

## SPARK PLASMA SINTERING (SPS) AS ADVANCED POWDER METALLURGY SINTERING METHOD

Mamedov V. A.

### **Abstract**

*Spark Plasma Sintering (SPS) is a newly developed rapid sintering technique with great potential in achieving fast densification results and minimising the undesired grain growth process and sintering time. It is proven by obtained experimental data, that enhanced sinterability of powders subjected to SPS mainly associated with particles surface activation and increased diffusion rates on the contact zones caused by applied pulse current. Application of rapid heating results in bypassing low-temperature regions where surface-transport-controlled sintering is dominant. This can preserve the powder surface area to temperature levels where bulk transport is significant. However, the nature of activation effects, and especially in regard to acceleration of diffusion processes, is not clearly established. A lot of research works report the occurrence of plasma during the application of pulse electric current. Interaction of particles surface layers with reactive chemical species of plasma are interpreted as the key factors in sintering mechanism. However, the appearance of thermal plasma during SPS process is a controversial issue and particle-plasma interaction is a complex phenomenon. It is clear that significantly more work is required for clear understanding of the nature of the activation effect or effects caused by pulse electric current.*

**Keywords:** *Spark Plasma Sintering, Electric Pulse Current, atoms with stable electron configurations, diffusion viscose creep, grain growth, concentration of vacancies, lattice diffusion, grain boundary diffusion.*

### INTRODUCTION

During the past decade there has been an increased interest in using electric field for activated sintering of various PM materials [1-5]. The possibilities of sintering PM materials by application of an electric field dates long back [6-13]. Lenel in 1955 had studied electric resistance sintering-the compaction of metal powders by passing a low voltage, high-density current through them. At the time when a current was passing through the loose powders, the external pressure was applied. G. De Groat and other investigators reported about the possibility to achieve a sustained activation of the powder particle surface by producing repeated electrical discharges [14-18]. The spark sintering process for sintering metal powders in short time ranges of 5-30 s was investigated in et al [19,20]. The process was characterised by passing a high-density electric energy at simultaneously applied low pressures. S. Saito and his co-workers studied the same process. The highly dense titanium compacts were obtained after passing an electric current of 1 kA for several

seconds under a relatively low external pressure of 10 MPa [21]. It was proposed that the high sintering rate was due to breakdown of oxide layer on the surface of the particles, and good bonding improved by application of a high-density electric current. In some other works the results using a high-density circuit to perform compaction of  $TiB_2$  and SiC powders were presented [22, 23]. It was reported that most of the power was drained through the graphite die and plunger and there was no considerable advantage to using this scheme. A method based on the application of high voltage discharge using capacitor had been developed by Saito et al. [24]. The powder compact was preliminarily isostatically pressed up to 58.5 MPa. In the next stage, electric discharge from 60  $\mu F$  capacitor charged up to 15 kV, was passed through the powder compact. The obtained resistance values were explained by breakdown of the oxide layer. In many cases the electrical discharge compaction method was utilised to produce high-density compacts used for further processing steps like forging or rotary swaging [24, 14-16, 25]. In some other works the possibilities of the application of high voltage and high-density current from a capacitor bank were evaluated [26-30]. The main goal was to obtain PM compacts of high density capable of withstanding rotary swaging. Tensile testing for PM compacts sintered at current densities of 20 to 94  $kA/cm^2$  revealed a marked strength increase.

Recent works in this field were mainly concentrated on the developments of sintering techniques using the plasma and electric current for activation of powders during sintering. Johnson and his co-workers studied plasma sintering of ceramic oxides. As reported by Johnson, using the rapid heating rates makes it possible to minimise surface diffusion and increase densification rates [31-35]. The Resistance/Spark sintering was developed in Korea [36], pulsed electrical discharge sintering with pressure in USSR [37-39], plasma sintering in Brazil [40] and Spark Plasma Sintering in Japan [41-46]. The main principle of these sintering techniques is the use of the pulse electro-discharge concept for achieving fast heating rates and at the same time applying external pressure for rapid bonding between the powder particles.

