

Fast Precipitation Pattern Formation in a Metallic Two-Component Dissolution–Reaction Process

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We here report the observation of precipitation patterns obtained when solid zirconium is allowed to react for few seconds with molten aluminum in the temperature range $720 < T < 850$ °C. The patterns are made by precipitates of the intermetallic compound Al_3Zr in the Al matrix. Generally, these precipitates show interconnected wavelike structures, but in a narrower temperature range ($780 < T < 820$ °C), part of these structures further organize into periodic bands. The pattern formation in the Al–Zr system is characterized by the strictly binary nature of the system, the short time scale for the pattern formation, and the presence, in the same sample, of different degrees of periodic organization.

Spatial pattern formation in macroscopic systems has been deeply investigated in connection with the development of theories on nonlinear instabilities, dissipative structures, and self-organization. So far, the main attention has been devoted mainly to occurrence of periodical patterns in fluidodynamics, homogeneous chemical reactions, and biological systems.¹ Relatively less attention has been given to the pattern formation in heterogeneous processes such as precipitation.^{2–19} Here we report the observation of precipitation patterns obtained when solid zirconium is allowed to react for few seconds with molten aluminum in the temperature range $720 < T < 850$ °C.

The observations have been conducted on quenched samples using the following procedure. The Al batch (~ 0.5 g of Al 99.9999% Strem) is placed in a graphite crucible ($\varnothing 5 \times 10^{-3}$ m, length 10^{-2} m) and enclosed in a vertical quartz tube under an inert gas flow (Ar 99.998% purified on a getter of Zr powder kept at 700 °C). A Zr wire (Aldrich 99+%; $\varnothing 10^{-3}$ m, length 2×10^{-2} m) or strip (Alfa 99.2+%; 1×10^{-3} m thick, 1×10^{-3} m wide, 2×10^{-2} m long) was thoroughly cleaned either mechanically and chemically (with a HNO_3 , HF, and H_2O 45:5:50 solution) in order to remove any surface oxide. The wire (or strip) was then connected to the lower part of a stainless steel bar. The bar was free to slide vertically through a flange placed on the top of the quartz tube. The bottom tip of the Zr wire was positioned a few millimeters above the Al batch. The entire apparatus was placed in a cylindrical furnace and maintained there to reach thermal equilibrium for at least 30 min. Then, the Zr wire was dipped into the melted Al by lowering the stainless steel bar. After a predefined reaction time (between 5 and 60 s), the entire assembly was removed from the furnace and quenched in water. Upon cooling, the Al ingot, incorporating the Zr wire, was removed from the graphite crucible, included in epoxy resin, and cut with a diamond saw perpendicular to the axis of the Zr wire. The exposed surface was prepared metallographically and observed with a scanning electron microscope using an electron backscattered detector.

The morphology of the observed reaction products depends considerably on the reaction temperature. When it is performed

at temperatures slightly above the melting point of Al, a typical morphology characterized by the presence of interconnected wavelike patterns made out of precipitates of Al_3Zr is observed. These precipitates are present in the region of the solidified Al matrix close to the Zr wire (Figure 1a). Their distribution, far from being completely random, shows a definite coherence length and resembles some analogous structures, sometimes referred as Turing instabilities, observed in the case of precipitation from homogeneous gels.^{6,12} When the reaction temperature is raised above a critical value (~ 780 °C), part of the precipitates start to show a more regular disposition, characterized by a sequence of concentric broken rings (Figure 1b,c), while the region closer to the Zr wire remains less regular. The rings disposition resembles closely the periodic precipitates already observed in gels^{17,18} when the concentration gradient of the reactants show a radial symmetry. When observed in a vertical section, these regular external rings show a massive sedimentation towards the bottom of the Al pool, while the less regular precipitates close to the Zr wire remain in suspension. The number of rings together with their spacing and regularity are well-reproducible in different experiments at the same temperature but are very sensitive to the reaction temperature. Upon increasing the temperatures, in fact, a larger number of more closely spaced rings are generally observed.

The rings do not show a clear time evolution at constant temperature, as their morphological appearance and their number are well-defined even in few seconds of reaction time and do not seem to change remarkably with longer interaction. On the contrary, the less regular internal region grows linearly with the reaction time, moving the region of the rings far from the Zr wire.

It must also be noted that the characteristics of the individual crystals present in the precipitates show marked differences in the various regions. The periodic rings are made out of relatively large cubic crystals (Figure 2), while the region closer to the Zr wire is characterized by extremely fine crystals, which cannot be resolved using the backscattered electron microscopy. In general the boundary between these two regions is very sharp.

