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SEGREGATION IN WELDED NICKEL-BASE ALLOYS

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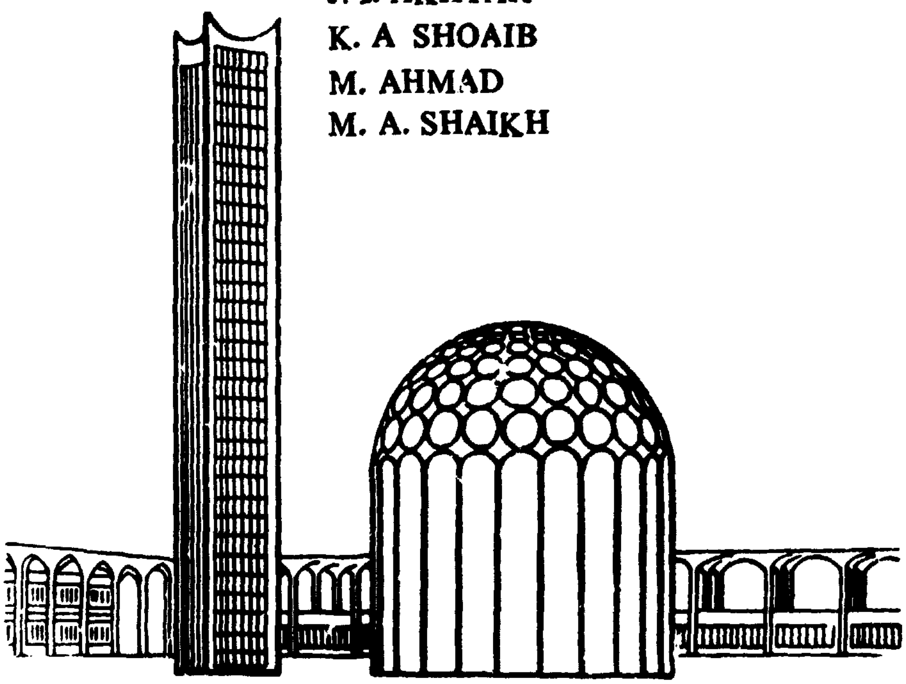

Radiation Damage Group
NUCLEAR PHYSICS DIVISION
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ABSTRACT

Segregation effects have been investigated in nickel-base alloys Monel 400, Inconel 625, Hastelloy C-276 and Incoloy 825, test welded under controlled conditions. Deviations from the normal composition have been observed to varying extents in the welded zone of these alloys. Least effect of this type occured in Monel 400 where the content of Cu increased in some of the areas. Enhancement of Al and Ti has been found over large areas in the other alloys which has been attributed to the formation of low melting slag. Another common feature is the segregation of Cr, Fe or Ti, most likely in the form of carbides. Enrichment of Al, Ti, Nb, Mo, etc., to different amounts in some of the areas of these materials is interpretted in terms of the formation of γ' precipitates or of Laves phases.

1. INTRODUCTION

Nickel-base alloys constitute an important class of materials which are used under demanding conditions of high corrosion resistance and high temperature strength. A wide range of these alloys exist due to the ability of nickel matrix to accomodate large amounts of elements, such as chromium, iron, copper, molybdenum, etc., while retaining essentially a single phase face-centred-cubic structure.[1]

The complete range of solid solutions of nickel-copper system offers a number of alloys of industrial importance. One of the well-known alloys in this series is Monel 400 which is characterized by good strength and ductility, and resistance to the corrosive action of a wide range of media such as sea water, acids and alkalis. This material is extensively used for components such as condenser tubing, pump shafts, marine fittings, etc.[2].

The nickel-chromium-iron metallurgical system, with additions of other elements such as molybdenum, niobium, tungsten, aluminium, titanium, etc., provides a very large variety of alloys with strength, ductility and corrosion resistance tailored to a whole gamut of industrial applications. Many of these alloys are being used, or are being contemplated for use, in nuclear engineering in high temperature reactors or in fusion reactors for parts such as hot gas pipes, heat exchangers, control rods or the vacuum vessel[3].

These alloys derive their high temperature strength from solid solution hardening as well as from precipitation hardening by γ' phase of the type $Ni_3(Al,Ti)$. Corrosion resistance to both reducing and oxidizing media is conferred upon these materials by the nickel matrix itself as well as by the additions of Mo, Cu and Cr [4]. Inconel 625 has relatively high Cr concentration and contains Mo and Nb in solid solution and retains better strength and ductility at elevated temperatures. Hastelloy C-276, containing high Mo and some W, is known to have high corrosion resistance. Incoloy 825 contains comparatively higher Fe than other Ni-base alloys and has good creep properties in addition to excellent corrosion resistance.

