions. Sulfur map after extended sputtering is shown in Figure d).
- Figure 5: Auger spectra for a) sputter-cleaned JBK-75 and b) for JBK-75 heated to 720 C for 248 min.
- Figure 6: Auger maps for b) sulfur, c) titanium and d) carbon after 720 C heat treatment. Figure a) is an SEM of the surface region associated with the Auger maps.

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TABLE I
NOMINAL COMPOSITION (AT.%)

	Fe	Cr	Mn	Ni	N	Si	C	P	S	Al	O
21-6-9:	62.9	20.1	8.7	6.6	1.1	0.46	0.08	<.03	<.01	0.005	0.001
	Fe	Ni	Cr	Ti	Mo	V	Al	C	S	P	
JBK-75:	52.6	28.2	15.2	2.4	0.75	0.38	0.33	0.89	0.01	0.01	

TABLE II
IMPURITY INTERACTION PROPERTIES

Repulsive	Attractive
N-S	N-Cr
Sn-S	Sn-Ni
Sn-N	S-Mn
	Ti-C

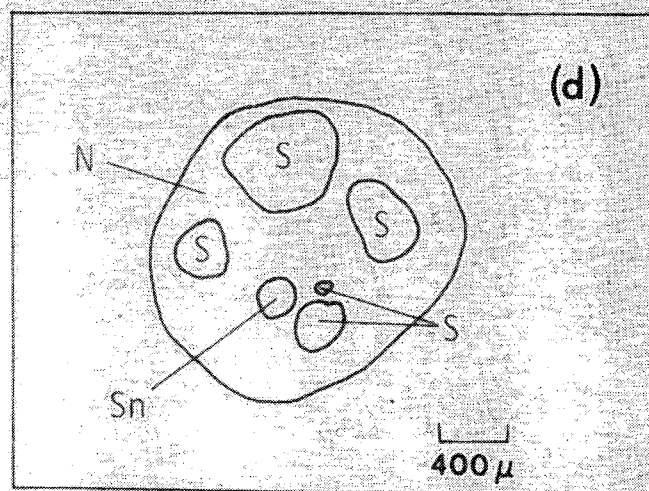
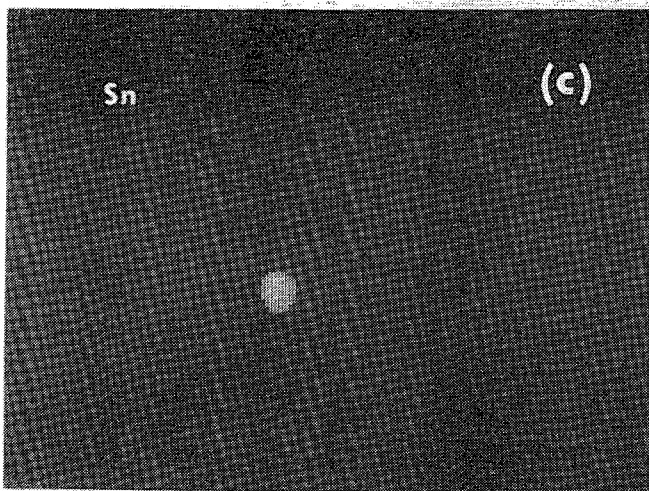
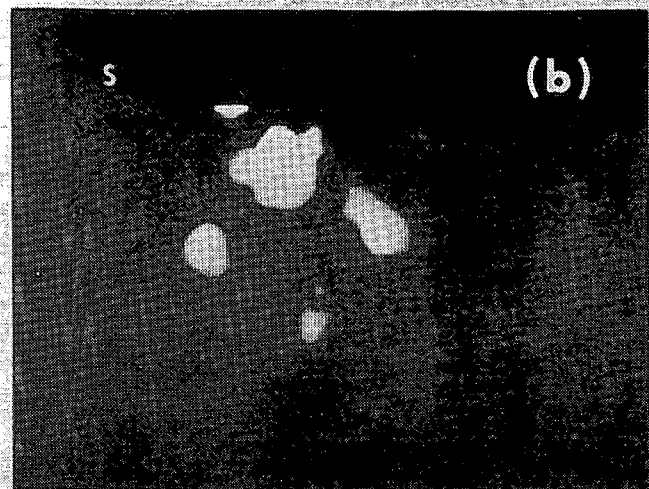
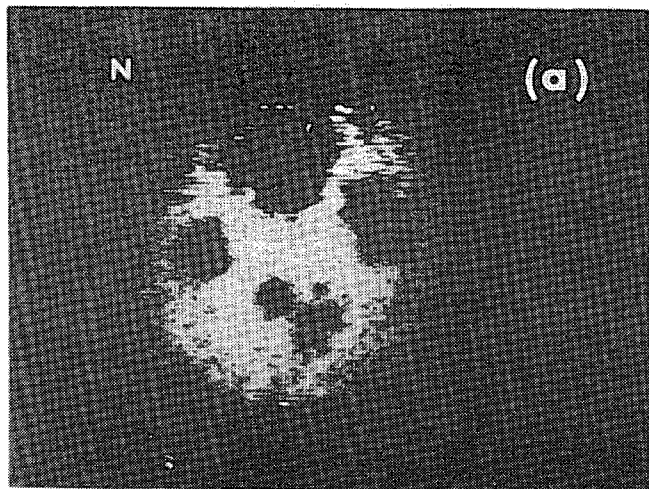


