

Distribution of chromium and nickel between the phases present in the borided layer of alloy steels

C. BADINI, C. GIANOGGIO and G. PRADELLI, Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Turin, Italy

Abstract

The preferential distribution of transition elements in the borided layer consisting of phases derived from the borides FeB (rhombic) and Fe₂B (tetragonal) has been verified using commercial steels containing chromium and nickel (UNI UX 100 Cr 13, UNI X 8 Cr 17 and UNI X 8 CrNi 1808). Boriding treatment was carried out at 900°C with powders enriched in KBF₄ and CB₄. The average content of the alloying elements was determined using the microanalysis of areas of dimensions comparable with those of the single phase layers.

It was found that chromium diffuses from the parent metal into the borided layer and is distributed preferentially in the phase which is more rich in boron, as we have already discovered in investigation of the two phase field [(Fe,Cr)₂B + (Fe,Cr)B] of the system Fe-Cr-B; nickel on the other hand tends to diffuse from the external layer into the bulk of the metal and the rhombic phase becomes depleted in this element in comparison with the tetragonal phase. These conclusions are in agreement with the generally valid observation which we have made in ternary systems between boron and pairs of transition metals as a result of which the element having the high atomic number is preferentially inserted into the phase which is less rich in boron in the distribution of the above mentioned metals between borides in equilibrium in the two phase zone. An intermediate zone between the borided layers and the bulk of the metal which is particularly rich in carbon, and, in the case of UNI X 8 CrNi 1808 steel only, nickel also, has been observed in all the steels examined.

Riassunto

Distribuzione di cromo e nichel tra le fasi presenti nello strato borurato di acciai legati

Utilizzando acciai contenenti cromo e nichel (UNI UX 100 Cr 13, UNI X 8 Cr 17 e UNI X 8 CrNi 1808), è stata verificata la ripartizione preferenziale degli elementi di transizione nello strato borurato costituito da fasi derivate dai boruri FeB (rombico) e Fe₂B (tetragonale). Il trattamento di borurazione è stato condotto a 900°C con polveri arricchite di KBF₄ e B₄C. La determinazione del contenuto medio degli elementi di lega è stata effettuata con microanalisi di aree di dimensioni confrontabili con quelle degli strati monofasici.

È stato riscontrato che il cromo diffonde dalla matrice metallica nello strato borurato e si ripartisce preferenzialmente nella fase più ricca di boro, come avevamo già evidenziato nello studio del campo bifasico [(Fe,Cr)₂B + (Fe,Cr)B] del sistema Fe-Cr-B; al contrario, il nichel tende a diffondere dallo strato esterno verso la matrice metallica e la fase rombica risulta più povera di questo elemento rispetto a quella tetragonale. Tali conclusioni sono in accordo con l'osservazione di validità generale da noi verificata in sistemi ternari tra boro e coppie di metalli di transizione in conseguenza della quale, nella ripartizione dei suddetti metalli tra boruri in equilibrio in zone bifasiche, l'elemento a numero atomico maggiore s'inserisce preferenzialmente nella fase meno ricca di boro. In tutti gli acciai esaminati è stata osservata una zona intermedia tra gli strati borurati e la matrice metallica particolarmente ricca di carbonio e, limitatamente all'acciaio UNI X 8 CrNi 1808, anche di nichel.

Considerable developments (1) in the investigation of the thermochemical process of the boriding of ferrous alloys, a treatment which provides surface layers of great hardness (approximately 2000 HV) and therefore optimum wear resistance, have been observed in recent years.

Techniques of producing surface borided layers using solid (2), liquid (3,4) or gaseous (5,6) boring mixtures have received a great stimulus.

The structure and character of these layers has been studied using different techniques such as X-Ray diffraction, optical and electronic microscopy, hardness and microhardness analysis (7) and, more recently, Mössbauer spectrometry (8). Although the techniques of obtaining borided layers are now well known, as is their generic characterisation on the basis of the type, structure and hardness of the phases present, investigations into distribution of the alloying elements between the parent metal and the phases making up the borided layer are incomplete and unreliable, above all in that they are not supported by thorough theoretical knowledge of the distribution equilibria for the metal atoms between the MB and M₂B phases present in the said layer. It should be pointed out that by the notation M₂B and MB we intend to indicate the solid solutions derived from the borides Fe₂B (tetragonal) and FeB (rhombic) through the replacement of iron atoms by atoms of transition metals. These solid solutions (and not iron borides as is generally stated in the literature) make up fundamental phases present in the diffusion layer.

