Laser-Melting Treatment of Thick Chromium Electrodeposits on Brass Substrate

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The effects of high-power laser treatment on thickly chromium-coated brass were studied. Microstructure observations, energy dispersive spectrometry (EDS), X-ray diffraction (XRD) analysis and microhardness measurements were carried out. During laser-melting treatment, part of the electrodeposited chromium always evaporated, so that the laser beam incised grooves on the metallic surface, under which two distinct zones were obtained—the laser melted zone (LMZ) and the heat affected zone (HAZ). The upper area of the LMZ consisted mainly of chromium and displayed about the same microhardness as the laser-softened electrodeposited chromium, while in the lower one CuZn, $CuZn_5$, Al_8Cr_5 phases and unalloyed chromium were identified. This area showed the highest microhardness-shout 1.5 times that of the substrate. The HAZ displayed the same composition and microhardness as the substrate.

Molybdenum-coated brass and hot wrought brass are widely used in the manufacture of certain parts of the automobile gear-box because of their good thermal and mechanical behavior. The basic idea of this study was to investigate the possible replacement of molybdenum with electrolytically deposited chromium as a more economical solution.

Thick chromium coatings display satisfactory mechanical properties, but poor adhesion to the brass substrate. Laser-melting treatment was employed in order to improve adhesion and possibly the mechanical properties. Earlier studies of this subject are limited to thin (up to 17 pm) chromium coatings on copper, subjected to laser-melting treatment by means of continuous or pulsed laser radiation. They resulted in surface alloys containing 10 to 40 percent chromium and displaying microhardness values between 100 and 160 HV_{100g}, twice that of copper. In the laser-melted zone, chromium was in the form of precipitates found inside the grains as well as at their boundaries.[1-3]

In the present work, chromium was deposited electrolytically on a rotating brass cathode from a chromic acid/sulfate bath. The deposit thickness was chosen to be 100 µm, as a simulation of molybdenum-coated brass, and 200 µm in order to probe the option of thicker coatings used in porous chromium coatings (ASM 2407C and MIL-C-20218).

The laser-melting process consisted of a single laser pass or partially overlapping passes. Microhardness measurements and microstructure studies were carried out before and after the laser-melting process, employing optical and electronic microscopy, X-ray diffraction analysis and energy dispersive spectrometry.

Experimental Procedure

Materials

A Cu-Zn alloy commercially denoted as brass 356 was employed. This is a special brass used for the manufacture of certain gear-box parts. Its chemical composition is given in Table 1. The specimens were disks (diameter 25 mm, height 3 mm) and the microhardness values given by the manufacturer ranged from 140 to 170 HB because this special brass displays a multiphase microstructure.

Electroplating Process

Chromium electrodeposition was preceded by the following cleaning treatment: The specimens were immersed in a 20-percent w/v H_2SO_4 solution for five min and then rinsed with acetone. After cleaning, they were immediately immersed in a bath containing 250 g/L CrO_3 and 2.5 g/L SO_4^{2-}. Each specimen was attached to the cathode and rotated at 1200 rpm.

The exposed area of the specimen to be electroplated was a disk with a diameter of 20 mm. Pure lead was used as the anode. The bath was operated at 30 ‘C and the current density was 18 A/dm^2. Details of the electrolysis set-up were reported earlier.[4]

The electrolysis duration was calculated according to Faraday’s law: 4 hr and 8 hr for deposits of 100 and 200 µm thickness, respectively. Current efficiency was determined as 30 percent. Both temperature and current density values were chosen so that the deposits were dull gray in order to absorb the maximum possible amount of the laser beam power.[5]

Laser-Melting Process

The laser-treatment was carried out using a continuous CO, laser beam (wavelength: 10.6 pm, maximum output: 3.2 kW and annular beam energy distribution in TEM_{01} mode). A special optical set-up was invented to protect the 250-mm focal length lens.[6]

Table 1
Chemical Composition of Alloy Used

	Cu	Al	Mn	Ni	Si	Cr	Zn
Min	57.5	1.5	2.0	<0.05	0.6	0.0	bal.
Max.	59.0	2.0	3.0	0.05	0.9		etc.

