

CORROSION RESISTANCE OF LASER-DEPOSITED COMPOSITE COPPER-BASALT OVERLAY

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Abstract

This paper deals with an assessment of the corrosion resistance of copper-basalt composite clad by laser. The filler powder for laser overlaying was a mixture of high-purity copper powder Oerlikon METCO 55 consisting of 45-90 µm particles and a basalt powder comprising particles 50-250 µm in size. Under this experimental programme, three series of specimens were prepared (5 wt. % basalt; 10 wt. % basalt; and 15 wt. % basalt). The substrate was C45 steel 20 mm in thickness. The corrosion resistance of the laser clads was assessed by potentiodynamic corrosion testing using the linear polarization method. The electrolyte was an synthetic prepared mine water. Metallographic evaluation of the laser clads was carried out using optical microscopy (OM) and scanning electron microscopy (SEM). Based on the outcomes of this study, a summary was developed of the application potential of the laser-deposited composite copper-basalt overlay for surface treatment of storage containers for underground spent nuclear fuel repositories located in the Czech Republic.

Keywords: Laser cladding, copper-basalt composite, potentiodynamic corrosion test, X-ray diffraction

1. INTRODUCTION

Laser cladding relies on the high-energy-density laser beam to melt the base material as well as the cladding material. The latter may be in the form of powder or wire. The cladding process produces a narrow region, in which the melted cladding material and base material become metallurgically bonded. Their solidification thus leads to strong metallurgical bonds which provide the deposit with good cohesion as well as adhesion to the base material. The goal of laser cladding is to create a weld clad with desired properties and chemical composition on the base material without extensive dilution (>10 %) between the two metals [1].

Laser cladding applications in the power generation and nuclear industries are not new. The first documented mention dates back to 1981 when a protective weld clad was deposited by laser on the joints between turbine blades and rotor in the Rolls Royce company [2].

Among them, there is the unique concept of composite laser weld cladding for protection of outer surfaces of storage containers for spent nuclear fuel in underground repositories. In the Czech Republic, the fundamental requirements on storage containers have been set out by the State Office for Nuclear Safety (SÚJB). They include an extremely high corrosion resistance of the outer surface. The SÚJB stipulates that storage containers should retain their corrosion resistance for at least 100,000 years in the underground repository environment. The composite material for the corrosion-resistant outer layer of storage containers for spent nuclear fuel is based on materials and constituents that have existed on Earth since time immemorial. Degradation processes in chemically-pure metals (such as copper) and igneous rocks can be assessed reliably in order to obtain corrosion resistance predictions for the 100,000-year period defined by the SÚJB.

2. EXPERIMENTS

The purpose of the experimental programme was to contribute to development of a composite laser weld clad/base material with high corrosion resistance in a defined environment. The base material was ČSN EN 10083-2 (C45) steel sheet of 20 mm thickness ground on both sides. The chemical composition of C45 steel is shown in **Table 1**.

Table 1 Chemical composition of C45 steel (base material), element content in weight per cent [3]

C	Si	Mn	Cr	Mo	Ni	P	S
0.40 - 0.52	0.43	0.46 - 0.84	0.45	0.13	0.45	0.04	0.04

A special laser cladding material was created by mixing high-purity copper powder and basalt. The copper powder was purchased from Oerlikon Metco under brand name Metco 55. Basic information on powder particle sizes, specifications and properties of Metco 55 powder are given in **Table 2**.

The basalt powder for this experimental programme was purchased in a store which sells materials for hand work and model building. The powder grain size was measured using SEM; and was found to be 45-250 µm. It was also examined using X-ray diffraction. The diffractogram of the basalt powder is shown in **Figure 1**. Phases identified in the powder are listed in **Table 3**.

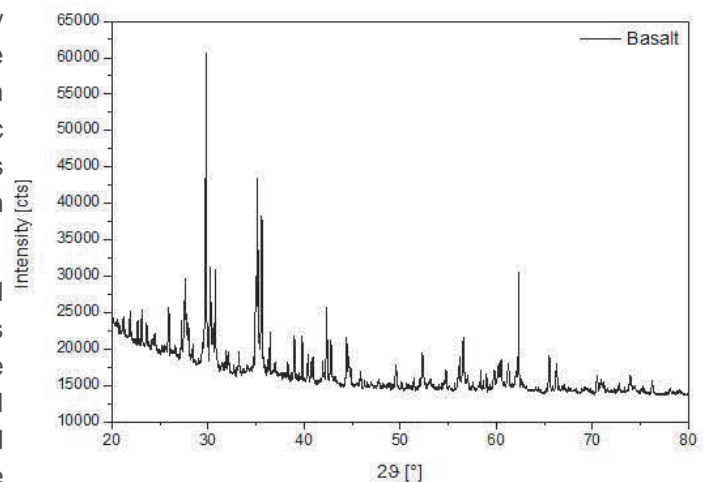


Figure 1 Basalt powder, diffractogram

Table 2 Metco 55 powder, specifications and properties declared by the manufacturer [4]