Fabrication of metallic structures often requires the use of welding and many modern alloys are optimized for this purpose. However, solidification during welding is an inherently non-equilibrum process and the microstructures so generated are often not those predicted by applying equilibrium considerations to existing phase diagrams [5]. Nickel-base alloys are, in general, susceptible to welding discontinuities such as microfissuring, hot cracking, porosity and strain-age cracking [6]. The solidification segregation patterns in these alloys exhibit depletion of Ni in the interdendritic volume and an accompanying increase of most solute species (Mo, Nb, Ti, etc.) while the reverse pattern is observed in the dendrite core [5].

The present report describes the results of the segregation effects in some of the nickel-base alloys which show relatively attractive welding behaviour.

2. EXPERIMENTAL

The alloys investigated in the present work were Monel 400, Inconel 625, Hastelloy C-276 and Incoloy 825 obtained from commercial sources. The normal composition of these alloys is given in Table 1.

The samples studied were in circular (disk) as well as in rectangular shapes. The size of rectangular samples of all the alloys was 12 mm x 12 mm while the diameter of circular specimens was about 18 mm for all the materials except Incoloy, where it was 12 mm. The thickness of the samples of Monel and Incoloy was 1 mm whereas that of the specimens of Inconel and Hastelloy was 3 mm. The latter had a V-groove of width and depth 2 mm along the middle of the sample for welding.

The test welds were produced using tungsten inert gas welding technique, with the shielding gas being argon flowing at a rate of 10 to 15 lt/min. The filler metal was derived from the parent metal in form of 1 to 2 mm wide strips. The tungsten electrode had a diameter of 1.0 - 1.6 mm and the weld travel speed ranged from 0.5 to 1.0 mm/sec. The welding current was about 30 A for the thick samples and 12 A for the thin samples. This was reduced to 5 A and and 2.5 A for the respective samples towards the end of the welding sequence in order to account for the heat accumulation. One set of samples was not subjected to any pickling or brushing treatment after welding while another was subsequently brushed on the surface with a hard steel brush. Yet another set of samples was quenched into water immediately after welding.

The welded specimens were examined both before etching and after etching with a suitable etchant to reveal weld microstructure and segregation. A JEOL JSM-35CF scanning electron microscope was used for this purpose. For microanalysis of various areas of the specimens an attached automated energy dispersive system, LINK 860-2, was used.

3. RESULTS

3.1 Monel 400

Welded samples of Monel were examined in the electron microscope after etching in a 1:1 solution of conc. HNO_3 in water for various intervals of time upto 3.5 min. In only very small areas on the weld beads was there any significant change in form of some increase in copper. Fig. 1 illustrates one of the very few areas which showed large deviation from nominal composition, giving considerable decrease in Ni content and a corresponding increase in Cu. X-ray microanalysis was done at various points along the straight line drawn across the micrograph and the content of Ni along the line is denoted by the accompanying profile. The profile indicates large fluctuations in nickel content in the segregated area. Quantitative analysis shows the content of Cu going upto 64% at some points in the segregated area in contrast to the normal value of 17%. The segregates seem to be in the form of thin flakes and the percentage of Cu decreases where the deposit has flaked off. The percentage of other elements does not change much in the segregated area.

3.2 Inconel 625

These samples were examined after etching in an equal volume solution of HCl, HNO_3, H_2O_2 and H_2O for 4 min at room temperature. Segregation of Al and Ti was a phenomenon observed in the fusion zone of all the samples. The segregates were in form of flakes or small precipitates on the welded surface. Fig.2 shows the weld microstructure as well as the surface segregates. The enhancement of Al is illustrated in form of a line profile of Al X-ray intensities from the points on the sample lying on the central straight line.

In all the specimens segregation of Nb was also observed in areas of weld beads adjacent to the heat affected zone. The surface structure of such areas was peculiar film-like as depicted in Fig. 3. In case of the circular samples, enhancement of Cr (accompanied by an increase of Fe) was observed at the last bead with its amount going upto 57% in the quenched specimen. In areas where Cr content was high the concentration of Nb was depressed. Representative compositions, rich in either Al/Ti, Nb or Cr/Fe, are given in Table II.

Three markedly different types of microstructures have been observed at the fusion zone: (a) the morphology of Al/Ti segregates like the bright areas shown in Fig. 2; (b) the plain structure of Nb/Mo segregates as shown in Fig. 3; and (c) somewhat less developed lamellar, eutectic, morphology at the last bead.