Table 2
Optimum Values of Laser Parameters

	Chromium deposit thickness	
	100 µm	200 µm
Laser beam power (P)	2500 W	2800 W
Defocused distance (d_{def})	40 mm	20 mm
Speed (v)	1.2 (m/min)	1.8 (m/min)

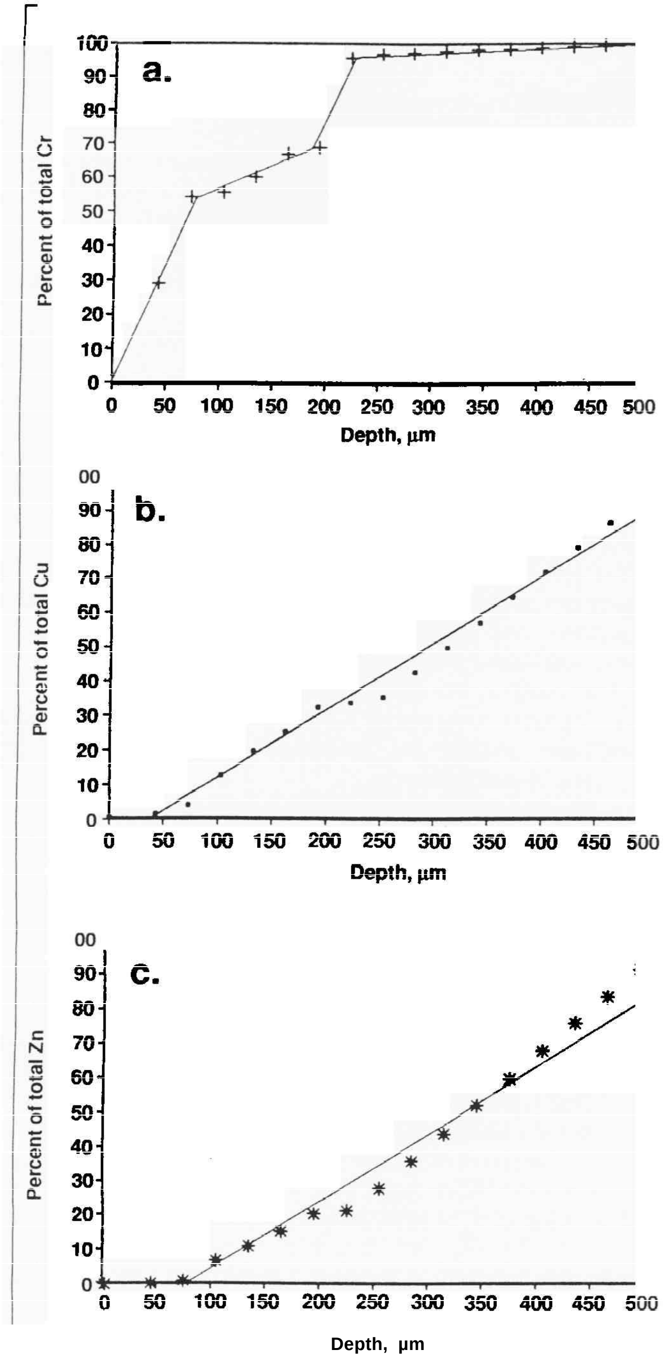

Fig. 4-Distribution of the total amount of (a) chromium, [b) copper, and(c) zinc, vs. depth, as determined by EDS.

Two distinct circular zones can be observed **in** all cases (Fig. 1, a and b): The upper one, close to the groove, is the laser melted zone (LMZ). It shows a rather uniform thickness of about 180 µm (for a chromium layer of 100 µm, Fig. 1 a) or about **240 µm (for** 200-µm chromium thickness, Fig. 1 b). It consists of a fine-grained cellular microstructure resulting from rapid solidification and containing unalloyed chromium grains of various sizes, in a random distribution (Fig. 3). This unalloyed chromium originated from parts of the electrodeposited chromium which cracked, were cut off and immersed in the molten substrate where they were encased without completely dissolving during the rapid solidification.

The zone below the LMZ is the heat affected zone (HAZ). Its thickness is about 220 µm (for chromium deposit thickness of 100 µm, Fig. 1a) or about 340 µm (for 200-µm chromium thickness, Fig. 1 b). It consists of grains of the same size as those of the brass substrate.