Copper content	Powder particle size	Morphology	Melting point	Density
Cu min. 99 %	45 - 90 µm	Spherical	1,356 K (1,083 °C)	8,960 kg/m ³

Table 3 Phase composition of the basalt powder found by X-ray diffraction

No.	Compound name	Chemical formula	No.	Compound name	Chemical formula
1	Magnesium oxide	MgO	11	Cristobalite II	Si8.0O16.0
2	Periclase (a = 0.4200)	Mg4.0O4.0	12	Calcium Aluminium Oxide	Ca5.0Al6.0O14.0
3	Periclase (a = 0.3952)	Mg4.0O4.0	13	Calcium-magnesium silicide	Ca4.0Si4.0Mg4.0
4	Quartz (a = 0.4702, c = 0.5256)	Si6.0O6.0	14	Alite	Ca54.0Si18.0O90.0
5	Quartz (a = 0.4973, c = 0.5267)	Si6.0O6.0	15	Pyroxene ideal	Mg8.0Si8.0O24.0
6	Quartz (a = 0.4722, c = 0.5267)	Si6.0O6.0	16	Sillimanite	Al8.0Si4.0O20.0
7	Silicon Oxide (Orthorombic)	SiO ₂	17	Enstatite	Mg16.0Si16.0O48.0
8	Silicon Oxide (Hexagonal)	SiO ₂	18	Tobermorite	Ca5.0Si6.0O18.0
9	Titanite	Ca4.0Si8.0O20.0	19	Mullite	Al4.8Si1.2O9.6
10	Cristobalite	Si8.0O16.0	20	Forsterit	Mg2SiO ₄

Laser cladding was carried out at New Technologies Research Centre (NTC) at the University of West Bohemia. Solid-state disc laser Trumpf TruDisk 8002 was used. Its wavelength was $\lambda = 1,030 \text{ nm}$ and the spot

size was 3.4 mm. Weld cladding powder was supplied via powder feeder GTV PF 2/2 MH to coaxial-feeding cladding head Precitec YC52 with a four-beam nozzle. The assist and shielding gas was 99.99 %-purity argon.

Using laser cladding, three samples of composite copper-basalt overlays were prepared. A special mixture of laser cladding powder Metco 55 and basalt powder was prepared for each sample:

- SAMPLE A (95 wt.% Metco 55, 5 wt. % basalt powder)
- SAMPLE B (90 wt. % Metco 55, 10 wt. % basalt powder)
- SAMPLE C (85 wt. % Metco 55, 15 wt. % basalt powder)

The substrate was C45 steel. Each overlay had an area of 60×95 mm.

3. METALLOGRAPHY

The laser overlays were examined using metallographic techniques and Carl Zeiss Z1M optical microscope (OM) with Axiovision software, and Philips XL 30 ESEM microscope with an EDX analyser (SEM). Their microstructures were revealed using a chemical mixture available under the name Robin. The interface between the laser overlay and the base material was etched with 3 % nital.

In the course of metallographic preparation of '95 % Cu, 5 % metal oxides' specimen, the adhesion of the composite laser clad to the base material proved insufficient; and the clad separated from the substrate. For this reason, '95 % Cu, 5 % metal oxides' samples were disqualified from subsequent examinations.

Figure 2 is a micrograph of the laser overlay on SAMPLE B (the cladding powder contained 90 wt. % of Metco 55 and 10 wt. % basalt). The matrix of the laser overlay consists of copper. The grain size of the copper matrix identified according to ČSN EN ISO 643 was G11. There is a dispersion of mostly round basalt particles in the matrix of the composite laser overlay.

Figure 3 shows an unmelted basalt particle at the fusion boundary of the laser overlay and the substrate in SAMPLE B. The hypothesis that it was an unmelted basalt particle was confirmed by EDX analysis (the point identified as EDX - M1 in **Figure 3**; the chemical composition is given in **Table 4**).