3.3 Hastelloy C-276

Rectangular shaped samples of Hastelloy have been examined without etching the surface layer. In the as-welded sample (unquenched and unbrushed) extensive segregation was observed in the welded zone even at low magnification in the scanning electron microscope. Elemental analysis in such areas gave extremely high values of Al. Such an area is shown in Fig. 4 where a scan of x-ray intensities has been taken along the central straight line. The curve at the top is the profile for Al while that at the bottom gives the variation of Ni. An excess of Mo has also been found in some of the regions of the weld.

In case of the samples water quenched after the welding process, low magnification inspection reveals a pattern of segregation very similar to that of the unquenched specimens. Widespread segregation of Al is found on the welded zones. However, a new feature is the observation of small iron-rich islands in the initial part of the welding sequence. Such an area, with line profile of iron at the top and of Ni at the bottom, is shown in Fig. 5. Some regions are observed where areas enriched in different elements co-exist side by side. In Fig. 6, an area rich in Al (top line profile) lies to the left of a high concentration of Cr (central profile) which is adjacent to an area containing a high amount of Ni (flakes on the surface, bottom profile).

In the third category of samples which have been brushed subsequently to the welding no large scale surface segregation has been observed. However, some areas rich in Fe have been found both on the weld beads and on the parent metal. Table III shows the composition of areas rich in Al, Mo, Cr, Fe and Ni respectively.

3.4 Incoloy-825

In a preliminary study, unbrushed samples of the alloy were studied in the electron microscope. Although the samples were unetched, a basket-weave type structure was observed which at higher magnification revealed a dendritic growth pattern. Fig. 7 illustrates such an area.

Extensive segregation is observed in the welded zone in form of platelet-like structure, shown in Fig. 8, which increases in area as one proceeds towards the last weld bead. In these areas the content of Ti, accompanied by that of Al increases at the expense of Fe and Ni. The concentration of Ti, as well as that of Al, is higher near the centre of each bead and also increases towards the last bead, with the Ti content going upto 37%.

In addition to the planar segregated areas, particles enriched in Ti and Al are also observed in the welded zone. The Ti content of these particles, which is generally around 30%, reaches upto 51% in case of those on the last bead.

Increase of Ti and Al is also found in the heat affected zone although it is not as high as that in the welded region. The concentration of various elements in the segregated areas of the heat affected zone and of the last bead is summarized in Table IV.

4. DISCUSSION

Complex metallurgical reactions are generated in a multi-component system on heat treatment. These reactions depend upon the type of the elements present and even small amounts of some solutes can produce significant effect. Monel 400 is free of solutes having precipitate forming tendency in the Ni-Cu system where the major elements have complete solid solubility. As expected, deviation from normal composition was observed infrequently in this alloy and, where this effect was observed, Cu was found to be in higher concentration. This can be easily understood with reference to the Ni-Cu equilbrium phase diagram where, in the region between the liquidus and the solidus, the liquid component solidfying last is Cu-enriched. Due to rapid cooling at the surface of the weld pool it is likely that this Cu-rich solution froze without having reached equilibrium composition.

In case of other alloy systems under consideration, additional elements such as Cr, Nb, Ti, Al, etc., are responsible for the production of secondary phases. The most common second phase present in superalloys is the coherent γ', the intermetallic compound $Ni_3(Al,Ti)$ which plays a major role in the strengthening of these materials. The extent of γ' formation is determined by the levels of Al and Ti. In alloys containing Nb, atoms of Ti and Al in the γ' phase are partly or completely exchanged with Nb[7]. For a Nb content more than 4% and ageing temperatures near 760 ^{o}C, γ' precipitates transform to the incoherent, stable, orthorhombic β -Ni_3Nb phase [1,8]. In addition to the γ' phase, carbides of the type MC, M_6C, M_7C_3 and $M_{23}C_6$ have been reported [3,9-12], where, depending upon the alloy composition, M has been variously observed to be rich in Cr, Nb, Mo or Ti. Prolonged ageing is known to produce intermetallic compounds such as Laves phases of the type $(Ni, Cr, Fe)_2$ (Nb,Mo,Ti) [12] or Ni_2 (Cr,Mo) [13,14], the Cr rich σ phase [5] or complicated compounds like μ and P[14,15] which may have the form $(Ni,Fe,Co)_3$ $(W,Mo,Cr)_2$.

Interpretation of the observed segregation phenomena for alloys other than Monel in the present case is not straightforward since complex effects are found to occur depending upon the particular alloy and upon the position on the fusion zone. Tables II, III and IV summarize the composition for only some of the selected areas of segregation although a whole range of varying compositions is observed.

