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SOLIDIFICATION MECHANISM OF THE D-GUN SPRAYED Fe-Al PARTICLES

The detonation gas spraying method is used to study solidification of the Fe-40Al particles after the D-gun spraying and settled on the water surface. The solidification is divided into two stages. First, the particle solid shell forms during the particle contact with the surrounding air / gas. Usually, the remaining liquid particle core is dispersed into many droplets of different diameter. A single Fe-Al particle is described as a body subjected to a rotation and finally to a centrifugal force leading to segregation of iron and aluminum. The mentioned liquid droplets are treated as some spheres rotated freely / chaotically inside the solid shell of the particle and also are subjected to the centrifugal force. The centrifugal force, and first of all, the impact of the particles onto the water surface promote a tendency for making punctures in the particles shell. The droplets try to desert / abandon the mother-particles through these punctures. Some experimental evidences for this phenomenon are delivered. It is concluded that the intensity of the mentioned phenomenon depends on a given droplet momentum. The droplets solidify rapidly during their settlement onto the water surface at the second stage of the process under consideration. A model for the solidification mechanism is delivered.

Keywords: Spraying; Rapid Solidification, Fe-Al droplets, Solidification model

1. Detonation gas spraying method

Intensive development of the detonation gas spraying method, [1-5] lead to significant innovation of the mentioned technology and to its practical use in the industry. First of all, it should be emphasized that the method is applicable to protective coating formation, [1]. The protective coating formation strongly depends on the dynamical parameters of the gas applied to the detonation powder spraying, [2].The gas used in the method not only causes the motion of the particles but the gas stream interacts on the particles during their movement towards the substrate as well, [3]. The analysis of heat transfer during the detonation and particles motion allowed to control the settlement of the particles on the substrate, [4]. Usually, the computer adding control of heat transfer promoted the further development of the gas detonation method, [5].

The current experiment performed in the Paton Electric Welding Institute – Kiev, Ukraine deliver some results dealing with the use of the mentioned method / technology to cover the water surface with the Fe-40Al particles. The model for the mechanism of solidification of these particles completely melted during the gas explosion is also developed.

2. Description of the Fe-Al particles solidification

The current model is associated with the Fe-40Al particles primary solidification occurring during their motion through air and gas situated between the gun barrel and substrate and secondary solidification occurring during the contact of these particles with water. The Fe-40Al [at.%] particles were settled on the water surface stand about 140 [mm] apart the gun tube.

2a. Settlement of the Fe-Al particles on the water surface

Generally, the particles form a kind of the layer on the water surface, Fig. 1.

The layer consists of large particles evincing some protruding small droplets and individual larger droplets which abandoned the mother-particles due to the centrifugal force activity.

The settled particles, generally od spherical shape, expose some protruding small and middle-sized droplets jammed in the solid shell of these particles. However, there are also some larger droplets distributed among the settled particles. Often, the middle-sized and large droplets are crashed and broken due to their strokes onto the water surface, Figs. 1-3.

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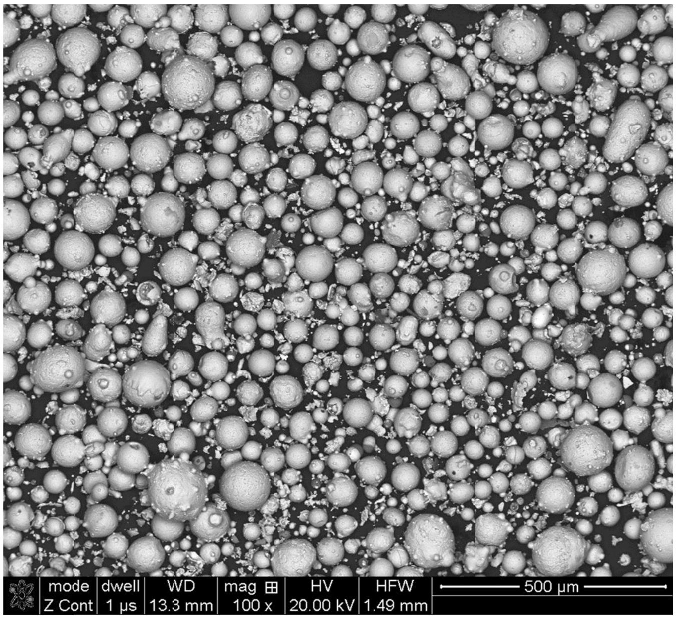

Fig. 1. A layer of the Fe-Al particles settled on the water surface due to the gas detonation spraying

A hypothesis arises:

1 – particles conserve the spherical shape due to their free / chaotic rotation; the heavier atoms (Fe) tended and displaced towards the particle periphery due to a centrifugal force which appears during the particle rotation,
Thus, the centrifugal segregation is created. It means that the particle core becomes enriched in low-melting element (aluminum) whereas its periphery gathers high-melting element (iron). This phenomenon promotes the formation of high-melting shell during the particle motion through the air / gas located between a gun tube and water surface;

