Brazeability of Ni-Cr Heat Resistant Cermets on Stainless Steel

Four Nicrocoat coatings are evaluated for wettability, diffusion and erosion on AISI 321

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ABSTRACT. Coating problems very often depend solely on the bonding between the substrate and the applied coating. Normally, thermal and mechanical stresses cause failure of the coatings and are the main reason for the short life of the coating. A program for the evaluation of the properties of Nicrocoat cermets coating alloys has been performed. Wettability and diffusion characteristics of these coatings on a substrate of AISI 321 have been determined to obtain the optimum process parameters.

Samples were prepared in accordance with these parameters, and tests were made to determine high temperature oxidation and thermal fatigue resistance.

Introduction

The increasing need for metallic materials capable of operating at higher temperatures has stimulated extensive efforts toward the development of protective coatings. The overall problem of producing satisfactory protective coatings resolves itself into two principal areas. The first has to do primarily with development of protective coating compositions which will combine with the substrate to form compatible, useful material systems. The second portion of the problem entails development of optimum techniques for application of the coatings which exhibit maximum reliability (Ref. 1).

The basic function of the coating is that of a barrier to prevent access between the environment and the metal substrate. This function requires that the coating remain in place, unchanged, throughout the duration of utility of the substrate. From the foregoing, it is apparent that coating problems very often depend solely on the bonding between the substrate and the applied coating. Normally, thermal and mechanical stresses cause the failure of the coatings and are the main reason for the short life of the coating. One of the best methods for solving this problem is to braze the coating to the substrate. In this way the diffusion and the solution of the brazing elements between the coating and the substrate assure a bonding sufficient to resist thermal and mechanical stresses.

General Considerations

Among the available coating materials, Nicrocoat* alloys show many interesting properties. These coatings are Ni-Cr base alloys with addi-
tions of alloying elements, such as silicon, boron, and titanium. Si and B lower the melting point and promote wettabiliy and diffusion properties. Ti forms intermetallic compounds, such as silicides and borides, which have very high melting points and are finely and uniformly dispersed in the metal matrix. The presence of a ceramic phase contributes to the creation of such attributes as:

1. High remelt temperature, varying with degree of diffusion and composition of base metal
2. High resistance to oxidation and erosion
3. Improved resistance to thermal fatigue and resistance to thermal shock
4. Relatively high ductility
5. Matching of thermal expansion coefficients between coating and most superalloys

Nicrocoat alloys are fusion bonded and the ceramic phase is formed by chemical reactions which take place during the fusing operations of multi-component metallic powders. Thus, the microstructure of the coating is that of an almost ideal cermet type (Ref. 2). The properties of the ceramic compounds, which explain to a great extent the behavior of these coatings are: resistance to scaling, corrosion resistance in various corrosive media, hardness, melting point, thermal conductivity and coefficient of expansion. With regard to resistance to scaling, high temperature compounds may be subdivided into several groups based on different oxidation mechanisms (Ref. 3). The protective capacity of an oxide layer may be estimated approximately by what is known as the Pilling-Bedworth ratio.
which indicates how much the specific volume of the oxide formed is greater or less than the specific volume of the oxidized metal, or in the present case the ratio:

\[
\alpha = \frac{M_d}{m_D}
\]

where \(M\) is the molecular weight of the oxide (or mixture) formed on the oxidation of 1g-mole of compound, \(m\) is the molecular weight of the compound, and \(D\) and \(d\) are the densities of the oxide and compound.

For \(\alpha < 1\), the film formed is discontinuous, resulting in continuous oxidation, while for \(\alpha > 1\), a protective oxide layer is formed, inhibiting the access of oxygen. For large values of \(\alpha\), the layer has considerable internal stress, spills, and loses its protective properties; therefore the best protective properties are possessed by compounds for which \(\alpha\) does not greatly exceed unity. \(\text{TiSi}_2\) and \(\text{TiB}_2\) have values respectively of 1.1 and 1.21 (Ref. 4).

Furthermore the stability of borides and silicides and their formation at various temperatures are related to their standard free energies of formation, \(\Delta G^\circ\); more negative values of \(\Delta G^\circ\) indicate stabler compounds. Of the metal diborides, those of the fourth and fifth odd (A) subgroups, e.g. \(\text{TiB}_2\), have the greatest stability. The same applies to disilicides (Refs. 5, 6).

In the oxidation of borides, volatile boric anhydride is also formed in addition to the oxides of the correspond-

Fig. 2 — Penetration of Nicrocoat alloys into AISI 321 base metal for various times and temperatures

Fig. 3 — Drop spreading on and penetration into AISI 321 base metal by Nicrocoat 610, after 1.5 hr at 1150 C in 10^-4 torr vacuum
the oxide film. This circumstance in conjunction with the low value of $\alpha$, determines the relatively high resistance to scaling of titanium boride.

The resistance to high temperature oxidation of silicides is related to the formation of a protective coating as a function of the volatility and solubility of the oxides of metals and silicon, formed in the high temperature heating of the silicides (Ref. 7). In the case of titanium silicides, a dense, vitreous layer is formed at definite temperatures and for definite ratios of the content of SiO and nonvolatile metal oxide. This vitreous scale is tightly adherent, resistant to oxidation, self-healing, and thus highly protective.

The above summarized properties of the Nicrocoat ceramic components explain at a great extent the potential interest of this type of coatings. However, their applicability depends mostly on their ability to create a bonding with a given substrate, that is by their wettabillity and diffusion characteristics. An experimental program was therefore carried out to determine the wettabillity and diffusion characteristics of several Nicrocoat compositions on AISI 321 stainless steel substrate.

