IMPROVING THE MECHANICAL PERFORMANCE OF UNIDIRECTIONAL CFRP BY METAL-HYBRIDIZATION

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Abstract
In CFRP primary structures the fraction of fibers aligned in load direction is limited due to the material's notch and impact sensitivity. As a result, stiffness and strength per unit weight of the laminate on a given direction are lower than the corresponding values for a unidirectional composite. The present investigations show that the on-axis residual-strength-after-impact of unidirectional laminates can be increased significantly by interleaving thin steel foils and highly orthotropic laminates become applicable. Grit-blasting, as a common pre-treatment process for stainless steel surfaces, is not feasible for thin foils due to the increased risk of damaging the metallic substrate. Therefore, different pickling processes are investigated as a non-mechanical alternative pre-treatment. Thus, superior adhesion properties are achieved compared to mechanical pre-treatments.

1 Introduction
In a variety of aerospace applications, the industry's increasing requirements for higher structural efficiency compete with the fundamental requirements for damage tolerance. Especially, when high specific uniaxial mechanical properties are aspired, notch and impact sensitivity properties limit the fiber fraction in load direction drastically, because laminates are created by stacking lamina with various orientations. Additionally, the thickness of equally orientated layers is limited to reduce crack distribution. Therefore, buckling endangered struts with high stiffness needs in particular, suffer a loss of their lightweight potential due to residual-strength evaluation. Recognizing these limitations, a new lay-up to increase the degree of capacity utilization of the CFRP is proposed [1]. The approach to reduce the aforementioned disadvantages uses a new laminate lay-up with metal layer thickness less than 0.08 mm and low metal volume fractions. The metal layers replace +/-45° and 90°-plies. Hence, stiffness and strength in 0°-direction are not reduced compared to the use of variant fiber directions, while residual-strength-after-impact is improved compared to pure unidirectional (UD-) laminates.
High specific stiffness and strength properties in uniaxial direction are in particular demanded in framework constructions. Also buckling or eigenfrequency requirements can increase the interest on materials with high stiffness properties. *Kolesnikov et al.* [2] worked out the weight saving potential of a framework design compared to an existing sandwich design of a launcher´s payload adapter. In this study, the weight reduction of the struts was regarded as primary optimization parameter. Struts of pure CFRP and CFRP-metal-laminates were investigated following a classical optimization method. First radial loads and bending moments in the frames were estimated as a function of the number of struts. Subsequently, for a given

optimal strut quantity, laminate thickness, strut diameter and lay-up were systematically varied to reach similar margin of safety for compression and tensile stress as well as for local and global buckling in the struts. As a consequence of the framework design, the struts are only loaded in longitudinal direction. This allows a unidirectional alignment of all carbon fibers as long as damage tolerance needs are sufficiently satisfied. Therefore, additionally to pure CFRP lay-ups, unidirectional fiber metal laminates (CFRP-titanium and CFRP-steel) with a metal volume fraction φ_M of 1.43 – 7 % were investigated analytically. The results showed a weight saving potential up to 37 % for a CFRP-steel lay-up compared to the CFRP-cone as sandwich structure. Therein, coupling elements are considered, neither for the framework nor for the sandwich design. This CFRP-steel lay-up also reaches 23 % weight saving compared to struts made of pure CFRP with high on-axis fiber fraction (75/25/0). The results were validated by a numerical simulation showing very similar values. These analytical and numerical results underline the demand for high on-axis specific stiffness properties. However, damage tolerance properties have to be proven for this novel material.

2 CFRP-UD-Steel Laminates

Research on Fiber Metal Laminates (FML) is performed since over 40 years to improve the material performance of the individual constituents and to overcome the disadvantages of both materials. Fiber metal laminates including aluminum alloys (ARALL, CARALL and GLARE) were investigated as well as FMLs including metal alloys like titanium or magnesium [3]. Each of these material combinations has its own motivations and requirements. The goal of the CFRP-UD-steel laminates is to increase the degree of capacity utilization for uniaxially loaded parts.