A common feature in case of these alloys is the observation of low melting slag of Al, Ti and Ca. Out of these, Ti has a high melting point but the liquidus temperature is lowered when it is in solution with Al [16]. Similar slag formation has already been noticed in welded Inconel-625 [6]. However, in the present work this effect was both widespread and of high content in Al and Ti. The nominal concentration of Al and Ti in all these alloy is much less than 1% and their segregation in high amounts suggests extensive depletion of these elements in the welded zone. A consequence of this would be a considerable reduction in the population of γ' precipitates and hence a reduction in strength in the welded area.

Another segregation product common to all the alloys studied seem to be the carbides. In case of Inconel these appear to be carbides of Cr and Fe while for Hastelloy these are enriched in both Cr and Fe or in Cr alone. Whether these carbides are of the form $M_{23}C_6$ or of the other types already reported [9-12,14] remains yet to be confirmed. In case of Incoloy the high concentration of Ti on the last bead is likely to be TiC.

The content of Al and Ti in the welded zone of Inconel 625 varies considerably from area to area and in some cases the composition is quite analogous to that of γ' phase Ni_3 (Al,Ti). Due to overlap of the L x-ray peaks of Nb and Mo it is not possible to separate the two elements in the EDS spectrum from this alloy. However, from the K x-ray line it is observed that, in the areas showing enhancement of these elements, it is generally Nb which is increased. Also, the quantitative value of these elements is depressed due to the inadequacy of standardization and of the lack of corrections because of roughness of the surface being analyzed. Because of these reasons, and because of a varying range of compositions, it is not possible to unambiguously identify whether Nb-rich areas are of the type Ni_3Nb or are Laves phase of the form $(Ni,Cr,Fe)_2$ (Nb,Mo) as has been previously reported [12].

In case of Hastelloy C-276, evidence in some of the high Cr and Mo areas indicates the formation of the ordered phase $Ni_2(Cr,Mo)$[13], while in Incoloy-825 some of the areas appear to be composed of the Laves phase of the type $(Ni,Cr,Fe)_2$ Ti. In none of the alloys investigated were the phases μ or P observed. Neither were these to be expected since their formation requires prolonged ageing, a condition which is not met in the welding process.

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Table 1: Nominal composition of the alloys investigated (wt%)

Alloy	Ni	Cr	Fe	Mo	Nb	W	Cu	Mn	Co	Al	Ti	Si	S	C
Monel-400	66.5	-	1.25	-	-	-	31.5	1.00	-	-	-	0.25	-	0.15
Inconel-625	62.3	22.0	1.9	8.8	4.2	-	0.03	0.12	-	0.17	0.23	0.25	0.01	0.03
Hastelloy C-276	57.0	15.7	5.6	15.8	-	3.3	-	0.49	1.9	0.26	0.01	0.04	0.01	0.01
Incoloy-825	39.4	22.2	31.0	3.3	-	-	2.0	0.13	0.63	0.16	0.80	0.22	0.01	0.09

Table II: EDS composition of areas enriched in Al/Ti, Nb/Mo, Cr/Fe in the fusion zone of welded Inconel-625 (wt%)

Area	Ni	Cr	Fe	Nb/Mo*	Al	Ti	Si	Ca
Normal matrix	64.8	23.1	4.8	6.9	0.1	0.1	0.2	-
Al/Ti segregation	1.0	2.2	0.4	-	91.4	2.8	-	2.2
	24.3	18.8	2.0	-	9.9	39.6	0.5	4.9
	45.8	25.8	8.2	6.1	7.0	2.5	0.1	4.5
Nb/Mo segregation	59.0	20.8	3.4	15.8	0.1	0.7	0.2	-
	43.7	36.1	2.8	11.7	1.4	4.2	0.1	-
Cr/Fe segregation	22.8	51.0	20.2	3.9	0.3	0.8	1.0	-
	28.3	31.7	24.7	4.7	4.2	1.1	0.7	4.6

*(1) Due to overlap of the main L x-ray spectrum in EDS analysis it is not possible to separate Nb and Mo. However, from the K x-ray lines it is found that, in segregated areas, increase is generally in the Nb content.

(2) Due to problems of standardization and of quantitative analysis because of roughness of the surface all the values of Nb/Mo are observed to be lower than the actual content.

Table III: EDS composition of areas enriched in Al, Mo, Cr, Fe and Ni in the welded region of Hastelloy C-276 (wt%)

Area	Ni	Cr	Fe	Mo	W	Al	Si	Cu
Normal matrix	66.5	16.0	6.0	7.8	2.5	0.2	1.0	-
Al segregation	2.1	0.8	0.3	0.4	-	71.6	-	24.8
Mo segregation	58.0	18.5	4.7	17.8	-	0.2	0.6	0.2
Cr segregation	5.4	80.1	1.5	0.3	-	9.6	1.6	1.5
Fe segregation	7.3	13.7	74.8	0.3	-	1.1	2.2	0.6
Ni segregation	87.1	4.3	8.0	0.5	-	0.1	-	-

Table IV: EDS composition of segregated areas on or around the last weld bead of Incoloy-825(wt%).

