

# Hard superalloy layers

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The vacuum coated green iron powder compacts with high-hardness layers of NiCrSiBC powders were prepared. Diffusion-coated layers have been obtained by compacting at atmospheric pressure. The microstructure, the hardness and microhardness of the coated layers in the diffusion zone and a diffusion model for carbon steel coated with NiCrSiBC superalloys are presented. The samples coated in a vacuum at the temperature of 1100°C (liquid phase sintering) have the lowest interface porosity and hardness between 700 – 1100 HV. The interdiffusion of nickel in iron substrate and iron in superalloy caused a good adhesion of the layer.

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## 1. Introduction

The NiCrSiBC form a class of hard alloys widely used for coating by thermal spraying. Chromium in these alloys (5-17 wt%) increases corrosion and oxidation resistance, and boron (2-4 wt%), along with silicon, have a marked effect on decreasing melting temperature. The boron and carbon form hard phases, thus increasing the wear resistance of the alloy [1, 2].

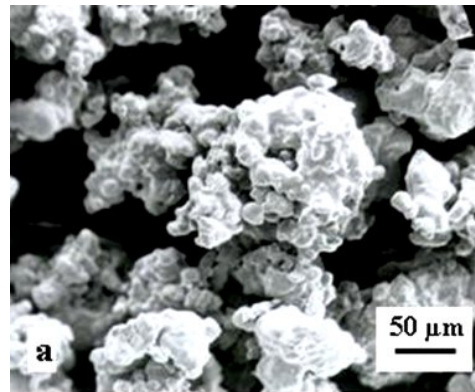
## 2. Materials and experimental method

The iron powders compacts were used as a substrate. The iron powders having a irregular shape and a mean diameter of 80 µm, were pressed at 0.6 GPa (Figure 1.a). The compacts were coated with an nickel superalloys powders (Table 1.).

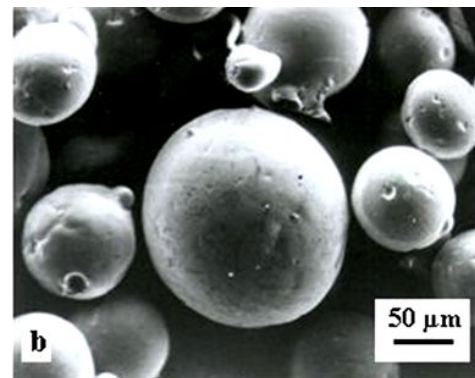
Table 1. Chemical composition of powders.

Chemical composition,wt.%.	Iron powder	NiCrSiBC
C	<0.01	0.9
S	0.013	-
Mn	0.082	-
Si	0.023	4.3
P	0.006	-
Cr	-	16.4
B	-	3.5
Ni	-	75.9
Fe	Rem.	-

These powders have a near spherical shape with a mean diameter of 80 µm. The surface of the particles is, to a large extent, smooth (Fig. 1.b), which indicates the formation of γ type supercooled solid solution.



a)



b)

Fig.1. Iron (a) and NiCrSiBC superalloy (b), powders

The compacting by air pressure (CAP) method was used [3, 4, 5, 13].

The compacts and coating materials were introduced in a pyrex glass container under vacuum and heated at 900°C and 1100°C, respectively (Figure 2). The heating rate was 7.5°C/min.

The diffusion was studied: in solid state (at 900°C), and as well in liquid phase (at 1100°C).

The samples were maintained at mentioned temperature 1 hour, and then cooled together with furnace.

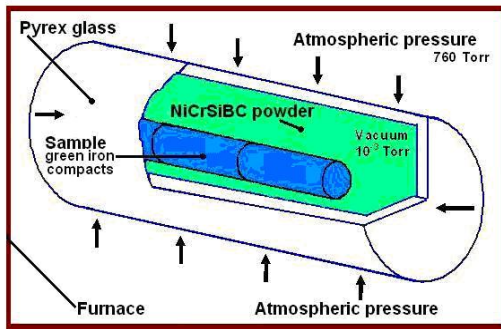


Fig. 2. Vacuum diffusion coating method at atmospheric pressure.

