Numerical calculation of laser welds nanocomposite formation parameters for solders based on proteins and carbon nanotubes

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Abstract. Laser welding is an alternative method of biological tissues joining. One of the actual tasks of laser welding of biological tissues is to determine the weld depth by a non-invasive method during surgery. The paper presents a model for calculating the duration of the formation of welds depending on the density of laser radiation power and the depth of the joint. The calculations were performed for the laser beam diameter $d = 1.1$ mm, power density in the range from 10 to 25 W cm$^{-1}$, weld formation depth $l$ in the range from 0.2 to 1 mm and solders based on aqueous dispersions of bovine serum albumin, indocyanin green and single-walled carbon nanotubes.

1. Introduction
Laser welding of biological tissues is an alternative to the classical methods of joining biological tissues: using threads, glue, etc. This is a non-contact sterile method for the reconstruction of biological tissues, which excludes the use of foreign materials (thread, staples, glue, etc.) and forms sealed welds.

An analysis of several ways of connecting blood vessels was carried out in [1]. The use of braces shortens the duration of the anastomosis, but is expensive, limited in size, and difficult to handle. The use of glue will shorten the time and facilitate the anastomosis, but may cause allergic reactions and the bond strength is low.

Laser welding is usually carried out at a temperature of 45-65 °C without [2, 3] or with a special solder [4, 5]. A solder is necessary to increase the tensile strength of welds and reduce the thermal necrosis degree of biological tissues. As a rule, these are aqueous dispersions of bovine serum albumin (BSA) and an exogenous chromophore indocyanin green (ICG). It is possible to add single-walled carbon nanotubes (SWCNTs) to increase the strength as a reinforcing framework [6].

As a consequence of the solder due to absorption of laser radiation, conformational changes of BSA molecules occur. The tertiary and quaternary structures of the protein are destroyed, and the chemical bonds that form these structures are released. Then, the broken chemical bonds are restored, but in a different, disordered sequence. As a result of the above process, chemical bonds appear between previously separate protein molecules and a spatial composite is formed from BSA. It is rather difficult to assess the weld nanocomposite formation degree during an operation. The surgeon is guided by his experience and the appearance of the weld. In this work, calculations of the exact laser welds formation time are carried out, depending on the depth and solder composition. The obtained data can be used during operations to ensure the required depth laser welds formation with a minimum area of thermal necrosis of biological tissues.
2. Materials and methods

2.1. Mathematical model

The composite formation degree is directly proportional to the number of newly formed chemical bonds, and this, in turn, to a BSA conversion $\alpha$.

By definition, the chemical reaction conversion is:

$$\alpha(t) = \frac{C'_t}{C_0}$$

(1)

where $C_0$ and $C'_t$ – the concentrations of native albumin at zero time point and time point $t$, $C''_t$ – concentration of denatured albumin.

The relation $\ln \frac{C_0}{C'_t}$ can be defined as a denaturation function $\Omega(t)$:

$$\Omega(t) = \ln \frac{C_0}{C'_t}$$

(3)

From 1, 2 and 3 it follows:

$$\alpha(t) = \frac{e^{\alpha} - 1}{e^{\alpha}}$$

(4)

According to the laws of chemical kinetics:

$$\Omega(t) = \int_0^\tau K(T) dt.$$  

(5)

According to the Arrhenius equation:

$$K(T) = A e^{\frac{E_a}{kT}}.$$  

(6)

Thus, the denaturation function $\Omega(t)$:

$$\Omega(t) = \int_0^\tau A e^{\frac{E_a}{kT}} dt.$$  

(7)

where $A$ – the preexponential factor of the Arrhenius equation, $E_a$ – the activation energy $R$ – the universal gas constant, $T$ – the temperature, $t$ – a time, $\tau$ – the moment in time. At the conversion level $\alpha = 0.63$, the welded joint nanocomposite was considered formed [7].

The power of laser radiation is directly proportional to the intensity; therefore, the Beer–Lambert law can be used in the following form:

$$P = P_0 e^{-k_\lambda l},$$

(8)

where $P_0$ – the initial intensity of laser radiation, $P$ - the intensity of laser radiation after passing through the solder layer with extinction $k_\lambda$ and thickness $l$.

The total absorbed energy of the $i$-th layer of the solder $Q_i$ is spent on heating the solder ($Q_i^{\text{heating}}$) and denaturation BSA ($Q_i^{\text{denaturation}}$):

$$Q_i = Q_i^{\text{heating}} + Q_i^{\text{denaturation}}.$$  

(9)

The heating value of the $i$-th layer of the dispersion was determined as follows:

$$Q_i^{\text{heating}} = c m \Delta T,$$

(10)

where $c$ – the heat capacity of the dispersion, $m$ – the mass, $\Delta T$ – the heating temperature of the $i$-th layer of the solder. It should be noted that this approach assumes a uniform distribution of physical characteristics in the volume of the $i$-th layer.

The necessary characteristics of laser radiation for calculating the laser weld nanocomposite formation parameters are taken from previous studies [8]. A diode continuous laser was selected with a wavelength $\lambda = 810$ nm, a laser beam diameter $d = 1.1$ mm and a power density from 10 to $25$ W-sm$^{-2}$. 

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Aqueous dispersions of BSA (25 wt%) + ICG (0.01 wt%) and BSA (25 wt%) + ICG (0.01 wt%) + SWCNTs (0.1 wt%) were considered as solders under investigation.