Area	Ni	Cr	Fe	Mo	Al	Ti	Ca
Normal matrix	41.2	23.3	33.0	2.0	0.1	0.4	-
Heat affected zone	38.3	25.7	29.8	1.9	0.5	3.8	-
	37.3	26.5	28.9	1.9	0.6	4.8	-
Last weld bead (area analysis)	17.4	22.8	14.4	0.5	7.8	29.8	7.3
	28.8	19.2	23.8	1.4	8.6	14.9	3.3
	20.7	17.4	17.7	0.8	4.4	37.0	2.0
Particles on last weld bead	17.9	17.1	17.9	0.2	3.2	41.5	2.2
	12.4	21.4	12.5	0.7	1.3	51.3	0.4

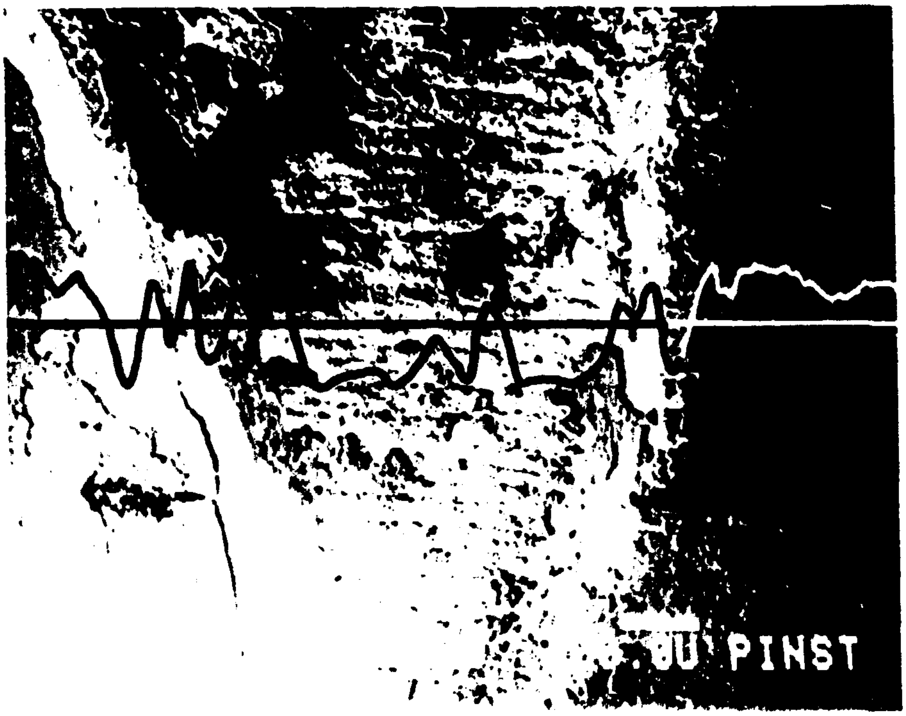

Fig. 1. Line profile of Ni in a welded area in Monel 400 showing enhancement of Cu.