Figure 1

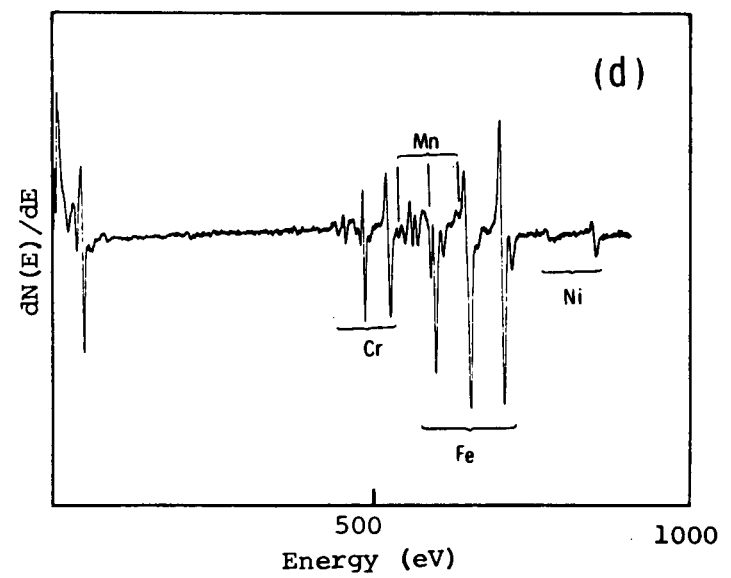
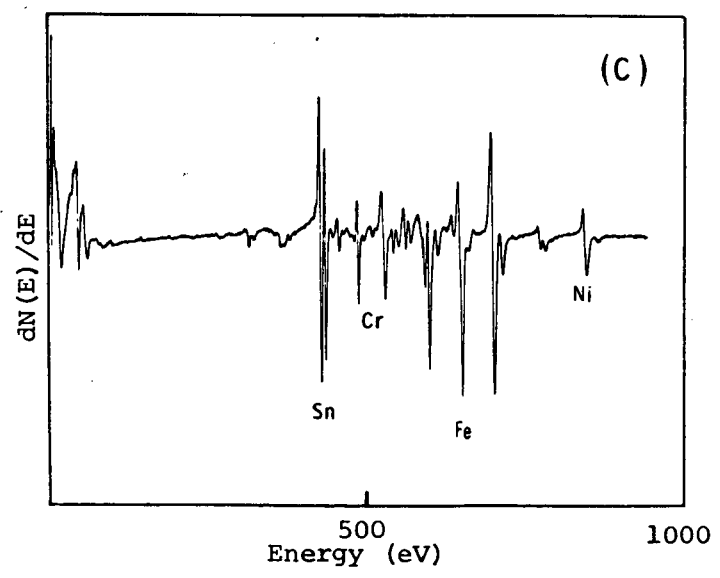
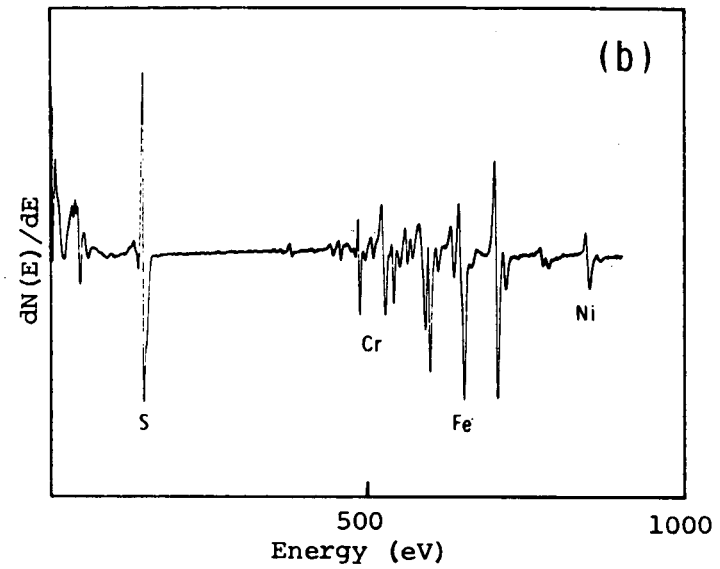
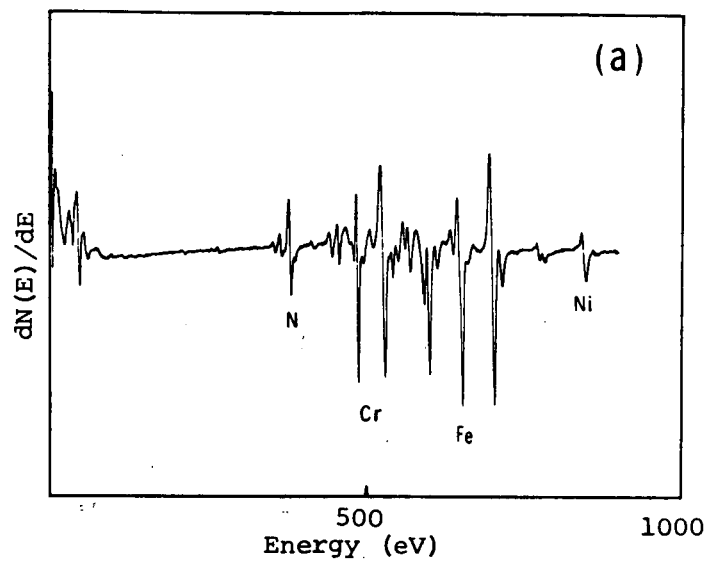