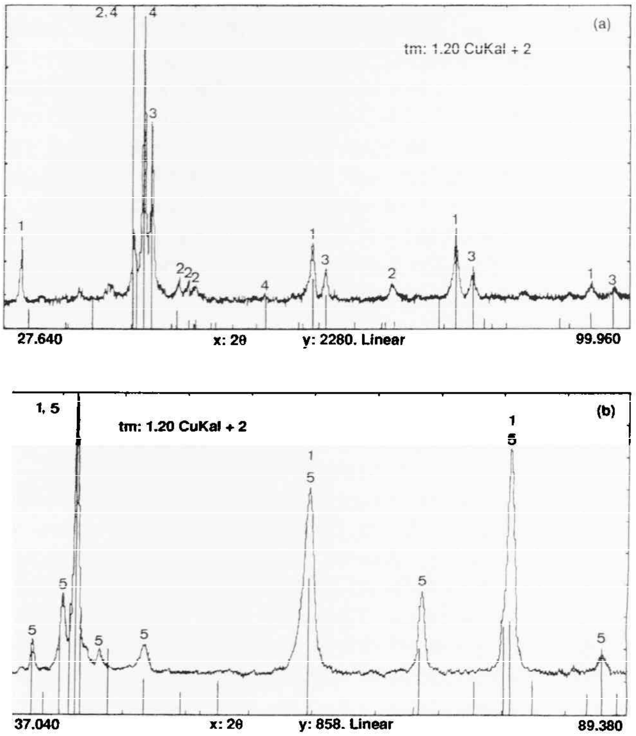

Fig. 5—XRD patterns and detected phases; (a) LMZ: β'-CuZn (1); Al_8Cr_5 (2); Cr (3); $CuZn_5$ (4); (b) HAZ: β'-CuZn (1); metastable β_1-CuZn (5).

Microstructure Characterization

EDS was employed to determine the distribution of chromium, copper and zinc. The measurements were made every 30 pm, for a total depth of 600 pm, beginning from the bottom of the groove. Figures 4 a, b and c show the total amount of the identified metal, up to the depth of each measurement expressed as a percentage of the total amount of this metal contained to a depth of 600 µm for a chromium deposit of 200 pm. For example, if the total chromium contained in 600 µm under the bottom of the groove is 100 mg, then the chromium contained in the first 60 µm is 55 mg (Fig. 4a). This determination is derived from the laser melting of a 200-µm chromium layer with a beam power of 2800 kW (Table 2).

Consequently, in the first 60 µm, 55 percent of the total amount of chromium is distributed (Fig. 4a), while copper and zinc are found in negligible percentages of their entire amounts (Figs. 4b and c). Almost the whole amount of chromium is distributed in the first 240 µm (Fig. 4a), while the distribution of copper and zinc is rather uniform after approximately the first 60 µm (Figs. 4b and c).

This indicates that there are two areas in the observed LMZ. The first (0 to 60 µm), consisting mainly of chromium, is attributed to the very low solubility of copper and zinc in chromium as indicated by Cr-Zn and Cr-Cu phase diagrams. The second area of the LMZ (60 to 240 µm) consists mainly of Cu-Zn phases and unalloyed chromium.

A negligible percentage of chromium is distributed in the remaining 360 µm (240 to 600 µm) which correspond roughly to the HAZ. The distribution of copper and zinc continues to be uniform in this zone. These results are in accordance with the very low volubility of chromium in copper and zinc.

XRD analysis performed in the LMZ (Fig. 1) resulted in detection of the phases β'-CuZn, CuZn$_5$, Al$_8$Cr$_5$ and unalloyed Cr (Fig. 5a). The LMZ was removed by polishing and XRD analysis was performed on the new surface which corresponds to the HAZ. Finally, XRD analysis was also performed on the unaffected substrate. Both β' brass and metastable β_1 brass were identified as the main phases of the HAZ (Fig. 5b), while the main phases of the substrate were β'-CuZn and (Cu, Zn), which indicates that the (Cu, Zn) phase was transformed to the metastable β_1-CuZn during the laser heating.