When the temperature is raised above a second critical value

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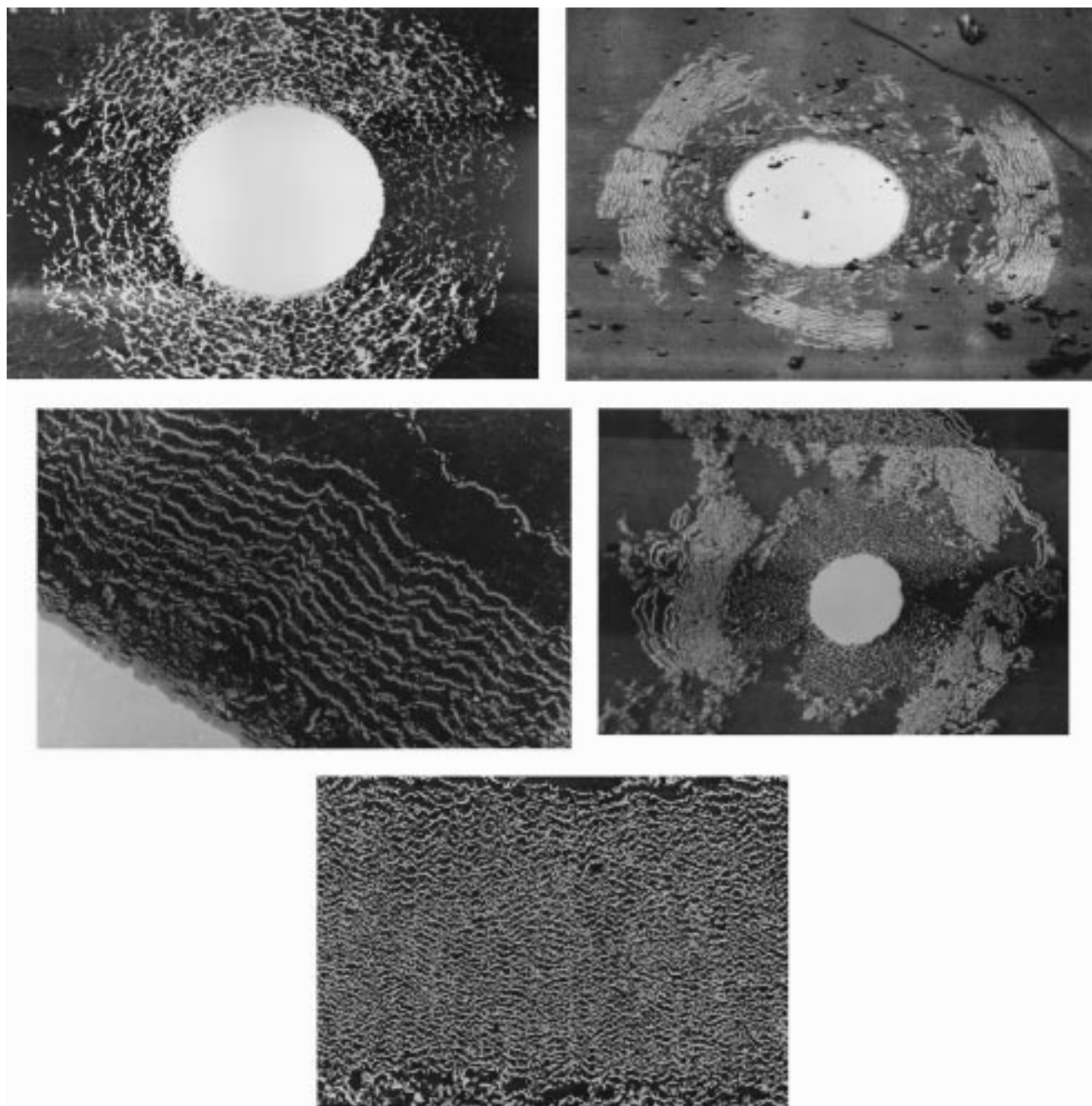


Figure 1. Backscattered electron micrograph of a transversal section of samples quenched after reaction at different temperatures for different times. The bright areas are Zr, the dark areas are Al, and the gray precipitates are Al₃Zr. (a, top left) Zr wire reacted at 720 °C for 5 s, magnification $\times 47$; (b, top right) Zr wire reacted at 802 °C for 20 s, magnification $\times 41$; (c, middle left) Zr plate reacted at 800 °C for 33 s, magnification $\times 80$; (d, middle right) Zr wire reacted at 820 °C for 20 s, magnification $\times 26$; (e, bottom) Zr plate reacted at 850 °C for 16 s, magnification $\times 120$.

