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Cold Spray Deposition of SS316L Powders on Al5052 Substrates and Their Potential Using for Biomedical Applications

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Abstract**—**The corrosion behaviour of 316L stainless steel coatings obtained by cold spray method was investigated in this study. 316L powders were deposited onto Al5052 aluminum substrates. The coatings were produced using nitrogen (N_2) process gas. In order to further improve the corrosion and mechanical properties of the coatings, heat treatment was applied at 250 and 750 °C. The corrosion performances of the coatings were compared using the potentiodynamic scanning (PDS) technique under *in-vitro* conditions (in Ringer's solution at 37 °C). In addition, the hardness and porosity tests were carried out on the coatings. Microstructural characterization of the coatings was carried out by using scanning electron microscopy attached with energy dispersive spectrometer (SEM-EDS) and X-ray diffraction (XRD) technique. It was found that clean surfaces and a good adhesion were achieved for particle/substrate bonding. The heat treatment process provided both elimination of the anisotropy in the coating and resulting in healing-up of the incomplete interfaces between the deposited particles. It was found that the corrosion potential of the annealed coatings at 750 °C was higher than that of commercially 316 L stainless steel. Moreover, the microstructural investigations after the corrosion tests revealed that corrosion preferentially starts at inter-splat boundaries.

Keywords**—**316L, biomaterials, cold spray, heat treatment.

I. INTRODUCTION

INCREASING human population leads to an increase in the number of medical devices addressed to bone related injuries [1]. Metallic materials are widely used in medical applications as implants on the purpose of restoring joints of body parts or with the intent of replacing organs functioning at acceptable levels. Recently, stainless steels (SS), cobalt-chromium alloys (Co-Cr), titanium (Ti) and their alloys are the most widely used metallic materials those aiming to extend service life of the biodevices in the human body [2], [3]. It has been well known that stainless steel is biocompatible with human hard tissues. Unfortunately, the mechanical properties of the implants are fairly high and this structural behaviour can make some limitations on their direct utilization as implant in load bearing applications. Aluminum is an extremely light material having low density, high specific strength, high stiffness, good castability and machinability, and high damping capacity [4]. In addition, it has a good corrosion resistance as a result of the formation of an inert oxide layer on its surface. However, direct usage of Al_2O_3 is not possible due to its brittle characteristics when used as an implant material. Thus, aluminum needs a specific surface modification in order to minimize the adverse effects to body electrolyte.

It is well known that the metallic biomaterials are physiologically inert and have a high corrosion resistance due to the formation of a passive film on the surface. However, the human body is an aggressive environment for the implanted metals and alloys. Thus, corrosion is one of the major problems that affect the biocompatibility of medical devices due to biodegradability of the metallic materials [3]. The deposition of stainless steel powder by means of cold spray process on Al alloys has a great potential for applications such as biomedical, high temperature oxidation and corrosion protection. For example, the coating cold sprayed with mixing SS and Co powders shows lower corrosion rate than bulk SS material, which was considered for new stent material [5]–[7]. It was shown that a significant reduction in porosity (less than 1%) can be achieved by applying a post treatment of the cold gas sprayed stainless steel coating [8]. On the other hand, it was shown that the post heat treatment of the cold 316L sprayed layers did not enhance the fatigue life of the component even with the presence of residual compressive stresses introduced during the cold spray process [5].

Reference [9] demonstrated that the cold sprayed 316L coatings with better inter-particle bonding and less porosity are prone to be less exposed to pitting attack in Cl^- containing solutions. However, [10] showed that the cold sprayed SS 316L coating exhibits a corrosion rate 20 times lower than that of mild steel substrate but 20–40 times higher than that of bulk SS 316L in 1 N HNO_3 solutions. In this study, the effect of the annealing treatment on the *in-vitro* corrosion response of the coatings in the Ringer's solutions were investigated in order to demonstrate a possible alternative usage of 316L cold spray coatings on Al5052 alloys.

II. EXPERIMENTAL PROCEDURE

Stainless steel coatings were deposited using the cold gas spray processing. Commercially available SS 316L stainless steel powder (Praxair, USA or Fujumi Inc., Aichi, Japan) was used as the feedstock (Fig. 1). The particle size range was 5 to 25 μm. Coatings were then deposited at the optimum conditions, i.e. a stagnation temperature of 800 °C and stagnation pressure of 4 MPa. In order to study the effect of

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annealing on the microstructure and investigate the corrosion behaviour of the coatings, the coating layers were annealed at 250 and 750 °C. The hardness of the annealed specimens was measured with micro Vickers hardness (HV) at a load of 100 gf for a dwell time of 15 s.

