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Novel approach for Reactive Bonding in Microsystems Technology

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Abstract: *In this work, first results of the development of highly reactive nanocomposites based on metallic nanoparticles for joining components for micro-electro-mechanical systems are presented. Reactive joining of micro-components received much attention in the last decade, as it enables the connection of components without the entire system being exposed to prolonged heat-load. This is important especially for the integration of different materials in microsystems as intrinsic stresses due to large differences in the thermal coefficient of expansion can be prevented. Here we present the general idea and very first results concerning the reactivity of different material combinations.*

Keywords: *reactive bonding, nano-composite, self-sustaining high-temperature synthesis*

I. Introduction

Exothermic reactions have been used since more than a century as an energy source for welding and soldering [1]. Thermite welding has a long tradition mainly in railroad track construction. Here, a self-sustaining, exothermic redox reaction is started at the joining point, forming elemental iron as a reaction product. The reaction temperature during the process is so high that the iron is liquid and fills the joining gap. In this way a permanent connection of the parts to be joined is formed after solidification.

In the last decade the ideas of self-sustaining high temperature synthesis have been adopted for microsystems technology [2,3]. They differ from the thermite process primarily by the materials used. However, the approach is comparable and the underlying ideas are basically the same. Reactive bonding, mostly used for wafer bonding applications, is performed by using highly reactive nanoscale multilayer systems as an intermediate layer between the bonding substrates. The multilayer system typically consists of a repetition of two alternating different thin metallic films where thousands of thin single layers are alternating. The reactive multilayer structures can be prefabricated in the form of nano-foils [4] or they can be deposited on the substrate surface prior to the bonding process. A commonly used deposition method for multilayer structures is magnetron sputtering. The self-propagating exothermic reaction within the multilayer system supplies the local heat to bond the solder films. Due to the large active contact surface between the reaction partners, the reaction front can spread very quickly, and the whole reaction takes place within a few milliseconds. Based on the limited temperature the rest of the substrate material is exposed to, temperature-sensitive components and materials with different CTEs, i.e. metals, polymers and ceramics, can be used without thermal damage. Especially for the packaging and soldering of micro-electro-mechanical systems (MEMS) this is very important as intrinsic stresses due to large differences in the thermal expansion coefficient can be avoided in this way.

While this concept relies on alternating nano-layers, here we present our ideas to expand this approach by the use of self-propagating reactive nanocomposites (RNCs) containing intermixed metal nanoparticles. In this approach we do not use a multi-layer system, but a nanocomposite consisting of nanoparticles of the reactants (e.g. aluminum, nickel, or titanium) [5]. Thus, with the use of a single reactive phase the joining can be performed in a single step. In the following we will outline this idea and present first results concerning the reactivity of different material combinations.

II. Concept

Bonding via reactive nano-composites relies on the idea to use of a single thick layer of intermixed metal nano-particles instead of a multilayer-structure of alternating nano-layers. The concept of the reactive nano-composite is schematically sketched in fig 1.

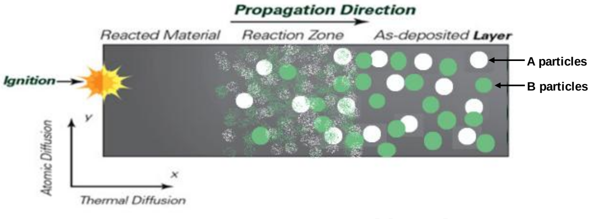

Fig. 1 Reactive Nanocomposite Material based on Nanoparticles

A mixture of reactive particles is deposited in a single, thick layer on a substrate. At a given position the mixture is ignited. The reaction front will propagate through the reactive layer until the whole layer has reacted to form the corresponding alloy. The heat generated throughout the process is used for bonding. For this approach to work, the generated heat must be sufficient in order to sustain the reaction and to lead to effective bonding of the substrates. Typically the substrates will have to be pretreated with some wetting layers and the nano-composite will be melting during the reaction process.

The advantage of this approach, compared to multilayer reactive bonding consists in the simplicity of the processing steps, since no multilayer structure has to be fabricated. A possibility for the whole sequence of process-steps is schematically outlined in Fig. 2. The nanoparticles with average diameters below 100 nm are homogeneously mixed and dispersed in a carrier liquid e.g. a volatile solvent to enhance handling properties and eventually to prevent unintended ignition. The solution is applied to the substrate and after solvent evaporation a dry layer of inter-mixed reactive nanoparticles is formed. The element to be bonded to the substrate (e.g. a cover lid) is aligned on top of the reactive layer and, while applying pressure, the reactive nanocomposite layer is ignited by a laser pulse or by the application of an external small heat-source. The resulting self-propagating exothermic reaction creates sufficient amount of heat to establish a bond between the substrates. During the reaction process an intermetallic phase is formed, which also briefly melts during the reaction and wets the joining partners. After cooling a stable compound is produced.