Recently, the Spark Plasma Sintering Method (SPS) launched commercially and significantly paid attention in PM. This technique is expected to be a new process for sintering various kinds of materials [47-52].

The SPS process is a solid consolidation sintering process with simultaneous application of a low voltage and high- density pulse current and uni-axial pressure. The key advantages offered by this new sintering method include very high densities being obtained in a short time and low sintering temperatures comparing to conventional sintering, hot pressing and HIP. However the mechanism of this new process, especially its effect on densification of sintered compacts, still remain unclear. It is generally proposed by many researchers, that the ON-OFF DC current in initial stage of sintering process generates the spark discharge and rapid Joule heating between the particles. The gas among powder particles can be ionised and transformed into newly generated plasma. This process promotes the elimination of absorbed gases and oxide layers on the surface of the powder particles and activates the sintering process.

The goal of present paper is to make an overview of the works on SPS process, its fundamentals and mechanisms and outline the perspective fields of application of this new sintering technology.

## **BASIC PRINCIPLES OF SPS PROCESS**

The basic SPS technique uses pulsed electrical current combined with rapid heating and application of pressure in order to achieve a final sintering in a short time. The schematic of the SPS process is presented in Fig.1. The powder mixture is directly loaded

into the graphite die. Punches are also made from graphite. The use of graphite as a material for die and punches limits the applied external pressure during sintering to the value of 100 MPa.

There is a variation of sintering environments for different initial powder mixtures. The most commonly used environments are vacuum, argon, hydrogen or air. The process starts with initial activation by applying a pulsed current. Later when the proposed activation level is achieved, the densification process takes place. Densification during SPS process normally is achieved by application of external pressure, which can remain constant during the entire process or increase gradually. Pulse discharge normally is achieved by the application of voltage of about 30 V and a current of 600-1000 A. The duration of each pulse may be varied from 1 to 300 ms. Total sintering time is dependent on the type of material to be sintered. Normally the conductive powders are heated according to Joule effect. For non-conductive powders, heating process occurs through heat transfer from the die and punches. In this case, the die and punches are heated through their own resistance. In SPS process an ON-OFF DC pulse voltage and current from a pulse generator is applied to loose powders. Basic stages of SPS process are illustrated in Fig.2. The current is forced to choose the path of least resistance.