### 3. Results and discussion

The microstructures of samples surface were studied by optical microscopy (Fig. 3). The coating layers both by heating at 900°C and 1100°C, respectively are constituted from near the same structure components: **solid solution matrix**  $\gamma(\text{fcc})\text{-Ni}(\text{Cr,B,Si})$ ; **binary eutectic**  $(\gamma\text{-Ni}(\text{Cr,B,Si}) + \text{CrB})$  as well as **polynary eutectic**  $(\gamma\text{-Ni}(\text{Cr,B,Si}) + \text{chromium carbides} + \text{silicon borides})$ .

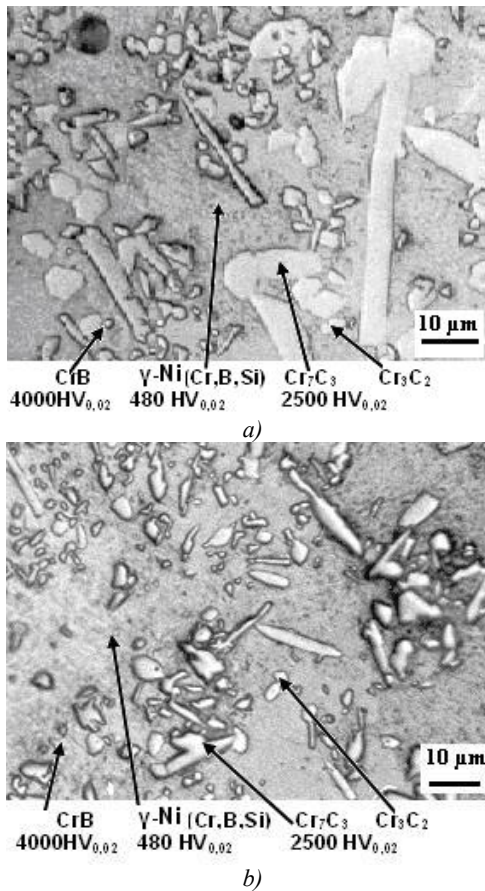


Fig. 3. Microstructures of samples (layer) vacuum coated at 900°C (a) and at 1100°C (b).

In the layer, there are also dispersed chromium boride (CrB) particles, having 1-4  $\mu\text{m}$  grain size (Fig.3). The nature of chromium carbides was determined by using X ray diffraction (Fig.4) and EDX spectrometry (scanning electron microscope, Jeol 5600LV type). The  $\text{Cr}_7\text{C}_3$ ,  $\text{Cr}_3\text{C}_2$  carbides were shown in Fig.5.

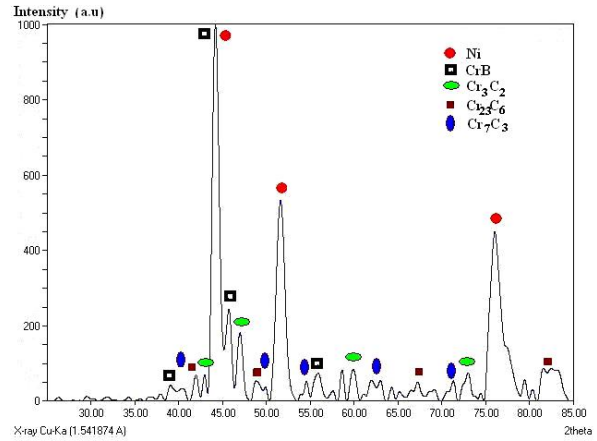


Fig. 4. X ray pattern of the vacuum coated NiCrSiBC superalloy layer

The microhardness of the coating constituents was studied. The microhardness was 480  $\text{HV}_{0,02}$  for  $\gamma\text{-Ni}$  solid solution, 4000 $\text{HV}_{0,02}$  for CrB and 2500  $\text{HV}_{0,02}$  for chromium carbide.

