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"Metal-Ceramic Interfaces: Laser Processing" Part III

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METAL–CERAMIC INTERFACES IN LASER COATED STEELS: A TRANSMISSION ELECTRON MICROSCOPY STUDY OF A MIXTURE OF IRON AND SPINEL GRAINS

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Abstract—This paper concentrates on laser coating of a Duplex steel SAF 2205 by bringing a mixture of Cr_2O_3 and Fe powder into a laser beam. After the laser treatment the Duplex steel transforms into a b.c.c. structure. Transmission electron microscopy observations indicate a proper bonding between substrate and coating consisting of a spinel structure around the composition $FeCr_2O_4$ near the interface. In addition, particles with a spinel structure have been observed in the b.c.c. substrate. Crystallographic orientation relationships have been identified for the interfaces of the spinel structure with the b.c.c. matrix using electron diffraction.

Résumé—Cet article est consacré au revêtement par laser d'un acier biphasé SAF 2205 par irradiation d'un mélange de poudre de Cr_2O_3 et de Fe sous un faisceau laser. Apres le traitement par laser, l'acier biphase prend une structure c.c. Des observations par microscopie électronique en transmission indiquent une liaison correcte entre le substrat et le revêtement qui consiste en une structure spinelle de composition voisine de $FeCr_2O_4$, située pres de l'interface. De plus, des particules de structure spinelle sont observées dans le substrat c.c. Par diffraction électronique, on a identifié les relations cristallographiques d'orientation des interfaces entre la structure spinelle et la matrice c.c.

Zusammenfassung—Diese Arbeit behandelt die Laserbeschichtung des Duplex-Stahles SAF 2205. Hierzu wird eine Mischung von Cr_2O_3 mit Fe in einen Laserstrahl gebracht. Nach der Laserbehandlung ist der Duplex-Stahl in eine k.r.z. Struktur umgewandelt. Beobachtungen im Durchstrahlungselektronenmikroskop zeigen eine gute Bindung zwischen Substrat und Überzug; es findet sich eine Spinell-Struktur in der Nähe der Grenzfläche mit einer Zusammensetzung um $FeCr_2O_4$. Zusätzlich werden Teilchen mit einer Spinell-Struktur im k.r.z. Substrat beobachtet. Die kristallografischen Orientierungsbeziehungen in der Grenzfläche zwischen Spinell-Struktur und k.r.z. Matrix werden mittels Elektronenbeugung aufgeklärt.

1. INTRODUCTION

The laser/particle injection process has proven to be a versatile technique of coating metals with ceramic particles to meet extreme requirements of wear and corrosion resistance. Because of its high energy density, the laser beam is able to melt the metallic substrate and may even partly melt the ceramic powder. As a result, a solid bonding can be formed between the ceramic and the metal. However, as the physical properties between ceramic and metallic materials are much different, e.g. the crystallographic structure and the thermal expansion, cracks usually develop at the ceramic–metal interface as well as inside the coating during the rapid solidification and cooling processes. In this paper, the orientation relationship and the coherency of laser melted Duplex steel 2205 interface with Cr_2O_3 is investigated by transmission electron microscopy. This system was chosen because of the small difference in thermal expansion coefficient between the oxide and Duplex

steel. The thermal expansion coefficient of Cr_2O_3 is $9.6 \cdot 10^{-7}$ [1] from 20 to 1400°C, of Duplex 2205 $3.6 \cdot 10^{-7}$ [2] from 20 to 400°C. The chemical composition of the Duplex SAF 2205 is listed in Table 1.

Obviously, a good adhesion of the ceramic–metal interface may prevent the formation of interfacial cracks. Chemical reactions between ceramics and metals may lead to a good wetting. Therefore a reaction bonding technique has been developed in the ceramic–metal joining [3]. A spinel phase has been reported [4] to form at the interface between liquid iron and the oxide Al_2O_3. Using X-ray diffraction we reported recently [5] on the presence of a $FeCr_2O_4$ spinel structure in Cr_2O_3 laser coated steel. It was concluded that a good adhesion and crack free ceramic coatings can be obtained if this spinel is formed at the ceramic–metal interface. On the other hand it should be noted that in some systems, e.g. alumina–nickel there is a critical thickness above which fracture occurs at or near the spinel–metal interface [6].