Figure 2

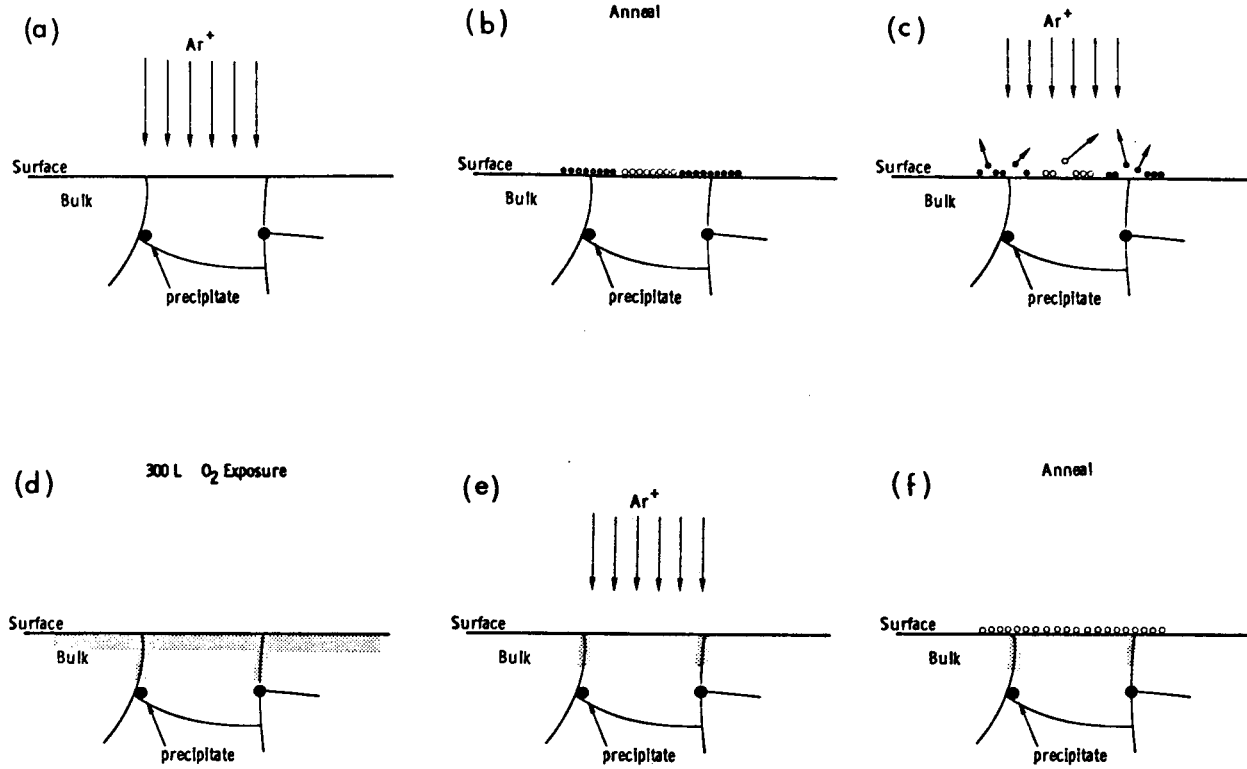


Figure 3

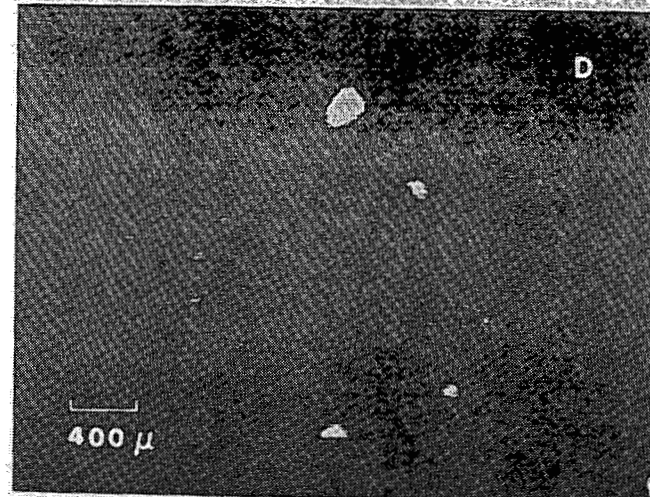