2.1 Mechanisms Improving Laminate Properties

The main advantages of the use of metal layers are stiffness and strength in 0°-direction, which are not reduced in comparison to the use of variant fiber directions. For lower metal volume fractions φ_M specific stiffness in 0°-direction is higher compared to common multiaxial CFRP-laminate lay-ups [4]. Additionally, transverse stiffness and strength are enhanced compared to unidirectional laminates. The longitudinal compression strength is increased as a consequence of the material combination and the ‘in-situ’-effect due to the high number of alternating interfaces [5]. In case of an impact or fracture, the metal layers deflect inter-fiber-fracture into delamination and serve as crack arrester layers (Fig. 1). FMLs are capable of absorbing energy through plastic deformation and through failure at the interfaces [6]. Thus, energy dissipation is elevated due to the increased number of interfaces within the laminate. Furthermore, peel-stresses at the free edges generated by the failure are reduced because the transverse contractions of a longitudinally loaded UD ν_{12} and metal ν_m are very similar in comparison to ν_{12} and ν_{21} in a multiaxial lay-up.

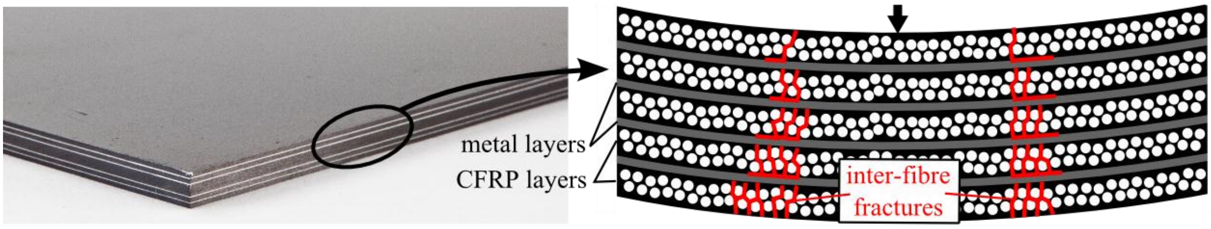

Figure 1: Deflection of inter-fibre-fractures [4].

2.2 Bilinear Material Model

Different constitutive uni- and biaxial material models were developed, accounting for lay-up, mechanical and thermal loading and the effect of plasticity and reversed plasticity (‘Bauschinger effect’) [7]. However, for a preliminary investigation, the bilinear model or

MVF-approach (Metal-Volume-Fraction) has the advantage of simplicity and its predictions of laminate stiffness E_L and yield strength $\sigma_{L,y.}$ are quite accurate [7]. For a narrow strip with fibers along the length and the Poisson effect free to occur, the stress-strain relationship can be described by Hook's law for the one-dimensional case (see Fig. 2). The laminate's longitudinal stiffness E_L and the thermal expansion coefficient in fiber direction α_L can be predicted by the rule of mixture as a function of the metal volume fraction φ_M [6]. In this approach the yield strength $\sigma_{M,y.}$ of the metal instead of the typically measured technical elastic limit $\varepsilon_{M,0.2}$ is needed, which can be determined as follows:

$$\sigma_{M,y.} = \left(\varepsilon_{M,0.2} - \frac{\sigma_{M,0.2}}{E_{M,pl.}}\right) \cdot \frac{E_{M,pl.} \cdot E_M}{E_{M,pl.} - E_M} \tag{1}$$

The required effective elongation at the technical elastic limit $\varepsilon_{M,0.2}$ and the plastic stiffness of the metal $E_{M,pl.}$ are calculated by:

$$\varepsilon_{M,0.2} = \frac{\sigma_{M,0.2}}{E_M} + 0.002 \tag{2}$$

$$E_{M,pl.} = \frac{\sigma_{M,ult.} - \sigma_{M,0.2}}{\varepsilon_{M,ult.} - \varepsilon_{M,0.2}} \tag{3}$$

Based on the permanent strain after failure $\varepsilon_{M,A}$, the effective elongation of the metal at failure $\varepsilon_{M,ult.}$ is:

$$\varepsilon_{M,ult.} = \frac{\sigma_{M,ult.}}{E_M} + \varepsilon_{M,A} \tag{4}$$