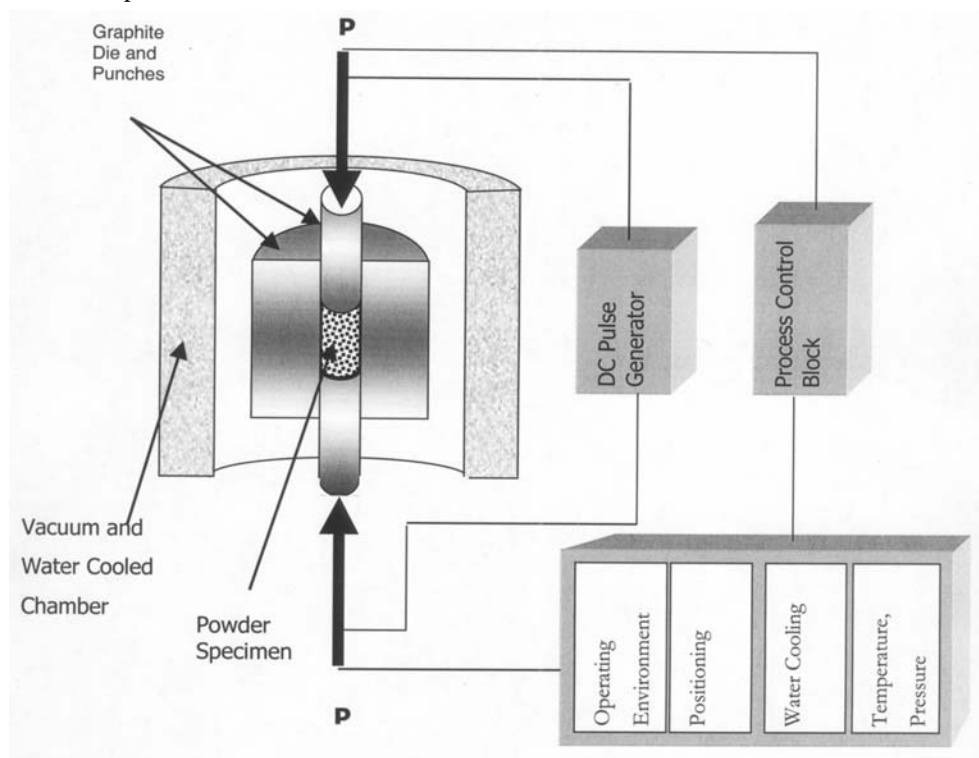


Fig.1. Basic Scheme of SPS Process.

That path normally goes through the contact points. The small capacitors are formed across the particle contact points because of the presence of oxide layers on the surface of the particles. Electrical discharges are generated across the capacitor gaps.

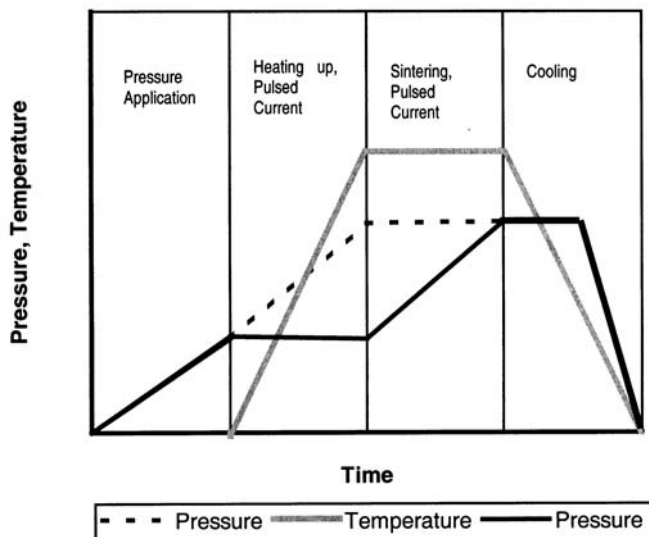


Fig.2. General processing stages during SPS.

The electrical discharges across the sample may generate spark discharge or plasma, that is, an ionised gas among powder particles. The surface layers of the powder particles are subjected to compositional modifications in a plasma environment. This process enhances the removal and elimination of oxide layers and surface impurities and absorbents, which are present on the surface of the powder particles as residual products of powder processing. The external pressure applied to activated powder particles, together with pulsed discharge, provides the diffusion bonding between particles and essential densification of the compact. In the initial stage of spark discharging by ON-OFF pulse current in the gap or at the contact points between the particles of conductive material, a local high-temperature-state of several to ten thousand Kelvin generates momentarily. The vaporisation and melting actions occur on the particle surfaces. M. Tokita reports the easy purification and activation of particle surface at the stage of plasma generation [53]. However, it seems that plasma generation occurs only in some cases, not yet well defined. The generation of the plasma requires special conditions. In some other works, the uncertain relationship between the effects caused by ON-OFF DC pulse current, electrical discharge, electrical field and the thermal effect and conductivity of the sintered material, which changes during the sintering process, were discussed. However, it is proven by experimental evidence that particle surfaces are “cleaned”, and grain-to-grain contact is observed in the sintered samples. A transmission electron microscopy (TEM) micrograph of aluminium nitride sintered by SPS technique, showed clean boundary layers [54].

It seems that during the process of application of pulsed current to the compact, the spark discharges occur between powder particles and intensive heating of the contact zones takes place. The mass transport through the newly formed high temperature arc accelerates. It can be proposed, that high temperature gradients between the surface and internal parts of the powder particles occur. The ionic interaction in the contact zone results in an intensive heat emission. It is possible that effectiveness of heat transport during this process is very high, as compared to normal heating by Joule effect. The compositional modifications and melting on the surfaces of the particles can be achieved in very short time. From the other side, the diffusion of ions on the space between powder particles is

enhanced by the applied electric field. Application of external pressure results in the plastic flow of heated material and in the diffusion bonding between particles.