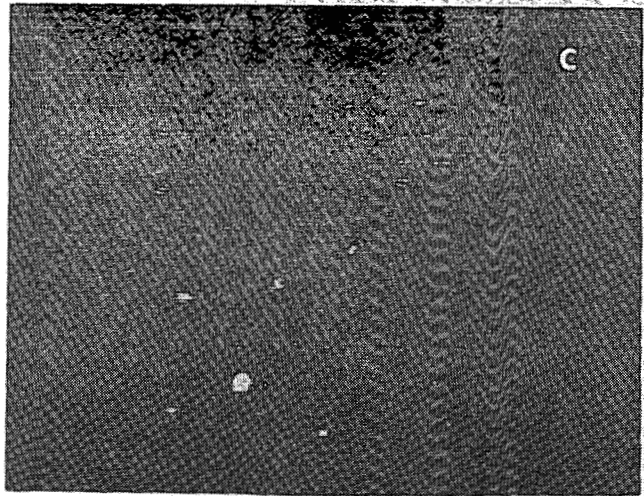
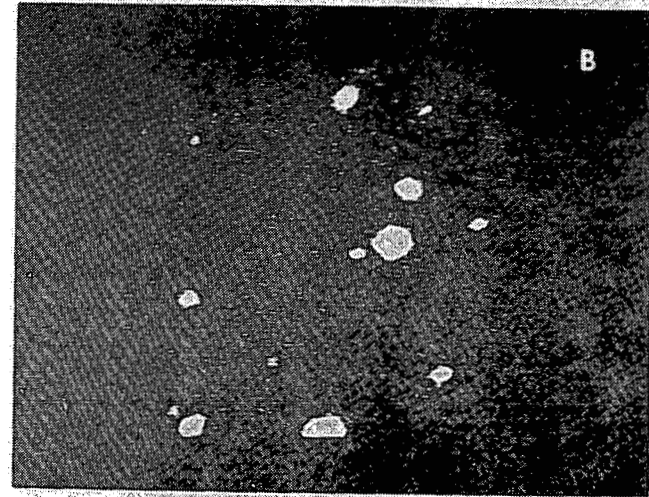
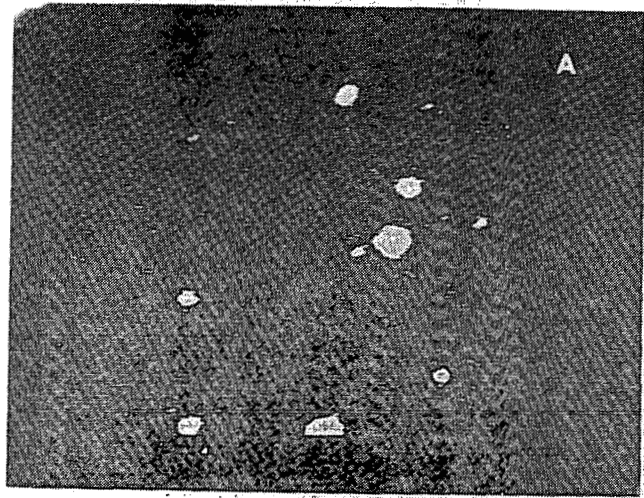