In literature it is assumed, that at cure temperature there are no internal stresses present and curing stresses are a function of curing temperature only [8]. Investigations performed by *Twigg et al.* [9] showed that there is even a stress transfer between tool and part and a stress is present at cure temperature. As a consequence, it is assumed in that stress free temperature T_{sf} is lower than curing temperature $T_{cure,max.}$ Further investigations by *Stefaniak et al.* and *Kappel et al.* showed that the stress is dependent on surface roughness as well [10, 11]. Therefore, an additional surface roughness dependency of the curing stresses in FMLs has to be assumed. The residual cure strain of the metal layer $\varepsilon_{M,R}$ and the composite layer $\varepsilon_{C,R}$ are estimated with the help of the differential temperature ΔT between the stress free temperature T_{sf} and the operation temperature $T_{op.}$. When the residual strains after cure are known, the yield strength $\sigma_{L,y.}$ and the ultimate strength $\sigma_{L,ult.}$ of the laminate can be predicted with the help of the corresponding elongations $\varepsilon_{L,y.}$ and $\varepsilon_{L,ult.}$. $E_{L,pl.}$ describes the plastic stiffness of the laminate after passing the yield point of the metal:

$$\varepsilon_{L,y.} = \frac{\sigma_{M,y.}}{E_M} - \varepsilon_{M,R} \tag{5}$$

$$\sigma_{L,y.} = [E_M \cdot \varphi_M + E_C \cdot (1 - \varphi_M)] \cdot \left(\frac{\sigma_{M,y.}}{E_M} - \varepsilon_{M,R}\right) \tag{6}$$

$$\varepsilon_{L,ult.} = \frac{\sigma_{C,ult.}}{E_C} - \varepsilon_{C,R} \tag{7}$$

$$\sigma_{L,ult.} = \sigma_{L,y.} + E_{L,pl.} \cdot (\varepsilon_{L,ult.} - \varepsilon_{L,y.}) \tag{8}$$

$$E_{L,pl.} = E_C \cdot (1 - \varphi_M) + \varphi_M \frac{\sigma_{M,ult.} - \sigma_{M,0.2}}{\varepsilon_{M,ult.} - \varepsilon_{M,0.2}} \tag{9}$$

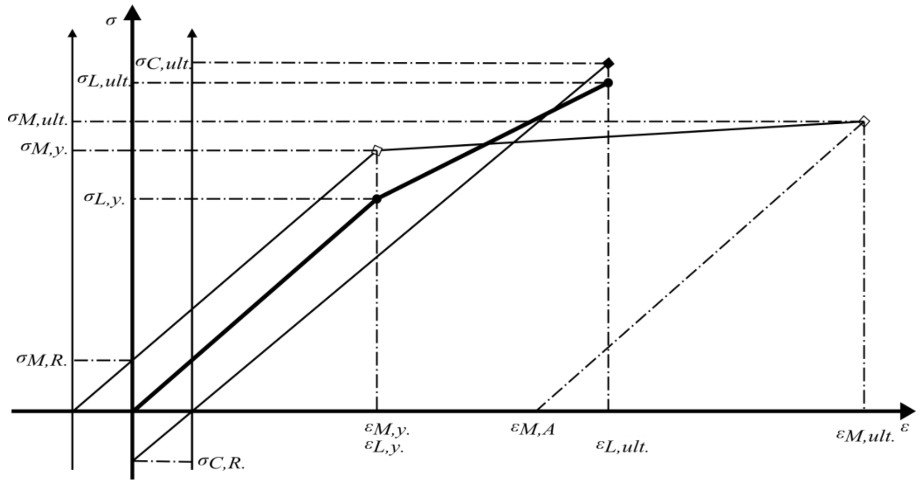

Figure 2: Stress-strain relations in bilinear model.

Due to the need of a high yield point of the metallic component and the galvanic corrosion between carbon and steel, 1.4310-stainless steel (X10CrNi18-8) is chosen for the following experiments. 8552/AS4 fabricated by Hexcel with 134 g/m^2 is used as prepreg for the experiments following the manufacturer's recommended cure cycle [12]. The basic properties of these materials are given in Table 1.

material°	tensile stiffness E_1 [GPa]	tensile stiffness E_2 [GPa]	density ρ [g/cm^3]	Source
steel 1.4310	185	185	7.9	[13]
CFRP 8552/AS4	141	10	1.58	[12]

Table 1. Specimens' material properties.

When creating the laminate lay-up of uniaxial loaded parts, designed as highly 0°-dominated as possible, the following stacking rules are common:

- Maximum number of similar orientated plies n ≤ 4 or maximum thickness t ≤ 1 mm
- Minimum 8 % of fibers in each of the four basic orientations.