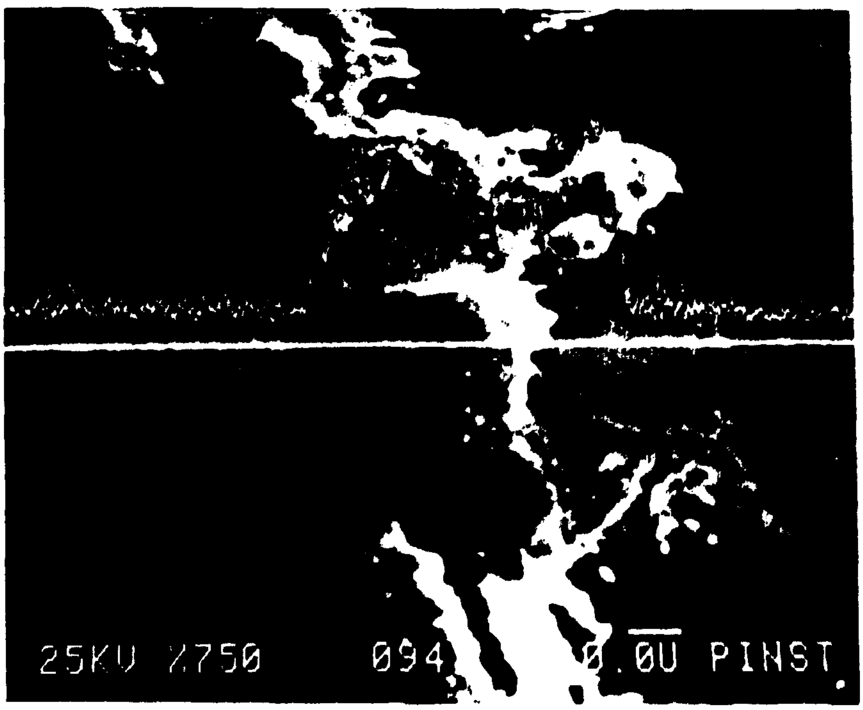

Fig. 2. Line profile of Al X-rays together with the Al segregates in Inconel.

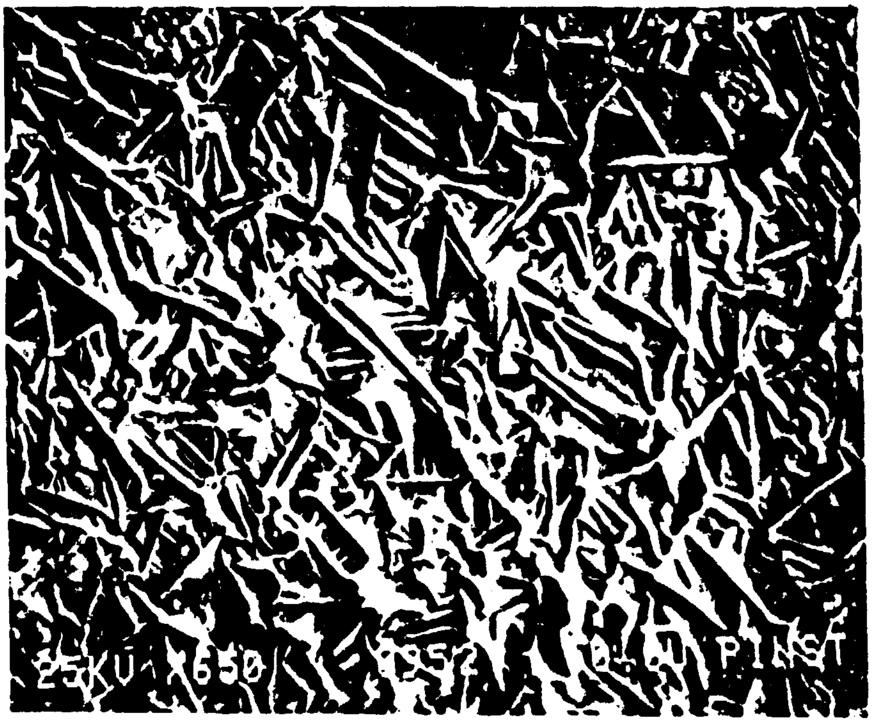

Fig.3. Nb-rich area on the weld bead of Inconel.

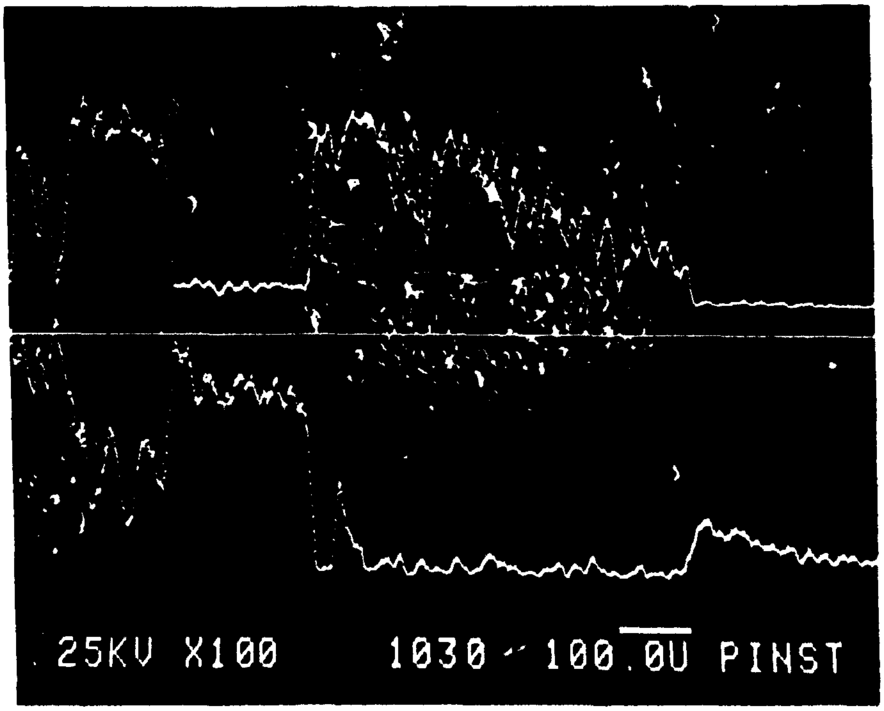

Fig.4. An area with segregation of Al in Hastelloy. Line scan done along the central straight line with line profile of Al on the top and for Ni at the bottom.