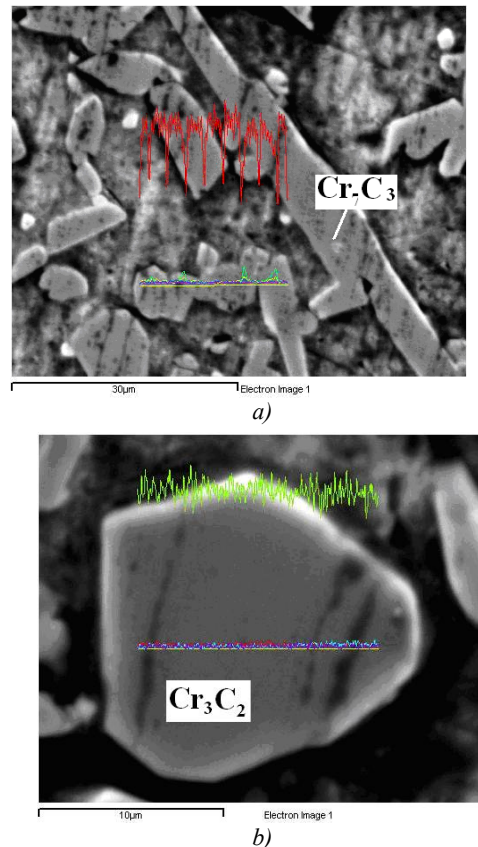


Fig. 5. Carbide particles in coating material.

The compositions and distribution of phases, at the interface between iron compact and coating layer was studied. Figure 6 shows the interface area of a vacuum coated sample at 1100°C and the distribution of the elements. Similar results were obtained of coating has been performed at 900°C. Thus the heat treatment temperature was shown to influence only to width of diffusion zone.

It was shown that iron difused in coating layer and nickel in the iron compacts as shown in Fig.7. We analysed the diffusion of the elements by using the Fick's

second law [6,7,8]. The time  $\tau$  evolution of atomic concentration can be described by the relation:

$$\frac{C - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{D*\tau}}\right)$$

where:  $C$  is the concentration of the atomic species at the time  $\tau$  and distance  $x$  from Matano plane.