These stacking rules are also used to design the multiaxial pure CFRP reference specimens (thickness t = 4 mm) for the following investigations. The resulting stacking for the particular laminate´s thickness to prepreg thickness ratio of the specimens is: (62.5/25/12.5). The on-axis stiffness E_R of this pure CFRP reference can be analytically calculated following Classical Laminate Theory (CLT) [6]. To provide an advantage of the CFRP-UD-steel laminates in specific stiffness properties compared to the CFRP reference, the selection of the metal volume fraction φ_M has to fulfill the following condition (ρ_L and ρ_R are the density of the CFRP-UD-steel laminate and multiaxial CFRP reference stacking respectively):

$$\frac{E_L}{\rho_L} < \frac{E_R}{\rho_R} \tag{10}$$

For the particular reference laminate, the metal volume fraction φ_M must be less than 12.3 % to fulfill the preceding condition (10). Fig. 3 shows the quantity of metal-CFRP interfaces n for three different metal layer thicknesses depending on the metal volume fraction φ_M and the corresponding specific stiffness E_L/ρ_L. It is obvious that for a metal foil thickness of 0.01 mm a volume fraction above 8 % is not achievable for the present material combination. For lower metal volume fractions the thicker metal foils only provide a few layers and interfaces. This relation indicates the need of preferably thin metal foils for common laminate and prepreg thickness ratios.

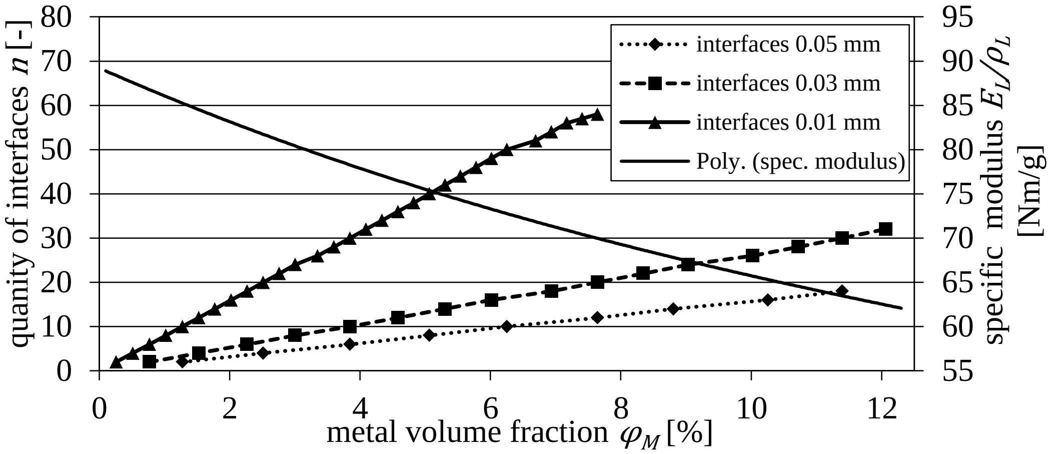

Figure 3: Quantity of interfaces n and specific modulus E_L/ρ_L dependency on metal volume fraction φ_M.

3. Surface Treatment

The surface treatment process can be subdivided into surface pre- and post-treatment [14]. There are two common surface treatments for Stainless Steel (SS), the 'grit-blast and silane process' (GBS) and the 'Boeing sol-gel process'. The GBS-process involves surface degreasing, abrasive removal of weakly adhered layers, grit-blasting and application of an epoxy-silane coupling agent [15]. Following the 'Boeing sol-gel process', the material is degreased and then deoxidized by using a wet or dry grit-blasting method. Finally, an aqueous sol-gel system, a dilute solution of a stabilized alkoxyzirconium organometallic salt and an organosilane coupling agent, is applied. Typically, an adhesive coating is then applied to the treated surface to generate a durable bond [16]. Thus, both treatments contain grit-blasting. However, grit-blasting cannot be used on thin metal foils (t < 0.08 mm) due to the serious risk of damaging the substrate or inhomogeneous work-hardening. Therefore, an alternative pre-treatment needs to be investigated.

Surface pre-treatments for metallic substrates are subdivided in physical, mechanical, chemical and electro-chemical treatments. Physical pre-treatments by plasma are not considered in the following due to their economic inefficiency for large surfaces. Additionally, electrochemical treatments are not considered because the possibility of pitting is increased for austenitic chromium-nickel steels [17]. Investigations of *Blohowiak et al.* [16] and *Mazza* [18] showed the poorest crack test performance for abraded surfaces. As a consequence, only chemical pre-treatments are considered in the present investigations.