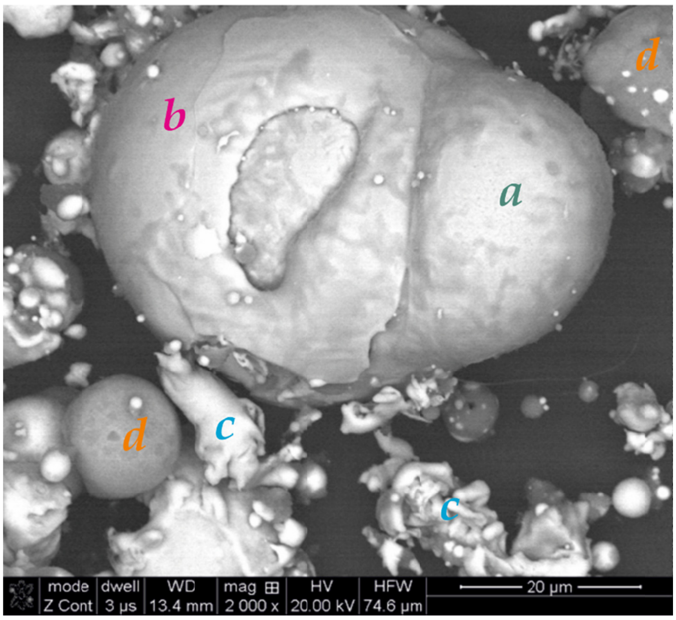

Fig. 2. The Fe-Al particle settled on the water surface; the single droplet, (a), protruded from the particle, (b); some of the large droplets, (c), damaged due to their stroke onto the water surface; the droplets significantly enriched in aluminum, (d)

2 – solidification of particles periphery forms the solid shell whilst the particle core remains liquid; both the solid shell and liquid core are separated between each other during the particle motion due to the shrinkage of solidifying shell.

Sometimes, the liquid core becomes a single droplet until its stroke against the water surface. Usually, the liquid core is subjected to the dispersion into many liquid droplets of differentiated diameters.

The liquid droplets rotate inside a given particle and therefore they are subjected to the centrifugal force.

In the case, when the liquid core is not dispersed into many smaller droplets, it breaks through the solid shell partially, Fig. 2, or completely in order to be subjected to the rapid solidification in the contact with water.

Tiny (small) droplets as well as some middle-sized droplets are not able to be born and released from the mother-particles. They get stuck partially in the solid shell of particles, Fig. 3.

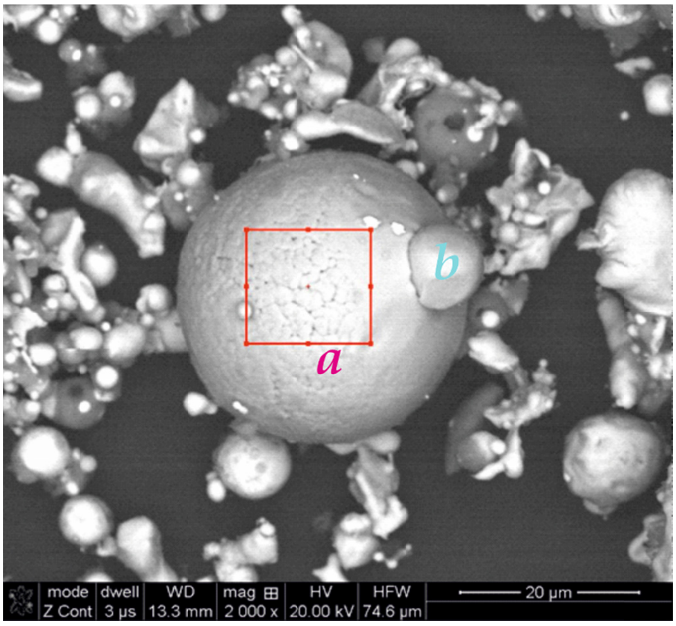

Fig. 3. The Fe-Al spherical particle, (a), settled on the water surface; the middle-sized protruded droplet, (b), trying to abandon the mother-particle; some (not all) of the middle-sized and large droplets crashed and broken due to their strokes onto the water; the cellular structure of the solid shell (in the marked windows)

The centrifugal segregation is more or less significant / intensive. Its intensity depends on the detonation force and centrifugal force itself. Generally, it results from the conditions of sedimentation. In the extreme case the liquid core becomes significantly enriched in aluminum, Fig. 4.

The performed chemical analysis confirms the significant / strong enrichment of the droplet in aluminum, Fig. 4, whereas iron was displaced by the centrifugal force into the solid shell.

A release of the Al-enriched core (droplet) from the particle is easier when the particle solid shell is partially crashed, Fig. 5.

