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THE INFLUENCE OF ALLOY MICROSTRUCTURE ON Al_2O_3 -PEG
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Rajendra Dattatraya Pendse
(M.S. thesis)

June 1982

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THE INFLUENCE OF ALLOY MICROSTRUCTURE ON Al_2O_3 -PEG
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To my parents.

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ABSTRACT

A comparative study of Al_2O_3 -peg morphologies in oxidized $\text{Co}_{10}\text{Cr}_{11}\text{Al}_{11}\text{Y}$ and $\text{Co}_{10}\text{Cr}_{11}\text{Al}_{11}\text{Hf}$ as-cast alloys was carried out with a view to examine the role of alloy/coating microstructure in the pegging process. No direct connection between the two was established. However, deeply penetrating internal Al_2O_3 -sheaths were observed associated with the microstructurally segregated yttride phase at the α/β boundaries in the oxidized CoCrAlY alloy; no sheaths were found in the CoCrAlHf alloys. These observations in conjunction with previous observations of 'sheaths' in vapor-deposited coatings are considered as evidence of an 'indirect' influence of microstructure on the pegging process.

A zone depleted of the β -phase was observed below the scale in all oxidized alloys. Simple observations and calculations on the zone-thickness were made with a view to elucidate the pegging mechanism. These were not entirely conclusive and additional work was found necessary.

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1. INTRODUCTION

1.1 Corrosion Resistance of High Temperature Alloys

The use of Ni-and Co-based superalloys for high temperature service is common practice in the gas turbine industry. The essential requirements of such high temperature alloys are:

1. Good high temperature mechanical properties (i.e., high temperature strength and ductility, high creep and fatigue resistance).
2. Resistance to degradation in high temperature environments (Corrosion Resistance).
3. Ease of fabrication.

However, more importantly, it is desired that the creep life of the turbine blades made from such alloys is utilized fully and that the life is not limited by the problem of high temperature corrosion. It is, therefore, vital to ensure the property of good corrosion resistance.

The present work is based on the development of Co-based superalloys (or coatings). These alloys are superior to Ni-base alloys in the temperature range 760-1000°C where 'hot corrosion' is the major problem. However, at higher temperatures ($\sim 1100^\circ\text{C}$ or higher) in oxygen atmospheres, their corrosion resistance is not as good; attempts have, therefore, been made to further develop these alloys and coatings.

In order to provide good corrosion resistance, the surface oxide film which forms on the alloy on high temperature exposure must satisfy the requirements of physical and thermodynamic stability, low thickening rate and good adherence to the underlying alloy. The first two requirements are usually met by making alloying additions of Al

and/or Cr and/or Si to the superalloy so as to promote the formation of the corresponding oxide films by selective oxidation. The fundamental aspects of selective oxidation have been developed in several earlier papers¹⁻⁸. Prediction of the minimum content of an element such as Al or Cr needed to form continuous protective scales can be made using diffusional models of growth which have been derived and reviewed by earlier workers⁸⁻¹².

An important problem with making Al-additions directly to Co-based superalloys is the resulting loss of ductility and workability. The presence of chromium helps in reducing the minimum Al-content needed to promote continuous Al_2O_3 -scale formation^{10,13}, however, the ductility does not improve appreciably. Therefore, corrosion-resistant protective coatings (typically, Co-Cr-Al) are used on the actual alloys thereby imparting desirable corrosion properties while not affecting the bulk properties of the alloy. Coating is performed either by physical methods such as plasma spraying, sputtering, evaporation and slurry, or by chemical methods such as chemical vapor deposition (CVD) and diffusion. The coatings may degrade during high temperature service in which case the alloys are re-coated thereby utilizing fully the creep life of the material.

1.2 Scale Adherence

It has already been pointed out that the thermodynamic stability and low thickening rate are essential requirements of a protective oxide film. However, an important requirement particularly in thermal cycling conditions is the adherence of the scale to the alloy. A poorly adherent scale is susceptible to easy failure under thermal cycling stresses. This exposes fresh alloy to the oxidizing atmosphere and in effect,

the scale ceases to be protective. Scale adherence is especially important in vehicular gas turbines, rocket engines, etc. where the nature of the application demands high temperature exposures of intermittent nature such that the scale withstands cyclic thermal stresses.

The term 'stresses' has been used rather loosely in the above; the exact nature and origin of the stresses during isothermal and cyclic oxidation are now explained briefly.

1. Stresses may develop during isothermal exposure due simply to the oxide having a greater specific volume than the corresponding amount of metal oxidized. The ratio of these quantities, the so-called Pilling-Bedworth ratio¹⁴ should, therefore, provide a rough guide of the magnitude and sign of such stresses. The above notion is valid when the scale grows by inward diffusion of oxygen ions so that the scale forming reaction occurs at the scale-alloy interface in a constrained manner. The dilatation stresses must be accommodated (in order to maintain geometric continuity) by the development of residual stresses in the scale as well as the alloy. Such stress-development is not expected in scales that grow by outward diffusion of cations (reaction at the gas-oxide interface). However, several other sources of stress are also possible and the Pilling-Bedworth model is not necessarily valid even in the former case, as was pointed out by Stringer¹⁵ and Tylecote¹⁶. For example, stresses could arise due to the growth of new oxide within an already established oxide layer¹⁷, (comparable diffusion rates of anions and cations), compositional changes of the oxide near the oxide-alloy interface, epitaxial

stresses at the interface due to mismatch of scale and underlying substrate, etc.

2. During thermal cycling, thermal stresses arise due to the difference in thermal expansion coefficients of the scale and the alloy. These are to be distinguished from the 'thermal stresses' that arise from thermal shock due to rapid cooling or heating. Investigators have often repeated thermal cycling experiments at much lower cooling/heating rates to ascertain that it is the former type of stresses that are really important in thermal cycling¹⁸.

The stress arising from cooling an oxide which is stress-free at the oxidizing temperature depend mainly on the difference in the expansion coefficients of scale and alloy and is given by¹⁹ (creep effects during cooling being disregarded)

$$\sigma_{ox} = \frac{E_{ox} \Delta T (\alpha_{ox} - \alpha_m)}{1 + 2 \frac{E_{ox}}{E_m} \frac{t_{ox}}{t_m}} \quad [1]$$

σ_{ox} = stress in the oxide

E_m, E_{ox} = Youngs moduli of alloy/metal, oxide

ΔT = Temperature range of cooling

α_{ox}, α_m = Thermal expansion coefficients of oxide, metal/alloy

t_{ox}, t_m = Thickness of oxide, metal/alloy.

Since in most cases $t_{ox} \ll t_m$ (' t_{ox} ' generally of the order of microns, ' t_m ' order of millimeters) therefore,

$$\sigma_{ox} \approx E_{ox} \Delta T (\alpha_{ox} - \alpha_m) \quad [2]$$

Using^{18,20,21} $E_{Al_2O_3} \approx 3.52 \times 10^{-10} \text{ N/m}^2 (50 \times 10^6 \text{ psi})$, $\Delta T \approx 1200^\circ\text{C}$,
 $\alpha_{ox} \approx 9 \times 10^{-6}$, $\alpha_m \approx 18.5 \times 10^{-6}$ for CoCrAl alloys gives $\sigma_{ox} \approx 3.87 \times 10^8 \text{ N/m}^2 (5.5 \times 10^4 \text{ psi})$ which is of the order of the compressive

strength of polycrystalline Al_2O_3 . (Assuming that [compressive strength of Al_2O_3] = 10 x [tensile strength] = 65×10^4 psi.) In addition, stresses arise from thermal shock and from the oxidation reaction, these add on in sign to the ' σ_{ox} ' calculated above. However, it is appropriate to point out at this stage that there is no obvious justification for assuming a connection between σ_{ox} as calculated above and the tendency to scale failure. This is because Al_2O_3 rarely fails by fracturing under compressive stresses. A detailed study of the mechanism of failure is required in order to establish such a connection. For the present work, a connection has been assumed a priori.

Either the stresses are accommodated by high-temperature plastic flow or failure of the scale results. An interesting analysis of the mode of scale failure was given by Evans²². It was pointed out that the mode of fracture ('blistering', 'flaking', 'shear-cracking') would be in fact determined by the degree of scale adherence; e.g., the failure mode is expected to shift from flaking to blistering or shear-cracking (although the latter is doubtful) by the improvement of adherence.

1.3 Improvement In Adherence-Rare Earth Effect (REE)

It is found²³⁻²⁷ that additions of rare earth or active elements or their oxide dispersions in relatively low amounts (~ 1 wt.%) to high-temperature alloys leads to a dramatic improvement in their oxidation resistance ('Rare Earth Effect'): 'dramatic', because of the magnitude of the effect and also because the effect has not yet been fully explained or understood. The REE has been used since, in practical

applications, notably alloys for heating elements, such as Thoria-Dispersed-Nickel-Chromium (TDNi-Cr) and TDNi. The effect has been generally observed in Cr_2O_3 and Al_2O_3 forming alloys, being more dramatic in the former. Some of the features of the REE are as follows:

1. Selective oxidation of Cr or Al is enhanced: the 'transient stage' of oxidation is curtailed in time²⁷, a fine-grained oxide forms and the establishment of a continuous layer occurs at lower Cr/Al contents in $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ forming alloys.
2. The scale growth process is modified: the scale thickening rate is appreciably lower^{30,31} and the mechanism of scale growth (outward diffusion of cations) is reversed in Cr_2O_3 formers³¹.
3. Probably the most dramatic effect is the improvement of adhesion between scale and alloy and the subsequent suppression of scale spallation; this is particularly important in cases of thermal cycling exposure.

It is to be noted that there is no way to satisfactorily distinguish between the presence of the active element-oxide dispersion and the active element itself: the active elements are highly oxygen affine and present in low concentration so they form a zone of internal oxide below the scale anyway.

Some of the proposed mechanisms for the observed increase in adherence are now mentioned and the pegging mechanism is explained in detail. Two types of mechanism have been proposed; the first type involves effects such as reduction in stresses and increases in scale plasticity (e.g., the 'enhanced scale plasticity mechanism', the 'graded seal mechanism', and the 'modification to growth process mechanism').

However, much evidence points to the more positive improvement of adhesion type of mechanisms and therefore, these will be discussed.

1. The Vacancy Sink Theory^{29,30,34}. In alloys not containing additions, voids are observed at the scale-alloy interface. These probably arise due to the collapse of vacancies; the vacancies could arise from two possible sources:

1. The cation diffusion contribution to scale growth, particularly in the early stages of oxidation when all elements oxidize, leads to a corresponding flow of vacancies towards the interface.
2. The selective loss of the scale-forming element from the alloy (Al in M-Cr-Al type alloys) leads to its depletion immediately below the scale so that an interdiffusion must occur in the alloy. Al being a slow diffuser, a lattice translation effect is present (Kirkendall Effect) and a corresponding flux of vacancies towards the interface results.

In the vacancy sink theory, it is firstly assumed that the void formation at the interface is a major factor determining scale-spallation. Then, the observed fact that the voids disappear on making additions is given as explanation of the improvement in adhesion. It is proposed tentatively^{30,34} that the presence of internal oxide dispersions below the scale provides vacancy sinks (since the interface between the dispersoid and the alloy is incoherent) thereby preventing the condensation of vacancies at the interface. Thus, the vacancy sink theory relies rather on circumstantial evidence. In fact, the precise role of

interfacial voids in scale failure is in the first place unclear.

2. The Pegging Mechanism ('Key-on Effect'). The addition of active elements/oxide dispersions leads to the growth of numerous oxide protrusions or stringers into the alloy^{23,28}, causing the scale-alloy interface to become characteristically tortuous. The mechanical keying effect of these intrusions has been suggested as the cause of improved scale adherence. Crudely, the stringers function like the roots of a tree which tend to firmly anchor it into the soil (recall the common sense meaning of the word 'pegs'). Earlier workers have investigated the nature of the pegs and found that these are Al_2O_3 (in M-Cr-Al type alloys) growing around the precipitates of active element-oxide below the scale³⁵. As would be expected, the size and distribution of the pegs has been found to be critical in imparting good scale adhesion.

There are no satisfactory models available for completely explaining the mode of formation of pegs. However, two mechanisms have been proposed as outlined below.

1. It is suggested that the oxygen ion transport is relatively rapid through the matrix of the active element oxide particle³⁶. (It is to be noted that these particles in fact precipitate ahead of the external scale but are eventually incorporated into it during its inward growth; they thus, provide high-diffusivity paths inside the scale.) The scale thus grows faster in certain localized regions and the scale underside is no longer planar but characteristically tortuous.

2. The formation of Al_2O_3 -pegs at the scale underside is essentially a case of internal oxidation of an element ahead of an external scale of the same element. A simple diffusional model for such a process was given by Wagner³⁷, and later, a more rigorous analysis presented by Whittle and Smeltzer³⁸. The main idea in this kind of mechanism is the enhancement of oxygen diffusivity in the alloy phase at the incoherent boundary between the alloy and the active element oxide particle. This raises the value of dissolved oxygen concentration locally at points the same distance below the interface but not lying along high-diffusivity (short-circuit) paths (i.e., incoherent boundaries). Further, there is an Al concentration gradient below the scale (which depends on the relative values of Al-diffusion rate in the alloy (D_{Al}) and the parabolic growth rate constant of the scale (K_C), D_{Al}/K_C so that the precipitation of Al_2O_3 can become thermodynamically possible at points below the interface, the product $[a_o(x)^{3/2} a_{Al}(x)]$ having exceeded the equilibrium constant, see Fig. 1.

A mathematical criterion for the possibility of the aforementioned type of internal oxidation was derived using a simplified diffusion model by Wagner³⁷. The criterion is posed in terms of diffusion and parabolic rate constants and concentrations of the oxidizing element in question:

$$(\pi/2)^{\frac{1}{2}} \left(\frac{1-N_A^o}{N_A^I} \right) \frac{(K_C D_O)^{\frac{1}{2}}}{\sqrt{D_{AB} \{1-F[(K_C/2D_{AB})^{\frac{1}{2}}]\}}} > 1 \quad [3]$$

where,

- N_A^o = bulk mole fraction of element A
 K_c = parabolic rate constant of the scale ($= x^2/2t$)
 D_{AB} = interdiffusion coefficient of alloy A-B
 D_O = diffusion coefficient of oxygen in the alloy
 $F(u)$ = the auxillary function for argument 'u' $F(u) = \sqrt{\pi} u \exp(u^2) \operatorname{erfc}(u)$
 N_A^I = concentration of A at the scale alloy interface
 and is given by (using mass balance),

$$N_A^I = \frac{N_A^o - F[(K_c/2D_{AB})^{\frac{1}{2}}]}{1 - F[(K_c/2D_{AB})^{\frac{1}{2}}]}$$

Substitution of approximate values for the case of Al in Co10Cr11Al (which may be treated as a pseudo-binary for the purpose of calculation) in the above-stated Wagner criterion (3) shows that the value of the expression is in fact not appreciably different from unity. It, therefore, seems reasonable that short circuit paths provided by the incoherent active element oxide-alloy boundaries (high local D_O) should indeed promote internal Al_2O_3 -peg formation as suggested by the model.