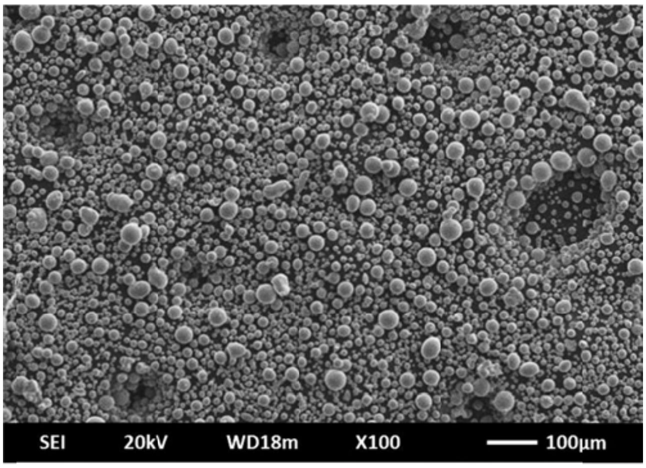

Fig. 1 Powder morphology of 316L SS before coating

Electrochemical investigations on the coatings were investigated by PDS technique under *in-vitro* conditions. *In-vitro* corrosion studies of the coatings were carried out in Ringer's solution and its constituents are given in Table I. Ag/AgCl and Platinum (Pt) wire electrodes were used as reference and auxiliary electrode, respectively. The obtained data were analyzed using the Gamry Echem Analyst software. The surface morphology of the coatings was carried out by using a scanning electron microscope (SEM, Jeol JSM–6335F) attached electron dispersive spectroscope (EDS). Also, the phase identification of the coatings was performed through using an X-ray diffraction (XRD, Oxford INCA).

TABLE I
COMPOSITION OF RINGER'S SOLUTION

Substance	NaCl	KCl	$CaCl_2$	pH
Composition ($g·L^{-1}$)	8.69	0.30	0.48	6.32

III. RESULTS AND DISCUSSION

Fig. 2 shows the cross-section of SEM image of the cold sprayed 316L SS coating on Al alloy substrate. The coating thickness of the samples was measured as ~900µm. The presence of some inter-splat voids and also the highly bonded inter-splat boundaries were evident in the coating. Fig. 3 shows XRD spectra of cold sprayed and annealed 316L powders. It can be seen that only the austenite (γ) and Al (α) phases were detected on the coatings and in the substrates, respectively. This shows that the annealing is applied in a such way that there is no indication of the no formation of oxidation and new possible phases. In addition, it is observed that peak intensities of the coatings increase with increasing annealed temperatures at 250 and 750 °C. Similar results were observed by [8] on 316L mixed with Co-Cr alloy powders.

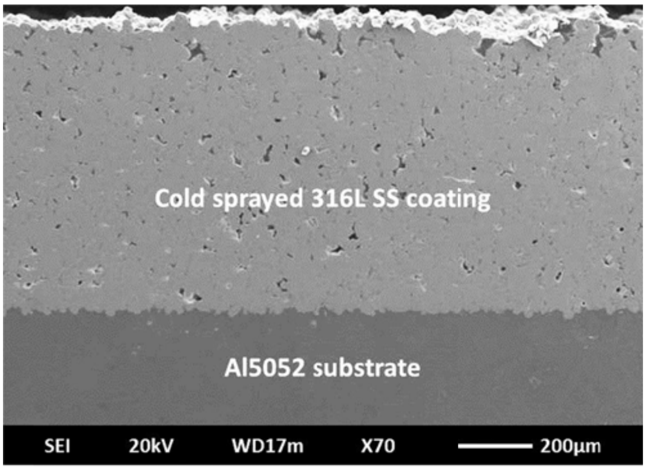

Fig. 2 Cross section SEM image of the cold sprayed 316L SS coating on Al alloy substrate

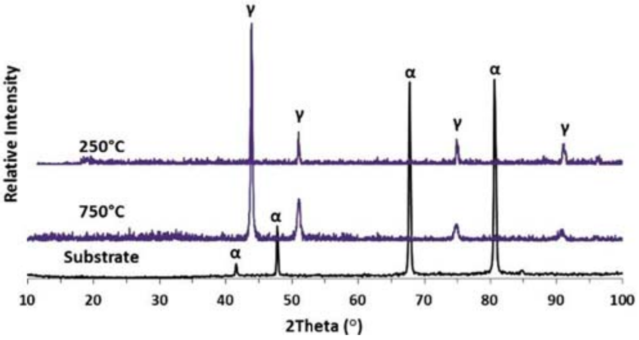

Fig. 3 XRD patterns of the annealed coatings and substrate

Fig. 4 shows the potentiodynamic polarization scanning (PDS) curves of the annealed coatings in the Ringer's solution and some important corrosion parameters obtained from the curves are collected in Table II. According to Fig. 4 and Table II, the E_{corr} values of the coatings decrease negatively with increasing annealing temperatures.