The remaining part of the crashed particle, (a), evinces: just born droplets; partially born droplets jammed in the particle

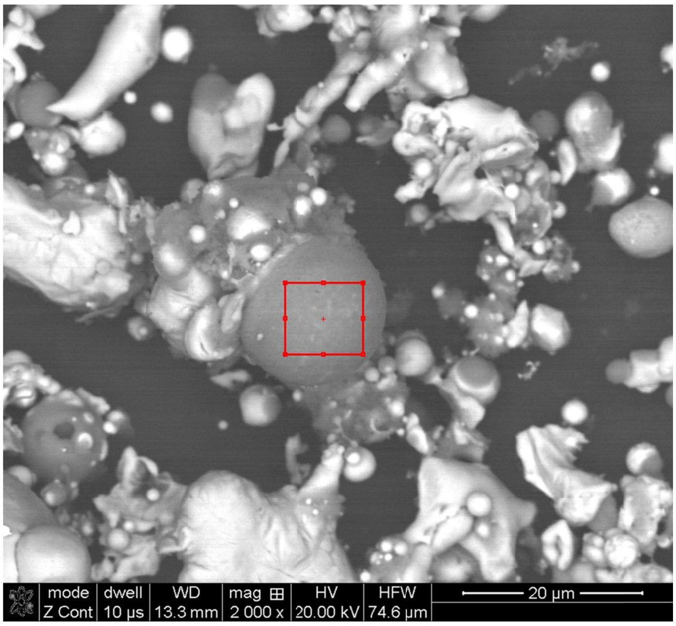

Fig. 4. Al-enriched core (droplet) released from the mother Fe-40Al particle

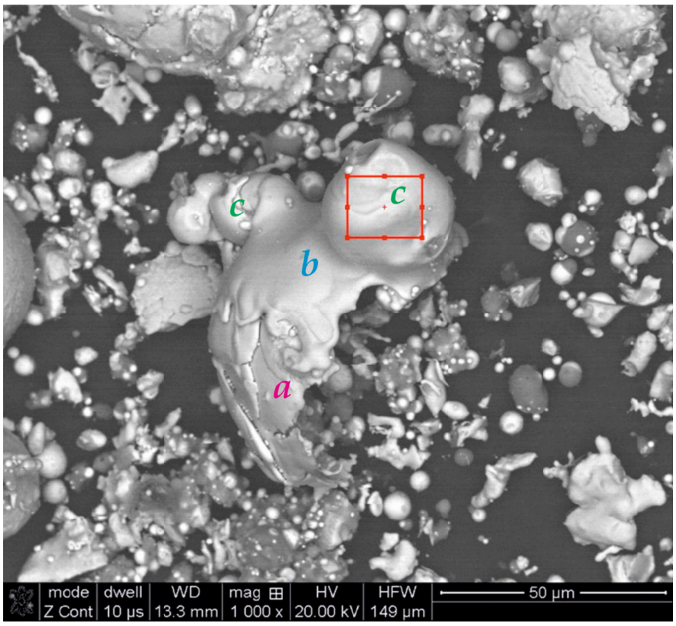

Fig. 5. Birth of some droplets, (c), from the Fe-40Al particle partially damaged, (a), due to the stroke of an accidental droplet, (b) and settlement onto the water surface

shell, (c), some small droplets inside the particle shell (enriched in aluminum); other particle, (b), completely melted due to the stroke / crash against the described particle. The marked area does not evince the cellular structure. It confirms the conclusion that the partially born droplet was subjected to a rapid solidification during its contact with water. The rapid solidification can lead to an amorphous / diffusion-less structure formation, [6].

In some cases, the one-axial revolution of the released / born droplets leads to an axial segregation, Fig. 6.

Moreover, the mentioned axial segregation promotes the division of a given droplet into an ellipsoidal part enriched in iron (b), and a semi-spherical part enriched in aluminum, (c), as visible in the left upper corner of the image, Fig. 6.

The phenomenon of the axial segregation (formation of some doublets) well visible in Fig. 7, is confirmed by the adequate measurement of the elements content, Table 1.

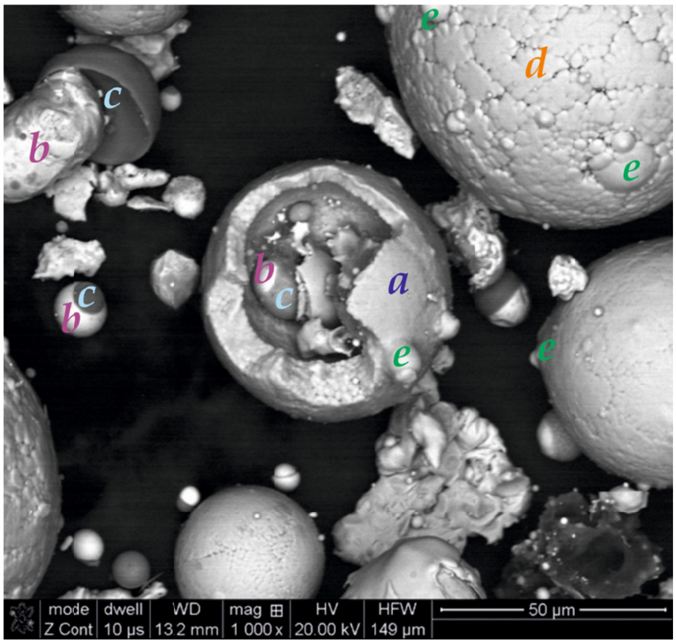

Fig. 6. Crashed particle, (a); the solid shell of the damaged particle with a varying thickness which results from a chaotic rotation of this particle and resultant unevenly occurring solidification during the particle motion through air / gas; axial segregation (separation into iron reach part, (b), and aluminum reach part, (c), due to the one-axial revolution of a given droplet); a cellular (honey-comb) structure of the particle shell, (d); some protruding droplets, partially born / jammed in the solid shell of the particle, (e)

