1. Introduction

Investigation into weld properties has become a key element of quality inspection in welding technology. It results from the fact, that a welding operation is the special process, what means, that possible imperfections can be revealed not earlier than after its completion. During the welding process various welding defects and imperfections can be formed what influences the weld strength significantly. As an example, it is shown in the table 1 [1,2] for pulsating loads.

| Ordinal number | Type of internal defects                  | Zrj, MPa | %   |
|----------------|------------------------------------------|----------|-----|
| 1              | Material with rolling skin                | 280      | 100 |
| 2              | Butt weld, sound, machined                | 260      | 95  |
| 3              | Very small pores                          | 250      | 90  |
| 4              | Pores visible on radiographs              | 195      | 70  |
| 5              | Errors in two layers                      | 180      | 65  |
| 6              | Slag inclusion, errors in the weld root   | 155      | 55  |
| 7              | Large errors in two layers                | 125      | 45  |
| 8              | Large clusters of slag inclusions         | 100      | 35  |
| 9              | Large errors in the weld root             | 70       | 25  |

Note: % - The percentage presentation of the weld fatigue strength in the tensile test with pulsating cycle; Zrj - weld fatigue strength in the tensile test with pulsating cycle, MPa.

The table shows to what a degree the weld fatigue strength falls in the tensile test with pulsating cycle depending on the type of internal imperfections. According to the PN-EN ISO 6520-1 the welding imperfection is defined as a discontinuity in the weld or a deviation from the intended shape or dimension whereas the defect is an unaccepted welding imperfection.

In order to prevent the occurrence of welding imperfections and defects, testing of welded joints is made what can improve welding quality and eliminate discontinuities which have already been formed. For detection of imperfections and defects as well as for assessment of their effect on welded joint properties it is applied both destructive and non-destructive testing. Destructive tests can be carried out on products, prototypes or samples, selected at random, which are destroyed in part or completely during testing. Because of damage which results from destructive tests, the non-destructive testing is preferred. Such a testing does not cause any disturbance in usability of the material while it gives information on material discontinuities occurring in products, on material properties and on the size of the objects under testing. One of the popular methods of non-destructive testing is that with the use of liquid- penetrant which enables to detect welding imperfections and defects getting outside the weld surface, either on the face side or on the root side. In this method, the movement of liquid and its ability to penetrate into material discontinuities are used [1].

Penetrant testing can be applied for all materials while its only limitation is porosity of the material under testing. In technical publications and in European standards the development time (i.e. the time of getting out the penetrant
from a discontinuity to the material surface) is specified from 10 to 30 minutes, without taking into account the material type. However, it results from the practice that the development time is closely connected with the material type and fluctuates from several minutes to 24 hours.

In literature, only the effects of the penetrant are described, whereas the effects of material, i.e. the influence of factors connected with material on adhesion between penetrant and material under testing, are not considered. Therefore it is necessary to undertake research aimed at explanation of this question. Specification of the factors influencing the penetrant development time as well as the determination of the degree to what they do it can be very helpful in research practice in order to make easier the choice of the correct development time[1].

2. Adhesion effect

In liquid-penetrant testing, the development time is affected by adhesion phenomenon. It is a physical phenomenon connected with the constitution of matter. It consist in bonding of surface layers of two different bodies caused by their attractive forces [3].

The basic configuration consists of solid body and liquid, what in case of penetrant testing occurs between the discontinuities surface of the tested material and the penetrant which has penetrated into them. Considering this effect in the aspect of mechanical theory of adhesion, the configuration is influenced, among other things, by the sum of intermolecular interactions, which appear between its components. The sum of intermolecular interactions is the greater the larger the solid body surface is. For that reason, the surface development, which increases proportionally to the surface roughness, is very essential. The surface roughness is tested on the surface profile which is formed by the line of intersection of this surface by a plane at right angle. The popular method of the roughness measurement is the determination of the arithmetic mean deviation of the roughness profile, marked usually by Ra symbol. It is defined by the arithmetic mean in the absolute value of deviations in surface profile from the determined line of the roughness profile mean within the specified test interval. Consequently, owing to the irregular shape, the number of valleys to which the penetrant can infiltrate increases. Penetration of liquid depends mainly on its viscosity, pressure, temperature, time of infiltration as well as on the depth and cross-section of the valleys. The process of infiltration of the penetrant into the surface of the test material can be expressed by the Poisseulle’s law and the capillary pressure equation. When these relations are combined, the following is obtained [1, 4, 5]:

\[
h_{\text{wp}} = \frac{r_w \cdot \gamma \cdot \cos \theta}{2\mu} \cdot \frac{a}{c} \cdot \left(1 - e^{\exp(-ct)}\right)
\]  

where:
- \( h_{\text{wp}} \) – depth of penetrant infiltration into the valley of rough material, \( m \)
- \( \theta \) – wetting angle, which is formed by the penetrant with rough material.