2. PRESENT WORK

2.1 Objective of Present Work

Some of the proposed models for explaining the improved scale adherence promoted by active element/oxide dispersion additions to the alloys have been explained in the previous section. Among the most accepted theories is the mechanical keying effect of oxide intrusions running into the alloy (pegging) presumably encapsulating the internal oxide particles. Although the general effect of pegging has been beneficial,

it was found from most work reported in literature that considerable differences in peg morphologies are possible and the resulting beneficial effects are not necessarily identical. Furthermore, it appeared that the peg-morphologies were related to the prior alloy microstructure not simply the presence of active element/dispersed oxide. In particular, the following key observations are of relevance:

1. Hf and Y containing alloys showed different peg morphologies on oxidation, there being a corresponding difference in the improved oxidation resistance promoted, Hf being more effective than Y³⁴.
2. Pt additions (note that Pt is a completely inert element) were found to have an effect⁴⁰⁻⁴², particularly in Hf-containing CoCrAl and in each case the origin of the effect was traced to be in the alloy microstructure^{41,42}; the precipitation of inter-metallic phases (e.g., Pt Hf₃) and their uniform dispersion in the alloy led to favorable peg-morphologies.
3. Among the most important observations (and in fact the one that primarily led to the present work) was the recent work on vapor deposited Co-Cr-Al coatings^{43,44}. These coating alloy structures showed on oxidation quite distinct peg morphologies, different from cast alloys, consisting of Al₂O₃ penetrating to relatively large depths preferentially down boundaries between α - β phases in the microstructure⁴⁴. It was suspected that these α - β incoherent boundaries could as well act as short circuit paths to promote peg-formation.

There have been no previous attempts at relating the observed peg morphologies with the characteristics of the underlying alloy and its behavior in the region below the scale-alloy interface during the oxida-

tion process. Some important factors could be: the alloy microstructure and the high-temperature response of the alloy to the stresses arising from the oxidation process. It was the objective of the present work to investigate the above possibilities particularly the micro-structural effects, in the light of the earlier observations (3) mentioned above.

It must be realized that such a study is of significance not only because it could lead to a new concept in pegging theory but also because it could probably help establish a dependence of the oxidation behavior on factors such as alloy (or coating) processing conditions and this is of great importance from the point of view of alloy design.

It was decided to investigate peg morphologies in cast alloys for three different compositions so that comparison with the case of vapor deposited structures mentioned earlier (observation (3) above) would prove meaningful.

2.2 Experimental Approach

Cast alloys with the basic composition Co10Cr11Al were selected for study with the three compositions (all compositions wt. % unless otherwise stated) indicated in Table 1. The reasons for the choice of the basic composition were as follows:

1. The Al-content in this alloy (11 wt.% Al) is well in excess of that needed for the formation of a 'compact' continuous Al_2O_3 scale⁹. The minimum Al-content required for this purpose is approximately 8%⁹. Thus, in studying peg morphologies inconsistencies that may arise due to difficulties in continuous scale formation are eliminated.
2. The alloy has a two-phase structure with approximately equal amounts of α and β phase. Fig. (2) shows a section of the

TABLE 1

Composition of the Alloys Studied (wt.%)

Alloy	% by wt. of				
	Cr	Al	Hf	Y	Ce
1.	10	11	-	-	-
2.	10	11	1	-	-
3.	10	11	-	1	-
4.	10	11	-	-	1

ternary phase diagram at 1100°C with the 'oxide map'⁹ superimposed on it. Typical microstructures are shown in Fig. (3). The α -phase (light phase) is a solid solution of Co-Cr-Al with maximum Al-solubility of approximately 5 wt.% and the β -phase is an intermetallic CoAl (dark phase) its relative amount in the alloy depending directly on the relative amount of Al in the alloy. The above type of microstructure is most suited for investigating the influence of phase boundaries on the peg morphology and for subsequent comparison with the observations on the vapor-deposited (VD) coatings. Furthermore, as pointed out earlier, the boundaries between the phases are incoherent because the relative amount of β -phase is large and the difference in structure and lattice parameter of the two phases is large enough as has been reported in literature⁴⁵.

The above alloys were to be suitably heat treated/processed so as to change the microstructure and then oxidized in identical conditions whereby its relationship (if any) with the pegging process could be studied.

The pegs are visible easily in cross section in a simple optical microscope at magnifications of 500X or higher. A more complete idea of the morphology, habit, and (sometimes) the qualitative analysis of the oxide peg can be obtained only by viewing the scale underside in 'three dimensional manner' in the scanning electron microscope (SEM) after the alloy has been dissolved. This technique (deep etching), described in detail in the next section, was to be used extensively since it is particularly suited for the study of the morphological features of the scale. The technique has proved quite useful in identifying the 'internal

sheaths' to be described in a later section.

Continuous weight change measurements during oxidation are necessary in most oxidation studies. However, since the main interest in the present work was a study of distribution and morphology, continuous weight change measurement was found unnecessary. A good idea of the oxidation behavior is obtained by examining carefully polished sections of the scale (which generally show breakaway very clearly) in the microscope as well as from weight gain measurements before and after the oxidation (sample and crucible weight changes, details in next section) which provide some indication of isothermal oxidation behavior and scale breakaway during a single cooling cycle from the oxidizing temperature to room temperature.

Further, it was noted that in most oxidation studies involving the rare earth effect, a zone of internally oxidized active element-oxide particles below the external scale and unoxidized active element in the bulk of alloy are present at once. There always exists therefore, an ambiguity as to whether the observed oxidation behavior has its origin in the zone of internal oxides or the unoxidized element which could possibly affect the microstructure and the diffusional process in the alloy. A good way to separate these effects could be to fabricate alloys (e.g., by powder metallurgy route) which contain the active element oxide phase itself dispersed already, but no active element, so that the oxidation behavior of such alloys would be independent of any possible active element effect. On the other hand, the role of unoxidized active elements could be tested by essentially simulating the oxidation process by a diffusion process in a simple diffusion-couple experiment (e.g.,

Co-CoCrAl)(This would not involve any active element-oxide formation and the effect of the active element could be singled out). Such a simulation is quite valid because the alloy-side of an oxidizing sample is essentially undergoing a diffusional loss of Al by oxidation, and in the simulated case this occurs by simple diffusion. The validity of this approach was partly established in the present work although conclusive experiments have not yet been performed.

3. EXPERIMENTAL METHODS

3.1 Alloy and Sample Preparation

Alloys of nominal compositions as shown in Table 1 were generally used throughout the present work. These alloys were prepared by vacuum melting in an inert gas induction furnace at $\sim 1500^\circ\text{C}$. Ingots of $4\frac{1}{2}$ cm and 5 cm diameter and 25 cm length were prepared by melting of the metals in calculated amounts at 1500°C and allowing to mix for 15-20 minutes. None of the ingots were homogenized mainly because sufficient mixing is ensured anyway via the rapid stirring motion in the molten bath introduced by the induction-melting process. Also, it is desired not to oxidize the active elements internally.

Attempts were made to prepare certain alloys by a powder metallurgy (P/M) route: calculated amounts of metal powders (Co: -300+400 # 49.9% pure, Cr 325 #, 99.9% pure, Al -9 μ , Y_2O_3 -325 #, 99.9% pure) were mixed in a mill containing Al_2O_3 pellets for 2 hours, then cold compacted at $3.5 \times 10^8 \text{ N/m}^2$ (~ 5000 psi) in a steel die and sintered in a step-wise manner (675°C -5 hrs. then 1250°C -20 hrs.). However, good densities were not obtained (voids were seen when observed in the microscope). Hence a hot-pressing technique was tried. Hot pressing was also done in a step-wise manner. A graphite die was used with a boron-nitride sleeve

to avoid contamination. The powder mixture corresponding to $\text{Co}_{10}\text{Cr}_{11}\text{Al}_{11}\text{Y}$ (i.e., 1.27 wt.% Y_2O_3) was initially held in the die at 700°C for 6 hrs. for the intermetallic phases to form. The temperature was then raised to 1250°C and pressure upto $3.5 \times 10^8 \text{ N/m}^2$ (5000 psi) applied gradually. The mixture was left under this pressure for $2\frac{1}{2}$ hrs. then subsequently cooled. The press was sealed from the atmosphere and filled with Argon to prevent oxidation.

Samples for oxidation studies were prepared by first polishing successively on silicon carbide paper of 180, 240, 320, 600 grit then washing in soap water and finally cleaning in ethyl alcohol by ultrasonic 'shaking' for 5 minutes.

3.2 Heat Treatments

Annealing of samples was carried out in an evacuated mullite tube, approximately 50 cm in length and 26 mm in diameter. The tube was attached with a glass fixture and rubber tubing to facilitate evacuation. The specimens were placed in an alumina boat and introduced into the tube alongside a similar boat containing tantalum foil to getter the traces of oxygen left over after evacuation. The tube was pumped down to a vacuum of $< 50 \text{ mm Hg}$, introduced into the furnace and the furnace temperature raised to the desired value. Heat treatment was done at several different time-temperature combinations (e.g., 1200° , 1100° , 1000° -50 hrs, 100 hrs) however, the 1200° -100 hrs and 1200° -50 hrs. treatment was usually used on most samples since it gave a noticeable amount of phase-coarsening. The samples were held for the desired time then removed, ground (to remove the tarnish layer formed on annealing) and prepared for oxidizing runs.

Attempts to radically change the microstructure by treatments such as quenching directly from the liquid-formation temperature and so forth

failed because of severe cracking problems, therefore, only the annealing heat treatments were used.

Annealing of diffusion couples (see later) was performed in vacuo similar to the heat-treatments already described. The two 'members' of the diffusion couples (approximately 1 cm x 1 cm x 1 cm in size) were initially polished (one face) to 1 μ m using diamond paste. They were then held face to face securely by means of a fine Nichrome wire and placed in the mullite tube for annealing. The tube was evacuated before introduction into the furnace.

3.3 Oxidizing Runs

The oxidizing runs were generally carried out in a horizontal Lindberg furnace with a mullite tube in air at 1000-1200° ($\pm 10^\circ$). The samples were placed in an Al_2O_3 boat which was directly introduced into the hot zone of the furnace tube. Some runs were done in a vertical furnace by placing the sample in a crucible and suspending the crucible by means of a Nichrome wire.

The samples were weighed before and after the oxidizing run to obtain isothermal weight change values. Many samples were weighed both separately as well as along with the crucible (before and after oxidation) in view of the possibility of scale spallation (in which case the sample would show weight loss but the [crucible + sample] would show weight gain, etc.) The surface area of the samples was calculated from the exact dimensions measured by means of a micrometer.

3.4 Microscopy

Typical specimens were examined after each treatment and oxidizing run. The specimens were mounted in epoxy and first polished through 600 grit (SiC paper), then, after washing, were polished on diamond paste through 1 μ m (sometimes down to $\frac{1}{2}$ μ - Al_2O_3 polish if x-ray analysis was

to be done).

Optical microscopy was used to view the scale in section and in plan. For the plan view (see Figs.4), the samples were polished at a slight angle to the plane of the scale resulting in a 'slanting' section so that the scale got removed to differing extents over the section (Fig. 4). For optical microscopy, the specimens were lightly etched (2:1:1 mixture of concentration HCl + Concentration HNO_3 + Distilled Water for ~ 20 secs.) before examination to reveal the microstructural features.

Samples were also examined in the scanning electron microscope (SEM). To get a better idea of the morphological features of the scale underside, several samples were examined after 'deep-etching'. This involves dissolving away the alloy in a warm ($\sim 80^\circ\text{C}$) solution of methanol-10% Bromine leaving the scale 'standing in relief'. (The mounted sample is held face down in the above solution for ~ 5 minutes then removed and held gently in water and/or methanol to completely remove traces of bromine). Such samples were examined in the SEM by suitably tilting the sample so as to directly reveal the scale underside.

X-ray analysis was done (usually, qualitative analysis and x-ray mapping) on polished samples using the Energy Dispersive Analysis (EDAX) attachment on the Scanning Microscope.

4. RESULTS AND DISCUSSIONS

4.1 Heat Treatment

The as cast and heat treated microstructures as revealed on etching are shown in Figs. 5, 6 and 7. Note that the Y and Hf-containing alloys tend to be fine grained. Also, phase coarsening occurs on heating which is essentially an Ostwald Ripening effect⁴⁷. The quantitative

aspects of this phenomenon are not important for the present work. Since our interest was mainly in examining a possible correlation between 'pegs' and phase boundaries, the wider spacing of phase boundaries is the only point to note.

Figs 8, 10, 12 show scale morphologies in cross-section (optical micrographs) for the as-cast and heat treated alloys. The same morphologies on deep etching of oxidized specimens (as seen in the Scanning Microscope) are shown in Figs. 9, 11 and 13. The corresponding micrographs should be compared. The following points must be noted:

1. In the Co10Cr11Al alloys (addition free) the scale-metal interface is flat and shows no inward growing protrusions or pegs; the scale on this alloy always spalled on cooling to room temperature. Weight change measurements for this alloy did not prove to be a useful guide of isothermal oxidation behavior because the scale spalls profusely on cooling and is probably lost out of the crucible due to pieces of scale being ejected while spallation occurs. Thus, one must rather rely on the micrographs (oxide cross-sections depleted zone thickness, etc. Figs. 8(c)-13(c)) for assessing the oxidation behavior and making comparisons for the different heat treated alloys.

It is found that the oxidation behavior of these alloys is not influenced by heat treatment. As noted earlier, heat treatment only causes phase-coarsening, thereby changing the spacing of the α/β phase boundaries. Therefore, in view of the fact that the suspected association of 'pegs' in case of addition-free CoCrAl vapor-deposited coatings with phase boundaries in the microstructure is completely absent in the

as-cast structure ('pegs' do not form at all), one would not expect a dependence of the oxidation behavior on heat treatment (and thus, phase coarsening) and this is indeed observed to be the case.

2. The CoCrAl-Y and CoCrAl-Hf alloys show a different, rather tortuous scale-alloy interface with oxide protrusions or pegs at the scale-underside; the pegs are Al_2O_3 encapsulating the internally precipitated active-element oxides³⁵ (also, see later). In the Hf-alloys they are relatively more branched and well-distributed compared to the localized pegs in the Y-alloys. As pointed out in earlier work^{35,39}, this is related to the segregated nature of the Y in the Y-containing alloy (in the form of yttride (CO_3Y)) as against the solid soluble Hf, in the Hf-containing alloy. The Hf-containing alloy shows superior oxidation resistance, the scale remaining completely adherent on cooling the sample to room temperature as against the Y-alloys where some spallation occurs. Secondly, the peg morphology in Hf-alloys does not seem to be associated with the alloy phase boundaries and is unchanged by heat treatment. In the case of the Y-alloy the Y_2O_3 (and therefore, the pegs) forms preferentially at the phase boundaries because of the presence of the yttride phase and a dependence of peg morphology on heat treatment is probable; but none was observed (see corresponding micrographs in Figs. 8(b)-13(b)). However, more importantly, it is seen (Figs. 14), that the size of the peg itself has increased considerably and the pegs are even more localized on heat-treatment, presumably due to the coarsening of the yttride phase itself during heat-treatment. This

notion is in agreement with the observation that the more severe heat-treatment leads to the more severe coarsening, Figs. 14. Also, there is no similar coarsening effect in the Hf-alloy as is to be expected because Hf is completely soluble and forms no intermetallic phase. Detailed calculations of the Ostwald ripening rate (i.e., the coarsening rate) have not been performed for lack of precise data but a good idea of such a process can be obtained from the original ripening equation^{46,47}:

$$r \left(\frac{dr}{dt} \right) = \frac{2v\sigma}{RT} \frac{D C_M}{C_p} \left[\frac{1}{r_A} - \frac{1}{r} \right] \quad [4]$$

where,

r = size of precipitate

r_A = average size of precipitates

C_M, C_p = solubilities of Y in the matrix, precipitate resp.

D = diffusion coefficient of Y in alloy

v = molar volume of precipitate

σ = surface tension between yttride phase and alloy matrix.

In the present case, Y is known to be a fast diffuser in the temperature range of interest⁵⁶ and further, the average particle size is extremely small ($\sim 1 \mu\text{m}$) as estimated from micrographs and therefore, an appreciable ripening rate of the yttride phase is to be expected at 1200°C.

4.2 Depleted Zone

An important feature in all of the three alloys studied is the appearance of a β -depleted zone below the scale on the alloy side. This zone is easily revealed in the optical micrographs (e.g., Figs. 8, 10, 12) but is less obvious in the deep-etched scanning micrographs (Figs.