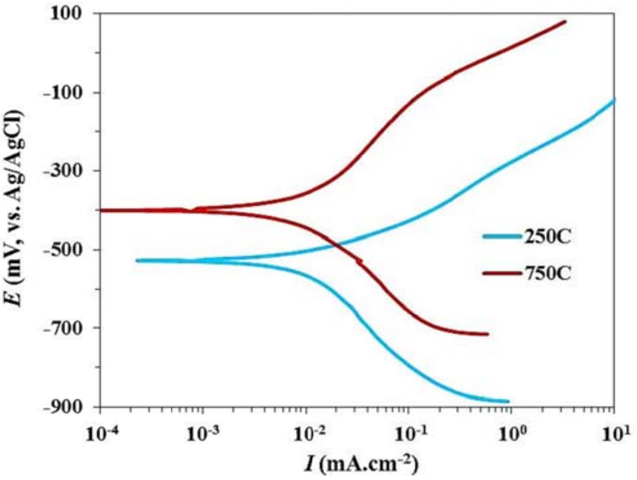

Fig. 4 PDS curves of the annealed coatings in the Ringer's solution

TABLE II
HARDNESS, POROSITY VALUES AND CORROSION PARAMETERS OF THE COATINGS

Annealing Temp (°C)	E_{ocp} (mV)	E_{corr} (mV)	I_{corr} ($\mu A\cdot cm^{-2}$)	Hardness ($HV_{0.1}$)	Porosity (%)
250	-485	-528	26.5	462	6.43
750	-316	-403	14.2	402	3.59

The annealed coating at 750 °C has higher E_{corr} and the lowest I_{corr} values in the physical simulated body fluid compared to the annealed coating at 250 °C. It can be said that thicker and nobler oxide film forms on the coating layer with increasing annealing temperature.

The E_{corr} and I_{corr} values of the commercially 316L were measured as -609 mV and 5.15 $\mu A\cdot cm^2$ in Ringer's solutions in [11]. In this study, the E_{corr} values of the annealed coatings are relatively nobler (> -600 mV) but the I_{corr} value of the annealed coating at 750 °C is higher (14.2 $\mu A\cdot cm^2$) (Table II) compared to the commercially 316L samples in [11].