The assumptions made for derivation of the formula do not illustrate fully the real conditions, because it was assumed that the valleys in rough material are of capillary tube shape, \( 2r_w \) in diameter, as well as it was excluded any chemical or electrostatic interactions between the penetrant and test material. Nevertheless, the equation shows the essential mechanism of the infiltration of the penetrant into the valleys of the rough material. On the basis of the equation it can be stated that the increase in the valleys diameter makes the penetration easier, whereas the penetrant viscosity reduces it. Viscosity depends on temperature what was not taken into consideration in the equation. Assuming that the pores and valleys in the material into which the penetrant infiltrates are the capillary tubes, \( r_w \) in radius, the penetration process is described by the Washburn’s equation. In this case the depth of penetrant infiltration into the rough material, \( h_{\text{wp}} \), is shown by the equation (2) [6]:

\[
h_{\text{wp}} = \left(\frac{r_w \cdot \gamma \cdot \cos \theta}{2\mu}\right)^{0.5}
\]  

The above equation enables to determine the time which is necessary for filling the material valleys by the penetrant. Moreover, the following relationship has been formulated [6]:

\[
cos \theta(t) = cos \theta_\infty \cdot \left[1 - a \cdot e^{\exp(-ct)}\right]
\]  

where:
- \( \theta_\infty \) – wetting angle after endless time duration; it is the stabilized \( \theta \) angle value which is achieved in the time from several seconds to several dozen minutes.
- \( a, c \) – constant values for the specified arrangement which depend on characteristics of the penetrant and the rough material.

However, when the equations (1) and (3) are combined, the following relationship is obtained:

\[
h_{\text{wp}}^2(t) = \frac{r_w \cdot \gamma \cdot \cos \theta_\infty}{2\mu} \cdot \left[t - \frac{a}{c} \cdot (1 - \exp(-ct))\right]
\]  

The infiltration of the penetrant into the valleys in material is affected mostly by the \( r_w \) value. It should not be considered uncritically, however, because of many simplifications and the fact that real arrangements are significantly different from the model ones. The penetrant and penetrated material characteristics are an additional aspect [6].

Adhesion phenomena are also interpreted following the electrostatics. According to this theory, the electron flux may flow, when two different materials are moved close one to another. Parameters defining the flow of electron flux, i.e. its intensity and time, depend on many factors. Among them is the distance to which the materials have been moved close one to the other as well as differences in electronic work function from particular materials. The principle is such: the higher electronegativity between materials is, the greater is the intensity of electron flux flow. As a result of such a flow, on the side of less electronegative material, on its surface layer, the layer of positive ions is formed what is an excess
positive charge. However in the surface layer of the more electronegative material electrons are settled, what, in turn, is an excess negative charge. The consequence of such a process is generation of so called double electric layer, situated in the interfacial zone, that is between the penetrant and the material into discontinuities of which the penetrant has got. Attractive forces formed in this way are described by the Coulomb’s law. They counteract the separation of materials, so they are one of the components of adhesion. Their force depends on the surface charge density, which occurs in the both parts of double electric layer [7, 8].

The adhesion can be considered also on the basis of diffusion, that is of reciprocal passage of particles of two different materials being in close contact. It happens as a result of the difference in thermodynamic potentials of particles in both adjacent materials. However, the adhesion effect can appear, if the solubility of materials in this arrangement is the same or similar. Such a situation happens mainly in case of polymeric materials.

The next theory of adhesion has been developed on the physical-chemical background. It is called also the intermolecular interaction theory. The adhesion effect is shown as the mutual interaction of intermolecular forces which occur between penetrant particles and the material into which the penetrant gets. Everything is based on physics, so if all forces and moments are known, each phenomenon can be described. In order to understand the physical-chemical theory of adhesion the nature and properties of intermolecular forces should be examined. The action of intermolecular forces is connected with their potential energy, i.e. the ability for doing a work. Therefore, it results from the above statement that the intermolecular force can be defined as the derivative of the potential energy relative to the path on which it acts [6].