### **DIFFUSION PROCESSES DURING SPARK PLASMA SINTERING PROCESS**

Experimentally observed phenomenon of fast contact zone enlargement can't be explained on the base of usual diffusion theory of mass transport. Apparently the short time of the thermal impulse is not enough for effective mass transport in the contact zone under capillary or external forces. Phenomenon of accelerated mass transport in the contact zone can be explained on the base of dislocation movement mechanism. The contact zone between powder particles can be considered as a source of dislocation glides [73-75]. In the case of pulse current sintering the process of emission and movement of dislocations could be very intensified due to fact that thermal gradient occurring in the contact zone create a remarkable tension gradient. Apparently this process is more active when there is no liquid phase in the sintering system. In case of liquid phase occurrence the mechanism of contact formation is more or less trivial due to easy mass transport through the free spaces between powder particles. In the initial stage of sintering process when minimal external pressure is applied to form contacts between powder particles the compact exhibit high porosity. With temperature increase the rate of grain boundary motion increases. Grain growth in this early stage is slow due to pinning action of open pores. Pores are attached to grain boundaries and acting like barriers reducing total grain-boundary area and energy. It can be proposed that during heating stage surface diffusion is an active process due to lower activation energy for surface diffusion that for other mass transport processes. As the temperature increase to critic level when spark discharges create melting on particles contact zones the surface diffusion slows down. Rapid heating rate would minimize the action of low-temperature surface diffusion. However, M. Nanko and his co-investigators studying the densification behaviour of cast-iron powder came to conclusion that neck growth is plastic deformation mechanism on the first stage, and this is basically the same as conventional hot pressing [55]. In other words when neck growth begins, no discharge occurs, or it does not give effect to the densification even if discharge occurs. Appearance of spark discharges involves the effective break down of oxide films and diffusion of impurities from the surface zones. At the stage of melt occurrence on the contact zones between powder particles the temperature is estimated to be close to boiling temperature levels of powder material. Active chemical interaction between melted surfaces and working environment can be expected at this stage. There is a great possibility that this process can be accompanied by compositional modification and creation of additional vacancies on the particles surfaces. Increase in vacancy concentration would enhance the mass transport in following sintering stages. Thereby high vacancy concentration on the particle surfaces and contact zones can be considered as main contributors to highest diffusion rates expected at high temperatures. The vacancies and atoms move mainly along grain boundaries (grain boundary diffusion) and through the lattice interior. Vacancies also can move between pores, leading to the growth of lager pores in the intermediate stage of sintering before yielding process started. The mass flows mainly along grain boundaries towards the bond between the particles. This process is leading to the increase of neck area between powder particles. Increasing the external pressure leading to the increase in inherent stress concentration in contact region. As the applied pressure exceeds the yield strength of the material the intensive plastic deformation and later creep processes take place. Depending on the level of applied pressure plastic deformation may occur through the entire particle or partially only on the contact zones. Applied pressure is expected to intensify remarkably the lattice and boundary diffusion through the increase in effective diffusion zones. This stage

of the sintering process can be characterized by effective elimination of porosity and particle movement.

Another interesting phenomena observed in microstructure of powder compact, which underwent SPS, is minimal coarsening. It is normally expected that grain growth becomes more active when pore structure becomes to collapse leading to minimization or elimination of porosity. Thereby the final stage of sintering during SPS process should accompany with rapid grain enlargement. Contrary to this proposal experimentally observed results demonstrated relatively small grain coarsening. Many researchers explain this phenomenon by effect of applied external pressure, which retards the grain growth process [56, 57]. It can be proposed that there are two main factors strongly influencing the grain growth process. First factor is fast heating rates allowing to avoid or to pass quickly the low temperature stages where surface diffusion dominates mass transport process. Initial stage porosity also can be considered as the factor retarding grain coarsening. Second factor is associated with the holding time in final stage of sintering process. At this stage when porosity is minimal and there are no barriers on the effective grain movement process, short time is a key factor.

