Hitachi and Tohoku University Developed additive manufacturing technology for high-entropy alloy with superior tensile strength and corrosion resistance using 3D printer for metals

Developed prototype of intricately shaped components providing 1.2-times-higher tensile strength and 1.7-times-higher pitting potential than conventionally possible

Tokyo, February 15, 2016 --- Hitachi, Ltd. (TSE: 6501) and Institute for Materials Research (IMR, Tohoku University) have developed an additive manufacturing technology for high-entropy alloy^{*1} (called HiPEACE^{*2})—with superior tensile strength and corrosion resistance— using a 3D printer for metals. This technology makes it possible to fabricate homogeneous components with intricate shapes but without compositional irregularities^{*3}. As shown in Figures 1 (B) to (C), compared to components made by conventional methods for manufacturing using a 3D printer for metals, these components provide 1.2-times-higher tensile strength (i.e., 1300 MPa^{*4}) and 1.7-times-higher pitting potential (an index of corrosion resistance; i.e., 0.85 V vs Ag/AgCl^{*5}). Applying the developed technology made it possible to successfully trial manufacture components with complicated shapes (see Figure 2). Utilizing this technology to fabricate components for facilities such as chemical plants (which require high strength and corrosion resistance) will contribute to enhancing lifetime and operation rate of such facilities.

Components of equipment used, for example, in chemical plants and for oil-well and gas-well drilling are subjected to an environment containing highly corrosive gases, so high strength and excellent corrosion resistance are prerequisites from the viewpoint of assuring safety. Targeting a high-entropy alloy (which is reported to possess high tensile strength and abrasion resistance as well as outstanding corrosion resistance under high-temperature-oxidation and alkaline environments), Hitachi and IMR have been developing manufacturing technology to create high-strength and high-corrosion-resistance components since 2014. A high-entropy alloy is composed of several different elements. Consequently, two challenges-namely, the likelihood of compositional irregularities occurring during casting^{*6} and the difficulty of processing due to high hardness—must be tackled. In the case of using a 3D printer for metals, intermetallic compounds^{*7} with a high degree of hardness are precipitated^{*8} in a net-like form during fabrication. As a result, tensile strength can be increased 1.4 times compared to that produced by using the conventional fabrication method (i.e.,

casting) [see Figures 1 (A) and (B)]. However, in consideration of practical applications, tensile strength and corrosion resistance must be improved even more.

Considering the circumstances described above, Hitachi and IMR have developed an additive manufacturing technology for a high-entropy alloy (called HiPEACE) with optimized local-melting and rapid-solidification processes (namely, two of the manufacturing processes using 3D printer for metals). The key features of the newly developed technology are as the following.

Additive manufacturing technology using a 3D printer for metals

Forming products by 3D printer involves repeated processing by which an electron beam is irradiated over an evenly spread metal powder (to a thickness of about 70 μ m) according to a design plan in order to form layers by selectively melting and solidifying certain areas. As for that processing, it is known that intermetallic compounds become finer and more uniformly dispersed as their solidification rate increases and that tensile strength and corrosion resistance are enhanced accordingly.

In consideration of the above-described knowledge, in addition to the electron beam energy and scanning rate^{*9} during irradiation time, a preheating process (by which a low-energy electron beam is irradiated onto the whole powder area before the HiPEACE powder is melted) was focused on. By keeping the preheating temperature of the powder to the minimum required and enlarging the difference between the preheating and melting temperature as much as possible, we can speed up the rate of solidification. As a result, an intermetallic compound (with high degree of hardness) uniformly dispersed (with spacing of several dozen nanometers) in a matrix phase^{*10} with high corrosion resistance was successfully formed [see Figure 1 (C)]. Accordingly, since it attained both 1.2-times-higher tensile strength and 1.7-times-higher pitting potential (an index of corrosion resistance) [see Figures 1(B) and (C)] as a structural material, the developed high-entropy alloy (HiPEACE) can be used to form intricately shaped and homogenous components without compositional irregularities. From now onwards, under the aim of commercial applications, HiPEACE will be further experimentally verified under actual-use environments.

The developed product was presented at TMS 2016 145th Annual Meeting & Exhibition of The Minerals, Metals & Materials Society from February 14 to 18, 2016 in Nashville, Tennessee, USA.



Figure 1: Comparison of features and metallographic structures of products fabricated by casting and 3D printer



Figure 2: Impeller with complicated shapes successfully formed by test molding

- *1 Defined as an alloy composed of more than five different elements at about equal addition fractions, a new alloy with great hidden potential.
- *2 <u>Hitachi Printable Extreme Alloy for Corrosive Environment: a high-entropy alloy developed by Hitachi.</u>
- *3 Elements of the alloy in question are unevenly distributed.
- *4 A unit of stress determined by dividing a force (N) applied to a tensile test piece by the cross-sectional area of the test piece (mm²); 1 N/mm² = 1 MPa.
- *5 Electrical potential when a corrosion current in a seawater environment (3.5 % NaCl) at 80°C reaches 0.1 mA/cm² (as a value measured in reference to a silver/ silver-chloride electrode).
- *6 A conventional technique for fabricating alloys as predetermined casting by pouring molten metal into molds.
- *7 Chemical compounds composed of more than two kinds of metals.
- *8 The formation of a solid substance separately from the solution it is dissolved in.
- *9 Rate at which the electron beam is being scanned.
- *10 A phase that forms a matrix, namely, the structural component that accounts for the bulk of an alloy.

About Hitachi, Ltd.

Hitachi, Ltd. (TSE: 6501), headquartered in Tokyo, Japan, delivers innovations that answer society's challenges with our talented team and proven experience in global markets. The company's consolidated revenues for fiscal 2014 (ended March 31, 2015) totaled 9,761 billion yen (\$81.3 billion). Hitachi is focusing more than ever on the Social Innovation Business, which includes power & infrastructure systems, information & telecommunication systems, construction machinery, high functional materials & components, automotive systems, healthcare and others. For more information on Hitachi, please visit the company's website at http://www.hitachi.com.

About Institute for Materials Research (IMR), Tohoku University

Institute for Materials Research (IMR) was the first to be established among the six research institutes of Tohoku University and marked 100th anniversary in 2016. Our institute's vital strengths include the merging of basic and applied sciences, and science with engineering. IMR has opened up new genres in terms of material science and engineering, developing high performance, high quality, and multifunctional materials. IMR serves "contribute to the well being of the human race and the development of civilization through the creation of new materials that are truly useful to society". Please access the website for more information about IMR: http://www.imr.tohoku.ac.jp/en/

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