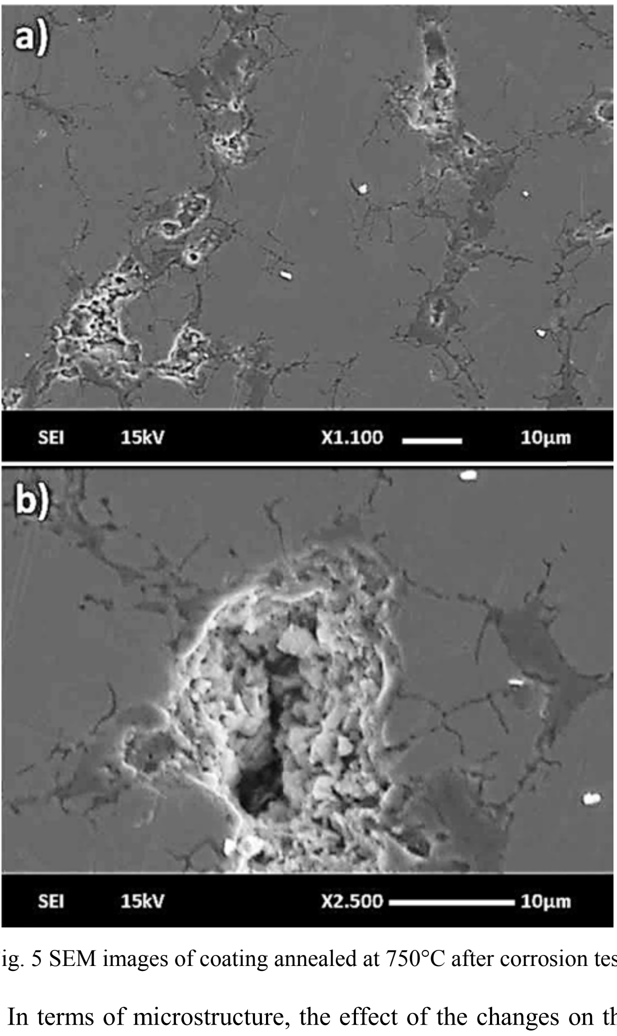

Fig. 5 SEM images of coating annealed at 750°C after corrosion test

In terms of microstructure, the effect of the changes on the corrosion behaviour is also important. Fig. 5 shows the corrosion propagation on the coating surfaces. According to the results, the corrosion is initiated in the inter-splat porosity of the coating (Fig. 5 (a)). It is shown that porosities act as preferential sites for nucleation of the corrosion. Then, the corrosion continues around the inter-splat boundaries (Fig. 5 (b)). In these regions, the electrolyte is stagnating which makes the oxygen transfer difficult. As a result of these mechanisms, inter-splat boundaries act as anode while the surroundings of the 316L powders act as cathode (1st stage). While increasing the potential, the porosities will be filled with corrosion products and passivate the upper surface by increasing the polarization (2nd stage, Fig. 6).

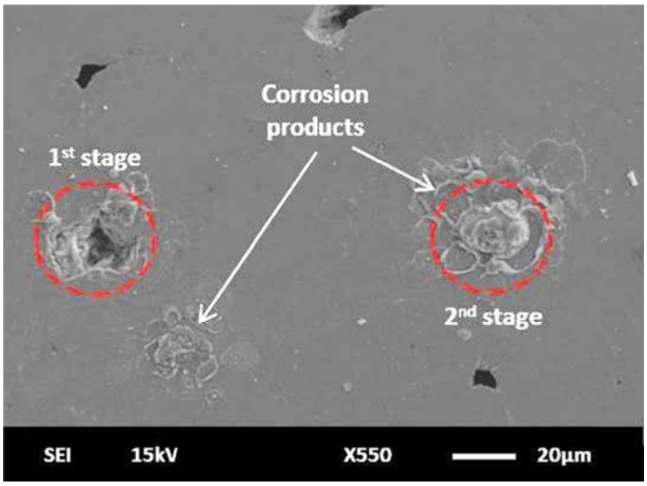

Fig. 6 Propagation stages of the corrosion in the coatings

The passivity of stainless steels is enhanced by modifying the chemical composition and morphology of the oxide layer which is generally rich in Cr_2O_3 [12]. In fact, the metal ion releasing from different grades of stainless steels depends on Cr content of the film which is responsible for passive film formation. Chromium and molybdenum in stainless steels are adjusted to improve corrosion resistance. Especially, in chloride containing solution, the corrosion resistance of stainless steels is improved by the presence of Cr and Mo in the steel. Mo inhibits the corrosion process by increasing the stability of passive film due to the formation of the protective molybdenum oxide film beneath the hydrated chromium-rich oxide film [13], [14]. Therefore, nickel causes a negative reaction when implanted into the body and may induce harmful effects due to release of nickel ions [12]–[15], which can be toxic to the human body. The X-ray mapping analysis of the corroded sample has verified the results (Fig. 7). The figure shows that Ni ions ejected from coating layer. However, the corrosion continues due to the absence of the sufficient oxygen under the effect of these corrosion products. Mixed surface oxide layer formed by surface compounds that involve different amount of oxygen, chloride, and hydroxide causes damage on this protective oxide film by forming local micro batteries having different electronic and ionic conductivities. With increasing potential, oxygen and Ringer solution leak more easily under this oxide film. Oxygen which leaks through the protective oxide film is locally accelerated to increase the volume of ferrous oxides, resulting with the surface oxide film cracking and increase in corrosion rate. According to these results, it can be said that the reason for nobler potential after the annealing process at 250°C is the inhibition of the formation of this sizeable irregular growing oxygen film on the coating. In other words, the formed heterogeneous oxide film and the protective film defects act as active sites for corrosion. This result is also supported with Fig. 8, which shows that the corrosion of the coatings is directly correlated to relative amounts of porosity. It is seen that the porosity and I_{corr} values of the coating substantially decrease with increasing annealing temperatures, so that the volume ratio of porosity becomes a decisive parameter that determines the cold sprayed surfaces against the corrosive attack under *in-vitro* conditions.