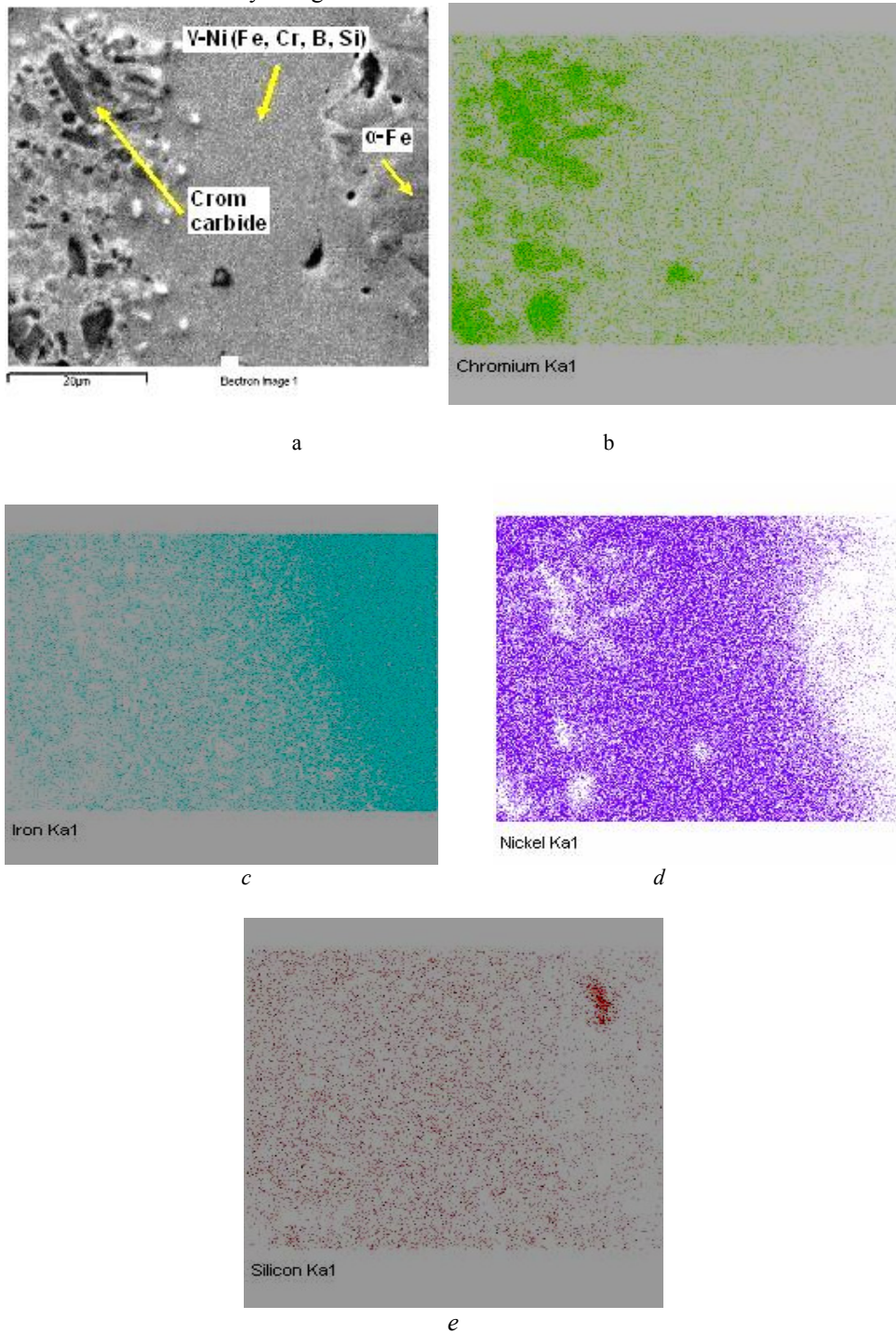


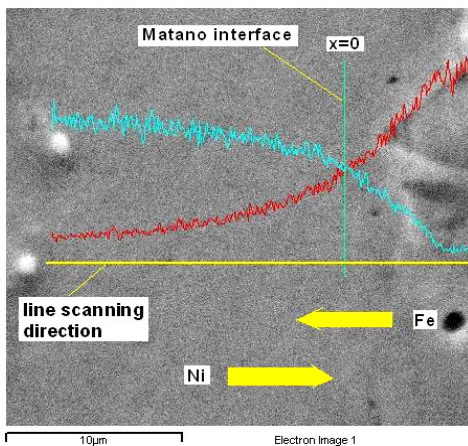
Fig.6. Distribution of elements in the diffusion (interface) area in a vacuum coated sample (1100°C).

The Matano plane is the interface corresponding to on equal amounts of atoms moved in the positive and negative direction during interdiffusion;  $C_0$  is the initial concentration;  $C_S$  is the concentration at the distance  $x=0$ ; and  $D$  – diffusion coefficient.

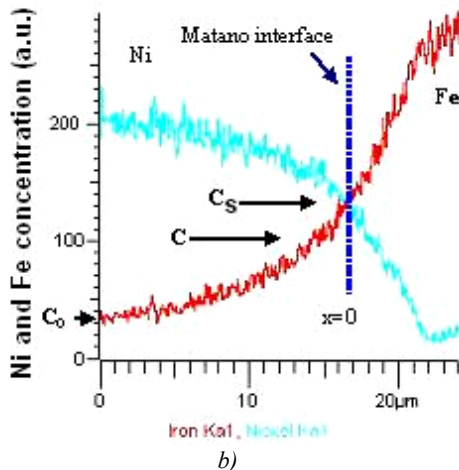
At relatively long distance for interface we have  $C_0 = 0$ .

The Matano interface is situated at  $C_S = 130$  (arbitrary units), as shown by the analysis of EDX measurements-Fig. 7. For,  $\tau = 3600$  s, and the diffusion distance (to the left of the Matano plane), between  $x=0$  and  $x= 6 \mu\text{m}$ , the mean diffusion coefficients were:  $9.21 \cdot 10^{-11} \text{cm}^2/\text{s}$  for the diffusion of Fe in  $\gamma\text{-Ni}$ , and  $4.52 \cdot 10^{-11} \text{cm}^2/\text{s}$  for the diffusion of Ni in  $\alpha(\text{bcc})\text{-Fe}$  (Fig. 7). We note that the above values are of the same order of magnitude as those found in literature [9, 10, 11, 12].