Each atom consists of the nucleus with the positive charge and electrons with the negative charge which rotate around it. Between atoms which are located sufficiently close one to another some repulsive or attractive forces can occur. The value and the direction of the forces of this type depend on the size and distance of atom nuclei as well as on the size and pattern of the electron cloud. Therefore, each molecules (atoms) arrangement has the potential energy which depends on the distance of their nuclei and according to the Lennard-Jones’ equation it is of the following form [9, 10]:

$$E = \frac{A}{r^6} - \frac{B}{r^3}$$  \hspace{1cm} (5)

where:
- \(A\) – repulsive constant, characteristic for the particular type of molecules, \((\text{pm} \cdot \text{meV})^1\)
- \(B\) – attractive constant characteristic for the particular type of molecules, \((\text{pm} \cdot \text{meV})^6\)
- \(r\) – distance between atom nuclei, .

From the equation (5) the value of intermolecular forces can be determined:

$$F = -\frac{dE}{dr} = \frac{12A}{r^{12}} - \frac{6B}{r^7}$$  \hspace{1cm} (6)

It results from the above equations, that the attractive forces take action in much larger range than the repulsive ones. The repulsive forces are generated only in case of direct contact of atom nuclei. On the basis of equation (6), between two atoms situated in the distance \(r\) [6] three cases can be distinguished:

1) for \(r > \left(\frac{2A}{B}\right)^{1/6}\) – attractive forces occur between atoms,
2) for \(r = \left(\frac{2A}{B}\right)^{1/6}\) – attractive and repulsive forces are balanced,
3) for \(r < \left(\frac{2A}{B}\right)^{1/6}\) – between . atoms there occur repulsive forces.

In order to achieve an adhesion junction, the molecules of the penetrant and the material which is wetted should be moved close one to another to such a distance which would enable to generate sufficient attractive forces between them. Too close position will not have a negative impact, because attractive forces are of much larger range than repulsive ones. The attractive forces between atoms or molecules are of essential importance [6].

Ones of the attractive molecular forces are the van der Waals’ forces which have been determined basing on the Clayperon’s law for ideal gases. After modification, the law can be expressed as follows [6]:

$$\left(p + \frac{an^2}{v^2}\right) \cdot (V - bn) = nRT$$  \hspace{1cm} (7)

where:
- \(p\) – pressure, \(\frac{N}{m^2}\)
- \(a\) – constant, characteristic for attractive forces, \(m^4\)
- \(n\) – number of moles,
- \(V\) – volume, \(m^3\)
- \(b\) – constant, characteristic for the particular gas, including the absolute size of molecules, \(m^3\)
- \(R\) – gas constant, \(\frac{J}{\text{mol} \cdot \text{K}}\)
- \(T\) – temperature, \(K\).

The van der Waals’ forces occurring among molecules and atoms of all bodies can be divided into several essential groups [6]:

- dispersion forces – called the London’s forces,
- orientation forces – called the Keesom’s forces,
- induction forces – called the Debye’s forces,
- multipole forces,
- conformation forces.

Dispersion forces are of the utmost importance. They are generated when the elementary dipoles are formed as a result of motion of electrons around the nucleus. Considering the insulated atom model, it is assumed that its spatial charge is distributed symmetrically within its nucleus. However, the quantum mechanics says that electrons are in the continuous motion what causes the lack of symmetry in the charge distribution. Then, the atom forms a dipole, and its dipole moment is changed continuously. Such a dipole, called a fluctuating dipole, generates quick-changing electric field through which it influences the other atoms and induces in them dipole moments. These atoms influence the first one in the same way. So, each atom is composed of the collection of instantaneous elementary dipoles and each dipole conforms to one of electrons. Every atom has as many instantaneous
The relationship is expressed in the following form:

\[ U_r \approx -\frac{3a^2}{4r^6} \]

where:

- \( a \) – polarization coefficient, characterizing the ability of an atom to deformation of the spatial charge distribution in the outer electric field, \( m^3 \)
- \( r \) – distance between two centres of the atoms attracting one another.

However, in case of two different atoms, i.e. between the penetrant and the material into which the penetrant infiltrates, the relationship is expressed in the following form:

\[ U_r \approx -\frac{3a_1a_2}{2r_{12}^6} \cdot \frac{l_1l_2}{l_1^6} \]

The subscripts 1 and 2 relate to the individual atoms, whereas the other symbols are of the same meaning as those in the previous equation. It results from the equations that the atoms have a part of electrons weakly bounded with their nuclei and thereby their mobility is greater. More frequent changes of electrons position bring about the stronger dispersion effect. The energy of these interactions is inversely proportional to the six power of the distance between molecules and directly proportional to the product of coefficients of molecular polarization. Dispersion forces appear between the same atoms as well as between the different ones. Each atom can interact simultaneously with many others. The reach of interaction is 1 nm what forces sufficient approach of molecules. Energy of these interactions is equal or less than 10 kJ/mole, indeed, but very often these interactions are those which determine the occurrence of the adhesion effect. The characteristic feature of these interactions is that they do not depend on temperature [6].