This work is intended to provide the preliminary results obtained with a view of revealing the effect which chromium and nickel have on the composition of the phases contained in the borided layer.

Our earlier investigations (9) carried out on the ternary systems M'-M''-B (M',M'' = transition metals), showed

that in the two-phase field (M',M'')₂B + (M',M'')B, the metal having a relatively lower atomic number occurs systematically in a higher concentration in the boride (M',M'')B which is more rich in boron. It can therefore be seen that Cr and Ni, which have an atomic number less than and greater than that of iron respectively, will have the opposite behaviour, in other words in the borided layer of steels chromium should occur predominantly in the outer boride (MB), unlike nickel which should be more concentrated in the M₂B phase. We therefore felt that it would be worthwhile investigating whether these assumptions would also be confirmed in the diffusion layer of commercial metal alloys and to investigate the effects of this distribution. The choice of steels with a high concentration of chromium (13-18%) and nickel (8%) resulted from the need to demonstrate the distribution of these two elements between the borides present in the diffusion layer in a sufficiently reliable fashion.

Procedure

Boriding treatment was carried out at 900°C using a commercial powder (CB₄ = 5%, KBF₄ = 5%, SiC = 80%, C = 10%) and steels of the type UNI X 8 CrNi 1808, UNI X 8 Cr 17 and UNI UX 100 Cr 13 for periods of time between 8 and 48 hours. The composition of the boriding powder was varied in relation to the type of steel treated by the addition of KBF₄ (max. 5%) and CB₄ (5-20%) in order to obtain layers of the two phases M₂B and MB of equal thickness.

Small steel discs of diameter 15 mm and thickness 3 mm, with a straightened and polished surface, were treated. The samples were placed in porcelain containers and covered with the boriding powder;

above this was placed a layer of alumina and sodium metasilicate which in melting prevents the escape of the reactive atmosphere which forms within the container (2). After treatment the metal discs, following surface cleaning on abrasive paper, were subjected to X-Ray analysis and then sectioned along a diameter using diamond coated discs capable of producing a good surface finish. The samples were then embedded and, after polishing, subjected to metallographic examination.

Examination of the borided layer

The embedded and polished testpieces were observed using an optical microscope before and after chemical etching, carried out using nital or Murakami's reagent. The samples which were not etched demonstrate the presence of two layers of solid solution MB and M_2B , which can be distinguished in that the former appears darker. The line separating these two phases was subsequently revealed after chemical etching with a 5% nital solution. Hot etching with Murakami's reagent gave greater prominence to the intermediate zone laying between the parent metal and the surface layers containing boron, the dividing front being irregular and not parallel to the surface of the borided piece despite the fact that the presence of the elements in the alloy would have suggested a more linear course in accordance with statements in the literature (10). Microhardness analysis, carried out with a Vickers microhardness meter with a load of 100 g, showed a clear difference in hardness between the parent metal and the borided layer, and between the outer zone consisting of MB and the underlying zone (M_2B) (1). In particular microhardness decreases with a reduction in boron content.

Finally each sample was subjected to X-Ray analysis, the investigation being carried out from the surface. The analysis was therefore repeated after measured thicknesses of material had been removed by abrasion to a depth greater than each diffusion layer, so that the

Fig. 1 - SEM micrograph of the borided layer obtained on UNI UX 100 Cr 13 steel ($\times 500$).



changes in the phases in relation to depth could be examined.

Samples which were polished but not chemically etched were used for observations by means of an electron microscope and analyses carried out using a microprobe; it was found that etching brings about a differential reduction in the concentrations of the elements in the alloy, thus falsifying the analytical results. The phases making up the borided layer can nevertheless easily be identified without etching (Fig. 1).

Quantitative determinations were made using the microprobe, with different procedures. Point analyses and concentration profiles do not provide significant values for the mean composition of the various layers in that the concentration is significantly affected by the localised presence of carbides and borocarbides. Therefore in order to obtain a percentage value for the element in question which represented the mean distribution throughout the single phase layer it was necessary to carry out the analyses over an area having a width equivalent to the depth of the layer (layer depth: 60 μm). The values obtained are shown in Table 1 and in the following figures by means of histograms,

TABLE 1 - Composition (% by weight with respect to the sum of the metal atoms) of the elements Fe, Cr, Ni in the borided layer and in the parent metal

Steel Diffusion layer	UNI UX Cr 13 % Cr	UNI X 8 Cr 17 % Cr	UNI X 8 CrNi 1808 % Cr	% Ni
Outer edge	11,20	13,60	15,40	8,60
MB zone	14,20	17,75	26,10	2,80
M_2B zone	13,30	17,03	19,90	5,96
Intermediate zone	13,15	15,80	19,80	11,96
Parent metal	12,90	16,20	19,50	8,30

the baselines for which show the extent of the single phase layer.