### DISCUSSION ABOUT POSSIBLE DENSIFICATION MECHANISMS DURING SPS PROCESS

It is generally reported that SPS process results in accelerated densification with a minimum grain coarsening. At the same time a good grain-to-grain bonding was reported. There are two major contributors to the densification process during SPS: the applied pressure and diffusion processes accelerated by externally applied pulsed current. Possible densification mechanisms under externally applied pressure (more usual for HIP process) were discussed et al. [58]. Authors considered three main contributors to the densification under applied pressure: plastic yielding, power-law creep and diffusion densification. It was stated that densification by plastic yielding is the dominant factor in pressure assisted plasma activated sintering process. However, the role of power-law creep also was not excluded as a contributor to the densification. Equations for both factors were given from et al. [59].

$$D_{yield} = 1 - \exp\left(-\frac{3P}{2\sigma_y}\right) \quad (1)$$

$$D_{p.creep} = \frac{3}{2} \left(\frac{\epsilon_0}{\sigma_0^n}\right) \frac{D(1-D)}{\left[1 - (1-D)^{\frac{1}{n}}\right]^n} \left(\frac{3P}{2n}\right)^n \quad (2)$$

where P is applied pressure,  $\sigma_y$  is the yield stress, D is the compact density,  $\sigma_0$ ,  $\epsilon_0$  and n are material creep parameters. Grain boundary diffusion and lattice diffusion were considered as main factors in diffusion densification process.

During application of external pressure in SPS process the viscose flow character of porous body is more obvious. This process can be similar to viscose flow of viscose fluids with difference that viscose porous body characterized by essentially greater compressibility. Another important factor characterizing the porous body is volume viscosity, which is dependent on the porosity of viscose body. On this base we can suppose that the theory of material viscose flow can be used for describing densification kinetics during EPCS processing. In the first stage due to high heating rates caused by applied pulse current some compositional modifications and melting of the surface layers of powder particles can be proposed. In the next stage partial evaporation and condensation process also is possible. There is a high possibility that apart from thermal interactions some

chemical interactions between the melted zones and operating environment take place. The chemical reaction process can also be dependent on the type of operating environment. The possible changes in chemical composition would affect the lattice constant of material subjected to sintering. Unfortunately there is a lack of studies investigating the changes in lattice constant during sintering. Chemical reaction can accelerate the removal of some atoms, which can result in occurrence of persistent vacancies and lattice modification. In the case of sintering powders with high oxygen content in initial condition there is a possibility for oxygen diffusion to the inner parts of the powder particle. Diffusion transfer of atoms through the formed vacancies accelerates the mass transport in contact zones. After application of external pressure powder compact is almost instantaneously consolidated to high density by plastic deformation. The external pressure reaches the equilibrium with the internally developed stresses. Consequently no further closure of pores is possible by plastic flow. However, if the value of applied external pressure is sufficiently high it can be resulted in very high densities. This process highly depends on the internal temperature during the process. The plastic flow equation in this case can be derived from reference [60].

$$\frac{dV}{Vdt} = -\frac{P}{\xi} \quad (3)$$

where  $V$  is the volume of porous compact,  $t$  is the time,  $P$  is the applied pressure and  $\xi$  is the coefficient of volume viscosity of porous material.

The equation for speed of densification for single volume of the material, in general principles, was given by Kovalchenko in et al. [94].

$$\frac{\gamma}{V} \cdot \frac{dS}{dt} + 2\phi = -\frac{P}{V} \cdot \frac{dV}{dt} \quad (4)$$

where  $\gamma$  is the surface tension,  $S$  is the surface area of porous compact,  $P$  is applied external pressure,  $V$  is the volume of porous compact,  $t$  is the time and  $\phi$  is the speed of energy dissolution. In case of viscous flow of the material:

$$2\phi = \xi \left( \frac{1}{V} \cdot \frac{dV}{dt} \right)^2 \quad (5)$$

where  $\xi$  is the coefficient of volume viscosity of compact material. Following equation can be derived for coefficient of volume viscosity:

$$\xi = \eta_c \frac{\rho^3}{1-\rho} \quad (6)$$

where  $\eta_c$  is the coefficient of shear viscosity of the compact material,  $\rho$  is the density of the material.