The orientation forces occur between molecules which are of durable dipoles nature. These molecules are characterized by different electronegativity, i.e. the ability of penetration of electrons from other atoms. According to quantum mechanics, the presence of electrons near the more electronegative atom is more probable than near the less electronegative one. This is shown by the arrangement of two different concentrated charges which are distributed in the distance \( d \) one from another and are of the opposite character. Such an arrangement is called the dipole and is characterized by the dipole moment value determined by the formula:

\[ \mu_{md} = q \cdot d_i \]

where:

- \( q \) – absolute value of each charge of this dipole, \( j, ES \)
- \( d_i \) – distance between two different concentrated charges of opposite character, \( \mu m \).

The dipole moment of the molecule is the sum of vectors of particular dipole moments which act in the molecule. However, the dipoles cannot be considered as stiffly situated arrangements because they have the rotation ability. The rotation possibility is the result of quantum effects, while the interaction energy of two dipoles can be shown as follows [6, 12]:

\[ U_r = -\frac{\mu_{m1} \cdot \mu_{m2}}{k \cdot T \cdot r_d^6} \]

where:

- \( k \) – Bolzman’s constant, \( \frac{J}{K} \)
- \( T_b \) – temperature, \( K \)
- \( r_d \) – distance between the centre of two dipoles, \( \mu m \).

If dipoles are considered as the stiff arrangement, the potential energy of their interactions depends on the product of their dipole moments, average distance between them and mutual position among themselves. In this arrangement their interactions are of electrostatic nature while the dipole moment originates from asymmetric distribution of electrons. Usually, the orientation forces energy does not exceed 10 kJ/mole, however these interactions decrease quickly when the temperature increases, because it gives rise to the molecule motion. This, in turn, disturbs the dipole orientation [6].

The Debye’s forces, called otherwise induction ones, arise between non-polar molecules which have not the stable dipole moment and the stable dipoles. When the electrons approach the stable dipole, they influence separately on each pole of the stable dipole. Therefore the non-polar molecule becomes the induced dipole as a result of displacement of electric charges. This is the mechanism of formation of induction influence of the type dipole-induced dipole which can be shown by means of the formula:

\[ U_D = -\frac{\mu_{m1} \cdot \mu_{m2}}{r_d^6} \]

Such a process of formation of induced dipole is called colloquially polarization. The polarization consists of three components: electronic, atomic and orientation ones. Every one of these components depends on the frequency of the external electromagnetic field. The induction energy is much lower than the disperse and orientation energies because usually it is 2 kJ/mole. In case of intermolecular actions its contribution in potential energy is lower than 10% of polar or disperse interactions what is an evidence that its importance in adhesion processes is rather minor. Just as in case of orientation interactions, the induction actions become weaker when the temperature increases [6].

The conformation forces arise in consequence of rotation of atoms or their groups around intermolecular bonds what results in changes in their positions. The rotation is connected with changes of atoms position within electrostatic field of an individual molecule what changes interactions between its fragments. Multipole forces are the result of internal
compensation of components of atom dipoles or atom groups within the molecule. Both conformation and multipole forces are very small but usually they appear so as dispersion forces.

Recapitulating, the van der Waals’ forces are the main source of adhesion phenomena but not the sole. They occur always when molecules or atoms have been approached themselves within the distance less than 1 nm [13].

During formation of adhesive junction, chemical bonds between atoms of adjacent bodies can occur. Formation of chemical bonds is connected with reconstruction of electron structure of these atoms. The electrons taking part in this process are called the valence electrons. In adhesion processes the following bonds are considered: covalent, ionic, hydrogen and acid-basic ones [14].

The covalence bond, called also atomic one, forms in consequence of arising of common electron pair for two coupling electrons. It is the result of penetration of atomic orbitals on which there are single electrons with the reverse spin orientation. In the result of such an action the molecular orbital comes into being which couples two atoms by means of the common electron pair. The covalent bond energy is within the range of 400 – 600 kJ/mole. In spite of so great energy, the covalent bonds rarely are an agent which brings about the adhesion of two different materials [14-17].

The next type of chemical bond which can take part in adhesion of two different materials is the ionic bond forming between two atoms differing considerably in electronegativity. The more electronegative atom takes over an electron from the less electronegative one and thereby it becomes the negative ion, i.e. the anion, whereas the atom which has emitted the electron has become the positive ion, i.e. cation. Therefore, in consequence of electrostatic interactions, ionic bonds are formed, the energy of which is within the range of 200-400 kJ/mole but their participation in creation of adhesive bonds is minimal [14, 19].

