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High performance zinc flake pigments for anti-corrosive coatings manufactured by HKP/powder metallurgy process

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***Abstract*— Metallic high performance zinc-flake pigments (ZFP) obtained by high kinetic processing (HKP) lead to a new generation of zinc-flake coatings in private sector as well as in industrial applications and provide a long-term corrosion resistance. Zoz ZN-CP301 anticorrosive paint establishes the cost-effective HKP-ZFP technology. Epoxy-resin based systems are proved and the development of water-based ZFP-systems shows great promises for coating systems without chemical H_2-gassing of zinc.**

Keywords – zinc flake coating; ductile metal flakes; Simoloyer®; high kinetic processing; high corrosion resistance

I. Introduction

Corrosion will stay one of the biggest global problems in the 21st century due to degradation of steel constructions, plants, rail tracks, tubes, vehicles and machines. As a given fact 5 tonnes of steel are destroyed by corrosion per second [1]. The German public railway is estimated to spend about 5.5 billion (10^9) € until 2016 as the calculated end of service life-time is reached for 70% of all steel and railway bridges [2]. 3.3 trillion (10^{12}) US$ was the annual cost of corrosion worldwide in 2011 which is over 4% of the world's GDP [3]. This cost includes maintenance, prevention, replacements of corroded parts and interruption of services due to maintenance. Hence, protection of steel from corrosion is an important economical and ecological issue. Typically, a protective effect is achieved by application of a coating as barrier layer to cut off the metal surface from the environment, or by a zinc layer as sacrificial anode. Both can be combined as corrosion protective coating with either zinc dust or zinc flakes as metallic pigments for the sacrificial anode effect. Zinc flakes perform better than zinc dust in this context, as they form a protective layer of only 8-12 µm with overlapping flakes [4]. This yields better protection with less amount of zinc, whilst all desired properties of the steel component are conserved, i.e. electrical conductivity, friction characteristics etc. Also, as in any zinc-based corrosion protective coating, there is no risk of hydrogen embrittlement of the steel matrix. This is in contrast galvanization techniques.

Despite its advantages, which can be seen from the fact that zinc flake coatings are widely used in the automotive sector, these products still face environmental and economic issues as the production process in drum mills requires large amounts of solvents and long milling times. It has been shown that these issues can be overcome when high kinetic processing (HKP) with Simoloyer® technology is used [5-6].

In this contribution it will be shown that dry manufacturing of zinc flakes by HKP with the Simoloyer® horizontal high energy rotary ball mill yields excellent zinc flake pigments, at superior economic and ecological effectiveness. The performance of an anti-corrosion lacquer using these pigments will be discussed.

II. High Kinetic Processing

The design of the Simoloyer® is based on a horizontally borne rotor, which allows a highly efficient and homogeneous energy transfer from the supplied power to the kinetic energy of the balls (grinding media), which are accelerated by the rotor. This yields collisions between the balls with relative velocities up to 14 m/s. In the high kinetic regime, these collisions transfer energy to the powder mainly as pressure, with only minor contributions of shear and friction. As a result, powder particles are deformed, broken, recombined by cold welding, and/or a combination of all [7-8]. Compared to vertical conventional attritors the horizontal design avoids dead zones of interaction between grinding media and powder. Furthermore, a well-defined atmosphere can be maintained throughout the milling process, i.e. inert gas atmosphere. This allows solvent-free production of ductile metal flakes with milling times up to 1000x faster than with conventional mills. As most of the collisional energy is converted into pressure and very little energy is lost to shear and friction, the overall amount of energy to be supplied to the grinding media is below conventional milling. This is both economically and ecologically highly effective and definitely competitive compared to drum mills.

The special design of the Simoloyer® allows full scalability from laboratory size (0.5 l) to full industrial scale (900 l) without changing the principle milling system [7-8]. A laboratory scale 2 l Simoloyer® is shown in Fig. 1.