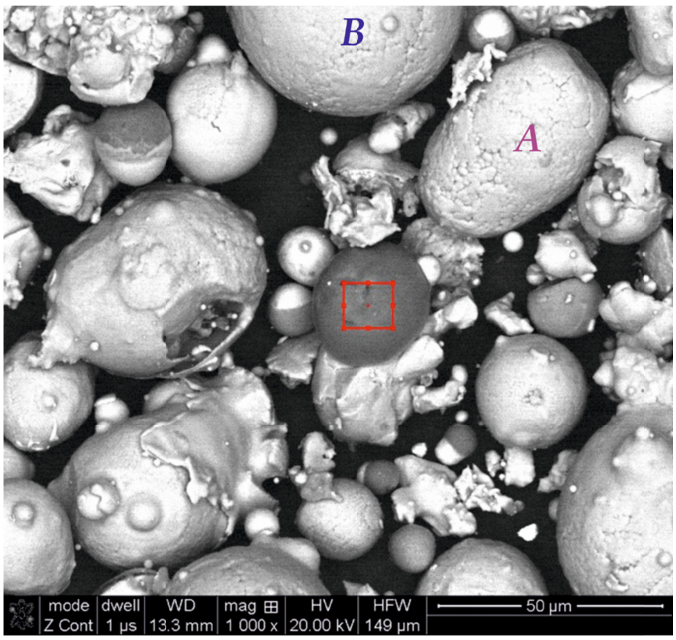

Fig. 7. Aluminum enriched part of a doublet visible in the image center (with the marked window / area for the measurement of the elements concentration)

TABLE 1

Concentration of some elements in the area marked in Fig. 7 due to the axial segregation

Element	at.%
oxygen	45.08
aluminum	47.64
zirconium	00.16
iron	07.12

The darker part of the droplet is enriched in aluminum, and depleted in iron, Table 1. The ratio of aluminum to iron, is equal to 47.64/7.12 = 6.69 whereas nominally this ratio in the particles used in the D-gun spraying was 4/6 = 0.67 [at.%/at.%]. The phenomenon of oxidation also occurred during the settlement of droplets, Table 1.

Some particles rotated chaotically during their motion through air / gas and therefore they conserve the spherical shape, B-particle in Fig. 7. However, when a given particle was subjected to one-axial revolution only, it conserves an ellipsoidal shape, A-particle in Fig. 7.

The phenomenon of the droplets birth from a given mother-particle results in the appearance of some punctures / holes in the particle solid shell, Figs. 8-10.

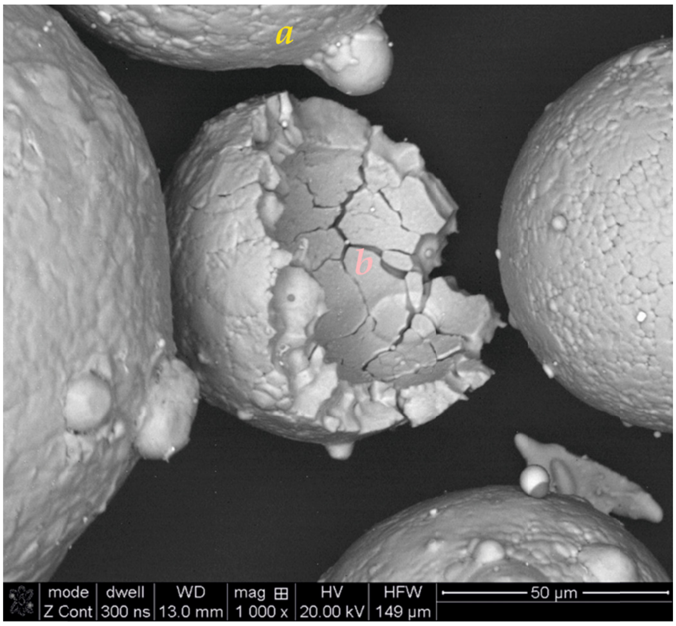

Fig. 9. Birth of some droplets from mother-particles; a/ not completed (the droplet jammed in the particle shell), b/ resulting in the puncture (the droplet released / abandoned the mother-particle)