In the adhesion process, hydrogen bonds are of great importance. The hydrogen bond, called also the hydrogen bridge, is the coupling of two atoms by means of hydrogen atom. The occurrence of the bonds of this type is usually limited to liquids and solid bodies. In order that the hydrogen bridge may be created, the coupling on the stage of hydrogen atom with another atom (for instance atom X) must be polarized. In this arrangement, the hydrogen atom is transferred to the joint electron pair and thereby the hydrogen atom becomes the partial positive charge. The last stage in formation of the hydrogen bond is the occurrence, in sufficiently close distance, an atom (for instance atom Y) which has a free electron pair and renders it accessible to the hydrogen atom. After moving atoms X-H close to the atom Y, the bond X-H----Y is created. The energy of these bonds is within the range of 15-50 kJ/mole. The energy of hydrogen bonds consists of the sum of the following interactions [6]:

- dispersion ones taking place at the momentary dipole moment,
- electrostatic ones which happen when X-H molecule approaches the atom Y while the original distribution of charges is not disturbed,
- those caused as a result of transition of an electron pair onto the orbital connected with the hydrogen atom.

Donor-acceptor bonds, otherwise called acid-basic ones, often occur between solids and liquids, that is to say between the test material and the penetrant. In these bonds, acids can be the acceptors of electrons, because their electron shells are not filled entirely. Bases, in turn, are in possession of a free electron pair which is transferred to acids whereby the bond is formed [6].

3. Summary

Non-destructive testing is applied successfully in many branches of industry. One of the most popular methods of detection of surface imperfections is penetrant testing. Owing to its simplicity and low costs, the method has been developed for almost hundred years. The testing consists in penetration of a bright liquid called penetrant into discontinuities having their outlets at the surface of the material under examination, and next “drawing up” of this liquid from discontinuities on the surface by means of the developer. The time of development, in accordance with European Standards, is 10-30 minutes. Practically, the time ranges from several minutes to a dozen or so hours and is different for particular materials. In technical publications, it can be found the description of reactions and interactions of the penetrant whereas the impact of the test material on these interactions is not explained. There is lack of information on the development time for individual materials.

The difference in development time for various materials is caused by adhesion effect occurring between penetrant and test material.

Although the number of publications on adhesion is still increasing, there is no uniform theory relating to this effect up to now. There are many theories and each of them has its own grounds, referring to selected observations. However in none of them there is the complete description of all phenomena connected with adhesion. Sometimes it happens that some theories refer to the same processes but apply different notions. In this situation it can be accepted the generalized theory of adhesion based mainly on physical-chemical grounds, more specifically, on van der Waals’ forces. The investigations explain why van der Waals’ forces, even though they are small, are the essence of the adhesion process. There are two reasons for that. The first one is the fact that van der Waals’ forces are of universal nature, i.e. they form between any molecules and atoms what means that their joint influence is considerable. The second reason is much longer range within which these bonds act in comparison with the other bonds. Substantial attraction under van der Waals’ forces can be achieved at longer distance than in case of other bonds. Recapitulating the adhesion theories, it can be formulated the following main conditions which must be met that adhesion joint may be formed:

- two bodies can create the adhesive joint when their molecules are in the distance less than 0,9 nm,
- great attractive force between the molecules should be connected with the lowest potential energy of the bond formed in this way.

The generalized theory of adhesion shows the direct connection between intermolecular forces and the distance
between molecules. The other theories, however, are focused only on selected issues connected with adhesion, what, sometimes, results in contradictory conclusions. In consequence, none of adhesion theories can be of universal nature and cannot be directly related to the time of development in penetration testing. The bibliography survey allows to designate the aim and scope of the work which will be shown in subsequent papers. The influence of selected materials should be verified and the result will show the adhesion value between the penetrant and material being wetted. In the literature survey given below it has been found that the surface roughness also influences the adhesion. Therefore, the surface roughness is the next material factor which should be tested. It is expected also that the development time can be affected by the volume of penetrant in the discontinuity. To this end, the discontinuity width will be also taken into consideration in further investigations.

Therefore, the investigations will be aimed at the determination of the development time for the main construction materials as well as of the influence of particular factors such as:

- type of material,
- surface roughness in place of the imperfection and
- imperfection width,

on this time.

The result of the investigations should be the formulation of the relationship of the development time vs. the above mentioned factors. The relationship should define the extent to which particular factors (independent variables) influence the development time (dependent variables). As it has been mentioned, in accessible nowadays scientific-technical literature there is lack of this information.

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