C	Si	Mn	Cr	Ni	Mo
0.03	1.0	2.0	22	5.5	3.0

2. EXPERIMENTS

A 1.5 kW CO₂-laser, Spectra Physics 820, was applied for the laser coating, which was operated at 1 kW with a scan velocity of 20 mm/s, beam diameter of 0.6 mm and 50% of overlap under a protective atmosphere of Ar as shielding gas. A powder mixture of Cr_2O_3 and pure iron was brought into the laser beam instead of pure Cr_2O_3, in order to form a spinel structure inside the coating. The composition of the precursor powder mixture is $Fe:Cr_2O_3 = 1:2$ (mol wt). The size distribution of the Fe powder peaks around 10 μm whereas Cr_2O_3 powder shows a broad distribution ranging from 5 to 45 μm. The melting point is 1535°C for Fe and 2266°C for Cr_2O_3. The composition analysis of the laser processed coating by EDS (energy dispersive X-ray spectrometry, see [5]) indicates that about 50% of the available iron powder has been diffused into the oxide particles. In this way, according to the composition, the product of the reaction between Cr_2O_3 and Fe will be $FeCr_2O_4$, or $(Fe_{1/3}Cr_{2/3})Cr_2O_4$.

Duplex steel SAF 2205 was used as substrate materials. After laser processing, the surface structure of Duplex SAF 2205 transforms into a single phase of b.c.c. A cross-section through the coating and substrate can be found in [5]. The thickness of the coating is in the order of 100 μm. The structure was investigated by X-ray diffraction and then identified by electron diffraction. A transmission electron microscope (TEM) operating at 200 kV was used (JEM 200 CX). The TEM specimens were dimpled to about 30 μm in the centre and thinned by ion milling afterwards.

3. EXPERIMENTAL RESULTS

3.1. Microstructure of the coating

Both by X-ray diffraction and electron diffraction it was found that the coating consisted largely of grains with a spinel structure of $FeCr_2O_4$. Here we should emphasize that the crystal structure, but not the composition, is that of $FeCr_2O_4$. EDS data and the phase diagram are presented in Ref. [5] from which it may be concluded that large deviations from stoichiometry are presumably due to this far from equilibrium processing route.

Figure 1 shows typical spinel grains inside the coating. Still there remain iron particles inside the coating which are distributed between the spinel grains. Figure 2 displays such a b.c.c. iron particle bound by spinel particles. During the phase transformation many planar faults, e.g. stacking faults and twinning, were induced in the spinel particles,

Fig. 1. Dark field TEM image of a few spinel grains inside the laser coated layer on Duplex steel.

some of which lie on the closest packed planes of {111} spinel. Cracks could be observed along some grain boundaries. No cracks appear in the spinel-b.c.c. interface, probably because of the good wetting between spinel and liquid iron, although stresses due to solidification and coefficient of thermal expansion mismatch could dominate this behaviour as well. The wetting angle of liquid iron with $FeCr_2O_4$ spinel is 72° at 1600°C in air [ ], i.e. smaller than 90° for wetting to occur.

In some cases, a cubic-on-cubic orientation relationship could be observed at the interfaces between iron and spinel particles. Figure 3 is a diffraction pattern which is identified to be the orientation relationship of (1$\bar{1}$1) spinel/(1$\bar{1}$0) b.c.c. and [110] spinel/[111] b.c.c.

3.2. Spinel particles in a b.c.c. matrix: Duplex steel SAF 2205

In contrast to the Fe particles inside the coating, the spinel particles found in the steel matrix have a spherical shape. Here we mean the spinel particles completely enclosed by the matrix. Figure 4 shows one spinel particle surrounded by the b.c.c. matrix. Similar to the spinel structure of the coating, many

Fig. 2. Dark field TEM image of a b.c.c. iron particle inside the laser coated layer on Duplex steel.
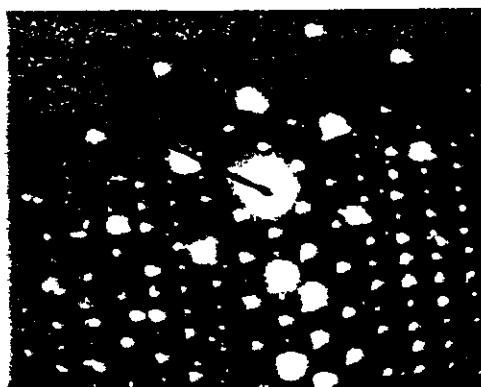
Fig. 3. Electron diffraction pattern of a b.c.c. iron particle in a spinel matrix showing the orientation relationship of (1$\bar{1}$1) spinel/(1$\bar{1}$0) b.c.c. and [110] spinel/[111] b.c.c.