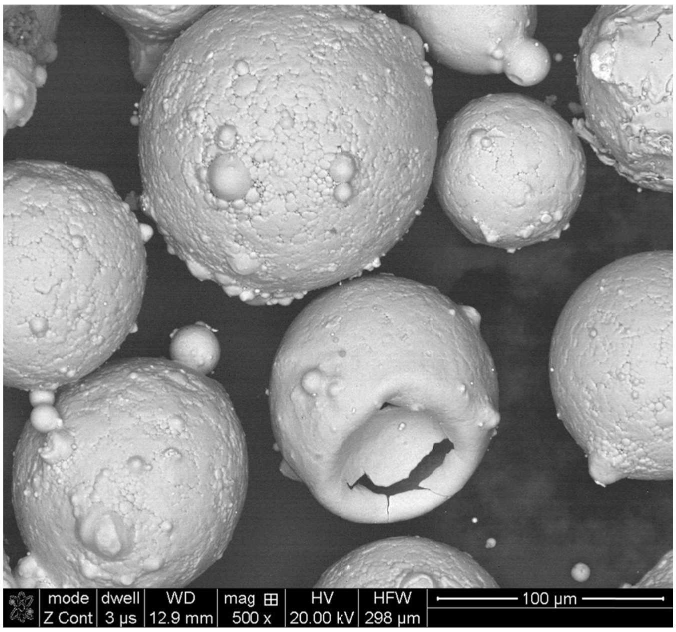

Fig. 8. Particle evincing the puncture after the droplet birth; some small droplets jammed in the particles solid shell

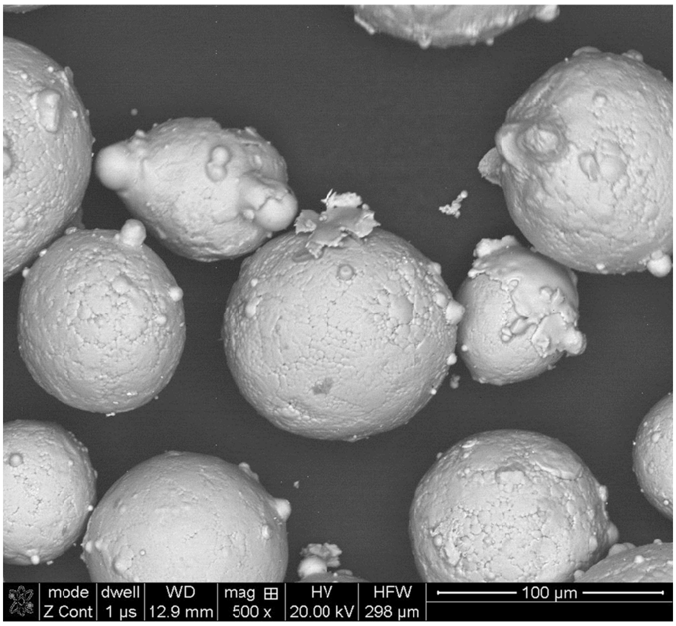

Fig. 10. Not completed birth of some droplets from particles; the jammed droplets subjected to rapid solidification in the contact with water; the droplets remaining inside the mother-particle subjected to slow solidification

The successful droplet birth (example b/ in Fig. 9) results not only in the formation of puncture / hole but in the mechanical cracks (along the grain / cell boundaries) as well.

The mentioned rotation of the particles and droplets result in the centrifugal segregation. Therefore, an adequate measurement of the elements content were performer to confirm the phenomenon of micro-segregation. Mainly, the measurement is dealing with iron, and aluminum located in the particle solid shell, Fig. 11.

It is confirmed that the centrifugal segregation caused almost complete elimination of aluminum from the particle shell. Thus, the shell became high melting material. Additionally, the presence of oxygen in the solid shell is significant, Table 2.

The nominal ratio of considered elements Fe / Al was 6/4 = 1.5 whereas this ratio changed significantly after spraying into: 86.15/2.45 = 35.16 [at.%/at.%].

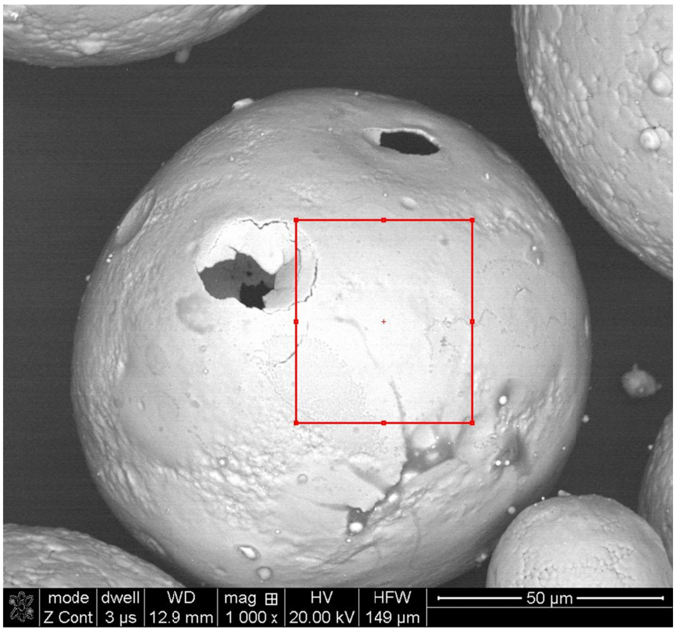

Fig. 11. Particle solid shell evincing two punctures / holes after the droplets birth

TABLE 2

Concentration of some elements in the area marked in Fig. 11 after the centrifugal segregation; nominal content of the mother-particle: Fe-40Al [at.%]

Element	at.%
oxygen	11.28
aluminum	02.45
zirconium	00.12
iron	86.15

2b. Solidification mechanism for the particles shell formation

The solidification of the particles shell occurs during the particles motion through air / gas with the presence of steep thermal gradient at the solid / liquid interface. This thermal gradient is imposed by a high temperature of the liquid particles leaving the gun barrel and a cold surrounding air. Thus, the oriented growth of cells / grains is expected. The cells grow radially towards the particle center. The cellular structure of the shells is confirmed by the SEM observations, Fig. 3, Fig. 6-8, Fig. 10, and exceptionally convincingly in Fig. 9.

