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The Impure Retardation of Interparticle Joining Surface Migration

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Abstract: An analysis of migration of the interparticle joining surface in the conditions of impure retardation is presented. An expression quantitatively connecting retardation work with the initial segregation on a metal surface and temperature conditions of formation of hot-deformed powder material is derived. The values of retardation work are calculated when some types of iron powder are used as the initial material.

Keywords: Impure segregation; Interparticle joining; Low-alloyed iron powder.

1. Introduction

Interparticle joining is the basic process of formation of hot-deformed powder materials (HDPM), defining morphology of their structure in the area of particle contacts, and consequently the level of structure-sensitive properties. In [1-3] it is found that maximum values of mechanical properties of HDPM are achieved when intracrystalline joining, occurring in the case of removal of the migrating interparticle joining surface (IPJS) from the structure defects, formed on coming in contact of free surfaces of powder particles or pores. It is true under such consolidation degree of powder preform, which allows to consider it not as a conglomerate of powder particles, but as a discrete body.

The relation of moving and retarding migration forces, effecting at different technological stages of HDPM obtaining, defines its structure in the joining area. One of the significant factors, effecting on IPJS migration, is its interaction with the segregation of impure atoms. That is why in this work the purpose is to analyze the effect of impure retardation of IPJS migration and to work out the procedure of its definition.

2. Experimental Procedure

In order to calculate the work of impure retardation $A_{ir}$ factual data are obtained as the consequence of the treatment of data of the Auger-electron spectroscopy (AES) of metal powders, performed on an Auger spectrometer model PHJ-680 of the “Physical Electronics” firm. The pressure of residual gas in the analytical chamber of the apparatus made up

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(1-2.5) \times 10^{-7} \text{Pa}.

The method of spraying of surface metal layers by argon ions was used to study the element distribution from the observed surface in the material volume. The energy of ion beam made up 10 keV, that corresponded to the etching speed $10^{-8}\text{m/min}$ [4].

The chemical composition of metal powders is presented in Table I.

**Tab. I Chemical powder composition**

<table>
<thead>
<tr>
<th>Powder grade</th>
<th>Component content, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo</td>
</tr>
<tr>
<td>ASC 100.29</td>
<td>-</td>
</tr>
<tr>
<td>Astaloy CrM</td>
<td>0.5</td>
</tr>
<tr>
<td>Atomet 4601</td>
<td>0.53</td>
</tr>
<tr>
<td>Atomet 4901</td>
<td>1.5</td>
</tr>
</tbody>
</table>

3. Theoretical and Experimental Estimation of the Impure Retardation Work

Let us examine the segregation influence on the mobility of IPJS. In the initial state the segregation of element $i$ is characterized by the definite atom distribution in normal direction to IPJS expressed by the maximum $C_{\text{max}}$, reduced $C_{\text{redi}}$ concentration and the concentration of solid solution $C_{\text{mi}}$, and by the width of segregation area $x_{\text{cdi}}$ (Fig.1).

![Fig. 1 Interaction of migrating IPJS with segregated atoms (a): removal of IPJS from the segregated atmosphere; (b): carrying away of segregated atoms by IPJS.](image)

The value of reduced concentration is determined according to the expression:

$$C_{\text{redi}} = \int_{c}^{d} C(x) \cdot dx / x_{\text{cdi}},$$

where $C(x)$ = function, descriptive of the $i$ – element distribution in the segregation area.

Two cases of IPJS interaction with the segregated atoms are conceivable: IPJS removal from the segregation atmosphere (Fig.1a) and carrying segregated atoms away by migrating IPJS (Fig.1b).

In the case of migrating IPJS removal from the segregated atoms motive migration work should excel the energy of their connection with IPJS, presenting the work of segregation retardation. In the second case the work of segregation retardation is defined by...
the difference of segregated atom concentration on either side of IPJS, expressed by the
difference of cross-hatched areas (Fig.1b).

Let us consider the first case when migrating IPJS is removed from the segregation
atmosphere.