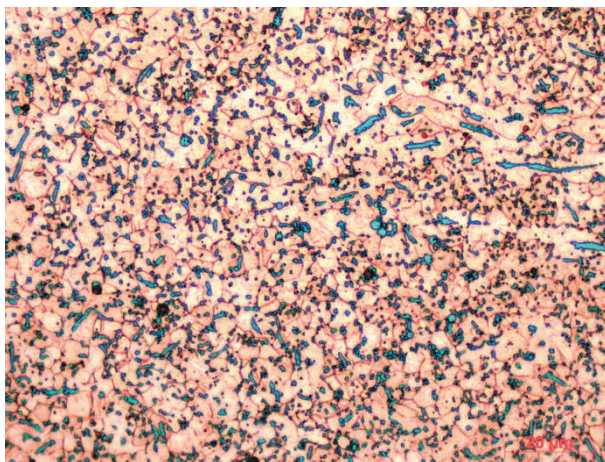


Figure 2 SAMPLE B; Cu-based matrix with a dispersion of basalt particles; etched with Robin reagent; magnification 1,000×

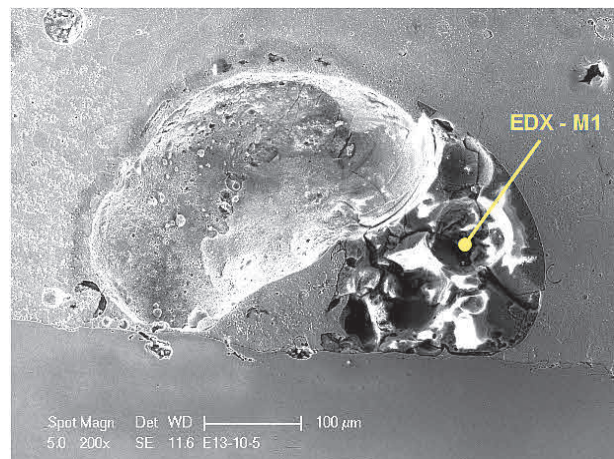


Figure 3 SAMPLE B; unmelted basalt particles; the region of EDX analysis of chemical composition is identified; SE image; magnification 200×

Metallographic examination of SAMPLES A, B and C revealed severe heterogeneity of the laser-deposited composite overlays. The Cu-based matrix of the overlay contained some areas with dispersion of basalt particles. As the laser cladding process progressed, the overlay became increasingly contaminated with iron

and other elements from the base material. Essentially, the joint between the composite copper-basalt overlay and the base material, a carbon steel, is a dissimilar weld. The fusion boundary is a problematic region, as it develops cracks during welding, which run into both the base material and the overlay. From the perspective of real-world use of laser-deposited copper-basalt composite overlays in highly-corrosive environments, the cracks in the overlay are a major weakness.

Table 4 Basalt; EDX analysis of chemical composition, element content in weight per cent

	Fe	Cu	Si	Mn	Ni	Ti	Cr	Ca	Al	Mg	O
EDX - M1	14.1	11.2	13.5	0.3	0.3	1	0.3	5.4	13.1	6.1	34.7

4. POTENTIODYNAMIC CORROSION TEST

Corrosion resistance of the composite laser overlays was assessed using potentiodynamic corrosion testing with the aid of BioLogic SP-150 potentiostat. EcLab 10.44 software was employed for data processing and evaluation. First, the time dependence was measured of the steady-state corrosion potential between *WE - WORKING ELECTRODE* and *RE - REFERENCE ELECTRODE*. The time for stabilization of free corrosion potential was identical in all measurements $t_R = 30$ min. Linear polarization was used for finding the dependence of corrosion current (converted to current density) on the mixed corrosion potential of the sample within the range from E_i to E_L ($E_i = E_{corr} - 0.025$ [V]; $E_L = E_{corr} + 0.025$ [V]) with respect to the reference electrode (*RE*). The Tafel lines obtained were extrapolated using software EcLab 10.44 and the polarisation resistance R_p [mV] and corrosion rate v_{corr} [$\mu\text{m}/\text{year}$] were determined [1]. The reference electrode ("*RE*") was a calomel electrode and the counterelectrode ("*CE*") was a 0.3 mm diameter platinum wire, which supplied electric current to the corrosion cell to induce voltage changes between the specimen and the calomel electrode [1]. The electrolyte was a pH 3.5 artificial mine water. Its chemical composition and method of preparation are described in [5]. The pH value was determined using a litmus paper. The conditions of potentiodynamic corrosion testing are summarized in **Table 5**.

Table 5 Potentiodynamic corrosion test - measurement conditions

Potentiodynamic corrosion test conditions	Quantitative values
Time for stabilization of free corrosion potential t_R	30 min
Corrosion potential measurement range (E Range)	-2; 2 V
Ewe working electrode potential recording vs. time (de/dt)	0.166 mV.s-1
Linear polarisation within the range (ΔE)	± 0.025 V
Specimen area (S)	177 mm ² ; 28 mm ²
Density of Copper	8.96 g.cm ³
Equivalent weight of Inconel 625	32 g.eq-1

As the composite copper-basalt laser overlays were considerably heterogeneous in terms of both chemical composition and structure, two types of corrosion cells were used for measuring their corrosion resistance. The first corrosion cell (designated below as C1) with an area of 177 mm² was supplied by the manufacturer of the potentiostat. The other corrosion cell (identified as C2) with an area of 28 mm² was specially designed for testing corrosion resistance of laser overlays, and 3D-printed in Felix 3.0 machine. The motivation for making the second cell for corrosion testing much smaller was to capture the heterogeneity of the composite laser overlays and measure and demonstrate it using the impedance method. Prior to corrosion resistance measurement, the laser overlays were ground in a magnetic grinding machine to their final thickness.