Finally the densification equation can be given in following form [61]:

$$\frac{\rho^2}{1-\rho} \cdot \frac{d\rho}{dt} = \frac{1}{\eta_c} (P_1 + P) \quad (7)$$

where  $P_1$  is capillary (Laplacian) pressure. In case of SPS process we can propose that  $P \gg P_1$  and  $P_1 \approx 0$ .

Apparently formula (7) does not include the value of shear viscosity of porous material. Dependence of volume viscosity from porosity of porous material is given in et al [62]



$$\xi = \frac{4}{3} \eta_p(\theta) \frac{1-\theta}{\theta} \quad (8)$$

where  $\eta_p^{(\theta)}$  - coefficient of shear viscosity of porous material,  $\theta$  is porosity. For small porosity levels shear viscosity degrades linearly with porosity increase [63].

$$\eta_p = \eta_c (1-\theta)^m \quad (9)$$

where  $m$  is coefficient, for spherical pores  $m \geq 5/3$ . Making a substitution of shear viscosity of compact material in formula (7) by Formula (9), following equation can be written:

$$\frac{\rho^2}{1-\rho} \cdot \frac{d\rho}{dt} = \frac{(1-\theta)^m}{\eta_p} P \quad (10)$$

The equation for densification kinetics in more comprehensive form (modified by Lersmacher [64]) is given by Kovalchenko and Samsonov in the following form [65]:

$$\theta = \theta_0 (1 + bt)^{-x} \quad (11)$$

$$x = \frac{3P}{3\eta_0 b} = \frac{D\Omega_0 15P}{kT 2r_0 b} \quad (12)$$

where  $\theta$  is porosity,  $\theta_0$  - initial porosity,  $P$  - external pressure,  $\eta_0$  - coefficient of viscosity for a polycrystalline body at  $t = 0$ ,  $t$  - time,  $b$  - rate coefficient for grain growth,  $D$  - coefficient of self diffusion,  $\Omega_0$  - atomic volume,  $k$  - Boltzmann's constant,  $T$  - absolute temperature,  $r_0$  - initial particle radius.

As it can be seen from formulas (11) and (12), that for obtaining high densities the pressure and temperature should be remarkably high. The time of sintering should be long (more usual for HP comparing to SPS).

From obtained experimental data it was clear that increase in holding time during SPS process was resulted in higher densities. Unfortunately there are small numbers of works where the influence of the initial particle size on the achieved during the SPS process densities have been studied. Therefore it can be proposed that initial particle size during SPS process affects more grain growth process rather than densification. Apparently the higher external pressure would result in higher densities achieved at lower temperatures.

Significant intensification of diffusion processes under externally applied load was reported by Naumov et al.[66]. Naumov made a proposal that during plastic flow the essential increase in lattice defect can take place.

The accelerated mass transport during sintering depends on increase of effective diffusion coefficient. As it is generally accepted the application of external pulsed electric current is one of the ways of activation of powder particle during SPS process. I. E. Geguzin made a proposal that in crystalline lattice of activated powders the concentration of vacancies is increased [67]. The increased concentration of vacancies is a factor contributing to diffusion acceleration [68]. T. Ishigaki investigating in-flight plasma treatment of titanium carbide powders came to conclusion that increased carbon site vacancies accelerate the diffusion transfer. This is in good agreement with Geguzin's proposal about the role of concentration of vacancies on diffusion processes. Johnson has reported about suppression of surface diffusion during rapid sintering process. As discussed by Johnson rapid densification originates from the suppression of surface diffusion [69]. It can be proposed that during SPS process the densification is mostly controlled by enhanced lattice diffusion and grain boundary diffusion.

It is generally accepted that the physical nature of the material affects the sintering of material powder. Therefore there is an interconnection between the activation energy of



sintering process of various materials and their electronic structure. According to electron theory of sintering of transient metals proposed by G. V. Samsonov, the valence electrons are partly locating around the atom skeleton during the formation of metal crystals. However some electrons partly get into non-located states. The localized part of electrons tends to form stable configurations [70, 71]. Such stable configurations for d-metals are  $d^0$ ,  $d^5$  and  $d^{10}$ . It should be stated that for d-transient metals the atoms in the metal crystal exist in stable configurations of  $d^0$  and  $d^5$ . With the increase of electron number on a d-shell ( $n_d$ ) the statistic weight of  $d^5$ - configuration also increases, but the statistic weight of  $d^0$ -configuration decreases and therefore the quantity of valence electrons, passing into a non-located state decreases as well. The relationship between the activation energy during self-diffusion and level of localization of valence electrons for transient metals is shown in figure 3 [72].