9, 11, 13). It arises from the fact that the Al-rich β -CoAl phase loses Al preferentially during oxidation, thereby transforming to the α -phase and causing recession of the α - β interface to occur into the alloy. Therefore, a region depleted of β -phase results.

By using a simple mass balance, the amount of Al lost to form the scale can be estimated from the 'measured' thickness of the depleted zone.

$$\begin{aligned}
 &\text{Approximate volume fraction of } \beta\text{-phase in} \\
 &\text{unoxidized alloy} \text{ ----- } v_{\beta} \\
 &\text{Thickness of depleted zone} \text{ ----- } t \\
 &\text{Approximate volume of } \beta \text{ 'lost' during oxidation} \\
 &\text{(per unit surface area of sample)} \text{ ----- } v_{\beta} \cdot t \\
 &\therefore \text{ wt. of } \beta\text{-phase 'lost' ----- } v_{\beta} \cdot \rho_{\beta} \cdot t \text{ (}\rho_{\beta} = \text{density} \\
 &\hspace{15em} \text{of } \beta\text{-phase)} \\
 &\therefore \text{ wt. of Al 'lost' ----- } \frac{M_{\text{Al}}}{M_{\text{CoAl}}} (v_{\beta} \cdot \rho_{\beta} \cdot t) \\
 &\hspace{15em} M = \text{atomic/molecular} \\
 &\hspace{15em} \text{wt.} \\
 &\therefore \text{ Approximate wt. gain/area of sample ----- } \frac{M_{\text{Al}}}{M_{\text{CoAl}}} (v_{\beta} \cdot \rho_{\beta} \cdot t)^{\frac{3}{2}} \frac{A_0}{M_{\text{Al}}} \\
 &\hspace{15em} = (v_{\beta} \cdot \rho_{\beta} \cdot t) \frac{3A_0}{2M_{\text{CoAl}}} \quad [5]
 \end{aligned}$$

The above quantity was evaluated for certain alloys using experimental values for ' v_{β} ' and ' t ' from optical micrographs at 640X and is reported in Table 2. The value of ' t ' was obtained as an average of values measured directly from the micrograph and corrected for by the magnification factor. ' v_{β} ' was taken approximately equal to ' A_{β} ' where ' A_{β} ' is the area fraction of the dark phase in the microstructure. This latter quantity was obtained by 'counting' the areas of dark and light phases by superimposing a graph paper on the micrograph.

It is clear from Table 2 that the agreement between the weight gain

TABLE 2

Isothermal Oxidation Behavior, → 1200°C 50 hrs. in Air

Alloy	Prior Heat Treatment	Wt. Change/Area (g/cm ²) (Average Value)	Wt. Change/Area Calcul. from depl. zone thickness
			$= \frac{3A_0}{2M_{CoAl}} (v_{\beta} \cdot \rho_{\beta} \cdot t)$
Co10Cr11Al		-	-
Co10Cr11-Al-1Y	As-cast	6.8×10^{-4}	14×10^{-4}
Co-10Cr11Al-1Hf		20×10^{-4}	30×10^{-4}
Co10Cr11Al	Annealed	-	-
Co10Cr11Al-1Y	50 hrs.	5.1×10^{-4}	20×10^{-4}
Co10Cr11Al-1Hf	at 1200°C	22.6×10^{-4}	19.8×10^{-4}
Co10Cr11Al	Annealed	-	-
Co10Cr11Al-1Y	100 hrs.	7.1×10^{-4}	16×10^{-4}
Co10Cr11Al-1Hf	at 1200°C	18.1×10^{-4}	27.6×10^{-4}

values calculated as above and those obtained from direct weight measurements is not very good. However, the values are of the same order. Recall that several assumptions were made in the above approach: ' v_{β} ' is calculated in a highly approximate manner, also the calculation is based on the oxidation of Al alone whereas actually all elements oxidize in the transient stage and internal active element-oxides form continuously; also, the scale-alloy interface recedes slightly, which has not been considered; etc.

It is to be noted that the depleted zone thickness (which is relatively easy to measure) is in fact an indirect measure of the scale thickness. Figs. 15 show the change of depleted zone thickness with oxidizing time. The thickness does not seem to change parabolically with oxidizing time for the Y-containing alloy ($x^2/2t \neq \text{Constant}$). However, the variation is very close to parabolic in case of the Hf containing alloy. Also, the thickness is lowest for the addition-free alloy and highest for the Hf-containing alloy under identical oxidizing conditions (cf Figs. 8, 10, 12, 15). The depletion zone thickness essentially depends on two properties of the alloy-oxide system: the diffusion rate in the alloy (the diffusion coefficient, D) and the oxidation rate in the scale (the parabolic rate constant ' k '). It is, therefore, clear that either of these quantities (or both) is influenced by the addition of active elements and/or oxide dispersion.

Since during a typical oxidation experiment, the alloy side of the sample essentially undergoes only a diffusional loss of Al, the effect of the active element on the oxidation process can be 'simulated' by a simple diffusion couple experiment in which one member of the couple is the alloy of interest (with the active element) and the other is an alloy poorer in Al which thus removes Al from the former by diffusion.

The main advantage of this simulation, of course, would be that it would involve no oxidation and the effect of the active element could be separated from that of the active element-oxide precipitating internally. The validity of the above approach has been established by observing qualitatively the profiles of annealed Co-Co10Cr11Al and Co-Co10Cr11Al1Y diffusion couples, see Figs. 16. Note the striking similarity with the alloy-side of the oxidized sample of the corresponding alloys Co10Cr11Al and Co10Cr11Al1Y in Figs. 8(b),(c) with the exception (as expected) that no internal Y_2O_3 is found in Fig. 16(b) but it is found in Fig. 8(b). Also, whereas the depletion zone is thicker for oxidized Co10Cr11Al1Y than for Co10Cr11Al (see Figs. 8(a), (b)), the reverse is true in the diffusion couples. Thus, the difference in depletion zone thicknesses between the oxidized Co10Cr11Al and Co10Cr11Al-1Y samples seems to stem not from corresponding differences in alloy-diffusion processes but more likely from differences in the oxidation rates in the scale (as suggested in the previous paragraph) presumably promoted by the incorporation of the active element-oxides therein.

It is to be further noted that although the scale alloy interface in the Hf- and Y-containing alloys is irregular due to pegging, the interface between the two-phase zone and the depleted zone is relatively flat, there being no corresponding irregularity at this latter interface. This supports an earlier pegging model involving HfO_2 -particles acting as high-diffusivity paths for oxide-ion transport in the scale³⁶. These particles would otherwise locally block the scale-growth causing lesser Al-loss from the alloy regions immediately below them and an irregular $\alpha/\alpha+\beta$ boundary would result. However, as already mentioned, this is not observed, the boundaries in all the samples being always flat (e.g., see Figs. 8 and 15).

An important morphological difference between the Hf- and Y-containing alloys is apparent in all micrographs: whereas in the Hf-alloys the oxide intrusions (pegs) are seen to lie completely in the depleted zone only, in the Y-containing alloys they penetrate deeply along phase-boundaries into the two-phase zone of the alloy. The significance of this observation may be realized by recalling that a primary objective of the present work was to assess the possibility of a correlation between the pegs and the incoherent phase boundaries which was suspected in the earlier work on oxidized VD (vapor-deposited) coatings. The nature of these deeply penetrating 'pegs' (later, to be called 'sheaths' rather than pegs) in Y-containing alloys has, therefore, been investigated in detail in the following.

4.3 Internal Sheath Formation

As is clear from the earlier micrographs, the 'pegs' in the Y-containing alloy have a rather characteristic morphology. They show two zones, Fig. 16, an upper zone of relatively branched short and fairly thick pegs connected with the scale underside and a lower zone of membranous sheath-like 'pegs' (hereafter to be referred to as 'sheaths' distinct from 'pegs') penetrating deeply and enveloping the dark phase in the microstructure, Figs. 17. The segregated growth of the sheaths in the Y-containing alloy in contrast to the Hf alloy in which the sheaths are totally absent, is seen more vividly in a plan view of a sample polished in a 'slanting' manner, see Figs. 18. A pronounced phase boundary network is seen in the two-phase region as well as in the single-phase region in the Y-alloy whereas the dark 'spots' (which are oxide pegs in plan) in the Hf-case lie only in the single phase region being entirely absent in the two-phase zone (Figs. 18). Further, whereas the pegs form an almost continuous network at the scale under-

side the sheaths seem to develop only occasionally, and in a segregated manner around the boundaries. Also, these sheaths are thin and two dimensional in shape (Fig. 19), but can extend upto $\sim 100 \mu\text{m}$ deep into the alloy, below the scale-alloy interface (Fig. 17). EDAX analysis of a sheath, Fig. 19, has shown that sheaths contain Al and Y (the Co and Cr peaks are quite insignificant) which implies that the sheath is essentially Al_2O_3 associated with Y_2O_3 . If the Al, Y were in metallic form, they would dissolve away during deep-etching, whereas in fact the sheaths stand out in relief. Observation of the heat treated alloys shows that the peg morphology is probably influenced by the heat treatment (cf Figs. 8-13), but the sheath morphology is relatively insensitive to it. However, it was found that the as-cast alloys show a more pronounced tendency towards sheath formation than the heat treated alloys.

It does not seem reasonable to expect depths of penetration of Al_2O_3 of the order of magnitude found (upto 150μ) in terms of a simple diffusional model for internal oxidation. In the first place, as was pointed out earlier, the Wagner criterion³⁷ for simultaneous internal oxidation and external scale formation is only barely satisfied for the present type of system, even if a high value for the oxygen diffusion coefficient in the alloy is assumed. The model proposed earlier for the formation of the pegs by short circuit diffusion of oxygen down incoherent Y_2O_3 -alloy boundaries is acceptable as long as the pegs are conceived of as 'short' ($\sim 1\text{-}5 \mu\text{m}$, order of magnitude) protrusions, but it becomes unreasonable for the depths of penetration of sheaths observed in the Y-containing alloys as will be shown below. The sheaths must, therefore, have a quite different mechanism of formation from

pegs (which is also a plausible reason for their different morphology).

A simple approximate calculation for the depth of penetration of Al_2O_3 in the phase boundary regions is presented using the original model of Wagner³⁷. The value of the permeability product ($D_0 N_0$) is evaluated using experimental values for depth of penetration and time. This is compared with values expected from reported data in literature and it is shown that such data give values too low to account for the observed penetrations, thus suggesting some form of rapid entry of oxygen.

The equations for internal oxidation ahead of an external scale have been derived originally by Wagner^{8,37} and later reviewed by Rapp⁴⁸. The following simplified expression is obtained by making the assumption of a small parabolic rate constant of internal oxidation and small thickness of external scale compared to the depth of the internal oxidation zone.

$$N_0^S D_0 = v N_{\text{Al}} \frac{(\xi - x)\xi}{2t} \frac{1}{F[\xi/2(D_{\text{Al}} t)^{1/2}]} \quad [6]$$

where,

N_0^S = oxygen solubility at scale alloy interface,

D_0 = diffusion coefficient of oxygen in alloy,

N_{Al} = bulk Al-mole fraction in alloy,

ξ = depth of internal oxidation zone (measured from original gas-alloy interface),

D_{Al} = diffusion coefficient of Al in alloy,

x = thickness of scale,

v = 3/2 for Al_2O_3 (BO_v),

and $F(u)$ is the auxillary function for arg. 'u' (defined earlier).

Further, by taking $x \ll \xi$ and $D_{\text{Al}} \ll D_0$ which are valid for the present case, the equation reduces to one of the simpler limiting cases

involving no external scale formation⁴⁸:

$$N_o^{(s)} D_o = \frac{v N_{Al}^2}{2t} \quad [7]$$

Taking

$$v = 3/2$$

$$t = 50 \text{ hrs.} \approx 50 \times 3600 \text{ secs.}$$

$$N_{Al} = 0.05 \text{ (bulk molefraction)}$$

$$\xi \approx 100 \mu \approx 10^{-2} \text{ cm}$$

gives

$$N_o^{(s)} D_o = 6.25 \times 10^{-12} \text{ cm}^2/\text{sec.}$$

Further, taking $D_o \approx 10^{-7} \text{ cm}^2/\text{sec.}$ from literature⁴⁹ for dilute Co-alloys, gives

$$N_o^{(s)} \approx 6 \times 10^{-5}$$

Considering reported values of oxygen solubility in liquid Co-Al and the fact that the oxygen solubility must be in equilibrium with the Al_2O_3 scale, (note that the Al-content in the alloy at the scale-alloy interface as determined by Wagner's diffusion model, $N_{Al}^I = \frac{N_{Al} - F[(k_c/2D_{AB})^{1/2}]}{1 - F[(k_c/2D_{AB})^{1/2}]}$, is close to the bulk Al content because $k_c \ll D_{AB}$ for the present alloys so $F[(k_c/2D_{AB})^{1/2}] \ll 1$ and also $F[(k_c/2D_{AB})^{1/2}] \ll N_{Al}$; here, N_{Al}^I - Al-content of the alloy at the scale-alloy interface, k_c - parabolic rate constant for the external scale measured in terms of the recession of the alloy-scale interface, D_{AB} - interdiffusion coefficient for the pseudo-binary Co-Al alloy), the value $N_o \approx 6 \times 10^{-5}$ is high by a few orders. Since this value is unreasonable, a simple lattice-diffusion mechanism for oxygen is unlikely unless the diffusion coefficient of oxygen is itself higher by a few orders of magnitude.

At a temperature of 1200°C (1473 K), which is close to $0.8-0.9 T_m$

for the present alloy, and for an interstitially diffusing species (oxygen), an appreciable enhancement in the diffusivity by a phase-boundary or grain-boundary mechanism is unlikely⁵⁰. It is, therefore, proposed that a gas-phase entry of oxygen is a more probable mechanism.

Gas-phase entry would require the formation of open channels or voidage during the oxidation process. It is proposed that these channels form preferentially along the α/β phase boundaries in the two phase region nearest the scale thereby admitting oxygen into the alloy to form internal Al_2O_3 -sheaths. Exactly, why and how these may form is discussed below; but initially it is shown that oxygen-transport through such a channel (if indeed the channel does form) is feasible by a mechanism suggested by earlier workers⁵¹: The part of the scale below which a porous channel is formed can dissociate in that region. Now, since there is an Al-depletion zone below the scale (see earlier), and therefore, an Al-depletion gradient towards the interior of the alloy, the oxygen activity at the dissociated region of the scale is sufficient to oxidize Al in the interior, thereby forming internal Al_2O_3 -sheaths (also, internal Y_2O_3 , because Y is an even more oxygen-affine element than Al).

Some voidage and porosity could be identified at the boundary regions associated with the Al_2O_3 -sheaths in the optical and scanning microscopes. However, this was not entirely obvious and therefore, a subsidiary experiment was attempted. Previously oxidized samples of the Y-containing alloy were polished in such a way as to remove the scale, the single-phase depleted zone in the alloy and some part of the two-phase region. These samples were then reoxidized. A similar experiment was performed on the Hf-containing samples. It was found that the Y-alloys show catastrophic oxidation behavior with considerable

oxide-penetration and weight gain, Figs.20, presumably due to a network of channels intersecting the surface after partial polishing of the oxidized samples. On the contrary, the Hf-containing alloys show an oxidation behavior on reoxidizing which is similar to the normally oxidized samples, Figs. 20. These facts support the idea of channel formation at the phase boundaries and the subsequent formation of internal sheaths.

Although the idea of porous channel formation may be reasonably inferred from some of the above observations, statements regarding the origin (i.e., mechanism of formation) of the channels can at best be of a speculative nature. Some of the possibilities are mentioned below; they are not mutually exclusive and could operate simultaneously.