Due to the highly localized heating by this mechanism, the surrounding parts of the system do not get any significant heat charge, which makes the concept applicable for joining heterogeneous materials.

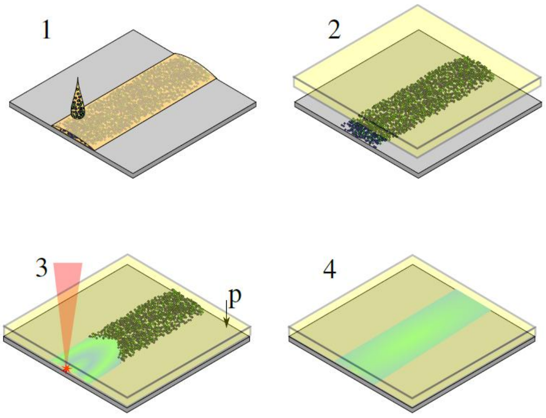

Fig. 2 sketch of the bonding process: 1: Deposition of the reactive nano-composites (which are dispersed in a suitable solvent) onto the substrate. 2: After solvent evaporation the nano-composite remains on the substrate and the device to be bonded is adjusted. 3: ignition of the reactive nano-composite, while the substrate and cover are held in place. 4: substrate and cover are bonded together

Furthermore, since the dispersion of the solution is a simple and fast process, patterning of complex joining structures can be done easily, without the use of complex multi-layer deposition techniques like sputtering or similar. Also inkjet printing techniques could be used for this step. However, this would require some addition effort in developing suitable printable pastes, instead of using solutions in a volatile solvent.

Overall there are a number of benefits of this process. As outlined above, it features high flexibility since the deposition of the bonding layer is possible by various means and in particular by printing techniques. This means it is a mask-less process and does not imply specific patterning. Notably, this leads to fast and affordable prototyping. As mentioned above the introduction of heat is very localized and thus it can be used for joining materials with a large CTE-mismatch or be applied to systems with temperature-sensitive components. Finally there is the possibility for contact-less ignition (via laser heating) which opens the possibilities to seal cavities under non-standard atmosphere.

On the other hand there are still a number of challenges, which have to be overcome. In particular one has to avoid oxidization of the reactive nano-particles prior to ignition. Also the choice of solvent in order to form stable solution without the risk of explosive evaporation is non-trivial and not completely solved at the current stage. And finally it is crucial to achieve a very close mixing of the particles and a dense structure in the reactive nano-composite after deposition. This point is important, in order to achieve a large effective contact area between the reaction partners.

III. Materials And Sample Preparation

As starting materials for the reactive process we used metallic nanoparticles in the form of solid samples obtained from IoLiTec. Spherical aluminum, nickel and titanium particles with nominal diameters from 18 nm to 60 nm were tested. In the remainder of the text we will label them in terms of the chemical element and the nanoparticle diameter e.g. "Al18" for the sample of aluminum nanoparticles with a nominal size of 18 nm. In the investigations we used different combinations of the materials, which are listed in Table 1. The metallic particles were handled under an argon atmosphere in a flow-box (see Fig. 3) as much as possible to prevent passivation with oxygen.

Table 1 Nanoparticles used and mixtures studied in this work.

Samples	Al 18	Al 40	Ni 20	Ni 60
Ti 60	X	X	X	X
Ni 60	X	X		
Ni 20	X	X		

Nano-composites of mixtures according to the above combinations were weighed in a stoichiometric ratio of the intermetallic phases AlNi and AlTi and dispersed in cyclohexane. To break up agglomerates of particles and obtain a homogeneous mixing of the dispersions an ultrasonic bath was used for at least one hour at 35 kHz. For the subsequent experiments individual droplets of the dispersion were dispensed on a metallized silicon substrate by hand as samples for further processing.

Ignition was performed with a 808nm diode laser, which was continuously driven with up to 500mW. The input power was continuously increased, while pointing the laser focus at the reactive sample. The reaction front can propagate throughout a sample only when the heat transferred laterally is sufficiently high for ignition of the adjunct material and at the same time the energy losses to the environment and the substrate is sufficiently low.

Ignition of thoroughly grinded Ni-Al samples was observed starting at 166 mW laser power. In the characterization tests presented here, only ultrasonic mixing of the components was performed without grinding. As we will see, this leads to localized reaction within the laser focus, without a self-propagating reaction front.

Fig. 3 Preparation of the nano-composites was done under protective atmosphere in a glove box.

IV. Experimental Results

In the following we present some first results. Analysis of the raw particles was done by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and x-ray powder diffraction (XRD). In general, the results showed high purity of the samples and low grade of oxygen contamination.