Therefore, the following model for the oriented structure formation can be delivered, Fig. 12.

The rotation of the liquid cores is facilitated due to the shrinkage of the solidifying shells.

The rotating liquid core cuts the tips of the cells and evens the inner surface of the particles shell. The contact of the liquid core with the growing cells promote a dispersion of the core into many droplets. The droplets are of different diameter, Fig. 13.

Some of the rotating droplets get stuck / sink in the solid shell (yellow droplets) or become partially born from the mother-particle (blue droplets jammed). The remaining droplets rotate and even the inner surface of solid shell (cut the cells tips).

The jammed droplets as well as the droplets which abandoned the mother-particles due to the centrifugal force are subjected to a rapid solidification as mentioned, Fig. 14.

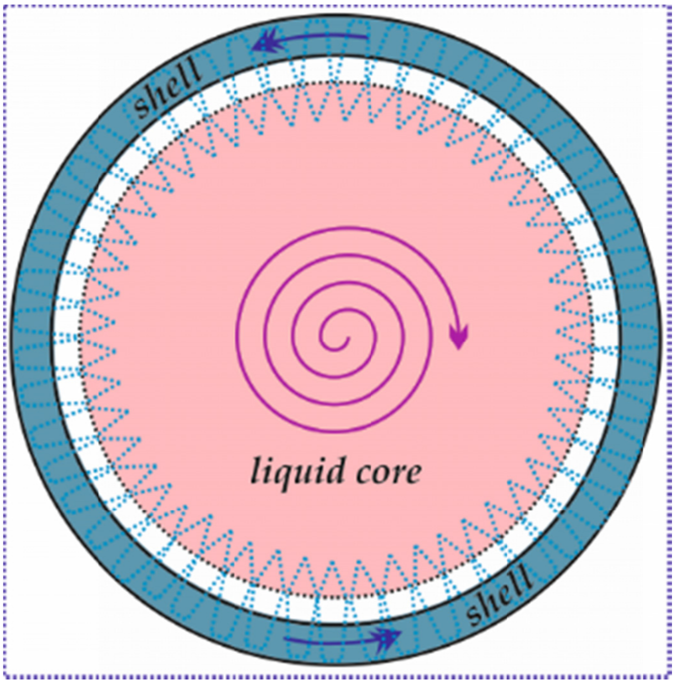

Fig. 12. Model for the particle solid shell formation; growing cellular structure marked; a shrinkage fissure between shell and rotating core introduced

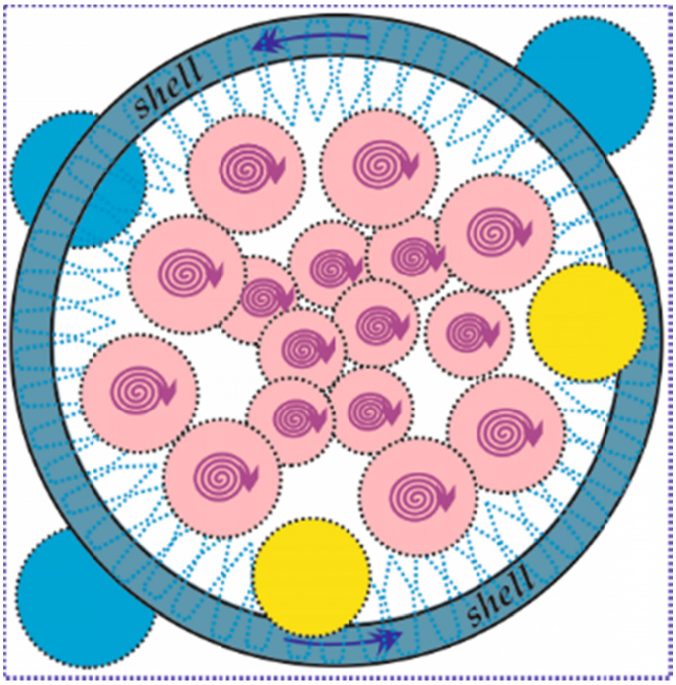

Fig. 13. Model for the liquid core dispersion into many droplets and for smoothness of an inner surface of the solid shell; arrows for particle / droplets rotation; cells protruding centripetally from the solid shell