Pickling is the most prevalent chemical pre-treatment for SS. For this purpose reducing or oxidizing acids are used. A nitric-hydrofluoric acid mixture is the most widely used solution for SS but involves problems such as the emission of NO_x fumes during the pickling process [19]. HCl-acid is usually not used because the formed $FeCl_3$ promotes pitting [17]. The main disadvantages of nitrate-free baths like H_2SO_4-HF-H_2O_2 are dark and adhesive deposits which can appear on the SS surface [19]. Essential constituents of these nitrate-free alternatives are hydrofluoric acid and an oxidizing agent. When hydrogen peroxide is used, it is common to utilize a secondary acid to account for the low stability of hydrogen peroxide in the presence of iron (ferric) ions [19, 20]. Usually, the initial ferrous ions are added to the idle bath as Iron-(III)-sulphate. The ferric ion (Fe^{3+}) participates in the pickling process and is converted to ferrous ion (Fe^{2+}). This reaction takes place at a specific potential that is obtained by the presence of hydrogen peroxide [20]:

$$2\,Fe^{3+} + 1\,Fe \leftrightarrows 3\,Fe^{2+} \tag{11}$$

Another function of the hydrogen peroxide is the conversion of the ferrous iron to ferric ion [20]:

$$4\,Fe^{2+} + 2\,H_2O_2 \;\leftrightharpoons 4\,Fe^{3+} + 2\,H_2O + 1\,O_2 \qquad (12)$$

The post-treatment process guarantees conservation and serves as coupling agent. For the 'Boeing sol-gel' process a dilute solution of an alkoxyzirconium organometallic salt and an organosilane coupling agent in combination with an acetic acid catalyst is used [16]. The schematic of the formed sol-gel layer is illustrated in Fig. 4.

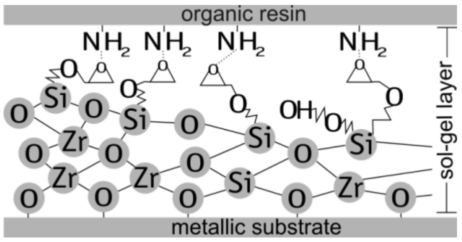

Figure 4: Schematic of sol-gel interaction [25].

In the present work different pickling processes were used as pre-treatment to replace mechanical treatment of the thin SS (1.4310) foils. Specimens for the evaluation of the adhesion performance were fabricated using nitric-hydrofluoric and nitric-phosphoric-hydrofluoric acid as well as the above mentioned nitrate-free solution. Acid concentrations and pickling durations were varied (see given numbering in Fig. 5) and the pre-treated metal foils were rinsed with deionized water before drying in an oven. After drying, the foils were post-treated with AC-®130 [21] and directly laminated with prepreg to prevent further oxidation. As reference pure UD-CFRP specimens and specimens with grit-blasted SS foils following the 'Boeing sol-gel' process were manufactured.

Adhesion performance is evaluated by determination of the apparent interlaminar shear strength by the short-beam method EN ISO 14130 [22]. The influence of the differing stiffness of the constituents in the hybrid laminate is neglected due to the low thickness of the single SS foil. It can be seen in Fig. 5 that the nitrate-free 3 pre-treatment in combination with the AC-®130 sol-gel post-treatment provides an even better apparent interlaminar shear strength than the reference 'Boeing sol-gel' process. Compared to the pure CFRP-UD reference, it has to be considered that the curing stresses do act on the same surface as the testing load. However, the specimens treated with the nitrate-free 3 process do all show cohesive failure in the matrix only. Furthermore, the environmental durability of the bond has to be evaluated by wedge crack extension tests.