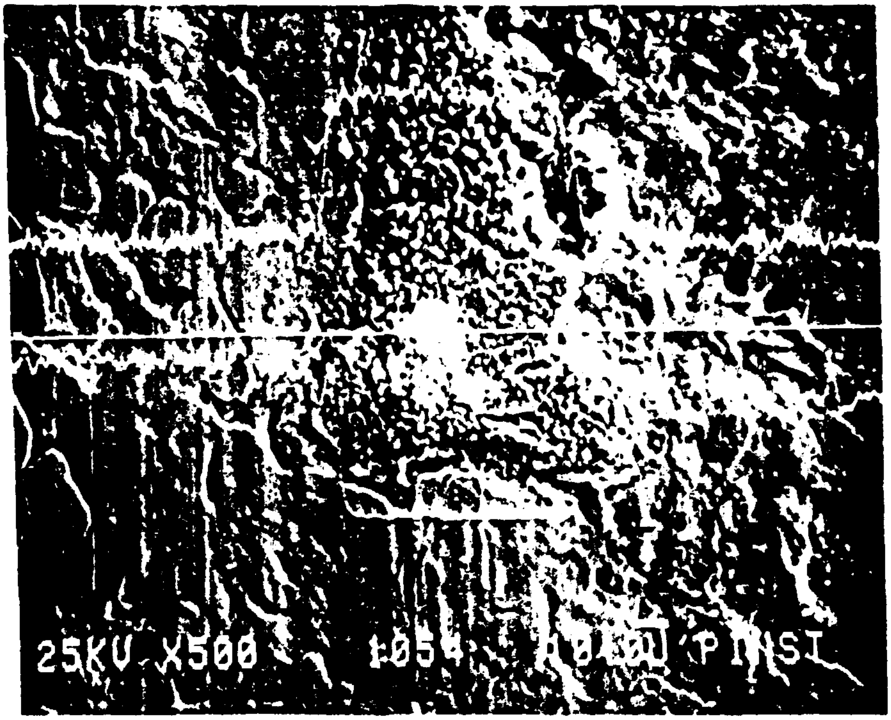

Fig.5. Segregation of Fe on the welded region of Hastelloy with line scan for Fe at the top and of Ni at the bottom.

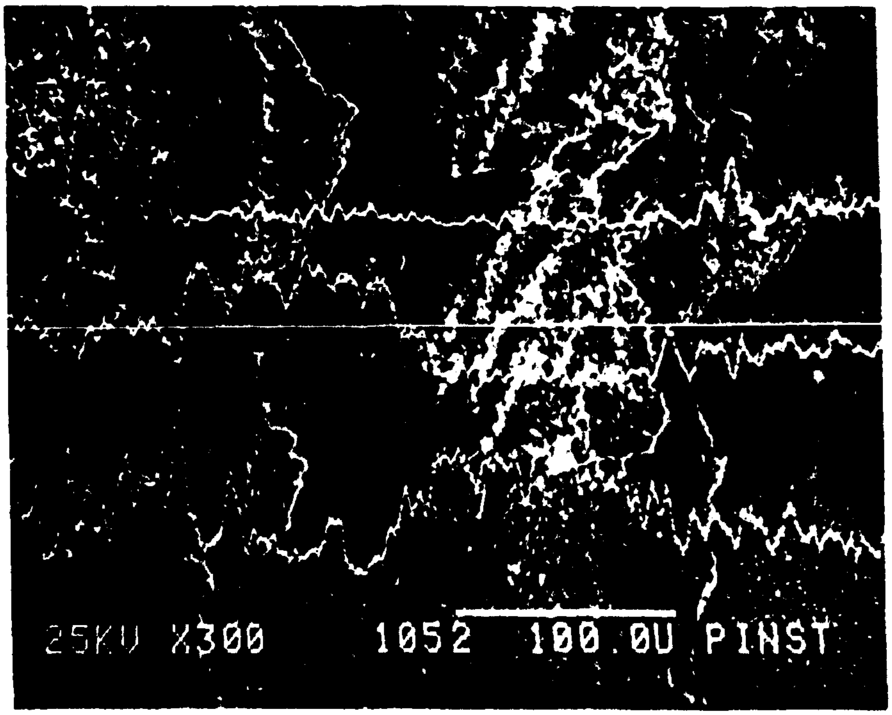

Fig.6. An area of welded Hastelloy showing regions with enhancement of different elements Al on the left (line profile at the top), Cr in the middle (Central line profile) and Ni, in form of flakes, on the right (lowest line profile).