Figure 4

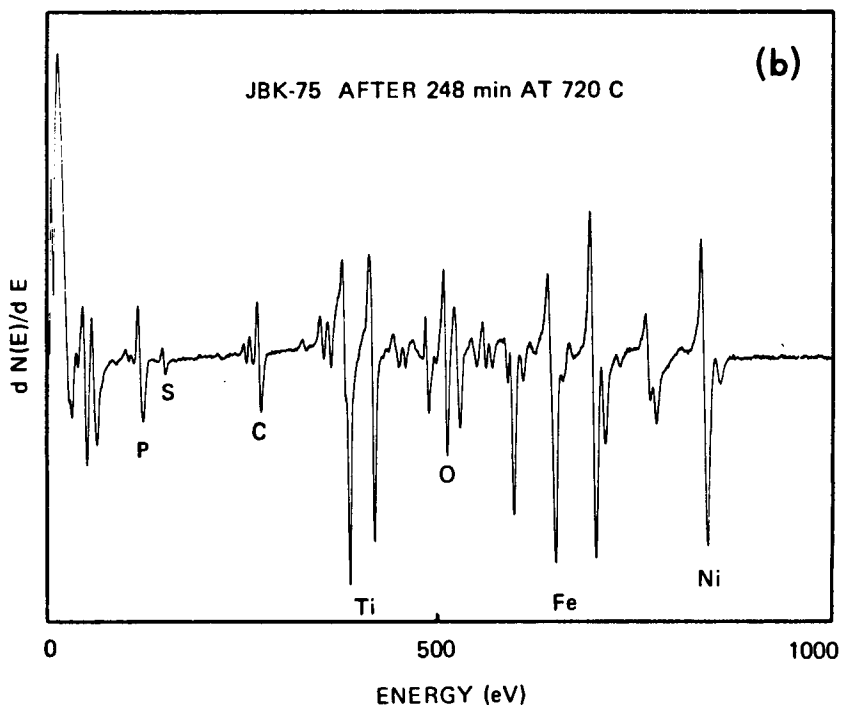
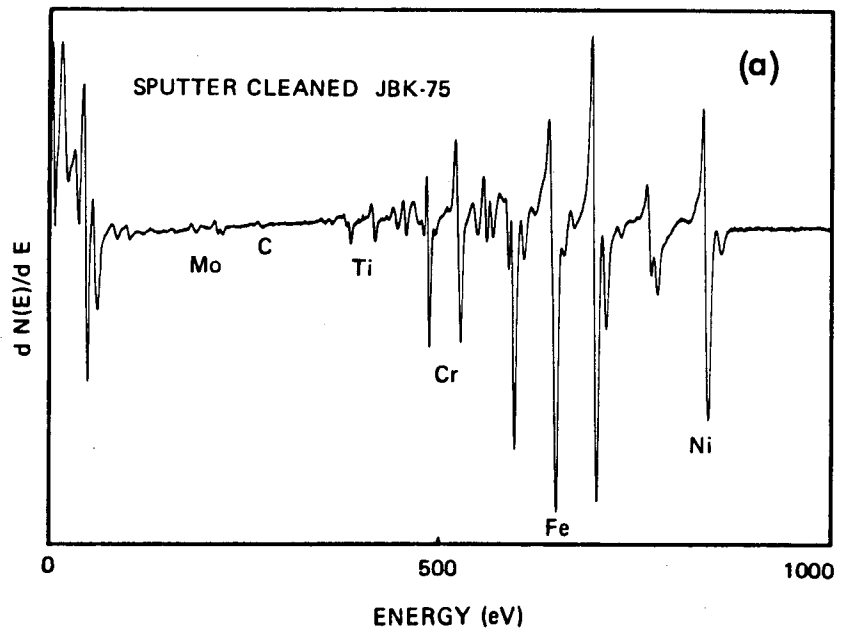