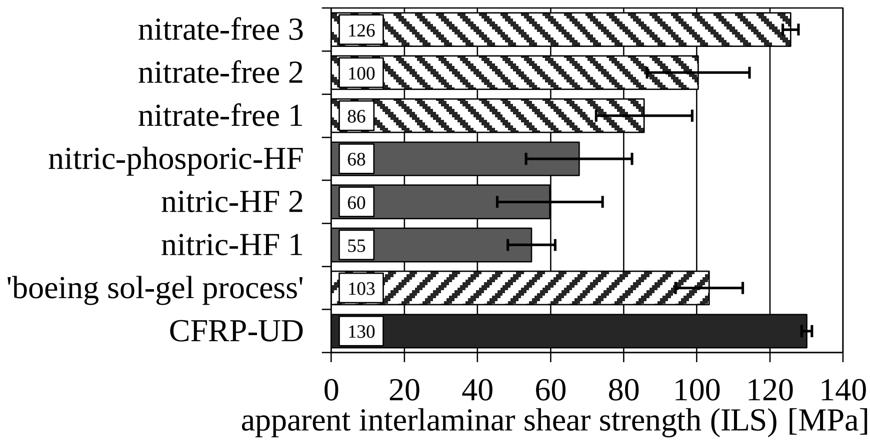

Figure 5: Apparent ILS using AC-®130 post-treatment.

4. RESULTS – MECHANICAL PROPERTIES

To evaluate the properties of the novel material, compression and 'compression-after-impact' tests were performed. Therefore, the unidirectional CFRP-steel specimens with a metal volume fraction φ_M of 7.5 % and metal layer thickness $t = 0.05$ mm were tested in comparison with a unidirectional and a multiaxial reference. Compression tests were performed following AITM1-008 [23] with combined shear and end loading. Compression-after-impact tests were based on AITM1-0010 [24] with 30 J impact only. The results in Fig. 6 show a catastrophic failure of the unidirectional specimens after impact and therefore no measurable residual strength. The 'compression-after-impact' strength of UD-CFRP-steel and CFRP-(62.5/25/12.5) are quite similar, whereas compression strength is increased by 49 % compared to the multiaxial reference. The compression modulus of UD-CFRP-steel is approx. 48 % higher than the CFRP-(62.5/25/12.5) reference. Regarding the specific properties of UD-CFRP-steel compared to CFRP-(62.5/25/12.5), specific compression strength and specific compression modulus are increased by 14 and 13 % respectively.

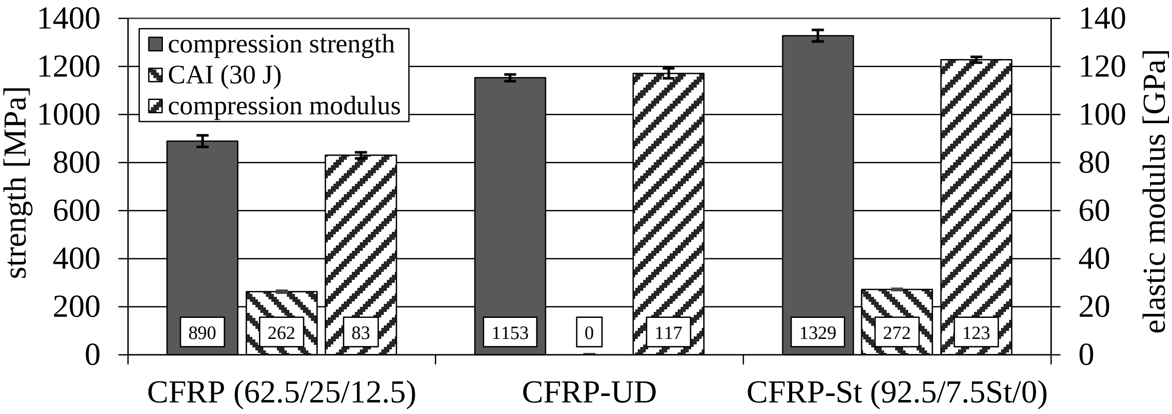

Figure 6: Compression properties.

5. Conclusion

Experimental investigations performed in this study show that residual-strength-after-impact of pure unidirectional CFRP laminates can be increased significantly by interleaving thin steel foils whereat compression strength and stiffness of the investigated unidirectional CFRP-steel laminates are improved in comparison to the unidirectional CFRP laminate. Compared to highly orthotropic pure CFRP laminates, composed confirm to stacking rules, specific compression strength and stiffness are increased by 14 and 13 % respectively. The investigations were performed for one particular metal volume fraction only. The investigated pickling process as pre-treatment of the foils provides even better adhesion properties than alternative processes, utilizing mechanical treatment. The pickling treatment in combination with the used sol-gel surface post-treatment offers the possibility to further reduce the thickness of the metal foils and to investigate the influence of metal volume fraction, metal layer thickness and lay-up on the residual-strength-after-impact.

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