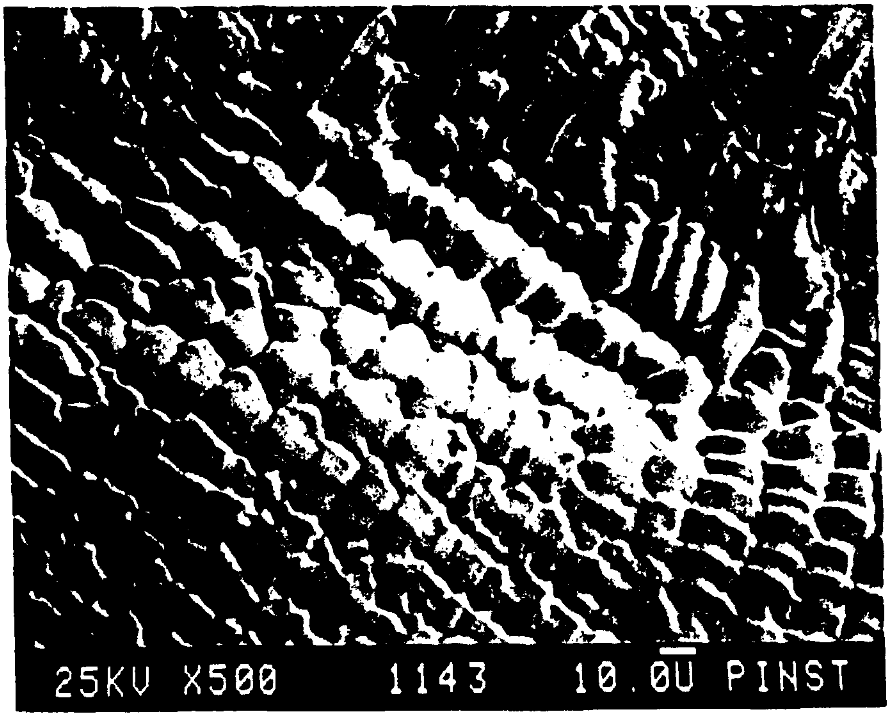

Fig.7. Dendritic solidification pattern on the weld bead of Incoloy 825.

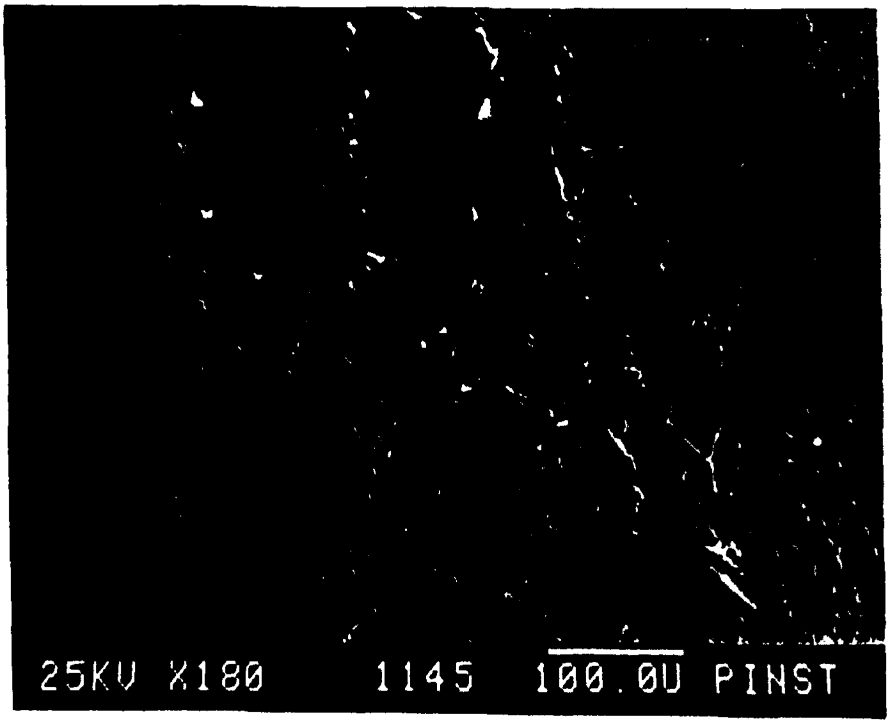

Fig.8. Area enriched in Ti and Al in the welded zone of Incoloy.