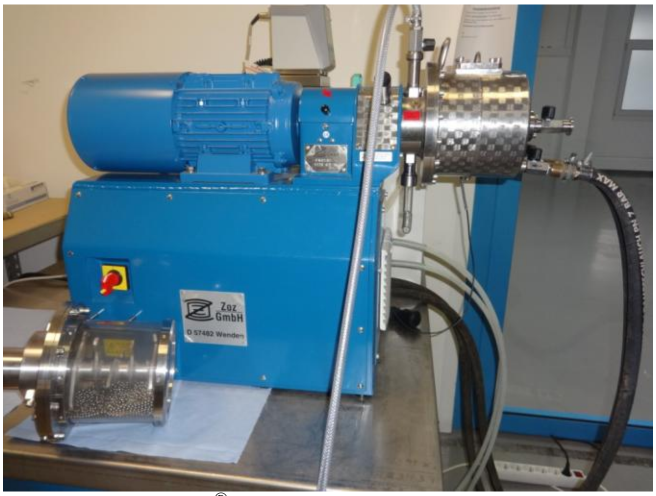

Fig. 1. Simoloyer® CM01-2lm high energy rotary ball mill and transparent grinding unit (front)

III. HKP-ZINC FLAKES AND LACQUER

Commercial zinc powder was milled under HKP conditions by Simoloyer®. This yielded HKP-zinc flakes (cf. Fig. 2). Different kinds of zinc powder raw materials with different d_{50} values were tested. Milling has reduced larger particle sizes and produced flakes of similar particle size, independent of the raw material (cf. Fig. 3).

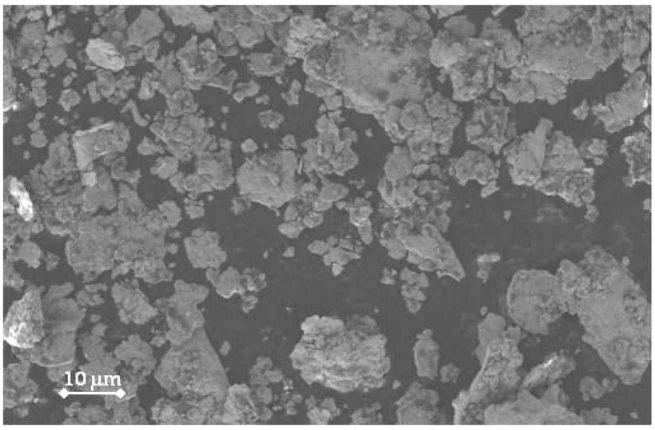

Fig. 2. Zinc Flakes by High Kinetic Processing

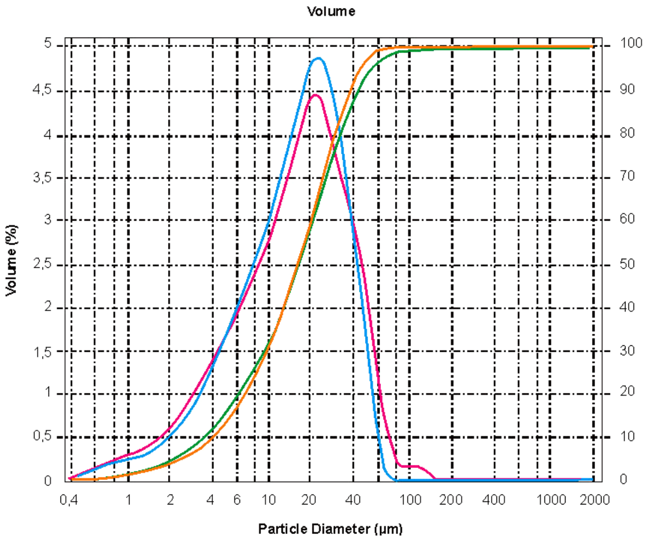

Fig. 3: particle size distribution of HKP-Zinc flakes

Stearic acid has been applied as grinding additive. It also stays on the flakes as a barrier layer to avoid direct contact with protons provided by water (Eq. 1), i.e. from humidity. This is important, as otherwise zinc would immediately react and form hydrogen (Eq. 2).

$$H_2O \quad \rightarrow \quad H^+ + OH^- \qquad (1)$$

$$Zn + 2\,H^+ \quad \rightarrow \quad Zn^{2+} + H_2\uparrow \qquad (2)$$

As these reactions are unwanted and reduce storage stability, a molecular agent is necessary to form a barrier layer on the flake surface. At the same time the barrier must not be too thick as otherwise zinc cannot work as sacrificial anode.