Using expression (1) it is possible to define the number of segregated atoms \( N_{\text{ati}} \) on the
IPJS:
\[
N_{\text{ati}} = N_A \cdot C_{\text{redi}} \cdot V_{\text{seg}} / V_m,
\]
where \( N_A \) - Avogadro’s number, \( V_{\text{seg}} \) – volume of examined segregation area of \( i \) – element,
\( V_m \) – molar volume defined according to the expression:
\[
V_m = N_A \cdot a^3 / K_{el},
\]
where \( a \) – parameter of an elementary crystal cell, \( K_{el} \) – the number of atoms, falling on one
elementary crystal cell.

Then the number of segregated atoms, falling on an unit of IPJS area is as follows:
\[
N_{\text{ati}}^{\text{sp}} = C_{\text{redi}} \cdot x_{\text{cdi}} \cdot K_{el} / a^3.
\]

Let us define the work of impure retardation in the case of IPJS removal from the
segregation atmosphere. The work, performed against the force of segregation retardation \( A_{\text{sr}} \),
should be dissipated on the account of segregated atom diffusion, taking place during IPJS
migration. The speed of dissipation of free energy, connected with diffusion currents, will be
defined by the product of current by moving force, which is the difference of chemical
potentials of element \( i \) on IPJS and in the matrix material [5]:
\[
\frac{dE}{dt} = \sum_{i=1}^{n} J_i \cdot \Delta \mu_i,
\]
where \( J_i \) – the current of segregated atoms of element \( i \); \( \Delta \mu_i \) – single moving diffusion force.

Then the work of segregation retardation will be defined by the following expression:
\[
A_{\text{sr}} = (dE/dt) \cdot \Delta t = \sum_{i=1}^{n} J_i \Delta \mu_i \cdot \Delta t,
\]
where \( \Delta t \) – time of dissipation of free energy and IPJS migration.

According to the definition of diffusion flow we have:
\[
J_i = N_{\text{ati}}^{\text{sp}} / \Delta t.
\]

The value of single chemical potential of real solid solutions is expressed as in
thermodynamic activity [6]:
\[
\mu_i = \mu_{0i} + k \cdot T \cdot \ln a_i,
\]
where \( \mu_{0i} \) – chemical potential in standard conditions; \( k \) – Boltsman constant; \( T \) - absolute
temperature; \( a_i \) – thermodynamic activity of \( i \) – element:
\[
a_i = \gamma_i \cdot C_i,
\]
where \( \gamma_i \) – coefficient of thermodynamic activity of \( i \) – element; \( C_i \) – atom concentration of \( i \) –
element. Considering that the coefficient of thermodynamic activity depends on atom element
concentration the expression can be written in the form:
\[
\Delta \mu_i = k \cdot T \cdot (\ln(\gamma_i^I \cdot C_{\text{maxi}})^{\text{ip}} - \ln(\gamma_i^II \cdot C_m)) = k \cdot T \cdot H,
\]
where \( \gamma_i^I \) and \( \gamma_i^II \) – coefficients of thermodynamic activity of \( i \) – element on IPJS and in the
metal matrix correspondingly.

Let us equate the energy of connection of segregated atom on IPJS, expressed through
equilibrium concentration, and the increment of free energy in a heterogeneous system in
order to define the value \( H \) in formula (10). The equilibrium concentration depends on the
energy of connection of IPJS with a segregated atom according to the following expression
[7]:
\[
C_{\text{maxi}} = C_m \cdot \exp(U_i/(k \cdot T)),
\]
where \( U_i \) – energy of connection of IPJS with segregated atom of \( i \) – element. From (11) it follows:
\[
U_i = k \cdot T \cdot \ln(C_{\text{maxi}} / C_m).
\]
Considering the joining area as a non-ideal solid solution, we express the connection energy, falling on one atom, in terms of the ratio of increment of molar free energy to the Avogadro number. That is:

$$U_i = \Delta \mu_i \cdot \Delta C_i = k \cdot T \cdot H \cdot (C_{\text{maxi}} - C_{\text{mini}}).$$

(13)

It follows from expressions (12), (13) that:

$$H = \ln \left( \frac{C_{\text{maxi}}}{C_{\text{mini}}} \right) / (C_{\text{maxi}} - C_{\text{mini}}).$$

(14)

Substituting expressions (4), (7), (10) and (14) in formula (6), we’ll get the equation for calculation of segregation retardation work, falling on the unit of area of IPJS, in case of its removal from the segregating atmosphere:

$$A_{sr} = \sum_{j=1}^{a} C_{\text{reali}} \cdot x_{cdj} \cdot K_{el} \cdot k \cdot T \cdot \ln \left( \frac{C_{\text{maxi}}}{C_{\text{mini}}} \right) \cdot (a^3 \cdot (C_{\text{maxi}} - C_{\text{mini}})).$$

(15)

Fig. 2 The element distribution on the surface of particles of powders ASC 100.29 (a), Astaloy CrM (b), Atomet 4601 (c), Atomet 4901 (d).