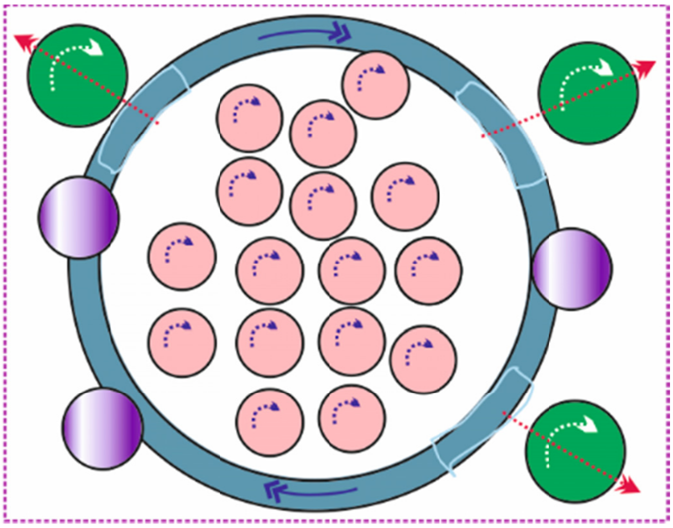

Fig. 14. Model for the larger droplets birth from the mother-particle; some punctures / holes in the solid shell after the birth marked

2c. Model for rapid solidification of the Fe-Al droplets

The differential equation for solidification can be formulated as follows:

$$d\left(x\bar{N}\left(x;\alpha\right)\right)=N\left(x;\alpha\right)dx+\frac{D}{R\,v}x\frac{dN\left(x;\alpha\right)}{dx}dx \qquad (1)$$

Eq. (1) shows the amount of solute (aluminum in the current model) which reached into the crystal / grain due to back-diffusion, when the currently appearing dx – layer (solid / liquid interface) appeared. The first term of the r.h.s. of Eq. (1) controls the amount of solute, which is currently within this layer, (s/l interface); the second term of the r.h.s. of Eq. (1) is associated with the amount of solute which passed across the s/l interface and entered into the cell / grain. Some notations used in Eq. (1) are:

- x – an amount of the growing cell / grain, *dimensionless*, $x \in [0,1]$,
- α – back-diffusion parameter (*Fourier Number*); $\alpha = D_S/(Rv_p) = D_S t^f/R^2$, $\alpha \in [0,1]$,
- $\bar{N}_S$ – average solute concentration in the growing cell, [mole fr.],
- N^S – solute concentration at the s/l interface, [mole fr.],
- D_S – diffusion coefficient into the solid, [m²/s],
- R – half the diameter of the growing cell (at its bottom), [m],
- v_p – average rate of the cell thickening, [m/s]; $v_p = R/t^f$,
- t^f – local solidification time, [s].

Since, the conservation of the mass balance for the considered solid-liquid system is: $d\left(\left(1-x\right)N^L\left(x;\alpha\right)\right)+d\left(x\bar{N}_S\left(x;\alpha\right)\right)=0$, thus the studied formula, Eq. (1) becomes:

$$\left[N^L\left(x;\alpha\right)-N^S\left(x;\alpha\right)\right]dx=\left(1-x\right)dN^L\left(x;\alpha\right)+ \\ +\alpha\,x\,dN^S\left(x;\alpha\right) \qquad (2)$$

N^L current solute concentration in the liquid, [*mole fr.*].

Eq. (2) is to be rewritten adequately to the current description which takes into account the phenomenon of back-diffusion and the following definition of partition ratio:

$$k=N^S\left(x;\alpha\right)/N^L\left(x;\alpha\right) \qquad (3)$$

$$\left(1-k\right)N^L\left(x;\alpha\right)dx=\left(1-x\right)dN^L\left(x;\alpha\right)+ \\ +\alpha\,k\,x\,dN^L\left(x;\alpha\right) \qquad (4)$$

The definition of the back-diffusion parameter satisfies the following limitation: $0 \le \alpha \le 1$, as it results from Eq. (4), [7,8].

However, the initial condition: $N^L(0;\alpha) = N_0$ allows to obtain the solution to Eq. (4).

$$N^L\left(x;\alpha\right)=N_0\left(1+\alpha kx-x\right)^{\frac{k-1}{1-\alpha k}},\ x \in [0,x_k] \qquad (5)$$

Eq. (5) is reducible to the so-called equilibrium solidification (*Lever Rule*), while applying $\alpha = 1$ and to the so-called non-equilibrium solidification when $\alpha = 0$.

The s/l interface path is: $N^S\left(x;\alpha\right)=k\,N_0\left(1+\alpha kx-x\right)^{\frac{k-1}{1-\alpha k}}$, according to an arbitrary phase diagram for the stable equilibrium. However, the solute redistribution path is to be formulated by an independent / additional relationship:

$$N^B\left(x;X^0,\alpha\right)=\begin{bmatrix}k+\beta^{ex}\left(x;X^0\right)\\ \beta^{in}\left(X^0,\alpha\right)\end{bmatrix}N^L\left(x;\alpha\right), \\ x \in [0,X^0],\ X^0 \in [0,x_k] \qquad (6)$$