It can be seen that the increase of activation energy is associated with the increase of localization level of valence electrons into  $d^5$ -configurations. Increase in statistic weight of  $d^5$ -state at the corresponding decrease of the statistic weight of  $d^0$ -state and the reduction of electrons going into non-localized state associated with the decreased number of electrons active in electron exchange during sintering process.

This corresponds to the increase of the activation energy of the process during sintering. Another important factor is the surface activation effect caused by applying pulsed electric current. On the surface of any crystalline formation the level of localization is less comparing to the volume. This attributed to the increased activity of the surface. This process can be explained by surface diffusion and increased mobility of surface atoms to move towards the direction were they could achieve more complete localization.

These phases are normally the contact zones between particles, because in contact zones there is a possibility for transfer of surface atoms with low localization level to the states

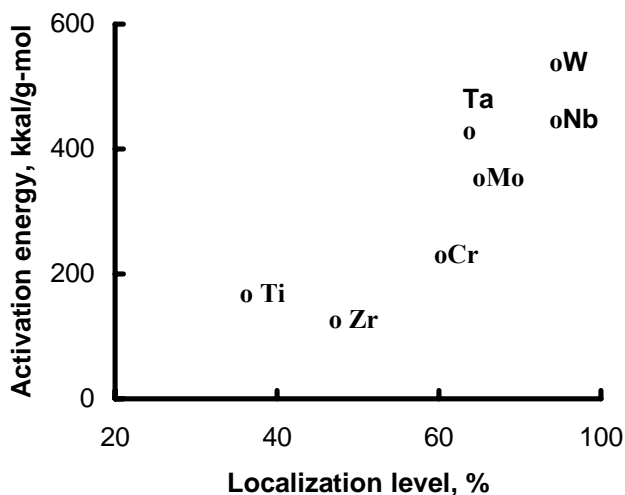


Fig.3. Relationship between self-diffusion activation energy and valent electron localization level for transient metals.

with higher localization of valence electrons. The activation effect caused by pulse current results in occurrence of large number of atoms with destroyed electron configurations. Occurrence of the liquid phase on the surfaces of powder particles results in extensive electron exchange. Severely destroyed localized states trend to rehabilitate and to transfer into states with higher localization level.

## CONCLUSIONS

As its seen from reviewed literature, SPS process finds more application mainly for sintering of materials that are difficult to obtain by conventional PM processing. It is also clear that there is an increased interest in applying SPS process for production of materials with metastable crystalline phases, amorphous phases and etc. The structural features of above mentioned materials and supersaturated solid solutions are very attractive due to their unusual physical properties. In contrast to SPS technique conventional PM methods cannot produce such materials without degrading their unique microstructure. The key advantages offered by this new sintering method include very high densities can be obtained in a very short time and low temperatures comparing to conventional sintering, Hot Pressing and HIP. However the mechanism of this new process especially on it's effect on densification of sintered compacts still remains unclear. It is generally proposed by many researchers, that the ON-OFF DC current in initial stage of sintering process generates the spark discharge and rapid Joule heating between the particles. This process promotes the elimination of absorbed gases and oxide layers on the surface of the powder particles and activates the sintering process.

Our proposal is based on the increased of concentration of vacancies on the crystalline lattices of powders subjected to pulse electric current passage. The increase in vacancy concentration results in a melting of surface layers in the initial stage of sintering and results in destroying the localised states of stable configurations. Application of external pressure enhances the diffusion-viscose creep process, which results in a fast densification of the material. Satisfactory interpretation of effects occurring during SPS process should be considered in complex form on the basis of electronic structure of sintered materials and the theory of diffusion viscose creep.

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