Table 1. The orientation relationships detected by TEM between particle and matrix

Particle	Matrix	Plane	Direction
B.c.c.	Spinel	(11$\bar{1}$)/(1$\bar{1}$1)	[112]/[11$\bar{1}$]
Spinel	B.c.c.	(111)/(110)	[110]/[11$\bar{1}$]
Spinel	B.c.c.	(11$\bar{1}$)/(110)	[110]/[1$\bar{1}$0]
Spinel	B.c.c.	(1$\bar{1}$1)/(1$\bar{1}$0)	[211]/[11$\bar{1}$]
Spinel	B.c.c.	(002)/(110)	[110]/[1$\bar{1}$0]
Spinel	B.c.c.	(31$\bar{1}$)/(0$\bar{1}$1)	[125]/[111]
Spinel	B.c.c.	(220)/(110)	[111]/[11$\bar{1}$]

planar faults are observed inside the particle, which are mainly on the closest packed plane of {111} spinel. However, only a few faults could be observed in some small spinel particles which are much smaller than the smallest size of the particles of the precursor Cr_2O_3 powders. They may be formed from the solidifying liquid. Sometimes, a superlattice diffraction pattern could be detected from the spinel particles. This pattern may be caused by the off-stoichiometric disorder of the spinel particles in comparison with the perfect $FeCr_2O_4$ spinel structure. Figure 5 displays such a pattern. Several types of crystallographic orientation relationship have been determined in our experiments at the interface between the spinel particles and the b.c.c. matrix. Table 2 compiles the results. However, in most cases the relation of {111} spinel/{110} b.c.c. could be identified. This means that the spinel-b.c.c. interface is mainly parallel to the closest packed planes of {111} spinel and {110} b.c.c. Very often, no crystallographic orientation relationship could be observed. No cracks were observed at the spinel-b.c.c. interfaces irrespective as to whether an orientation relationship exists.

Fig. 4. Dark field TEM image of a spinel grain inside the b.c.c. matrix of Duplex steel.

4. DISCUSSION

There are two types of spinel, normal spinel and inverse spinel [7]. In normal spinel with the stoichiometric composition of AB_2O_4, the oxygen atoms form an f.c.c. sublattice whereas A occupies tetrahedral interstices and B octahedral ones. In inverse spinel of $B(AB)O_4$, half of B occupies tetrahedral interstices and the rest of B and A are at octahedral sites. According to the size of both the interstices and the ions of iron and chromium, the inverse spinel is more favourable at the stoichiometric composition $FeCr_2O_4$. However, in general, oxides exhibit deviations from the stoichiometric composition [8]. Furthermore, since in our case the spinel does not match with $FeCr_2O_4$ stoichiometry, based on EDS observation, and is heavily distorted, there is not much of a point in distinguishing whether the spinel is of the normal or the inverse type. Table 3 lists two references of the ASTM data about this spinel $FeCr_2O_4$. One is cubic and another is tetragonal. Our X-ray diffraction data suggest that both of the spinels exist. For simplicity, the cubic spinel was selected for our discussion, because there is only little difference as far as the lattice constants are concerned.

According to the EDS results from which it was concluded that 50% of Fe has diffused into the Cr_2O_3, the product of the reaction between Fe and Cr_2O_3 could be $(Fe_{1/3}Cr_{2/3})Cr_2O_4$. In comparison with the stoichiometry $FeCr_2O_4$, two thirds of the interstices for iron are occupied by chromium. If the interstice for Fe in the oxide is not occupied by Fe, some Cr_2O_3 cell may be preserved because the product is a non-stoichiometric and inhomogeneous spinel. Here the stacking sequence of hexagonal Cr_2O_3 on the closest packed plane is ABABAB ..., and that of spinel is ABCABC .... Supposing the spinel is directly transformed from the closest packed plane of Cr_2O_3, i.e. some planes of the hexagonal structure will move $\frac{1}{6}\langle 112 \rangle$ by shearing to form a cubic structure of spinel. Twinning may be induced during the shearing and some hexagonal cells or planes remained in the spinel crystal may act as stacking faults on the closest packed plane of {111} spinel. For

Table 3. ASTM data of structures

Name	Cr_2O_3	$FeCr_2O_4$	$FeCr_2O_4$	Fe	Fe
Phase	R-3c.	Tetra	Fd3m	Im3m	Fm3m
a (nm)	0.4959	0.8497	0.8379	0.28664	0.35925
c (nm)	1.3594	0.3115			

instance, the stacking sequence of twinning could be ABC(ABA)CBA, and those of stacking faults may be ABC(AB)ABC and ABC(B)ABC. More detailed transmission electron microscopy is underway to be more specific about the nature of these faults.