Figure 5

SURFACE SEGREGATION OF JBK-75

720 C / 248 min

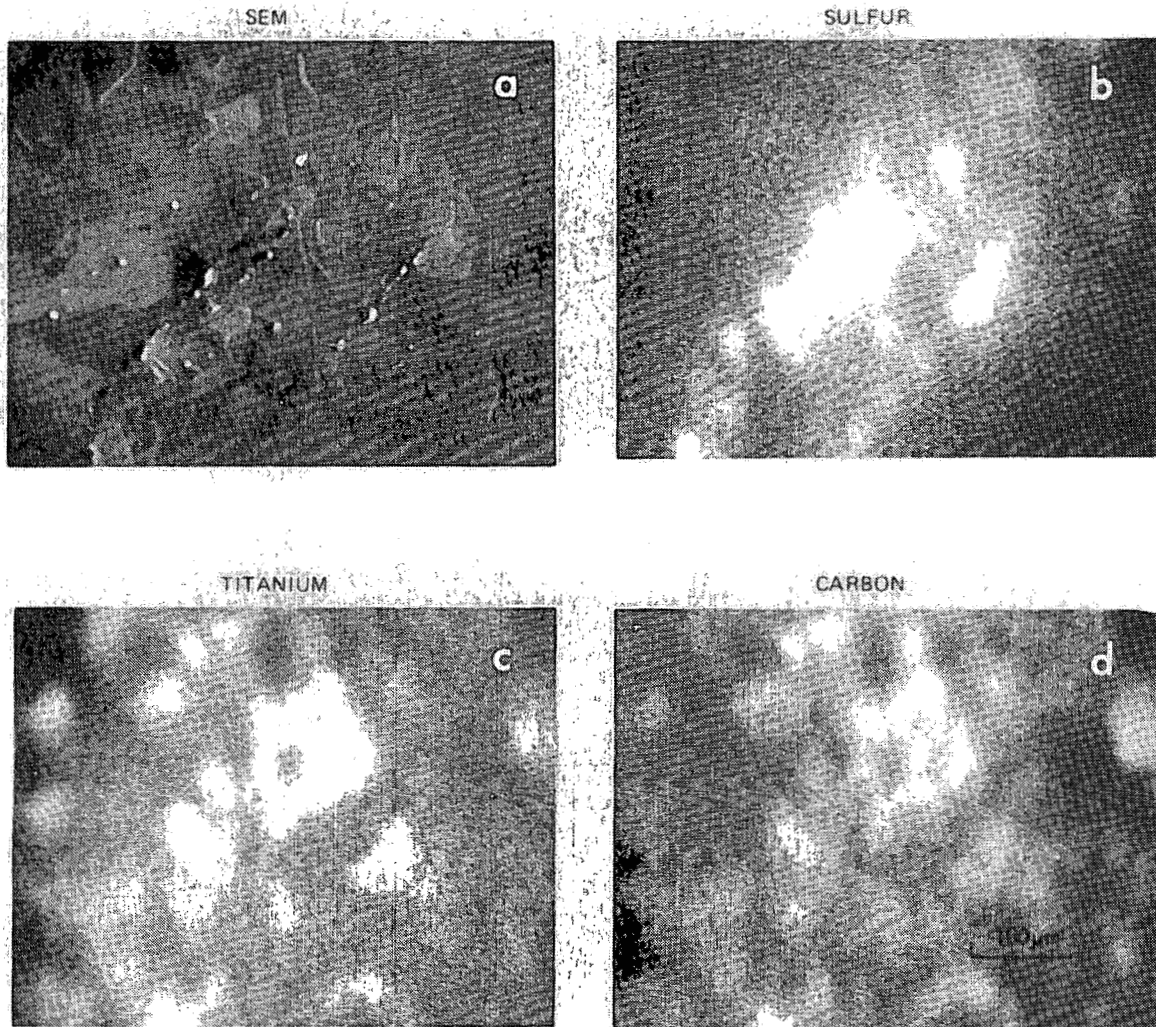