The analyses made over extended areas did not include the transition zones, where there is a reciprocal interpenetration of the phases in contact brought about by the growth of crystals in preferential directions (7). In these zones there is a difference in the composition of the adjacent phases with a different boron content, which is much more pronounced than that which can be deduced from the histograms. In fact, because these zones can be regarded as two phase zones, equilibrium conditions which are comparable with those found in the two phase fields of ternary boron-transition metal systems must be set up within them, with a highly differentiated distribution of the metal atoms. Investigation of the changes in the concentrations of the metal atoms in these zones was therefore carried out by means of microanalyses in areas of restricted dimensions (approximately $25 \times 3 \mu\text{m}$) so that insofar as possible single phase zones were examined. The centre of these, on the normal to the surface of the sample, was moved progressively outwards from the core of the sample.

The frequency of the measurements was increased in the zones in which the different layers interpenetrated. Using this criteria determinations were also carried out within each layer in order to show any discontinuities in composition in the regions where phases other than the dominant phase were locally present.

The results obtained are shown in Figures 7, 8, 9 and 10 in which the individual values are superimposed on the histograms for convenient comparison. The solid lines which connect these values in the zones where different phases coexist show the changes in composition more clearly.

Examination of the results

Figure 2 shows the change in the percentage of nickel for UNI X 8 CrNi 1808 steel in relation to distance from the edge of the testpiece. From an examination of the histogram it will be seen that there is an external layer of thickness approximately $30 \mu\text{m}$ which consists of the MB phase with a mean nickel content of approximately 30%; beyond this layer, that is on the edge of the testpiece, there was also found a limited zone with a high nickel content. A layer having a thickness of approximately $80 \mu\text{m}$ consisting of the phase M_2B (mean nickel content = 6%) lies between the outer MB edge and an intermediate zone in which, as will be specified below, there was noted a build-up of carbon and nickel (approximately 12% by weight for the latter element) which reached concentrations above those found in the parent metal.

The distribution of nickel between the two borides is in accordance with the statements made with regard to

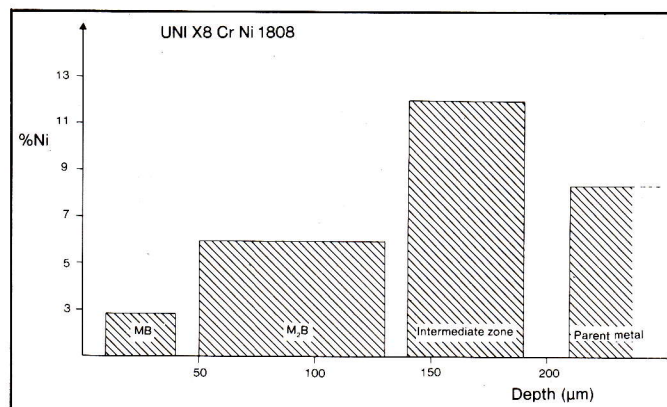


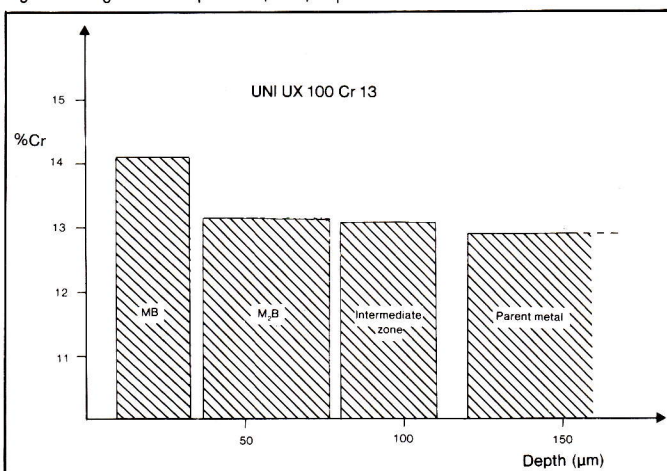
Fig. 2 - Histogram of composition (% Ni)/depth for UNI X 8 CrNi 1808 steel.

the distribution of metal atoms within the two phase files $M_2B + MB$ of $M'-M''$ ternary systems on the basis of which nickel should be systematically and preferentially distributed in the phases which are less rich in boron. The increasing concentration of nickel in the MB and M_2B layers from the edge of the test piece is therefore explained.