According to the lattice parameters in Table 3, the most favourable interface of spinel—b.c.c. is (001) spinel//(001) b.c.c. in the direction of [100] spinel//[110] b.c.c. It has to be added that according to the X-ray diffraction data performed on these coatings [5] non-stoichiometry of the spinel structure does not seem to affect the lattice parameter. Therefore, the lattice misfit on this particular interface orientation is estimated to be only about 3%. However, this type of orientation relationship was not observed. In most cases the interfaces are parallel to the closest packed planes although the lattice misfit on the (1$\bar{1}$1)spinel//(1$\bar{1}$0) b.c.c. interface is very large, of about 20% in the direction of [110] spinel//[111] b.c.c. and 2% in the direction of [101] spinel//[010] b.c.c. Therefore, the spinel—b.c.c. interface may not be coherent. Similar results have been reported by HREM and CTEM [9–12] about the interface of an oxide and a metal matrix. A cubic-on-cubic orientation relationship was observed but the interface was not coherent.

It is not exceptional that the orientation relationship does not coincide with the lattice misfit, since a lattice having almost identical atom matching often exhibits no tendency for easy heterogeneous nucleation and liquid-phase epitaxy may occur between lattices of widely different lattice spacing instead [13]. As early as 1955, Turnbull [14] has already pointed out that the energy of an interphase boundary has both a structural and a chemical component. The chemical component arises because atoms at the boundary have a certain proportion of neighbours of the "wrong" species across the boundary. Usually, however, because of metal—metal interfaces interest is mainly focused entirely on the structural component [15]. Then the orientation relationship should coincide with the interface coherence to attain the lowest free energy. In contrast to the metal—metal interface, the chemical component may play a crucial role for the oxide—metal interface, since there might exist a strong interaction between ions of oxygen and metals. Beside ions, in particular structural defects in ceramic materials carry localized charges and consequently a substantial bonding is expected based on image charges of these localized defects in the metallic jellium. Therefore significant binding between metals and ceramics can be attained even for incoherent boundaries [16–18].

No cracks have been observed at the interface between a spinel particle and the b.c.c. matrix irre-spective as to whether a crystallographic orientation relationship exists. This observation is in line with the observed difficulty to coat SS304 in comparison with duplex steel [5, 19].

5. CONCLUSION

After laser processing, the hexagonal Cr_2O_3 has reacted with liquid iron and transformed to the spinel phase. As the coating is a rapid melting and solidification process, iron could not react with the Cr_2O_3 grain completely, and the spinel becomes nonstoichiometric, in which many planar faults exist mainly on the closest packed plane of the spinel phase.

Crystallographic orientation relationships have been observed for the interfaces of spinel—b.c.c. But these interfaces can not be completely coherent because of the large lattice misfit on them. Even though no cracks have been observed at the interfaces at which a crystallographic orientation relationship exists.

REFERENCES

1. G. V. Samsonor, *The Oxide Handbook*, pp. 452, 125, 170. Plenum Press, New York (1973).
2. Sandvik SAF 2205, UNS S31803, Sandviken, Sweden, S-1. 347-ENG (1989).
3. W. E. Borbidge and P. T. Whelan, *Mater. Sci. Forum* 34–36, p. 439 (1988).
4. J. A. Yeomans and T. F. Page, *J. Mater. Sci.* 25, 2312 (1990).
5. X. B. Zhou, P. M. Bronsveld and J. Th. M. De Hosson, *Lasers Engng* 1, 145 (1991).
6. K. P. Trumble and M. Ruhle, *Acta metall. mater.* 39, 1915 (1991).
7. W. D. Kingery, *Introduction to Ceramics*, pp. 116, 471, 625. Wiley, New York (1967, 1960).
8. *Diffusion*, pp. 310–320. Am. Soc. Metals, Metals Park, Ohio (1973).
9. F. Ernst, P. Pirouz and A. H. Heuer, *Mater. Res. Soc. Symp. Proc.* 138, 557 (1989).
10. G. Necker and W. Mader, *Phil. Mag. Lett.* 58, 205 (1988).
11. J. D. Boyd and R. B. Nicholson, *Acta metall.* 19, 1379 (1971).
12. D. J. Pedder, *Metall. Trans.* 9A, p. 659 (1978).
13. G. A. Chadwick, *Metallography of Phase Transformations*, pp. 183, 67. Butterworths, London (1972).
14. D. Turnbull, *Impurities and Imperfections*, p. 121. Am. Soc. Metals, Metals Park, Ohio (1972).
15. *Phase Transformation*, p. 341. Am. Soc. Metals, Metals Park, Ohio (1970).
16. A. M. Stoneham and P. W. Tasker, *Phil. Mag. B* 55, 237 (1987).
17. M. W. Finnis, *Acta metall. mater.* 40, S25 (1992).
18. P. J. Jennings and R. O. Jones, *Adv. Phys.* 37, 341 (1988).
19. X. B. Zhou and J. Th. M. De Hosson, *Acta metall. mater.* 39, 2267 (1991).