Materials and Experimental Procedures

The substrate chosen for the program was AISI 321 stabilized stainless steel; the typical chemical composition is given in Table 1.

The coating alloys used were: Nicrocoat 610, Nicrocoat 620, Nicrocoat 621, Nicrocoat 630. Their chemical composition after fusing is given in Table 2.

The tests were carried out by placing fixed quantities of Nicrocoat, as powder dispersed in organic vehicle, on plates of AISI 321 and heating the specimens under a vacuum of the order of $10^{-4}$ torr.

Spreading and penetration determinations were carried out at different temperatures for various times. After heat treatment the drop enlargement and its penetration were measured. The summarized results are the average of four measurements.

Results and Discussions

The results of the wettabillity determinations are summarized in Fig. 1. Nicrocoat 610 shows that, after an initial increase, the drop diameter becomes stable at higher temperatures. However, the initial increase, varying between 30 and 70%, indicates the good wettabillity characteristics of Nicrocoat 610 on AISI 321.

Nicrocoat 620 and 621 show almost the same characteristics as Nicrocoat 610, even if there seems to...
be a stronger dependence of the drop enlargement on temperature.

Nicrocoat 630 shows unsatisfactory wettability characteristics; in fact its initial drop diameter is the lowest and has a maximum increase of about 40%.

The criteria used for penetration determination were those usually employed in brazing (Ref. 8) and the results are summarized in Fig. 2. Nicrocoat 610 shows the strongest aggressive effect, due to its diffusion and erosion, as can be seen in Fig. 3. Due to the presence of boron, diffusion into the base metal is particularly high. The same is true of erosion, which brings the penetration to a maximum of about 1000 microns.

Figure 4 shows the more limited diffusion of Nicrocoat 620. The penetration, at maximum value of 200 microns, is mainly due to erosion. Also for Nicrocoat 621 the penetration into the substrate is mainly due to erosion and reaches a maximum of 180 microns, as can be seen in Fig. 5.

Nicrocoat 630 shows penetration only at the highest temperature (1200°C), where it reaches a maximum value of 200 microns, as shown in Fig. 6.

The above results show good wettability and diffusion characteristics for the coatings examined and indicate the optimum parameters (temperature and time) to be used in obtaining satisfactory coatings. For all four coatings the optimum fusing temperature seems to be 1200°C, which results in both the formation of the ceramic compounds and the brazing of the coating to the substrate. To avoid excessive erosion, the soaking time should be limited to 0.5 hr for Nicrocoat 610; while the other types need a soaking time of 3 hr.

Using these parameters, AISI 321 samples were coated to determine the resistance of these coatings to high temperature oxidation and thermal fatigue. Figure 7 shows the four types of Nicrocoat under examination in the as-fused condition. All coatings appear dense and satisfactorily bonded to the substrate.

Oxidation resistance tests were carried out in air at various temperatures: 900 - 1000 - 1100°C for 50 hr. Figures 8, 9 and 10 show the coatings and reference samples of base metal after the oxidation tests. Nicrocoat 620, 621 and 630 resisted very well at 900°C, while Nicrocoat 610, even if its resistance may be considered satisfactory, suffered oxidation of its metallic matrix mainly due to diffusion of boron into the substrate and thus depletion of the protective ceramic components.

After the 1000°C test, the coatings were severely corroded. However, the substrate appears to be protected in all cases except that of Nicrocoat 610, where intergranular corrosion of the base metal can be observed.

The protective effect of the coatings at 1200°C is very limited, and in the case of Nicrocoat 610 the erosive effect of the coating itself has been such as to bring the substrate to complete destruction.

To determine thermal fatigue resistance, samples of AISI 321 coated with the four types of Nicrocoat, using the same parameters as before, were subjected to 500 cycles in the range 200-1100°C. Figure 11 shows the specimens after the cycles. As can be seen, Nicrocoat 620, 621 and 630 resisted very well, with no evidence of cracking, spalling or detachment of the coating. Nicrocoat 610, on the contrary, was almost completely destroyed, perhaps through a corrosion mechanism rather than by action of thermal stresses.

Conclusions

The main conclusions that can be drawn from the experiments performed are as follows:

1. Nicrocoat 610 has good wettability and diffusion properties and can be easily applied, even to difficult joint configurations. However, penetration, due to its boron content (which causes erosion of the base metal) is very high, limiting the maximum useful temperature of application.

2. Nicrocoat 620 and 621 have good wettability and diffusion properties and can assure a satisfactory
bonding with the substrate without any particular erosive effect.

3. Nicrocoat 630 has limited wetability and diffusion properties in the examined fusing temperature range, resulting in poorer bonding.

4. Nicrocoat 610 has satisfactory oxidation resistance up to 900 °C. This is due to boron diffusion into the substrate.

5. Nicrocoat 620, 621 and 630 have satisfactory oxidation resistance up to 1000 °C and for shorter times can have a protective effect up to 1100 °C.

6. All the coatings under examination have excellent thermal fatigue resistance.

References


5. Glasson, D. R. and Jones, J. A.,
Fig. 10 — Oxidation of base metal and Nicrocoat alloys after 50 hr at 1100°C in air.

Fig. 11 — Nicrocoat alloys after a 500 cycle thermal fatigue test, with temperature cycling from 200°C to 1000°C to 200°C over a time of 6.5 min per cycle.


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