2.2. Thermodynamic characteristics measurement

A preexponential factor of the Arrhenius equation and an activation energy in solder were determined using the dynamic scanning calorimetry method.

Researches were conducted with use of the differential scanning calorimeter of Netzsch DSC 204 F1 Phoenix (Netzsch-Geratebau GmbH, Germany). The results were processed in Netzsch Proteus.

The activation energy of the BSA denaturation process ($E_a$) was determined by the Ozawa-Flynn-Wall method:

$$\ln \beta = -1.0516 \frac{E_a}{RT} + \text{const.}$$  \hspace{1cm} (11)

where $\beta$ – the heating rate, $R$ – the universal gas constant, $T$ – the temperature.

The pre-exponential factor of the Arrhenius equation ($A$) was determined by the Kennedy-Clarke method:

$$\ln \left( \frac{bg(\alpha)}{T - T_0} \right) = \ln A - \frac{E_a}{RT},$$  \hspace{1cm} (12)

where $\alpha$ – the conversion, $E_a$ – the activation energy, $T$ – the temperature.

The conversion for the Kennedy-Clark method was determined by:

$$\alpha = \frac{\int_{t_S}^{t_F} DSCBL - DSC dt}{\int_{t_S}^{t_F} DSCBL - DSCBL dt},$$  \hspace{1cm} (13)

where $t$ is the time, $t_S$ is the denaturation peak start temperature, $t_F$ – is the denaturation peak end temperature, $DSCBL$ – is the denaturation process baseline, $DSC$ is the albumin denaturation process curve.

2.3. Spectroscopy

Absorption ranges for dispersions were received by Thermo Fisher Genesys10 sUV-vis spectrometer. Measurements were made in the wavelength range 190-1100 nm using a quartz cuvette 5 mm thick. For comparison, a cuvette with water was used. The attenuation coefficient $k_\lambda$ wavelength dependencies $\lambda$ were measured.

3. Results and discussion

3.1. Dynamic scanning calorimetry

Figure 1 shows the activation energies and the pre-exponential factors logarithms depending on the conversion of solder based on BSA (25 wt%) aqueous dispersion.

![Figure 1](image.png)

**Figure 1.** Dependence of activation energy and pre-exponential factor logarithm on conversion of solder based on BSA (25 wt%).
The average albumin thermal denaturation activation energy in the 25 wt% BSA aqueous dispersion was 437 kJ·mol\(^{-1}\) and in the 25 wt% BSA + 0.1 wt% SWCNTs dispersion was 711 kJ·mol\(^{-1}\). Figure 2 shows the activation energies and the pre-exponential factors logarithms depending on the conversion of solder based on BSA (25 wt%) + SWCNTs (0.1 wt%).

![Figure 2. Dependence of activation energy and pre-exponential factor logarithm on conversion of solder based on BSA (25 wt%) + SWCNTs (0.1 wt%).](image)

The average pre-exponential factor logarithm in the BSA (25 wt%) aqueous dispersion was 141 and in the BSA (25 wt%) + SWCNTs (0.1 wt%) dispersion was 230.

### 3.2. Spectroscopy

The absorption spectrum results are shown in Figure 3. Solders solder based on BSA (25 wt%) + ICG (0.01 wt%) and BSA (25 wt%) + ICG (0.01 wt%) + SWCNTs (0.1 wt%) were analyzed. The using solders absorption range is in the range of 790-810 nm, which corresponds to the used laser wavelength. For comparison, BSA (25 wt%) and BSA (25 wt%) + SWCNTs (0.1 wt%) graphs are presented.
Figure 3. Used solders absorption spectrums: a – BSA (25 wt%) + ICG (0.01 wt%) (solid line) and BSA (25 wt%) (dashed line); b – BSA (25 wt%) + ICG (0.01 wt%) + SWCNTs (0.1 wt%) (solid line) and BSA (25 wt%) + SWCNTs (0.1 wt%) (dashed line).

3.3. Numerical modeling
Modeling was carried out at the following values of the preexponential factor of the Arrhenius equation ($A_{SA+ICG} = 1.88 \times 10^6$ s$^{-1}$, $A_{SA+ICG+SWCNTs} = 8.93 \times 10^9$ s$^{-1}$) and the BSA denaturation activation energy ($E_a^{SA+ICG} = 437$ kJ·mol$^{-1}$, $E_a^{SA+ICG+SWCNTs} = 711$ kJ·mol$^{-1}$) received by the differential scanning calorimetry.

Figure 4 shows the weld nanocomposite formation duration depending on the laser radiation power density for depths $l = 0.2\div1$ mm for solders based on water dispersions BSA (25 wt%) + ICG (0.01 wt%) (a) and BSA (25 wt%) + ICG (0.01 wt%) + SWCNTs (0.1 wt%) (b).

Figure 4. The laser welds formation duration depends on the laser radiation power density and the joints formation depth for solders based on BSA+ICG (a) and BSA+ICG+SWCNTs (b).

4. Conclusions
The used laser weld formation mathematical model has been described. Thermodynamic and optical characteristics of the used laser solders based on BSA, ICG and SWCNTs has been measured. The laser welds formation duration has been numerically calculated for different solder compositions. The findings can be used in laser welding of biological tissues during surgical interventions.

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