The analysis of the electron microscope patterns show the presence of small circular micropores (Kirkendall type) in addition to porosity resulting from compacting the material (Figures 6 and 7). The micropores are the result of different diffusion coefficients of Fe and Ni as above mentioned. The variation of the hardness along the diffusion zone was also studied-Fig. 8. The diffusion of the iron is higher as the temperature increases and there is a decrease of the hardness for samples thermally treated at  $1100^\circ\text{C}$ .



a)



b)

Fig. 7. Diffusion curves of iron and nickel at the interface.

In this case the hardness near the surface of the layer decrease due to diffusion of borosilicate glass. Thus, higher hardness can be obtained at 0.5-1.5 mm from interface.

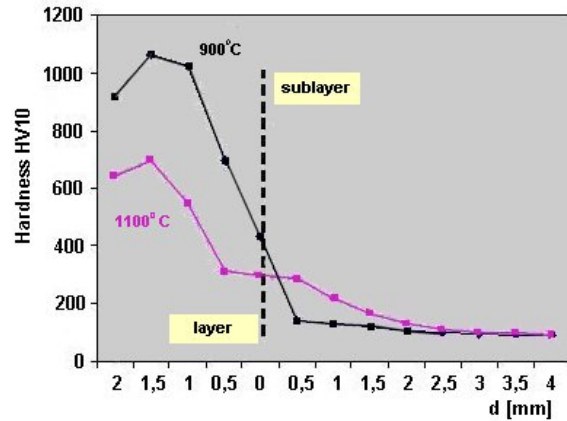


Fig. 8. Variation of the hardness for samples coated at  $900^\circ\text{C}$  and  $1100^\circ\text{C}$  normal to interface.

According to the above experimental results, the coating process can be described by the following scheme, Figure 9 [13].

Layer $\text{NiCrBSiC}$	Diffusion zone	Sublayer $\text{Fe}_3\text{C}$
<ul style="list-style-type: none"> <li>• Solid solution: <math>\text{Y-Ni}(\text{Cr,B,Si})</math></li> <li>• Binary eutectic: <math>\text{Y-Ni}(\text{Cr,B,Si})+\text{CrB}</math></li> <li>• Polinary eutectic: <math>\text{Y-Ni}(\text{Cr,B,Si})+\text{Chromium carbides} + \text{Ni}_3\text{Si borides} +</math></li> </ul>	<ul style="list-style-type: none"> <li>• Solid solution: <math>\text{Y-Ni}(\text{Cr,B,Si})</math></li> <li><math>\text{Y-Ni}(\text{Fe})</math></li> <li>• Complex eutectic: <math>\text{Y-Ni}(\text{Cr,B,Si,Fe})+\text{compounds}</math></li> <li>• Carbides; Borides; Silicides</li> <li>• Alloyed ferrite ; perlite</li> </ul>	<ul style="list-style-type: none"> <li>• Ferrite: <math>\alpha\text{-Fe}(\text{C})</math></li> </ul>

Fig. 9. Stages and structural components in the layer-substrate interface in reciprocal diffusion.

#### 4. Conclusions

The diffusion coefficient of iron is twice than of nickel. As a result, the presence of Kirkendall types pores were shown. The higher hardness were obtained at 0.5-1.5 mm from interface. The diffusion is solid state process ( $900^\circ\text{C}$ ) leads to a higher hardness.

This fact was correlated with a smaller number of iron atoms which diffused into coating material. In the case of coating by liquid phase sintering ( $1100^\circ\text{C}$ ), the hardness are lower due to higher number of Fe atoms wich diffuse in the layer, at higher temperatures. The interdiffusion of nichel in iron substrate and iron in superalloy caused a good adhesion of the layer.

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