Microhardness Measurements

Figure 6 shows microhardness measurements taken every 40 µm on the specimen shown in Fig. 2, along a line parallel to the initial surface of the chromium deposit at a depth of 100 µm. The thickness of the deposit was 200 µm. The starting point of the measurements was the center of the laser beam trace.

The laser-heated chromium coating shows a decisively lower hardness (200 to 500 HV$_{30g}$) than that of the initial unaffected electrodeposited coating (1020 HV$_{30g}$). The higher the temperature induced by the laser beam, the lower the microhardness value. This may be a result of release of hydrogen that was inserted into the chromium crystal lattice during electrodeposition, inducing strains and therefore high microhardness values.

Figure 7 shows microhardness measurements as a function of depth, starting from the bottom of the groove incised by the laser beam, to a depth of 800 µm.

Two main sets of values are observed here. The first one, corresponding to the LMZ, has a mean value of 320 HV$_{30g}$, except for the first 60 µm that show a mean value of 270 HV$_{30g}$ (about the same as that of the heat-affected electrodeposited chromium, Fig. 6) and it corresponds to the surface layer of the LMZ, which consists of almost pure chromium (Fig. **4a).** The main part of the LMZ shows a greater amplitude of fluctuation, as well as the highest mean value of microhardness. This is attributed to its microstructural heterogeneity as identified by XRD (Fig. 5a). The second set of microhardness values, corresponding to the HAZ and the substrate, has a mean value of 230 HV$_{30g}$, which is identical to the value found for the unaffected brass substrate. The HAZ area (1) neighboring the LMZ is characterized by a constant microhardness value, which indicates homogenization of the area as a result of alloy component interdiffusion, apparent at the grain boundaries (Fig. 3). Similar results were obtained with macro and micro-scale observations, EDS, XRD analysis and microhardness measurements, for 100-µm chromium coatings.

Findings

1. After laser-melting treatment of a chromium-coated brass, either through a single pass or partially overlapping passes, part of the chromium deposit evaporated, while the beam incised a groove on the metallic surface.

2. Optimum values of the laser parameters to achieve melting of the chromium coating are:

For 100 µ m thickness, P =2500 W, d$_{def}$= 40 mm and **v = 1.2** m/min

For 200 µm thickness, P = 2800 W, d$_{def}$= 20 mm and **v = 1.8** m/min

3. Less intensive energy radiation did not incise grooves on the metallic surface, but it was also not able to melt the electrodeposited chromium. In this case, the chromium softened and sank into the molten substrate.

4. No replacement of molybdenum by electrolytically deposited chromium could be suggested because of the failure to obtain a surface zone, almost flat, having geometrical homogeneity, under the laser conditions used.

5. After melting, two distinct zones were observed:

   a. The laser-melted zone (LMZ), having a thickness of about 180 µm and 240 pm, for 100 µm and 200 µm chromium layers, respectively.

   b. The heat-affected zone (HAZ), having a thickness of about 220 µm and 340 µm, for 100 µm and 200 µm chromium layers, respectively.

6. EDS and XRD analysis were performed on the LMZ and HAZ, derived from the melting of a 200-µm chromium coating. They showed that the LMZ consists of two areas:

   a. Upper, being close to the bottom of the groove (0 to 60 µm), and consisting mainly of chromium.

   b. Lower, (60 to 240 µm) consisting of the phases β'-CuZn, CuZn$_5$, Al$_8$Cr$_5$, and unalloyed chromium. In the HAZ, mostly β'-CuZn and β_1-CuZn were identified; the main phases of the substrate were β'-CuZn and (Cu,Zn).