1. It was pointed out earlier that Y is present as an yttride phase segregated at phase-boundaries. Further, the oxidation of yttrium occurs with an increase in volume (Pilling Bedworth Ratio for Y, $PBR_Y = \frac{\text{Vol. of oxide formed}}{\text{Vol. of Y oxidized}} = 1.133$). Therefore, an internally oxidized Y_2O_3 particle acts as a dilatation center giving rise to a stress field in the alloy, the nature of which depends upon the shape of the particle and the magnitude on the size⁵². It is possible that the stresses arising from such internal oxidation of yttride particles initiate a crack-like channel along the weaker incoherent α - β phase-boundary region.
2. Some investigators have emphasized the importance of oxidation stresses in studies relating to the high-temperature oxidation of alloys⁵³. In Al_2O_3 forming alloys, the scale grows by inward diffusion of oxygen ions via short circuit paths^{34,54}. Thus, the site of the reaction is the scale-alloy interface.

The volume increase during the oxidation of Al ($\sim 30\%$, because PBR for Al = 1.38) is therefore, accommodated by the development of biaxial compressive residual stresses in the scale and tensile stresses in the alloy. It has been pointed out by Harris⁵³ and originally by Hull and Rimmer⁵⁵ that it is energetically favorable for voids (of a minimum critical size $\gamma_{crit} = \frac{2\gamma}{\sigma}$, γ -surface energy, σ -stress) to grow under such a stress by the so called Hull-Rimmer creep mechanism. Such voidage develops in a channel-like form along boundaries lying perpendicular to the plane of the scale⁵⁵. The morphology of the channels (and subsequently of the sheaths) observed in the present work is very similar to the above. However, experiments directed at obtaining further evidence for the validity of this mechanism were not attempted.

3. The possibility of voidage forming preferentially at incoherent boundaries⁵⁰ by the condensation of Kirkendal vacancies in the alloy³⁴ or vacancies injected from the scale during the transient stage of oxidation has also been pointed out by earlier workers but no reproducible 'channel formation' was reported.

An important point seems to be the segregated nature of the yttride phase, because sheaths are completely absent in the Hf-containing alloys. Therefore, it appears that the channel-formation is probably triggered off by a mechanism of the type suggested in 1. above.

5. CONCLUSIONS

1. In Y-containing CoCrAl alloys (and presumably also in other similar alloys where active elements from segregated phases) the pegging process

needs to be further characterized: These alloys show internal Al_2O_3 formation in two distinct zones. An upper zone of relatively short, branched 'pegs' directly connected with the scale and a lower zone of morphologically different 'sheaths' developing along α - β boundaries. Whereas the former may form by a short circuit diffusion mechanism and have a beneficial effect, the latter probably form by gas-phase entry and could be detrimental.

2. The phase boundaries between α and β phases in the microstructure of CoCrAl alloys do not seem to influence directly the pegging process. However, it cannot be denied that the above effect may be preemptively suppressed by the appearance of a β -depleted zone below the scale.

3. Although α - β boundaries do not seem to play a direct role, the alloy microstructure can have a role to play in specific cases. For example,

1. In vapor deposited alloys the processing technique introduces microstructural defects at the α - β boundaries which then act as sites for channel formation and oxygen is admitted into the alloy.
2. In alloys containing active elements that can form segregated phases in the microstructure (e.g., Y in Y-containing alloys), channel formation is triggered by the internal oxidation of these segregated elements and gas-phase entry of oxygen occurs.

It is to be recognized that the relevance of the points mentioned above goes farther than the specific problem of elevated temperature oxidation resistance: They constitute vital consideration in the general problem of high temperature alloy design.

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7. FIGURE CAPTIONS

Figure 1. Illustrating mechanism for peg formation.

- a. The oxygen-profile is modified near an internal oxide particle (dashed curve)
- b. The modification of profile in (a) causes $a_{Al}(a_o)^{3/2}$ to exceed the solubility product and so a 'peg' forms.

Figure 2. The 'oxide-map' for Co-Cr-Al system superimposed on the ternary phase diagram.

Figure 3. Typical as-cast microstructures:

- a. Co10Cr11Al, etched, 640X
- b. Co10Cr11Al-1Y etched, 640X
- c. Co10Cr11Al-1Hf etched, 640X

Figure 4. Schematic of a plan-view from a polished low-angle 'slanting' section.

- a. In the case represented, pegs lie completely in the depleted (i.e., single phase) zone. e.g., Hf-containing alloy. (However, in Y-containing alloys, Al_2O_3 -sheaths enter 2-phase zone and decorate phase boundaries, see later Figs. 17) Region 3: 2 phase zone; Region 2: pegs in depleted zone; Region 1: scale.
- b. A typical micrograph from a Hf-containing alloy to be compared with (a) above. Note the correspondence with the different 'regions' in the schematic diagram, Fig. 4a.

Figure 5. As-cast microstructures:

- a. Co10Cr11Al-1Hf, 256X
- b. Co10Cr11Al-1Y, 256X
- c. Co10Cr11Al, 256X.

Figure 6. Heat-treated microstructures: As-cast, then annealed at 1200°C for 50 hrs. in vacuum.

- a. Co10Cr11Al-1Hf, 256X
- b. Co10Cr11Al-1Y, 256X
- c. Co10Cr11Al, 256X

Figure 7. Heat-treated microstructures: As-cast then annealed at 1200°C, 100 hrs. in vacuum.

- a. Co10Cr11Al-1Hf, 256X
- b. Co10Cr11Al-1Y, 256X
- c. Co10Cr11Al, 256X.

Figure 8. Cross-section through oxidized specimen showing also the alloy microstructure. Note depleted zone and 2-phase region. (As-cast, then oxidized 1200°C for 50 hrs.)

- a. Co10Cr11Al-1Hf, 640X
- b. Co10Cr11Al-1Y, 640X
- c. Co10Cr11Al, 640X.

Figure 9. Scanning Electron Micrographs corresponding to the micrographs in Figs. 8. Obtained by 'deep-etching' (i.e., alloy dissolved away; scale stands in relief.)

- a. Co10Cr11Al-1Hf
- b. Co10Cr11Al-1Y
- c. Co10Cr11Al.

Figure 10. Cross-sections of oxidized samples (As-cast, heat-treated 1200°C 50 hrs, then oxidized 1200°C 50 hrs. in air.)

- a. Co10Cr11Al-1Hf
- b. Co10Cr11Al-1Y
- c. Co10Cr11Al.

Figure 11. Scanning Electron Micrographs corresponding to the micrographs in Figs.10. Obtained by 'deep-etching' (i.e., alloy dissolved away, scale stands in relief.)

- a. Co10Cr11Al-1Hf
- b. Co10Cr11Al-1Y
- c. Co10Cr11Al.

Figure 12. Cross-sections of oxidized samples. (As-cast, heat-treated 1200°C, 50 hrs, then oxidized 1200°C, 50 hrs. in air.)

- a. Co10Cr11Al-1Hf
- b. Co10Cr11Al-1Y
- c. Co10Cr11Al.

Figure 13. Scanning Electron Micrographs corresponding to the micrographs in Fig. 12. Obtained by deep-etching (i.e., alloy dissolved away; scale stands in relief).

- a. Co10Cr11Al-1Hf
- b. Co10Cr11Al-1Y
- c. Co10Cr11Al

Figure 14. Pegs in Co10Cr11Al-1Y ('deep-etched' Scanning Electron Micrographs). Note yttride phase coarsening suggested by increase in average peg size from a-c.

- a. Sample as-cast then oxidized at 1250°C, 50 hrs.
- b. Sample as-cast, annealed 1200°C, 50 hrs. then oxidized at 1200°C for 50 hrs.
- c. Sample as cast, annealed 1200°C, 100 hrs., then oxidized at 1200°C, 50 hrs.

Figure 15. Increase in the 'depleted zone' thickness with time.

- a. Co10Cr11Al-1Y, oxidized 22 hrs. at 1200°C in air.
- b. Co10Cr11Al-1Y, oxidized 49 hrs. at 1200°C in air.
- c. Co10Cr11Al-1Y, oxidized 192 hrs. at 1200°C in air.
- d. Co10Cr11Al-1Hf, oxidized 22 hrs. at 1200°C in air.
- e. Co10Cr11Al-1Hf, oxidized 49 hrs. at 1200°C in air.
- f. Co10Cr11Al-1Hf, oxidized 192 hrs. at 1200°C in air.

Figure 16. Optical micrographs showing cross-section through diffusion couples annealed at 1200°C at 100 hrs. in vacuum.

- a. Co10Cr11Al-Co, etched.
- b. Co10Cr11Al-Co, etched. Note 'islands' of β -phase.

Figure 17. Morphology of the scale-underside in Co10Cr11Al-1Y. Note the localized penetration of 'sheaths.'

- a. Optical micrograph of oxidized cross section (As-cast, then oxidized 1200°C 50 hrs. in air).
- b. Deep-etched Scanning Electron Micrograph of the above.

Figure 18. Plan view of pegs/sheaths; see first the explanatory Figs. 4. Figs. 18(a) and 18(b) are from the depleted zone while Figs. 18(c) and 18(d) are from the two-phase zone, deeper in the alloy.

- a. Co10Cr11Al-1Y, as-cast, oxidized 1200°C-50 hrs; section through depleted zone shows segregated pegging.
- b. Co10Cr11Al-1Hf, same treatment as above; section through depleted zone shows randomly distributed pegging.
- c. Co10Cr11Al-1Y, same treatment as above; section through two-phase zone shows 'sheaths' decorating phase-boundaries in microstructure.
- d. Co10Cr11Al-1Hf, same treatment as above; section through two-phase zone shows total absence of sheaths unlike as in (c) above.

Figure 19. Typical morphology of 'internal sheaths' in Co10Cr11Al-1Y alloys (as-cast, oxidized 1200°C-50 hrs.)

- a. Scanning Electron Micrograph of deep etched sample.
- b. EDAX-analysis on sheath (labelled 'b' in figure) and surrounding alloy (labelled 'a' in figure) suggests that the sheath is probably $[Al_2O_3 + Y_2O_3]$.

Figure 20. Profuse oxide formation in 'channels' in reoxidized samples of Co10Cr11Al-1Y.

- a. Co10Cr11Al-1Y, reoxidized after polishing.
- b. Co10Cr11Al-1Hf, reoxidized after polishing; here, oxidation is very similar to the directly oxidized sample.

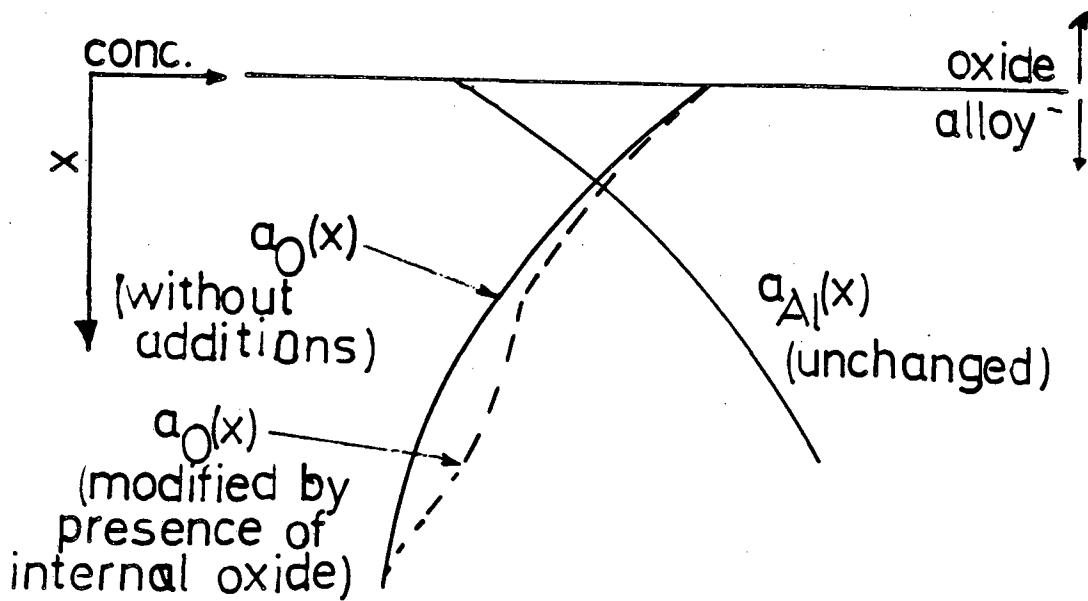


Fig. 1(a)

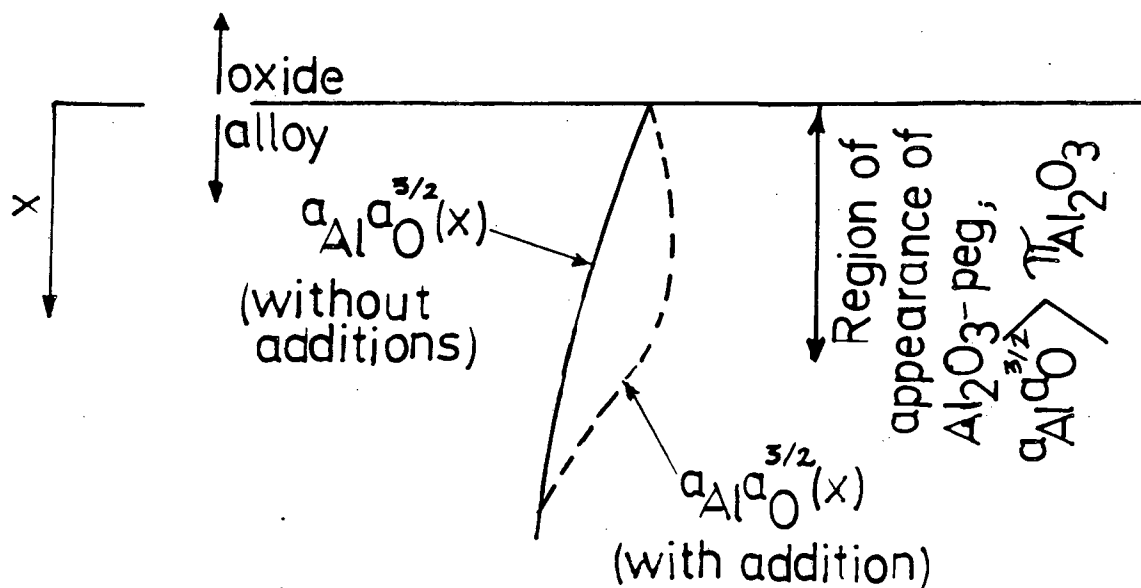


Fig. 1(b)