If a water-soluble lacquer is desired, different additives are necessary to induce the right setting behavior of the zinc flake pigments on the treated surface, which is solvent-dependent.

For this contribution an epoxy-resin based two component lacquer has been chosen. Upon curing the epoxy resin polymerizes and forms a matrix which fixes the pigments onto the surface. The lacquer is of dull gray color and sets well on a steel surface (cf. Fig. 4).

Fig. 4. Zoz zinc flake lacquer ZN-CP301

Corrosion protection of the lacquer, Zoz zinc flake lacquer ZN-CP301, has been tested with the salt spray test (cf. Fig. 5). It is obvious that ZN-CP301 performs better, especially on long timescales. Reasons for this behavior may be a more favorable particle size distribution, better coverage of the particles with barrier coating to prevent too high reactivity with aqueous media, and/or other influences of the milling process. This effect is even more dramatic if ZN-CP301 is compared to conventional zinc-rich coatings. This is not surprising, as already conventional zinc flake coatings outperform these.

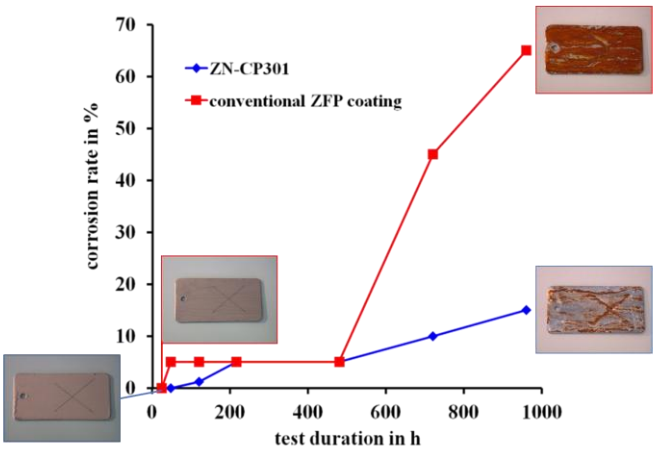

Fig. 5. Corrosion protection of ZN-CP301 and conventional zinc flake coating in salt spray test.

These results show clearly that HKP-zinc flakes are superior to conventional zinc flakes and by far superior compared to zinc-rich coatings. This superiority is not only in the application, where superb corrosion protection is achieved, but already in the production process. When using the Simoloyer® horizontal high energy ball mill also time and energy are saved and solvents are unnecessary at all in the milling process. Altogether, this yields a cost-effective and environmental-friendly product.

In principle, water-dispersible lacquers are also possible. Preliminary tests have been performed with HKP-zinc flakes covered by additives other than stearic acid. Here, the advantages of HKP are even more evident as the dry milling process already yields additive-covered zinc flakes. If these are brought into aqueous solution, they show less gassing (see Eq. 1 and 2) than conventional zinc flakes. Still, storage stability is low if the flakes are stored in aqueous solution. It is physically impossible to apply a sufficiently thick layer of additives to the flakes to withhold liquid water for a long period and maintain corrosion-protective activity at the same time. This is a problem all water-based zinc coatings face regardless of their formulation.

The solution to this problem is a two-component system, where the zinc flake pigments are stored separate from the aqueous acrylate dispersion. This allows much longer storage times unless the components are mixed. Drying is like in any water-based acrylate dispersion lacquer.

IV. Conclusion

Zinc flakes have been manufactured by HKP using the Simoloyer® horizontal high energy ball mill. The particle size distribution of these zinc flakes is the same regardless of the zinc powder raw material. A lacquer made with these zinc flakes as anti-corrosion pigments has been formulated and tested versus conventional zinc flake lacquers, where superior performance of HKP-zinc flakes has been proven. In addition, a route to water-dispersible HKP-zinc flake lacquers has been discussed.

The overall economic and environmental superiority of the HKP as provided by the Simoloyer® has been explained clearly. This results from dry milling, short milling times and energy-efficiency. As these effects are intrinsic properties of HKP, this method shows great potential for highly cost effective production of zinc flakes with almost no negative environmental impact.

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