The existence of an intermediate zone between the borides and the parent metal containing a high concentration of nickel ($Ni = 12\%$) can be attributed to the poor solubility of this element in the M_2B and MB phase which causes impoverishment of the nickel concentration at the surface. As a result this tends to diffuse into the sample accumulating between the M_2B layer and the parent metal; similar reasons can be used to explain the presence of a thin layer (approximate $10 \mu\text{m}$) which is also particularly rich in nickel (up to about 9%) on the outer edge of the test piece.

As regards the distribution of the percentage of chromium within the diffusion layer, histograms of the percentage of chromium in relation to distance from the edge are shown for UNI UX 100 Cr 13, UNI X 8 Cr 17

Fig. 3 - Histogram of composition (% Cr)/depth for UNI UX 100 Cr 13.



and UNI X 8 CrNi 1808 steels in Figures 3, 4 and 5 respectively.

Examination of these figures shows a build-up of chromium in the single phase zones consisting of MB and M_2B with a greater percentage of the element in the outer zone, in accordance with the conclusions on the preferential distribution of the metal atoms already mentioned.

With regard to the intermediate zone in which the chromium concentration is not appreciably different from that in the parent metal it will be seen that complex borocarbides are widely present, and this is even more obvious in the case of UNI UX 100 Cr 13 steel which is relatively more rich in carbon. The increase in the concentration of the latter element in this zone can be attributed to both the formation of phases of the type $(Fe, Cr)_3(B, C)$ and $(Fe, Cr)_{23}(B, C)_6$ and the impossibility of making a substitution between boron and carbon in phases of the MB and M_2B type as verified experimentally in the course of an extensive series of preliminary tests.

Fig. 4 - Histogram of composition (% Cr)/depth for UNI X 8 Cr 17.

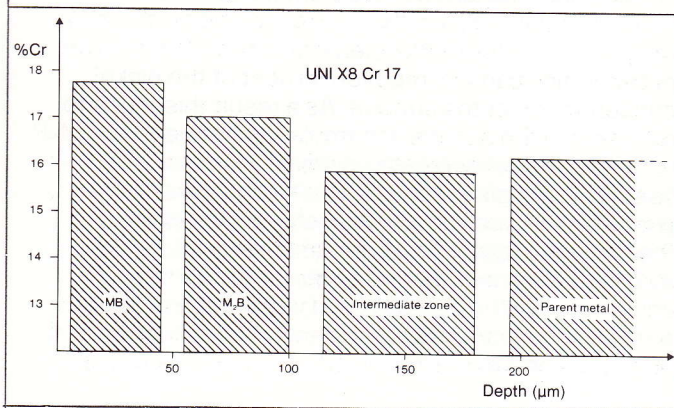


Fig. 5 - Histogram of composition (% Cr)/depth for UNI X 8 CrNi 1808 steel.