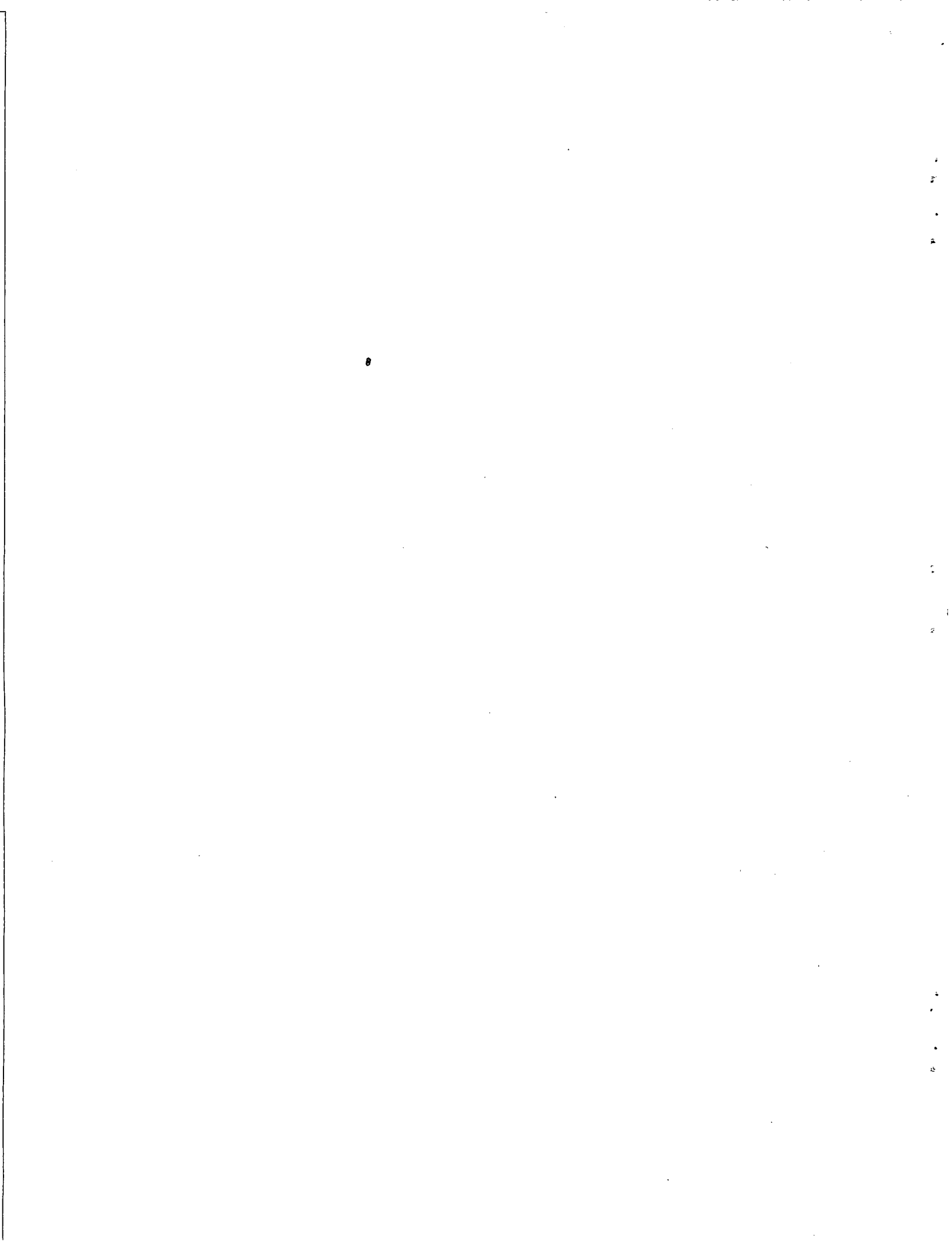


Figure 6



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