XBL 824-9051

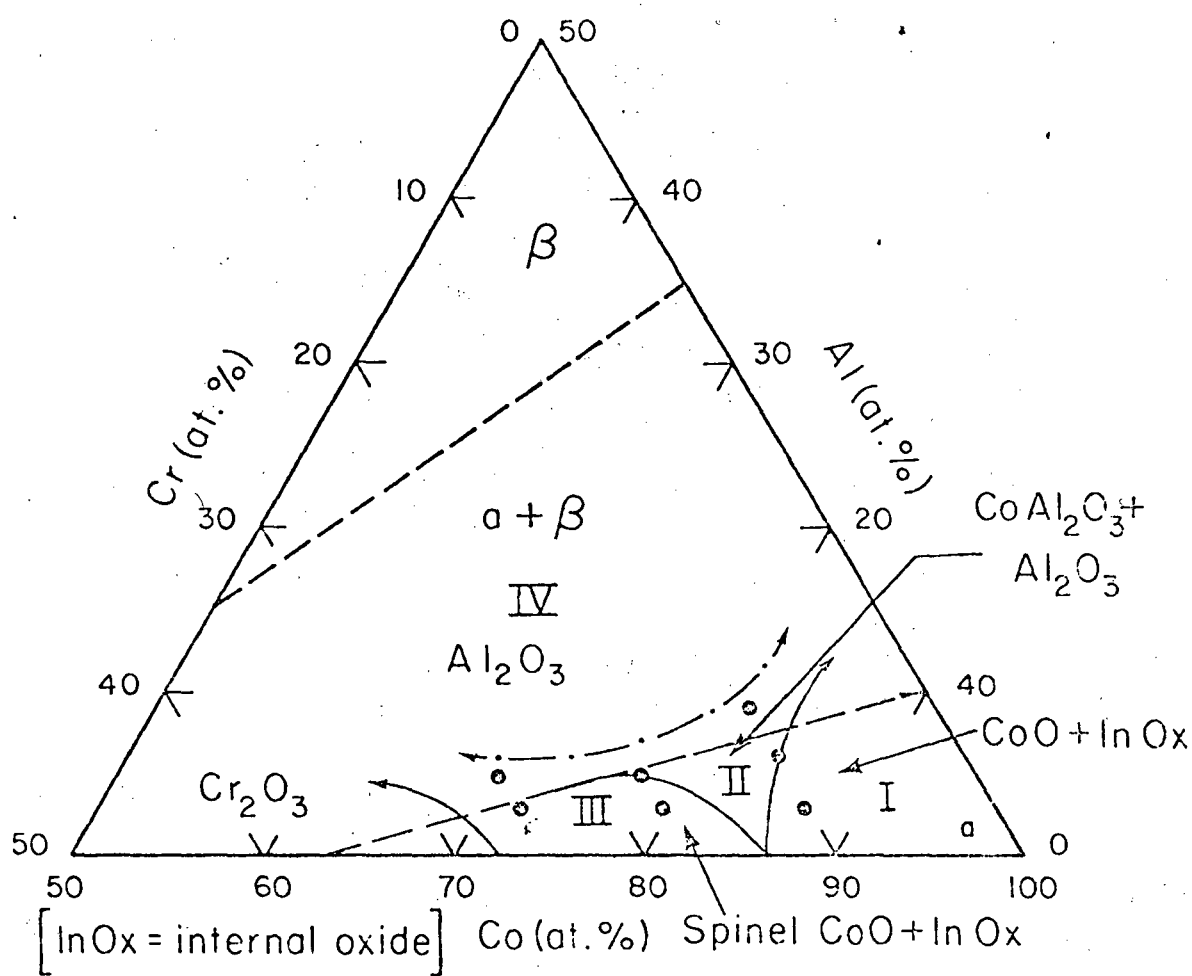
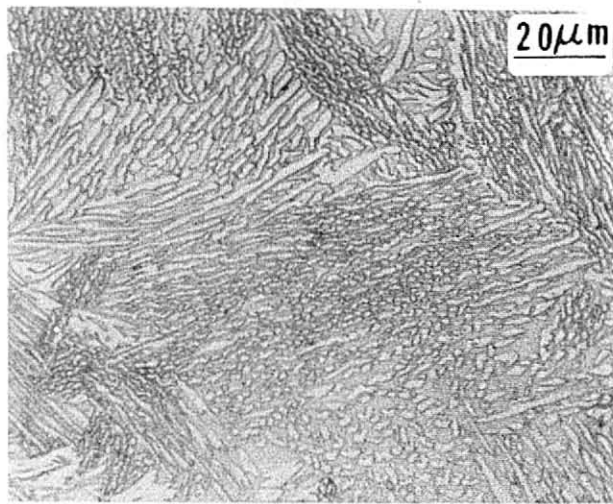
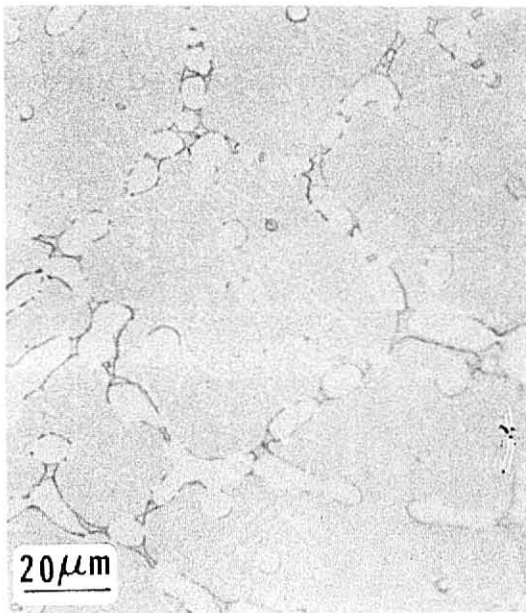


Figure 2.

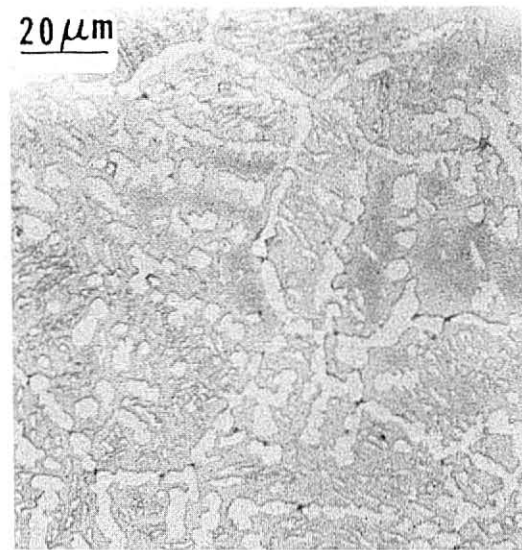
XBL 827-10739



(a)



(b)



(c)

Fig. 3

XBB 823-2831

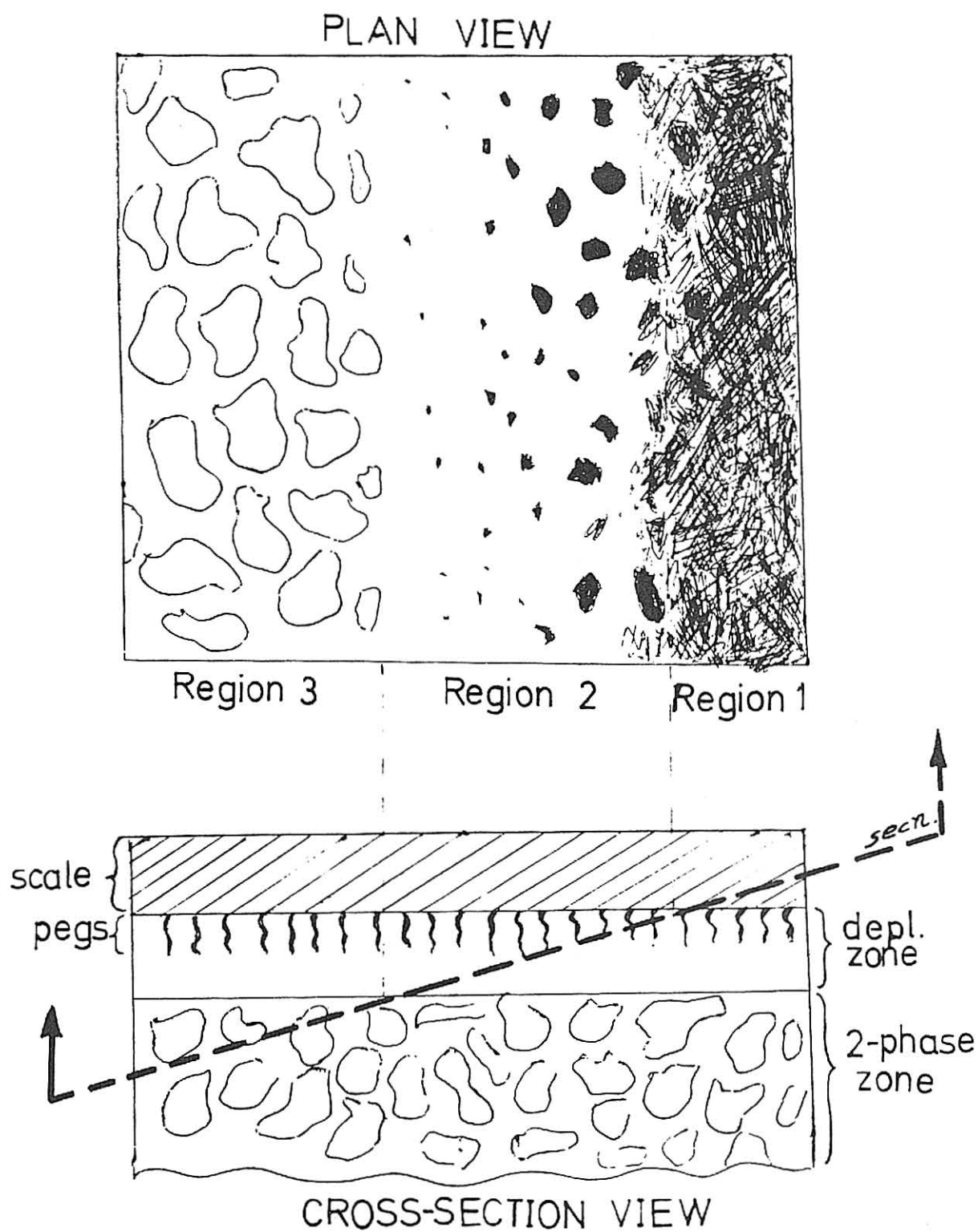


Fig. 4(a)

XBL 824-9050

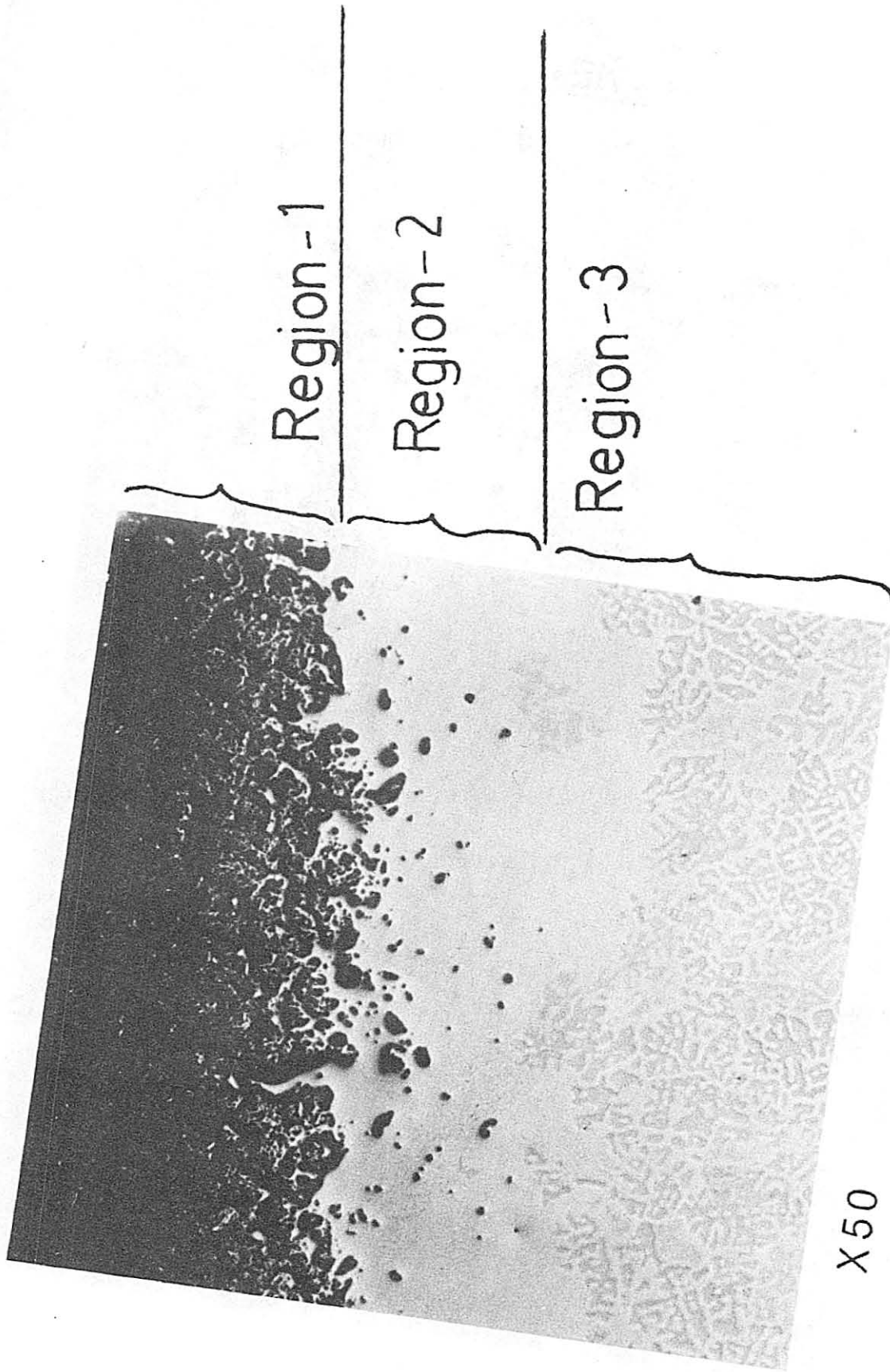
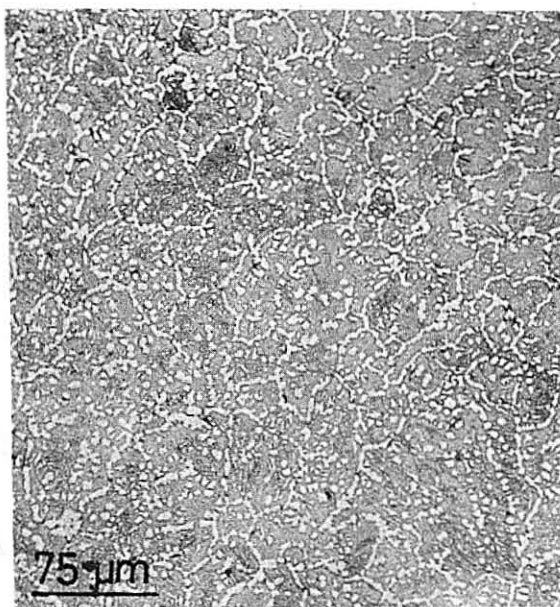


Fig. 4

XBB 824-3225



(a)



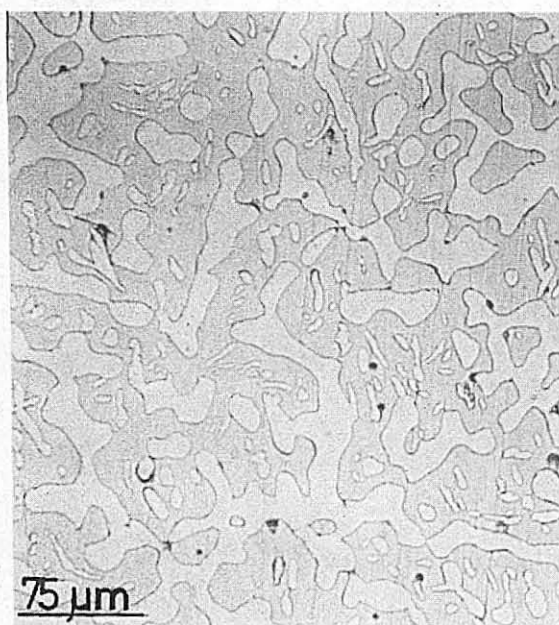
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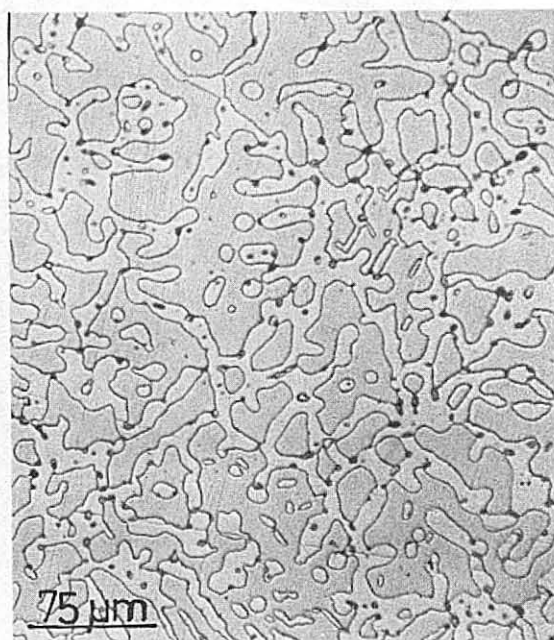
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Fig. 5