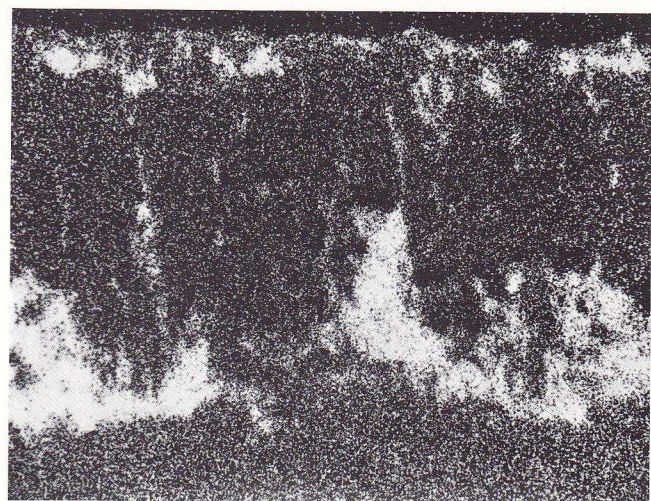
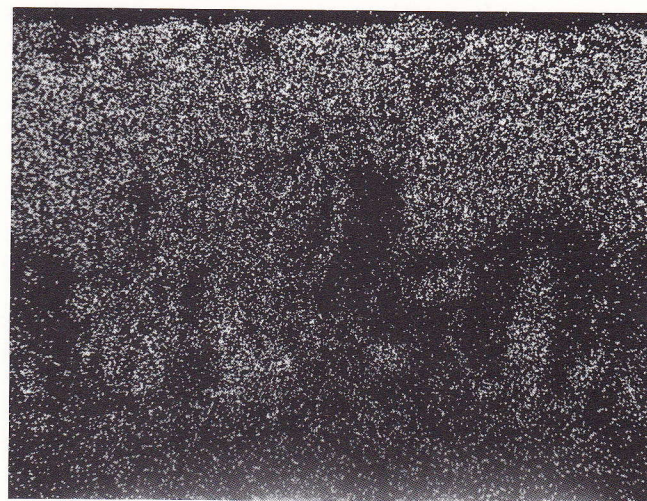
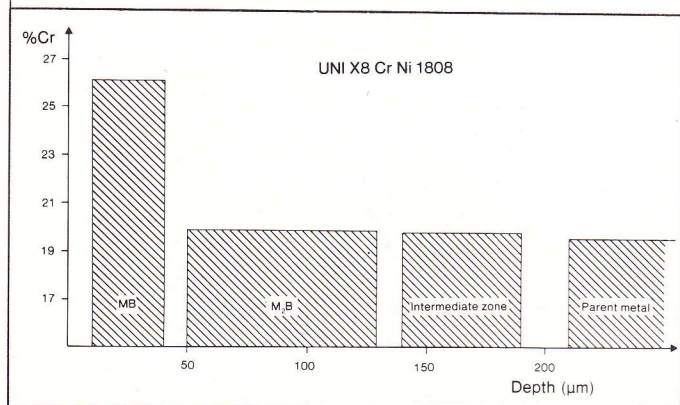


Fig. 6 - Map of the concentrations of boron and carbon obtained on UNI UX 100 Cr 13 steel.

Figure 6 shows maps of the concentrations of carbon and boron obtained in the borided layer of UNI UX 100 Cr 13 steel. It is clear that the latter element is preferentially located at the edge whereas the carbon accumulates in the intermediate zone. The presence of considerable quantities of carbides in this zone tends to modify the distribution of chromium between the layer consisting of M_2B and the parent metal. It is worthwhile making a quantitative examination of the distribution of the metal atoms Fe-Cr and Fe-Ni only at the interface of the single phase zones in which quasi-equilibrium conditions may be achieved which are comparable to the experimental data reported in previous work (9, 11) obtained using powder samples. The change in the percentage of chromium and nickel in these zones is shown quantitatively (solid line) in Figures 7, 8, 9, 10. The previous histograms are shown by a dashed line for comparison. The presence of large

crystals of carbides and borocarbides segregating irregularly in the intermediate zone explains the resulting scatter of values which is hardly representative of the actual mean situation.

Fig. 7 - Change in the concentration of nickel in the transition zones - UNI X 8 CrNi 1808 steel.

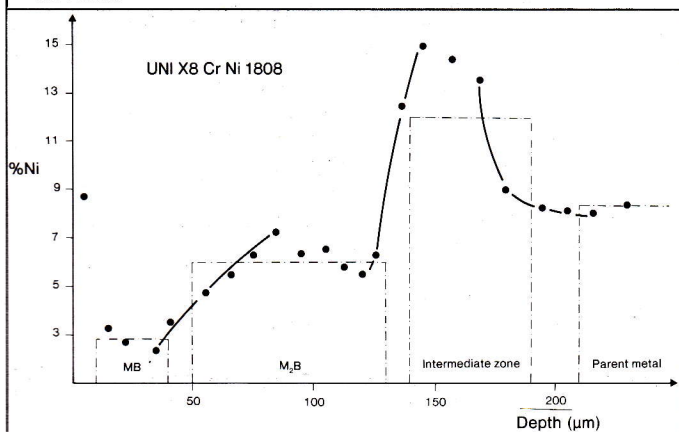


Fig. 8 - Change in the concentration of chromium in the transition zones - UNI UX 100 Cr 13 steel.