The results of AES of metal powders are presented in Fig.2. Calculation results for hot repressing temperature 1000 °C are presented in Table II.

<table>
<thead>
<tr>
<th>Powder grade</th>
<th>ASC 100.29</th>
<th>Atomet 4601</th>
<th>Atomet 4901</th>
<th>Astaloy CrM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{sr}, 10^{-5}$ erg/sm$^2$</td>
<td>1.48</td>
<td>4.6</td>
<td>8.5</td>
<td>4.43</td>
</tr>
</tbody>
</table>
In the second case, when the moving IPJS migration force is not sufficient for its removal from segregated atoms, and migration is accompanied by their entrainment, the arguments cited above are true for the IPJS segregation retardation work calculation. Definition of the value of diffusion flow as the difference in the quantity of atoms, forming segregation on each side of IPJS forms the calculation basis. In order to use formulas, deduced when observing the previous case, let us introduce the notion of reduced concentration, calculated from the following expression:

\[
C_{\text{red}} = \frac{\int_{e}^{d} C(x) \, dx - \int_{e}^{d} C(x)_{0} \, dx}{x_{\text{cdi}}},
\]

where \( C(x) \) – function, describing the distribution of the second component in the segregation area; \( x_{\text{cdi}} \) – the width of segregation area.

It is worth noting that in this case \( A_{sr} \) is a variable value, depending on the elementary act of IPJS migration, characterized by the \( x_{fe} \) value (Fig.1b). The higher the value of moving IPJS migration force, the more extended is the \( x_{fe} \) length and the higher is the segregation retardation work (Fig.3). One can pick out three sections for all investigated materials on the examined dependence. In the field of small migration of IPJS (5 – 10nm) the work of segregation retardation is not relatively great, but is very sensitive to argument change. On reaching the definite \( x_{fe} \) value corresponding to the width of segregation accumulation of one of the components, the motion dependence becomes smooth up to the attainment of the maximum value of the retarding effect.

![Fig. 3](image)

**Fig. 3** Dependence of the work of segregation retardation of migration of IPJS on the value of its transfer for HDPM, produced out of powders Atomet 4601 (1) and ASC 100.29 (2).

The transfer from entrainment of IPJS of segregation atmosphere to its removal takes place in the third section, corresponding to the drastic \( A_{sr} \) drop. In this case IPJS migration ceases to depend on the segregation factor.

The retarding effect increases with an increase in the hot deformation temperature. In our opinion this circumstance can be explained by the increase of the mismatch of initial segregation and equilibrium. Equilibrium segregation decreases with temperature increase until complete disappearance.

Values of work of impure retardation of migration of IPJS are in the interval of variety of moving forces of its migration, making up \( 10^{4} – 10^{7} \) erg/sm\(^{2}\) [8].

4. Conclusion

The suggested procedure of impure retardation work calculation enables control over the process of the formation of a HDPM joining area structure, basing on the recognized law
of element distribution on a metal particle surface.

References


Резюме: Приведен анализ миграции межчастичной поверхности сращивания в условиях примесного торможения. Выведено выражение, количественно связывающее работу торможения с исходной сегregationей на металлической поверхности и температурными условиями формирования горячедеформированного порошкового материала. Вычислены значения работы торможения при использовании в качестве исходного материала некоторых марок низколегированного железного порошка.

Ключевые слова: Сегрегация примесей, межчастичное сращивание, низколегированный железный порошок.

Садржај: Дата је анализи миграције додирне површине између честица у условима успоравања примесама. Дефинисан је израз који квантитативно повезује рад успоравања са почетном сегрегацијом на металној површини и температурним условима формирања топлодеформисаног прашастог материјала. Вредности рада успоравања израчунате су када се као полазни материјал користе неке врсте праха гвожђа.

Кључне речи: Сегрегација примеса, срастање честица, нисколегирани прах гвожђа.