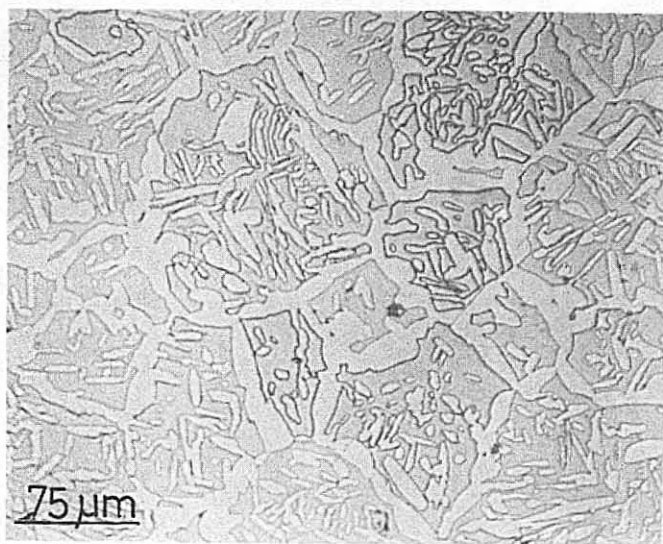
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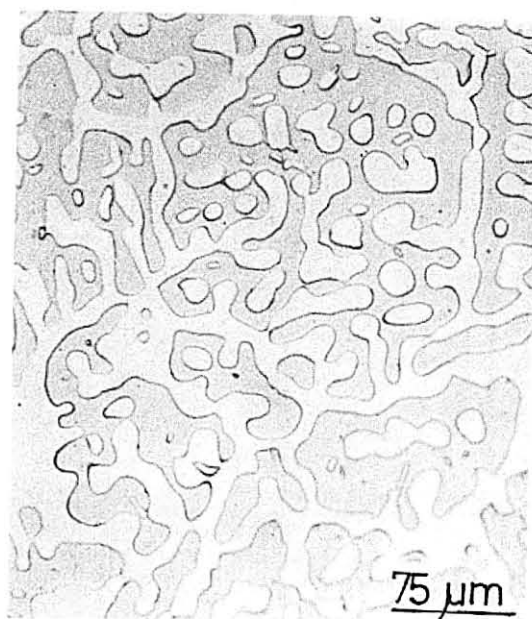
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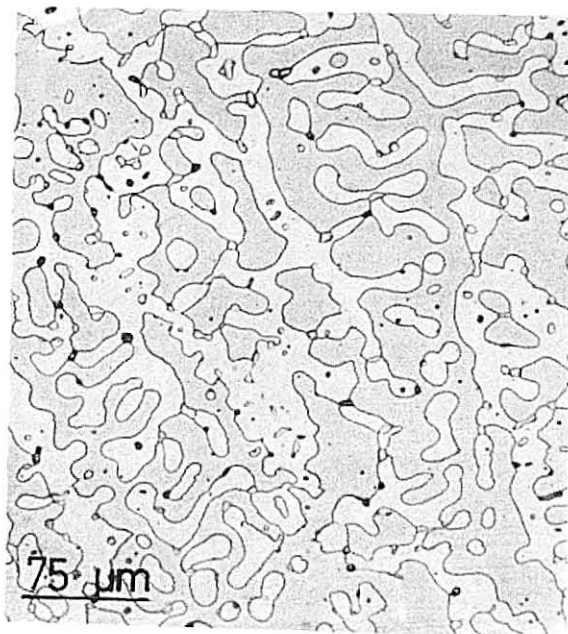
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Fig. 6

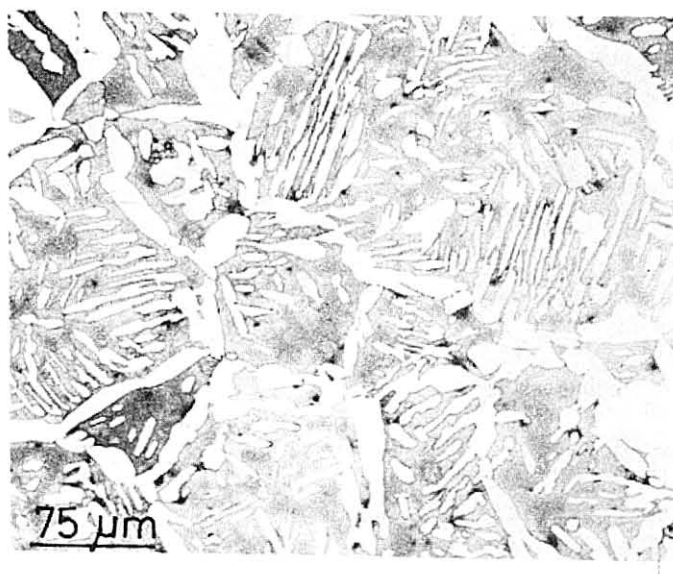
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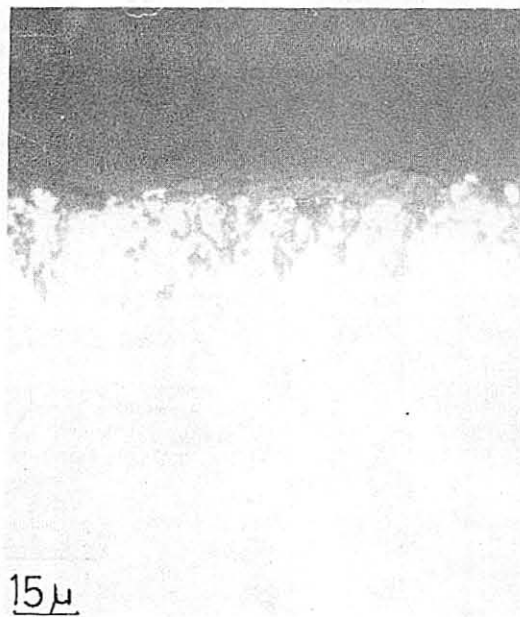
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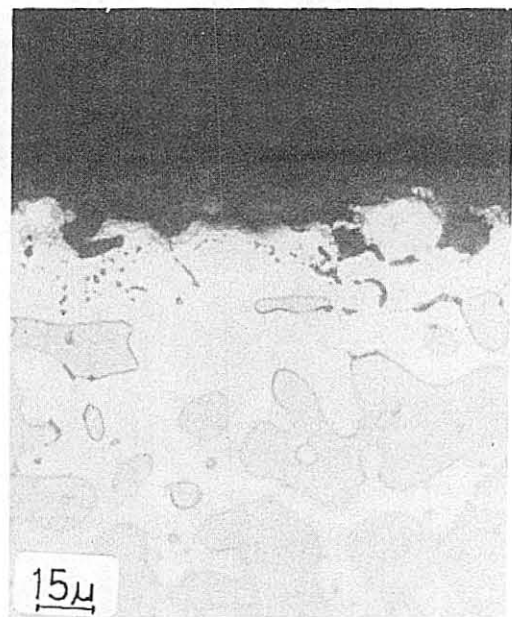
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Fig. 7

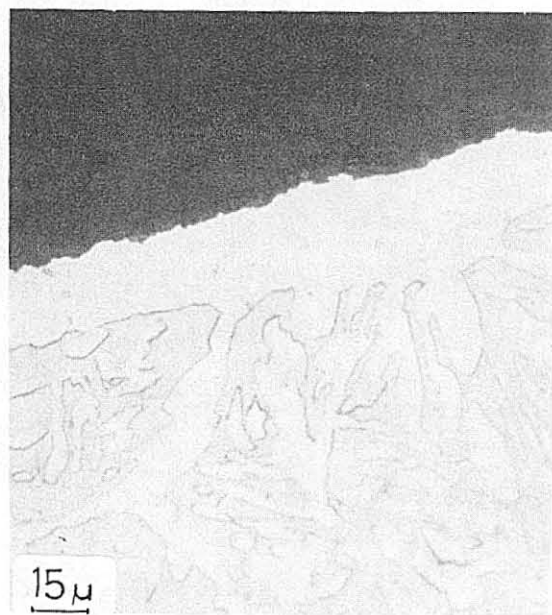
XBB 823-2834



(a)



(b)



(c)

Fig. 8

XBB 823-2835-

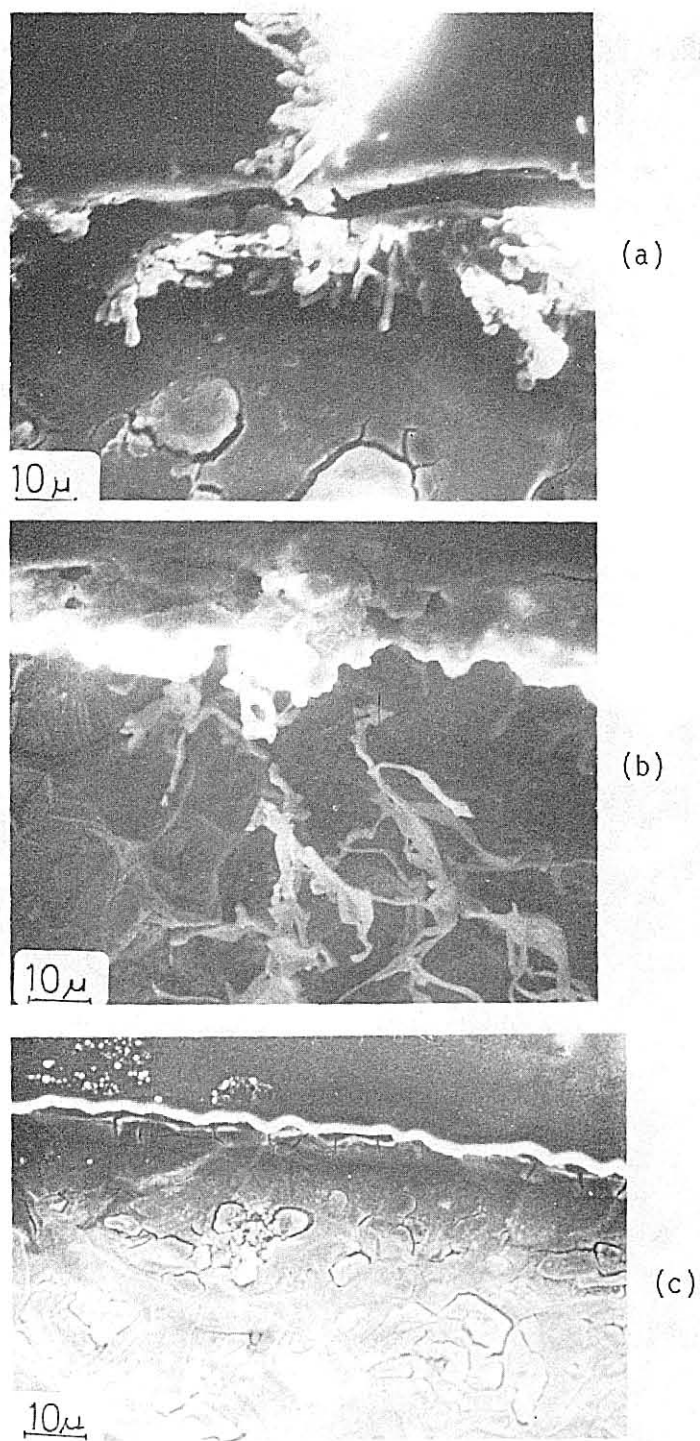
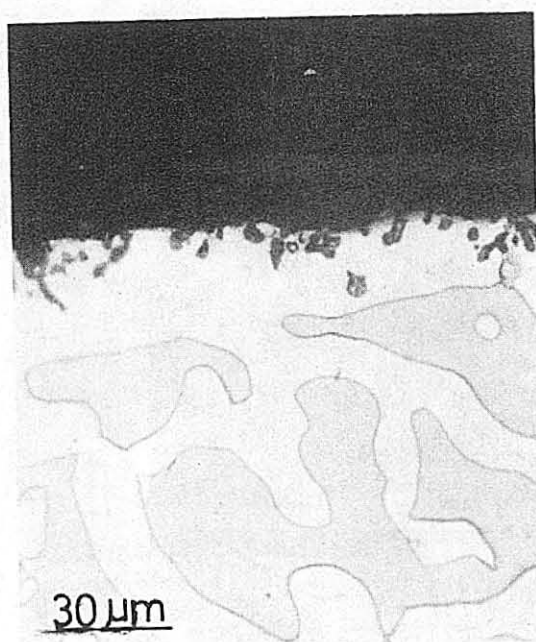
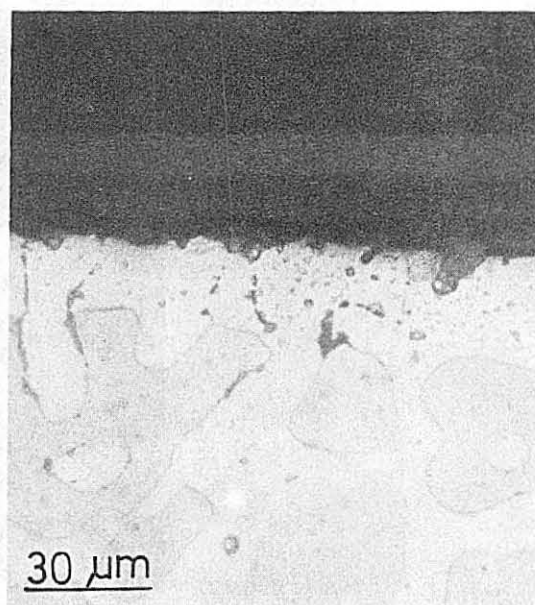


Fig. 9

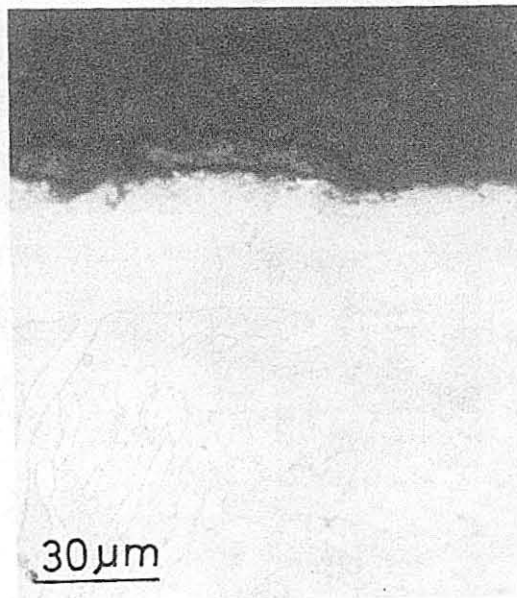
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(a)



(b)



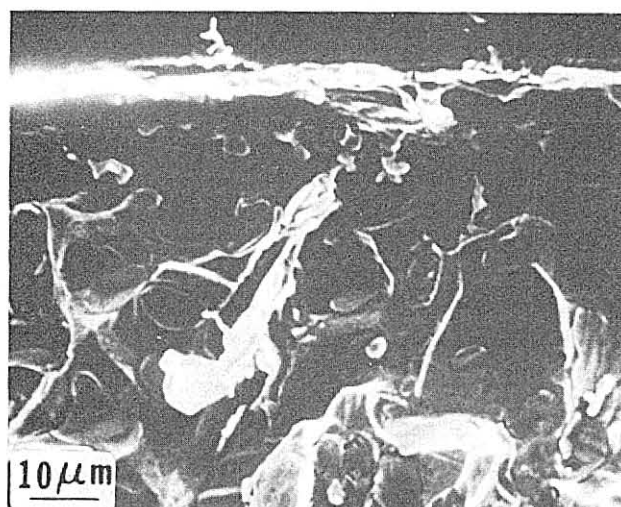
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Fig. 10