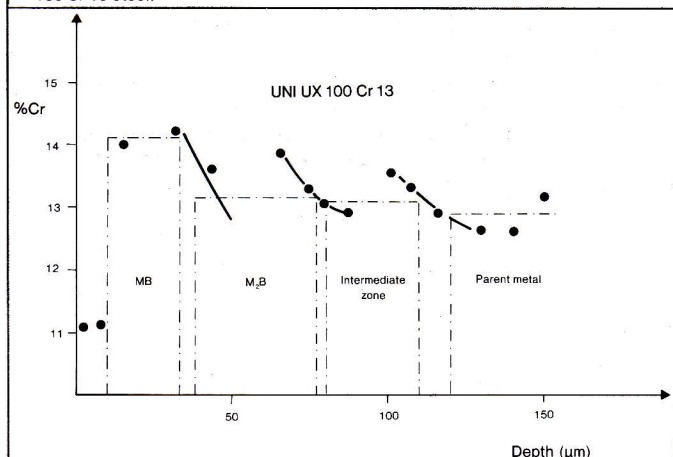
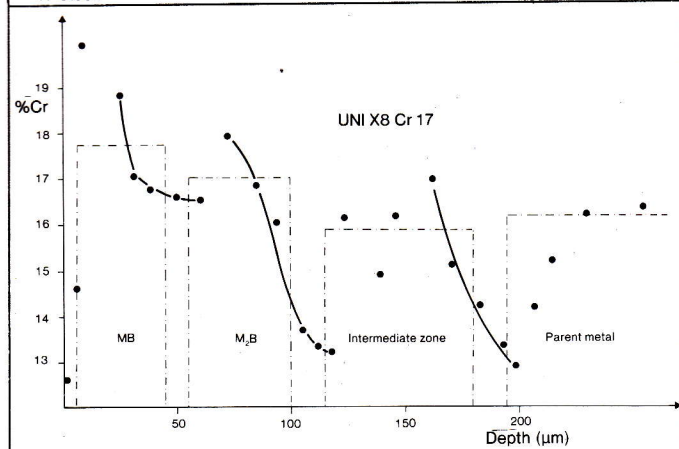


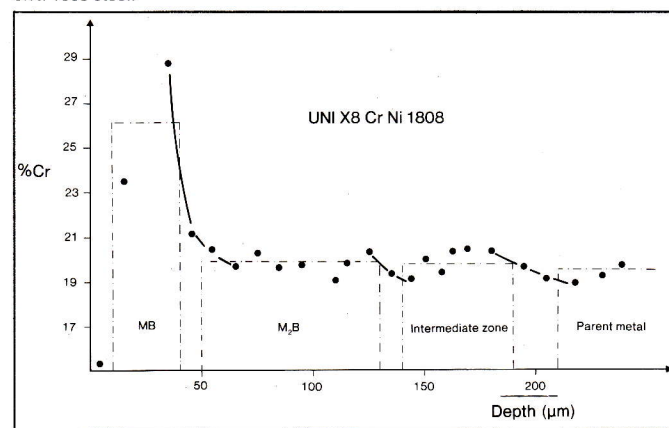
Fig. 9 - Change in the concentration of chromium in the transition zones - UNI X 8 Cr 17 steel.



From all the data obtained it is found that nickel (Figure 7) is distributed in the two phase zone in the highly differentiated manner, with preferential insertion into the phase which is less rich in boron. On the other hand, as far as chromium is concerned, it will be seen that this is preferentially inserted into the phase which is more rich in boron (Figures 8, 9, 10), with an appreciable difference in the values of the concentration between the two-phase boundaries in the interpenetration. In UNI X 8 CrNi 1808 steel : Fig. 10) the limiting boundaries in the zone of the boride layer consisting of MB and M_2B have a chromium concentration which changes from 29% to 20% respectively for the phases MB and M_2B . The data obtained at 900° C in the investigation of the Fe-Cr-B system indicate a wider difference in values. We are of the opinion that the dynamics of the boron diffusion process, and consequently of the diffusion of the other elements (Cr, Ni, C, Fe) do not make it possible to achieve the equilibrium conditions which in fact do occur in powder samples. There must therefore be a concentration gradient for each metal element from the interface zone towards the interior of each contiguous zone.