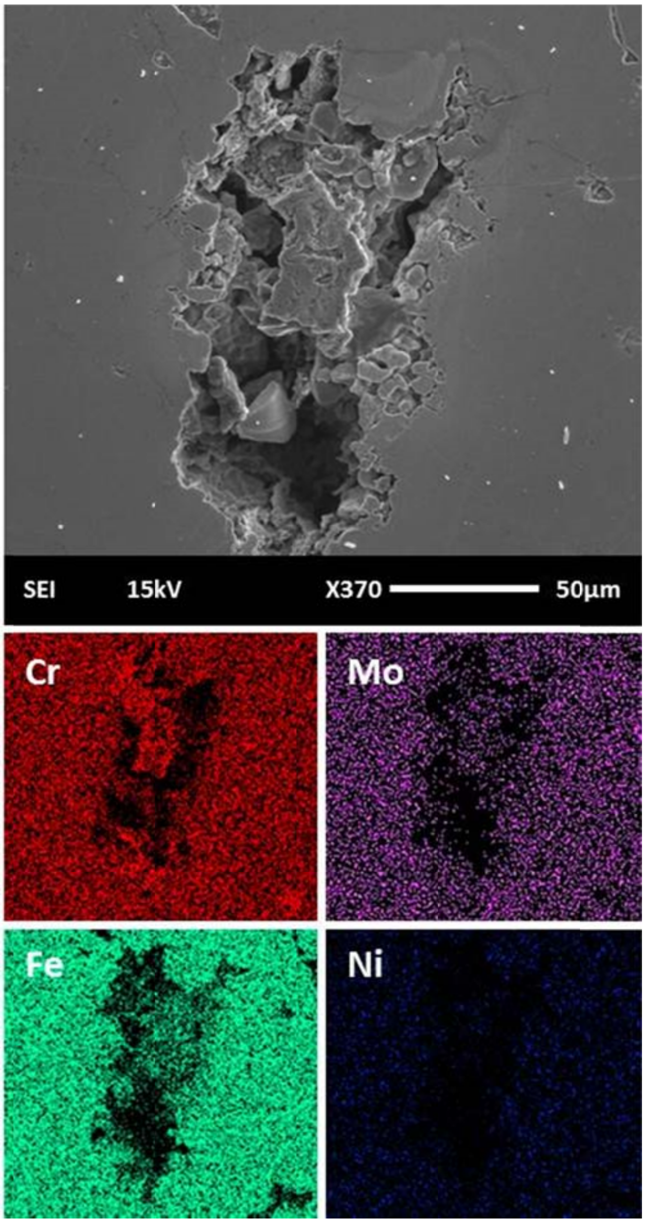

Fig. 7 SEM image and X-ray mapping results of formed pit on the coating after corrosion test

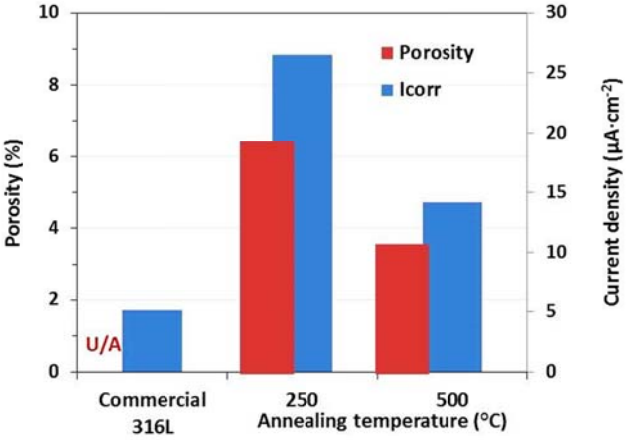

Fig. 8 I_{corr} and porosity values the coatings comparing with commercially produced 316L (the I_{corr} value get from Ref. [6] and its porosity value is unavailable)

IV. CONCLUSION

In this study, 316L powders have been successfully coated on the Al5051 alloys via cold spray deposition technique. The following conclusions can be drawn from the above study.

- The study showed that there is no diffusion to substrate (Al5052) during the cold spraying of the 316L SS powders.
- The E_{corr} values of the coatings decrease negatively with increasing annealing temperatures.
- The annealed coatings have higher E_{corr} values in the Ringer's solution compared to the commercially 316L samples.
- It can be concluded that a thicker and nobler oxide film forms on the coating layer with increasing annealing temperature.
- The microstructural observation showed that inter-splat porosities act as preferential sites for nucleation of the corrosion.

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