XBB 823-2839



(a)



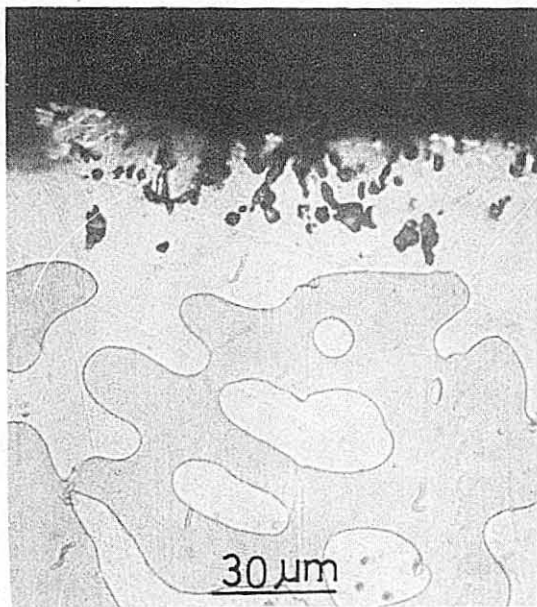
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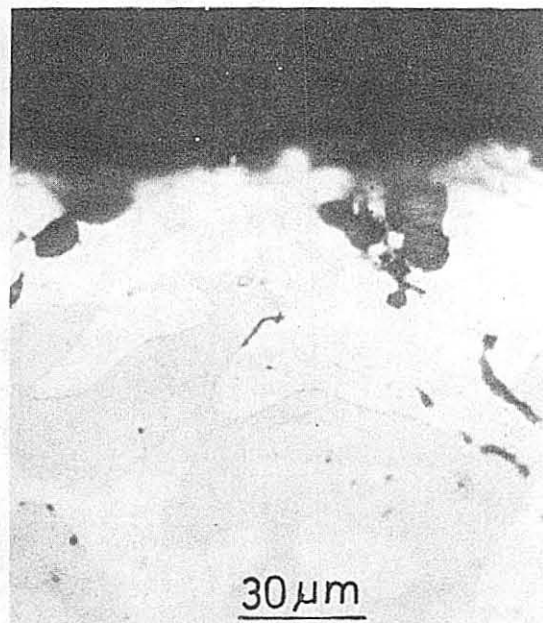
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Fig. 11

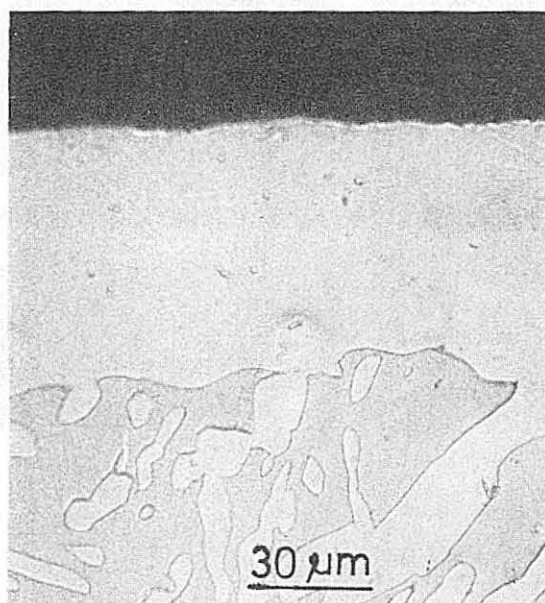
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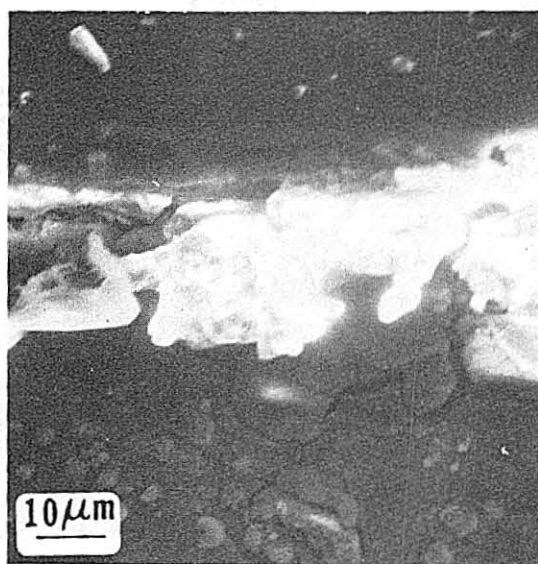
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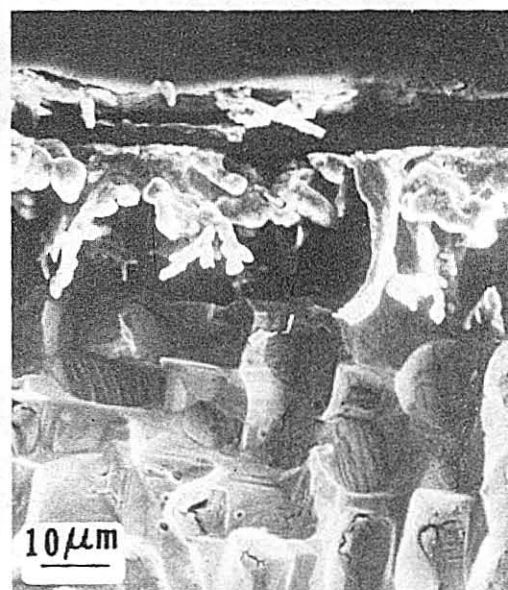
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Fig. 12

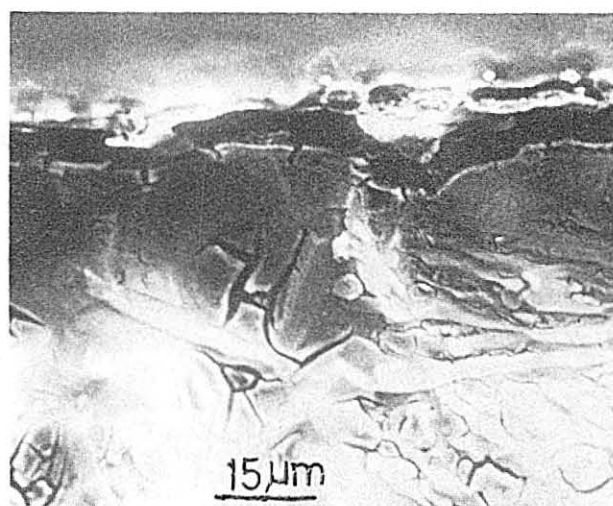
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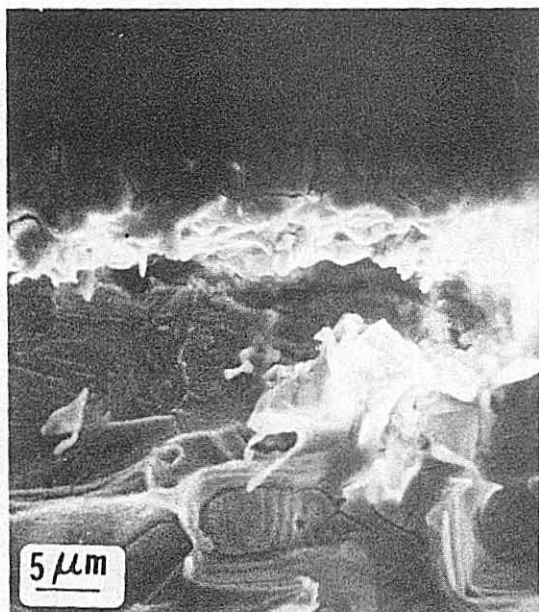
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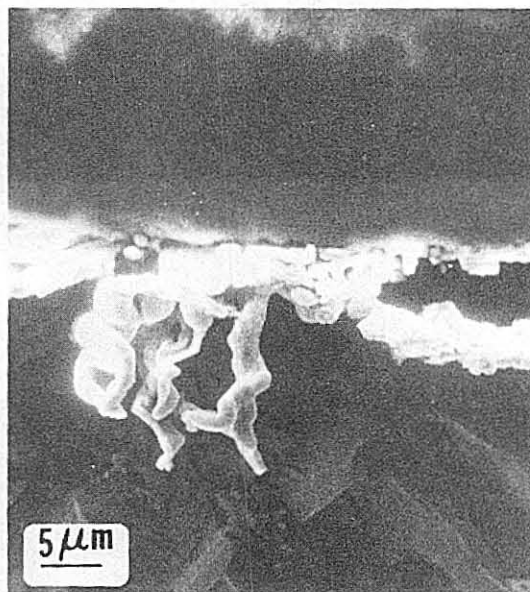
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Fig. 13

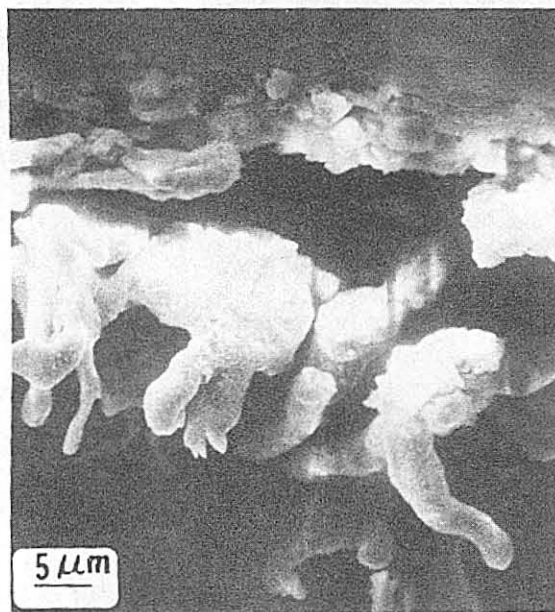
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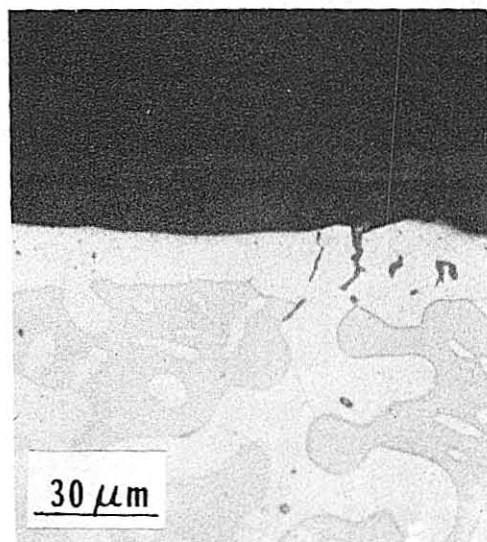
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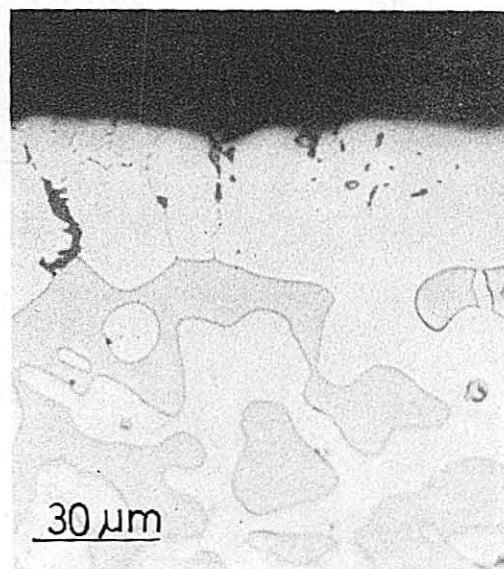
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Fig. 14

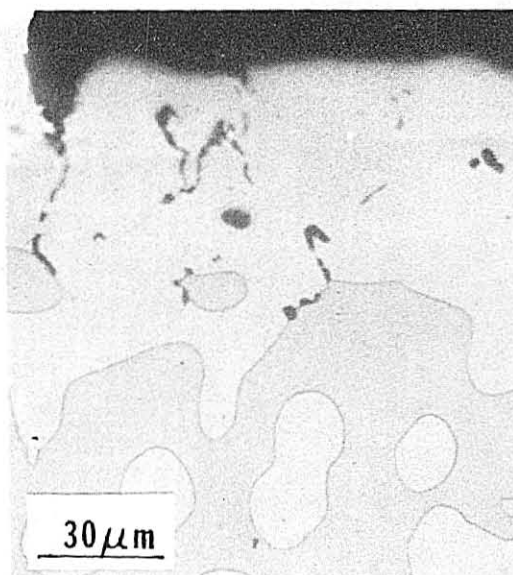
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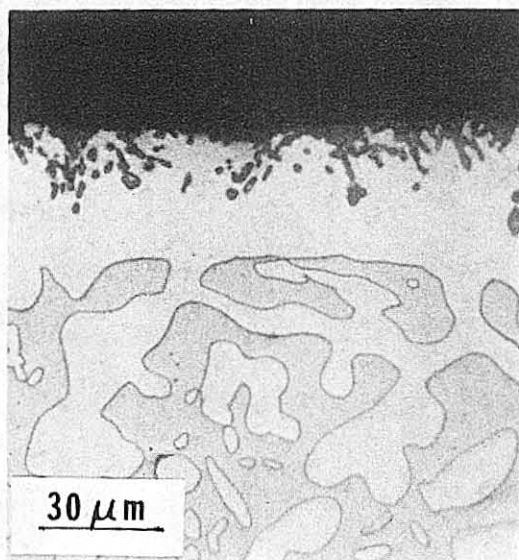
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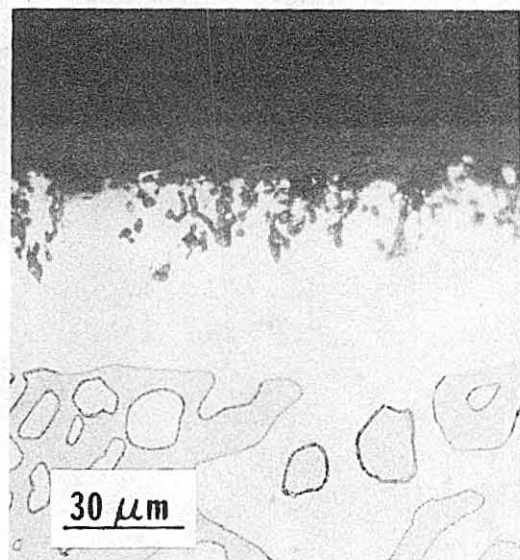
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Fig. 15

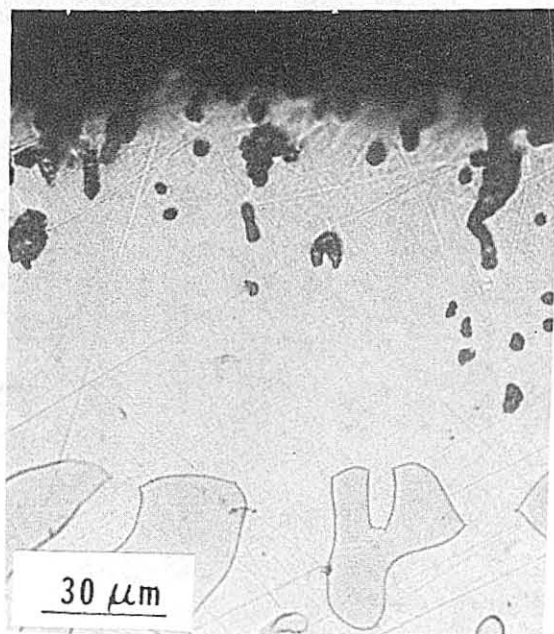
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(d)