The existence of an outer layer of restricted dimensions, which is particularly poor in chromium, is also explained by the fact that the diffusion layer is on average more rich in this element than the parent metal; it therefore tends to diffuse and dissolve in the borides thus impoverishing the outer edge which has a different appearance and composition to the MB phase. Chemical analysis of the edge shows the presence of silicon (in concentrations greater than those in the original steel) and of potassium, which is absent in the parent alloy. These elements may originate from the powder used in the treatment. The intermediate zone which is rich in particularly stable borocarbides seems to slow down the diffusion

Fig. 10 - Change in the concentration of chromium in the transition zones - UNI X 8 CrNi 1808 steel.



of chromium from the parent metal to the outer layer affected by the diffusion of boron.

Conclusions

On the basis of the above considerations we consider that the following major conclusions may be drawn.

- It has been confirmed that the surface layer of borided chromium-nickel steels tends to become enriched in chromium as a result of the considerable solubility of this element in the borides FeB and Fe₂B.
- In all the steels examined the outermost zone of the borided layer which consists of MB is more rich in chromium than the adjacent M₂B in accordance with the distribution equilibria for chromium between the borides FeB and Fe₂B observed in investigation of the Fe-Cr-B system.
- It is therefore confirmed that chromium is preferentially and systematically inserted into the phase which is more rich in boron even in the borided layer of steels in a similar manner to that previously demonstrated in powders, consistent with a dynamic situation for the diffusion of the elements in the borided layer.
- The differential distribution of chromium between the borided layer and the parent metal involves enrichment of this metal in the borides and impoverishment in adjacent zones. This is particularly obvious at the edge, while the presence of an intermediate zone which is rich in carbides and borocarbides of the type Fe₃C and Cr₂₃C₆ appears to present an obstacle to the outward diffusion of chromium from the parent metal.
- The magnitude of the nickel concentration, which is less in the borided layer than the average found in UNI X 8 CrNi 1808 steel, indicates diffusion phenomena towards the outer edge and towards the parent metal where this element accumulates to a substantial extent (approximately 12%).
- Also as far as the distribution of nickel at the interfaces is concerned the results obtained are in accordance with other experimental data in our possession: nickel, an element with a higher atomic number than iron, is predominantly inserted into the phases which are less rich in boron.

REFERENCES

- (1) Minkevitch, A.N. Couches des borures obtenues sur les métaux par diffusion. *Rev. Mét.*, (1963), 807-814.
- (2) Galibois, A., O. Butenko, and B. Voyzelle. Mécanisme de formation des couches borurées sur les aciers à haut carbone. II. Technique des poudres. *Acta Metall.*, 28 (1980), 1765-71.
- (3) Ornig, H., and O. Scaaber. Beobachtungen beim Oberflächenborieren von Stahl I. *Hartereitechn. Mitt.*, 17 (1962), 131-140.
- (4) Galibois, A., O. Butenko, and B. Voyzelle. Mécanisme de formation des couches borurées sur les aciers à haut carbone. I. Technique des pates. *Acta Metall.*, 28 (1980), 1753-63.
- (5) Casadesus, P., C. Frantz, and M. Gantois. Boriding with a thermally unstable gas (diborane). *Met. Trans. A*, 10 (1979), 1739-43.
- (6) Lyakhovich, L. S., F.U. Dalmanov, and S.A. Isacov. Boriding of steels in a gas medium. *Metalloved. Term. Obrab. Met.*, 4 (1982), 25-28.
- (7) Casadesus, P., and C. Frantz. Etude structurale des couches borurées élaborées par bombardement ionique sur le fer et les aciers au carbone. *Mem. Sci. Rev. Mét.*, 76 (1979), 9-21.
- (8) Carbucicchio, M., L. Bardani, and G. Palombarini. Mössbauer and metallographic analysis of borided surface layers on Armco iron. *J. Mat. Sci.*, 15 (1980), 711-719.
- (9) Pradelli, G., and C. Gianoglio. Equilibri di ripartizione tra gli atomi metallici nei campi bifasici dei sistemi ternari tra boro e metalli di transizione. *Atti I Conv. Naz. A.S.M.I.*, (1983), 143-151.
- (10) Palombarini, G., G. Sacchi, W. Dumini, and L. Cento. Borurazione: un trattamento termochimico che migliora la resistenza all'usura degli acciai *Riv. Meccanica*, 28 (1977), 85-93.
- (11) Gianoglio, C., and G. Pradelli. Sul sistema Cr-Fe-B: equilibri di ripartizione degli atomi metallici in campi bifasici. *Atti Accad. Sci. Torino*, 116 (1983).