SAMPLE A was not included in the measurement because its overlay had shown poor adhesion to the base material. Potentiodynamic corrosion testing involved three measurements on each corrosion cells C1, C2 on

laser clad SAMPLES B, C. One measurement on a copper sheet of 99.98 % purity was used as the reference standard for comparing the measured and calculated corrosion rates. The corrosion rates obtained were converted to corrosion rates over a 100,000-year period (as stipulated by the SÚJB), assuming linear loss of laser clad and copper sheet with time. Data from the potentiodynamic corrosion test are summarized in **Table 6**.

Table 6 Potentiodynamic corrosion test; measured and calculated steady-state corrosion potential, polarisation resistance and corrosion rate

Designation of sample	Corrosion cell	Number of measurements	Corrosion potential E _{corr} [mV vs RE]	Polarisation resistance R _p [Ω]	Polarisation resistance.S [Ω.cm ²]	Corrosion rate [μm/year]	Corrosion rate over 100 000 years [mm]
Cu sheet	C1	1	-175	6,334	11,211	0.023	2
SAMPLE B	C1	1	-352	82,499	146,023	0.284	28.4
	C1	2	-402	79,541	140,788	0.332	33.2
	C1	3	-505	76,917	136,143	0.442	44.2
	C2	1	-288	223,337	63,204	0.743	74.3
	C2	2	-505	5,070,000	1,434,810	0.041	4.1
	C2	3	-484	104,34	29,529	1.899	189.9
SAMPLE C	C1	1	-491	9,270,000	16,407,900	0.003	0.3
	C1	2	-535	8,120,000	14,372,400	0.003	0.3
	C1	3	-510	9,870,000	17,469,900	0.003	0.3
	C2	1	-512	9,042	2,559	14.741	1,474.1
	C2	2	-517	12,412	3,513	13.37	1,333.7
	C2	3	-324	26,479	7,494	7.45	794.5

The last column in **Table 6** contains converted corrosion rate measurements for a copper sheet and SAMPLES B and C. The corrosion loss in a copper sheet submerged in an electrolyte of artificial mine water was found to be 2 mm/100,000 years.

In SAMPLE B, the corrosion loss of the laser overlay was 4.1-189.9 mm/100,000 years, depending on the type of the corrosion cell used. In SAMPLE C, the corrosion loss of the laser overlay measured in C1 cell was 0.3 mm/100,000 let. However, SAMPLE C exhibited completely different levels of corrosion loss of its laser overlay when tested using corrosion cell C2 and the potentiodynamic method. The discrepancy between the corrosion losses in laser overlays in SAMPLE B and SAMPLE C suggests that they are very heterogeneous in terms of local chemistry and structure. The considerable discrepancies between the corrosion rate values are an indication of cracks in the laser overlays. In the potentiodynamic corrosion test, these cracks are manifested by an extreme local rise in the corrosion rate.

5. CONCLUSION

This paper deals with an assessment of the corrosion resistance of laser-deposited composite copper-basalt overlays. The substrate was C45 steel of 20 mm thickness. In this experimental programme, three laser-deposited composite overlays were prepared. Each of them had a different basalt content in copper-based Metco 55 laser cladding powder. The overlay which consisted of 5 wt. % basalt and 95 wt. % copper was disqualified from the experiments owing to poor adhesion of the overlay to the base material. The corrosion rates in SAMPLE B (10 wt. % basalt and 90 wt. % Cu) and SAMPLE C (15 wt. % basalt and 85 wt. % Cu) were

determined by the potentiodynamic corrosion test. The electrolyte was an artificially-prepared mine water. Corrosion resistance was measured in two corrosion cells of different types. The C2 type was specially designed and 3D-printed for corrosion resistance testing of laser overlays. The lowest corrosion loss was found in SAMPLE C: 0.3 mm/100,000 years. Although the measured and converted corrosion losses for SAMPLE C and for the environment were extremely low, metallographic examination identified local cracks in the laser-deposited composite overlays. The application potential of laser-deposited composite copper-basalt overlays is now difficult to determine with certainty because research into preparation of laser overlays is still under way.

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