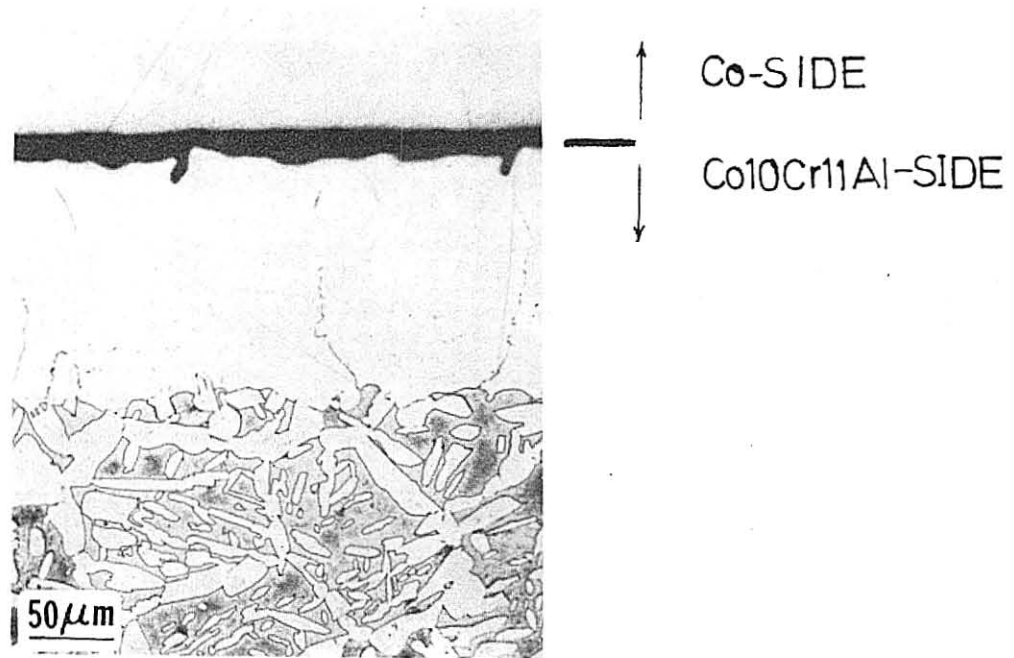
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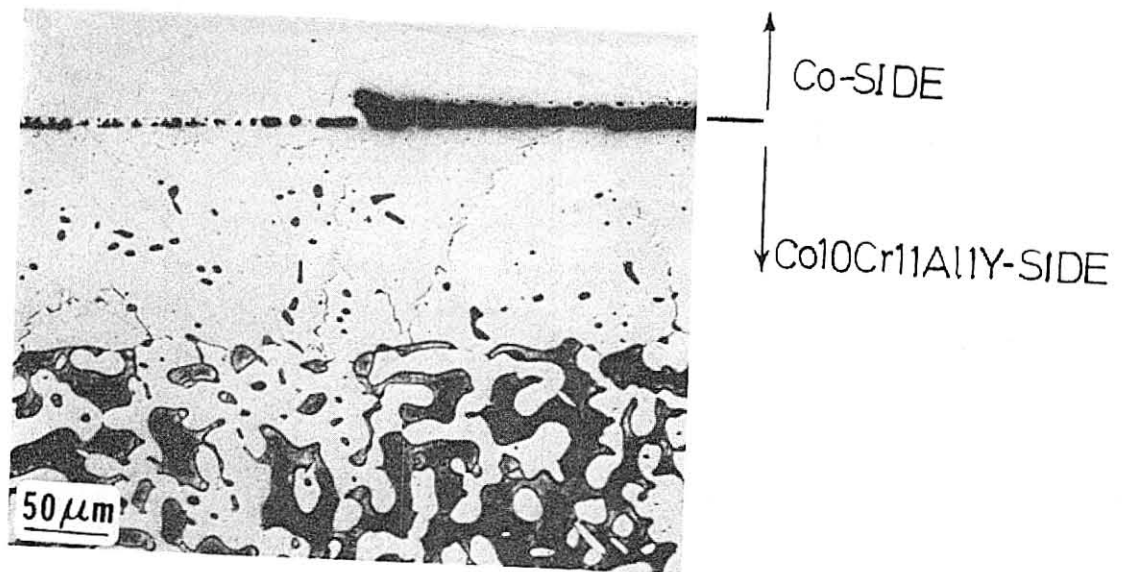
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Fig. 15

XBB 823-2844



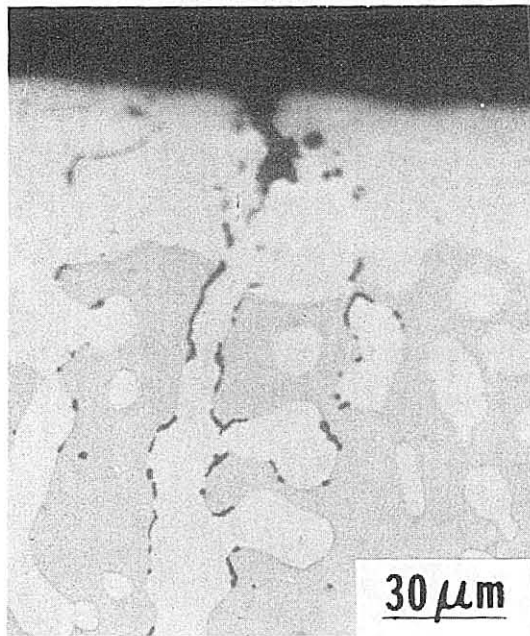
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Fig. 16

XBB 823-2830



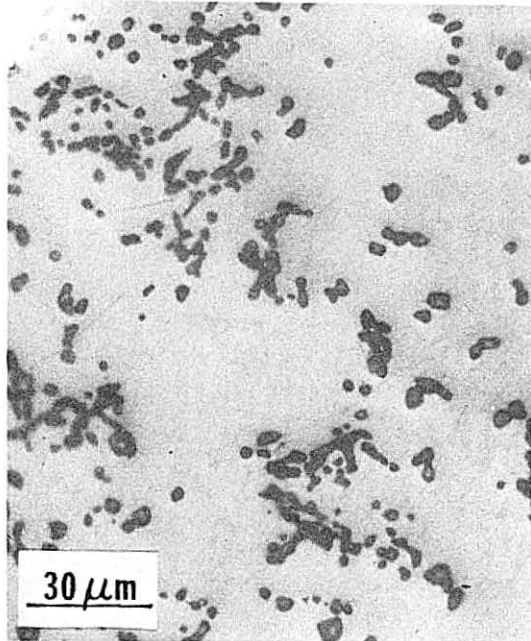
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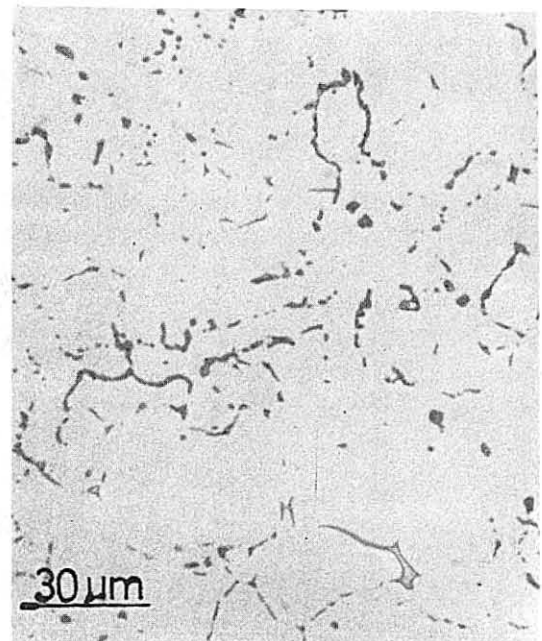
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Fig. 17

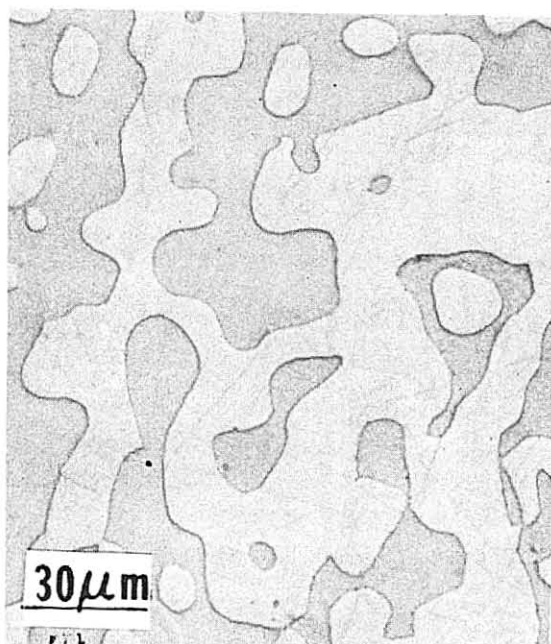
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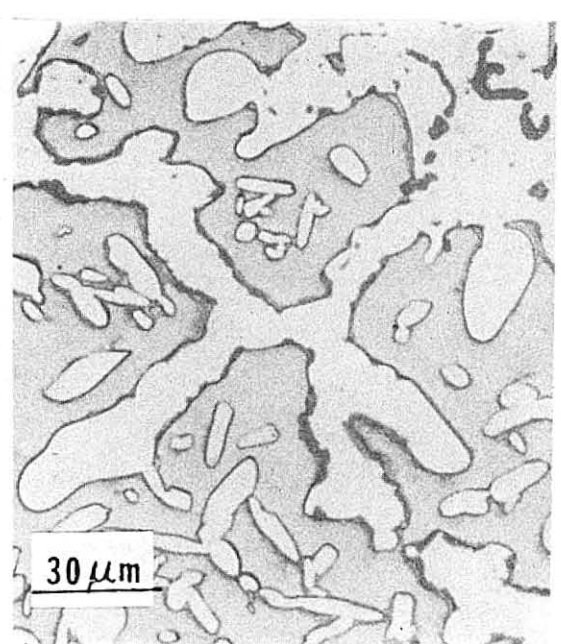
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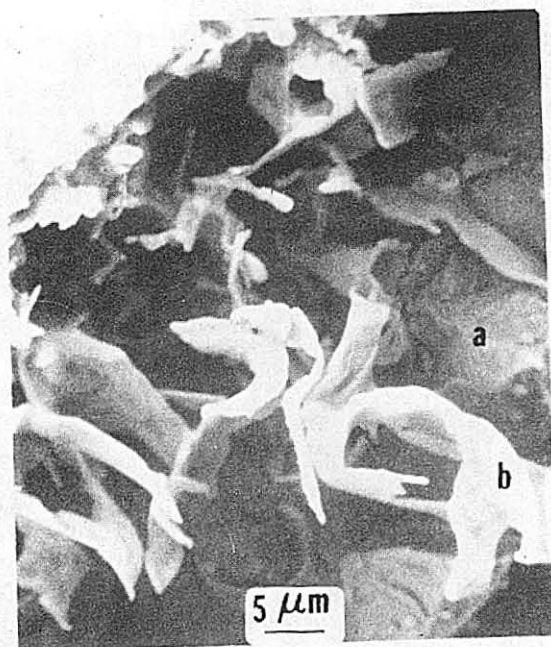
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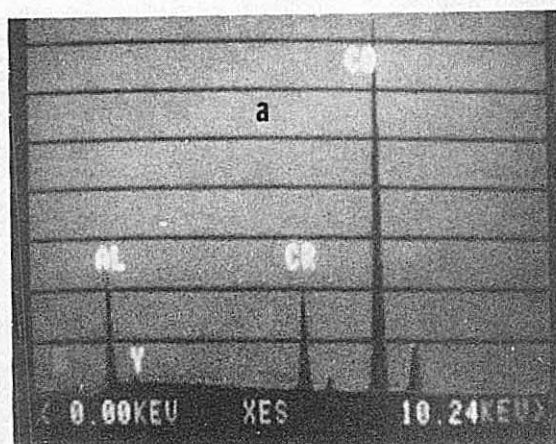
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Fig. 18

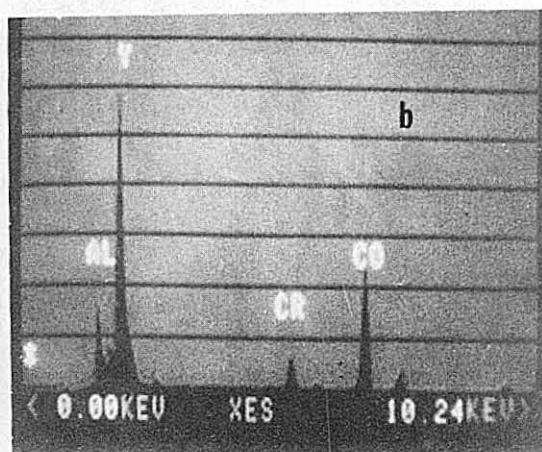
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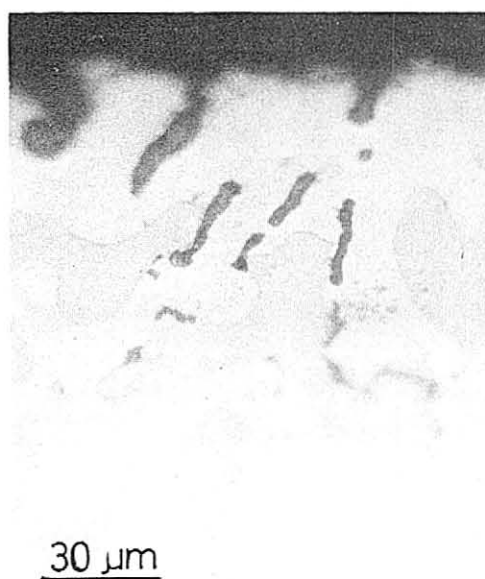
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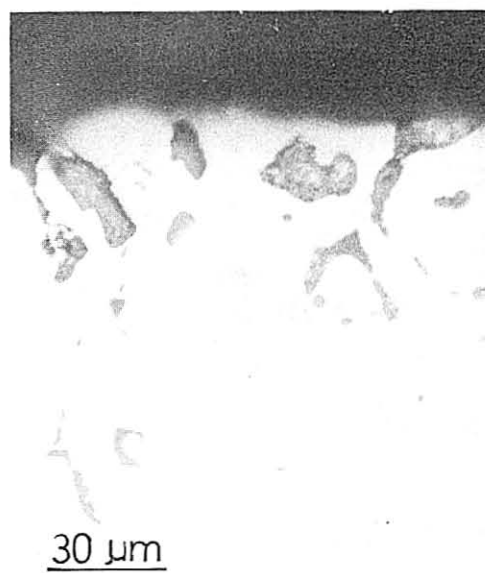
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Fig. 19

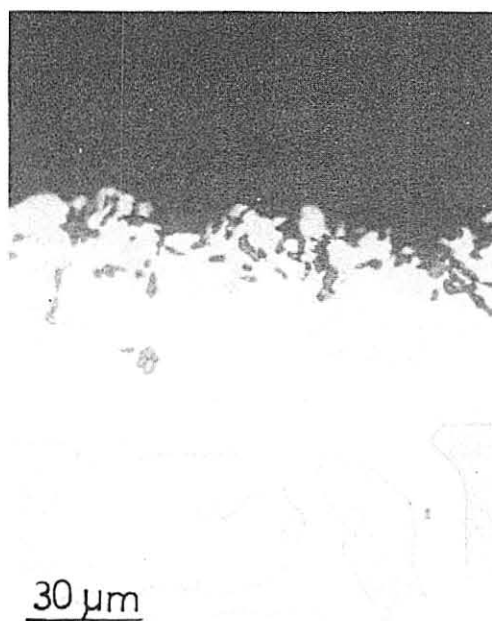
XBB 823-2837



(a)



(b)



(c)

Fig. 20

XBB 823-2838

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