(~ 820 °C), the organization of the periodic rings gradually reduces (Figure 1d,e).

Clearly, it must be considered that some of the described features can derive from the quenching of the high-temperature Al bath. In principle the distinction between structures developed during the high-temperature reaction and the ones derived from the rapid crystallization following quenching is difficult. The size of precipitates is generally considered a good indicator of the crystallization rate. On this basis the larger crystals present in the regular rings should be the result of a longer crystallization process, while the regions closer to the Zr wire show the characteristics of fast crystallization related with a quenching process. However, other factors influencing the nucleation density and/or crystals growth are possibly involved in the definition of the observed evidence.

Close analogy can be noted between some of the present experimental findings and the precipitate pattern formation process first described by R. E. Liesegang in 1896²⁰ and deeply investigated in the last 20 years.^{2–19} Liesegang patterns have been reported for a number of systems where a poorly soluble product forms ordered bands of colloids or precipitates in ternary or higher order systems. Such periodic precipitation is usually obtained in a gel, which effectively prevents convection and sedimentation of the precipitate phase, although analogous phenomena has been observed even in the solid state.^{2,3,5,9,14,19} In all these cases, the systems contain two or more components, in addition to the low-diffusivity inert medium. The time scale for pattern formation is generally very long (hours or days). None of these characteristics can be observed in the case of pattern formation in the Zr–Al system. A further unique

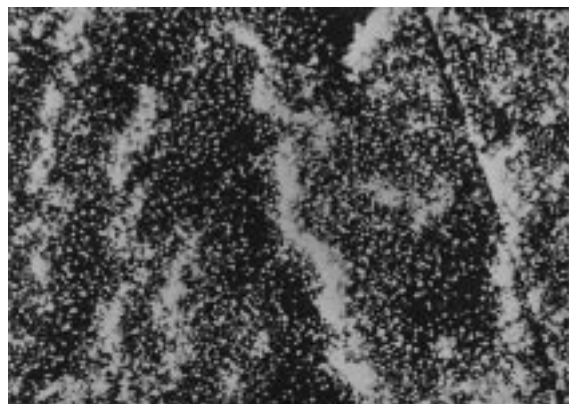


Figure 2. Detail at higher magnification of a region characterized by the presence of periodic precipitates. The individual crystals of Al_3Zr can be observed. Backscattered electron micrograph, magnification $\times 451$.

characteristic of this system is represented by the presence in the same sample of a different degree of organization, with a sharp transition between a Liesegang-type to a differently organized patterning. It is worth noting that such a transition does not appear to be related to any change in the external macroscopic parameters. Alternative approaches to the interpretation of our experimental findings can be based on the analogy with other solid-state processes driving the formation of periodical patterns. Van Loo^{21–23} and Chang²⁴ observed that solid-state diffusion processes in multicomponent systems can drive the formation of periodic bands parallel to the reaction interface. Such a morphology has been analyzed on the basis of a complex mechanism that involves a large difference in the diffusivity of the species. Hence, despite the close morphological similarities, these phenomena cannot be related to the periodical patterns observed in the system Zr–Al, which is strictly binary in nature. A closer similarity can probably be found with the formation of periodical structures observed during the oxidation of some metals and alloys, as described by Bertrand and co-workers.^{25–27} In this case two different kinds of layering were observed: a chemical layering, characteristic of systems containing at least three components, and periodical rupture, observed when Ni, Ti, or Nb are oxidized in pure oxygen in a narrow temperature range. These processes have been analyzed on the basis of a model involving chemical bistability with thermal feedback. This interpretation is probably very promising in view of an understanding of the processes involved in the Zr–Al system due to the large exothermicity of the reaction between these two metals. However, it must be observed that the chemical steps involved in the oxidation

processes are very different from the ones related with the formation of periodical patterns in the Zr–Al system. In the former, in fact, solid-state diffusion and mechanical blistering are involved, while in the latter only dissolution–precipitation processes must be considered.

Other possible explanations for the formation of periodical patterns in the system Zr–Al can invoke phenomena related to the presence of a liquid phase, like the formation of hydrodynamic patterns such as Bénard structures.¹ This approach, however, seems to be less promising owing to the short time scale of the process and the high viscosity of the melted aluminum.

Owing to the presence of several unique features, the pattern formation in the Zr–Al system appears as an original process that hardly fits into the phenomenology of other heterogeneous pattern formation processes. More experimental and theoretical work is necessary in order to achieve a firm understanding of the phenomena.

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