with $\beta^{ex}(x;X^0) = k(1-k)(X^0-x)/(1+k\,X^0-X^0)$ which yields from the condition: $N^S(x;1)+\beta^{ex}(x;X^0)\beta^{in}(X^0,1)N^L(x;1) = N^S(X^0;1)$ and

$$\beta^{in}\left(X^0,\alpha\right)=\frac{\alpha\left(1+k-2\alpha k\right)\left(1+k\,X^0-X^0\right)\left[\left(1+k\,X^0-X^0\right)\left(1+\alpha\,k\,X^0-X^0\right)^{\frac{k-1}{1-\alpha k}}-1\right]}{\left(1-k\right)\left[k\,X^0\left(1-\alpha\right)+\left(1+\alpha\,k\,X^0-X^0\right)\left(\left(1+\alpha\,k\,X^0-X^0\right)^{\frac{k-\alpha k}{1-\alpha k}}-1\right)\right]}$$

which yields from the mass balance: $\int_0^{X^0} N^B(x;X^0,\alpha)dx+(1-X^0)N^L(X^0;\alpha) = 1N_0$

- N^B – current solute redistribution in the solid, [mole fr.],
- N_0 – nominal solute concentration of a studied alloy, [mole fr.], Table 1, or Table 2,
- x_K – final / total amount of the growing cell / grain, [dimensionless],
- X^0 – amount of a growing cell / grain due to the possible after freezing, [dimensionless],
- β^{ex} – coefficient of the extent of redistribution, [dimensionless],
- β^{in} – coefficient of the intensity of redistribution, [dimensionless].

Eq. (5), and Eq. (6) describe the droplets slow solidification as that which occurred inside the mother-particles shell, Fig. 10.

The current model for solidification, Eq. 5), and Eq. (6) can also be used to describe the rapid solidification of the droplets jammed into the solid shell, Fig. 3, Fig. 6, Fig. 8, Fig. 9, Fig. 10, or completely released / born from the mother-particles, Fig. 4, Fig. 7.

In this case, for the rapid solidification, when, $k \Rightarrow 1$, according to the Aziz's concept, [9], Eq. (5) changes its form into: $N^L(x;\alpha) = N_0$. It means that the Fe-Al droplet solidifies rapidly, and the diffusion cannot appear (segregation-less, and diffusion-less solidification), and the liquid does not change its concentration.

Thus, the solute concentration at the solid / liquid interface is equal to: $N^S(x;0)|_{k=1} = k\,N^L(x;0) = N_0$. As a result, *liquidus* line is juxtaposed by *solidus* line, in the Fe-Al phase diagram for the stable equilibrium when, $k = 1$, and additionally $\alpha = 0$.

Finally, the redistribution is defined as follows: $N^B(x;X^0,0) \equiv N^S(x;0) = N_0$. Thus, the back-diffusion phenomenon is not forced to occur in this experiment (in the technology of the detonation gas spraying) when the partially or completely born droplets are subjected to the rapid solidification.

3. Concluding remarks

Solidification of the liquid particles occurs in two stages:

a) formation of the cellular structure of the particle solid shell during the particle contact with surrounding air and gas; the inner surface of the solid shell is evened due to the cutting of the cells tips by the rotating droplets,

b) rapid (amorphous) solidification of the droplets: jammed in the solid shell or born and released the mother-particle through the punctures made in the solid shell; the droplets remaining inside the solid shell are subjected to the slower solidification.

Not only the droplets diameter decides on the droplets birth from the mother-particle but first of all the droplets momentum. The higher the momentum is, the easier is the droplets birth. The threshold momentum is expected for a given particles used in the detonation gas spraying above which the droplets can be jammed in the solid shell or released from the particle.

A formation of some doublets is revealed; one part of the doublets is enriched in aluminum and depleted in iron, the second is enriched in iron and depleted in aluminum, Table 1, Fig. 7.

Two types of micro-segregation is observed: a centrifugal segregation which leads to the enrichment of the solid shell in the high melting elements, Table 2, Fig. 11, and an axial segregation which leads to the separation of iron and aluminum, Fig. 6.

The micro-segregation intensity depends on the intensity of a given droplet rotation, its diameter and generally, on the conditions of detonation.

The rapid solidification is described by the simple model for the formation of the solid.

It is proved that the solidification is **diffusion-less** (back-diffusion parameter tends to zero, $\alpha \Rightarrow 0$), and **segregation-less** (no changes of the liquid and solid is to be ensured and partition ratio tends to unity, $k \Rightarrow 1$).

When $\alpha = 0$, then $\beta^{in}(X^0,0) = 0$, and $N^B(1;1,0) = k\,N^L(1;0)$ for $x = 1; X^0 = 1$. $N^B(1;1,0) = N^L(1;0)$, for $k = 1$, according to the Aziz's theory, [9]. Finally, $N^B(1;1,0) = N^S(1;0) = N^L(1;0) = N_0$. It means that that the Fe-Al droplet solidifies rapidly, and the diffusion cannot appear (diffusion-less solidification). The liquid does not change its concentration neither the solid (segregation-less solidification), $N_0 \Rightarrow N_0$. No grains are expected in the rapidly solidified droplet, as confirmed by Fig. 5c.

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