7. Microhardness measurements confirm the existence of two areas in the LMZ and indicate two areas in the HAZ. The first area of the LMZ (0 to 60 µm) shows a microhardness mean value of 270 HV$_{30g}$, which is very close to that of the laser-softened chromium. The second area of the LMZ shows the

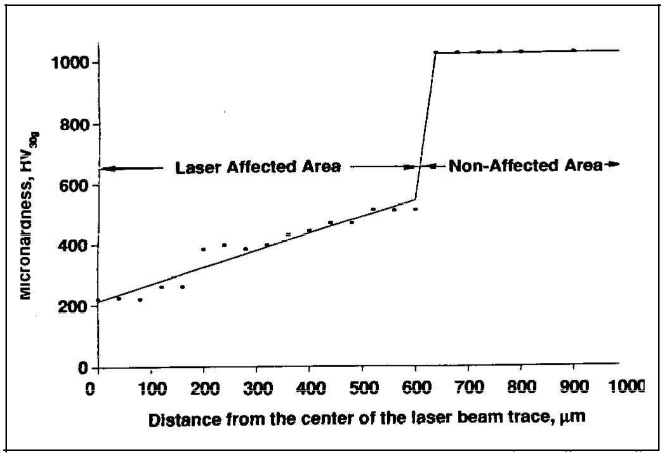

Fig. 6-Microhardness measurements of *specimen of Fig. 2 along a line parallel* **to the** *initial surface of the chromium deposit at a depth of 100µm. Measurement starting point: Center of laser beam trace.*

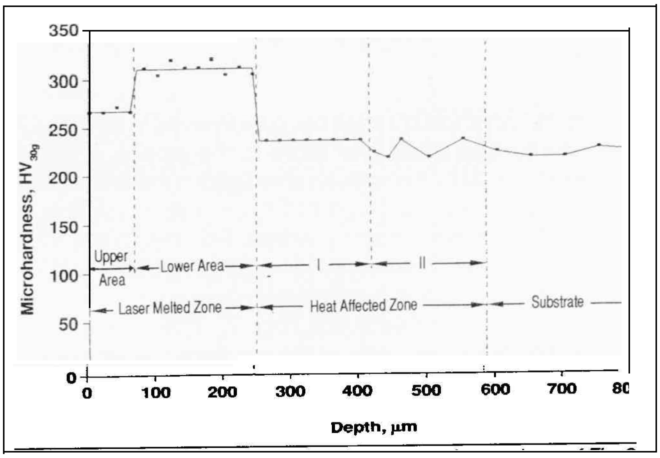

Fig. 7-Microhardness measurements vs. depth for the specimen of Fig. 3.

highest microhardness mean value of 320 HV_{30g}, about 1.5 times that of the substrate.

The HAZ showed a microhardness mean value of 230 HV_{30g}, identical to that of the substrate. The first area of the HAZ showed a constant microhardness value, indicating homogenization of this area as a result of alloy component interdiffusion, which can also be observed in the micrographs.

The laser-softened chromium coating displayed distinctly lower microhardness values (200 to 500 HV_{30g}) than the unaffected electrodeposited chromium (1020 HV_{30g}).

8. Similar results were obtained with macro and micro-scale observations, EDS, XRD analysis and microhardness measurements, for 100-µm chromium coatings.

References

1. S. Magnanelli et al., *Proc. XXII Int'l Metallurgy Congress: Innovation for Quality,* Bologna, Italy, 393(1988).
2. N. Ammannati et al., *Proc. Cu* **'86,** *Copper Tomorrow.* Technology-Products- Research, Barga, Italy, (1986), *Proc. Europa Mets//i-LM/,* **214 (1 989).**
3. **L.M.** Galantucci et al., *High Power Lasers,* Pergamon Press, Oxford, U. K., 1989; p. 57.
4. Th. Skoulikidis, S. Polymenis and A. Kostoudi, *Mol. Cryst. and Liq. Cryst.,* **158 B, 197 (1988).**
5. **F.A.** Lowenheim (cd.), *Modern Electroplating,* 3rd cd., John Wiley and Sons Inc., New York, NY, 1974; **p. 96.**
6. **R. Marini, D. Pantelis, C. Prioul and L. Ledoux,** *Material et Techniques, 9-10,* **27(1 990).**
7. **L.J. Durney (ed.),** *Electroplating Engineering Handbook,* 4th cd., Van Nostrand Reinhold Co., Inc., New York, NY, 1984; p. 242.
8. A. Houndri, S. Polymenis, Y. Chryssoulakis and D. Pantelis, *Metallurgical Transactions, 23 A, 1801* **(1992).**


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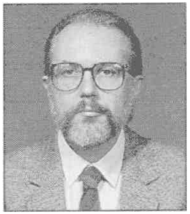

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