SEM analysis provides detailed micrographs of the samples, enabling the measurement of particle size distribution. In Fig. 4 a representative image is shown for the case of Ni20. To measure particle sizes, a semi-automatic image processing based approach was chosen. The SEM-micrographs were edited to enhance contrast and find edges between particles. These tasks were conducted using Gimp. After applying a color threshold, a watershed algorithm was used to differentiate between combined particles and finally. ImageJ was used to automatically find circular shapes and measure their diameter, area and ferret. (see Fig. 4(b))

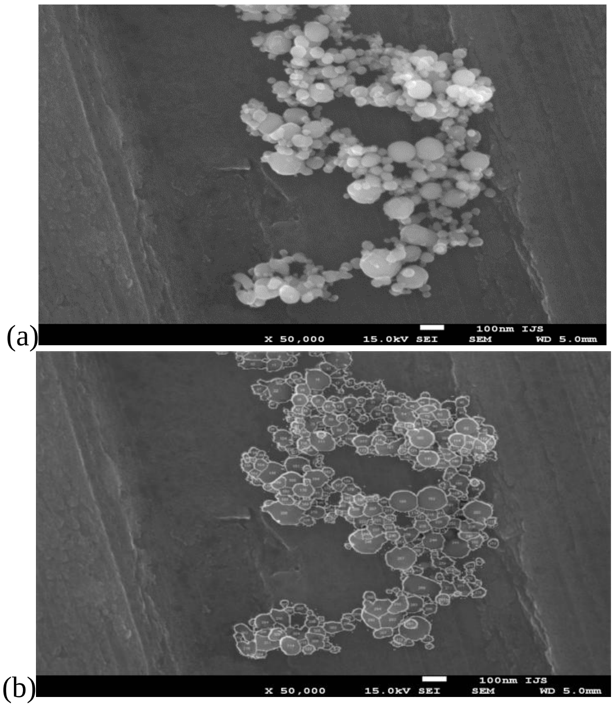

Fig. 4 (a) SEM image of Ni20. (b) Size estimation of Ni20 reveals that the average particle diameter is 47 nm, with 50% of the particles having a diameter below 43 nm.

The resulting data was used to calculate mean particle diameters and plot size distribution. For this sample the average particle diameter is 47 nm, with 50% of the particles having a diameter below 43 nm. Generally we observed, that in all samples the size distribution was rather large and also the average value of the diameter obtained by our estimates often deviates significantly (up to 100%) from the nominal size.

Fig. 5 shows the SEM images of a mixture of Ti and Al reactive nanoparticles. It can be seen, that the film, after evaporation of the solvent has a rather sponge-like structure. This comparatively porous structure is expected to be sub-optimal for a fast and efficient reaction spreading throughout the nano-composite. On the other hand, this fact allows precise control of the reaction spot, because reaction only takes place in the focal spot. For this reason it has advantages for first characterization experiments.

Indeed, in the first tests, no stable propagation of the reaction front was obtained. For the whole bonding process to work as a self-sustaining high temperature synthesis it will be necessary to obtain a denser structure with a reduced amount of cavities and more defined particle mixing. This can be obtained by high-energy ball milling which will provide more mixing energy compared to ultrasonic mixing, which was used here.

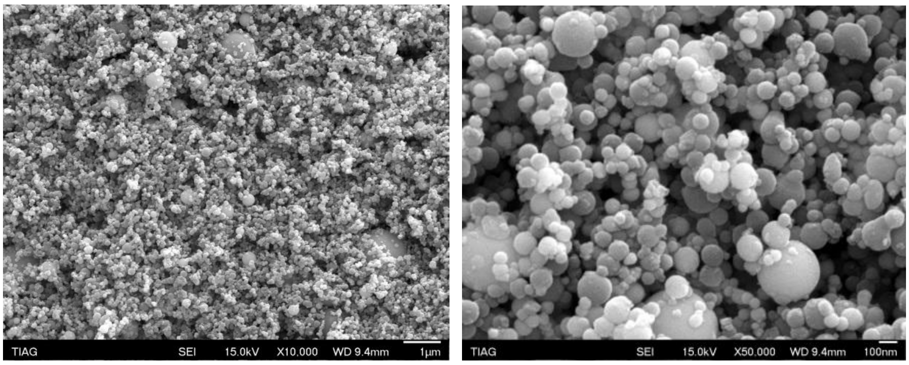

Fig. 5 SEM images of an unreacted mixture of Ti60 and Al40 taken with different magnification

If the laser is moved over the sample, we see that the reaction stays localized within the laser focus and that the amount of reaction can be steered by the speed of the laserspot, which limits the temperature obtained in the heating area. In Fig. 6 we see, that the laser effectively introduced a sintering of the nano-particles rather than complete melting and solidification. The energy generated by the exothermal reaction in this case was not sufficient to overcome non-adiabatic losses and to completely melt the nano-particles in order to propagate in a self-sustaining manner.

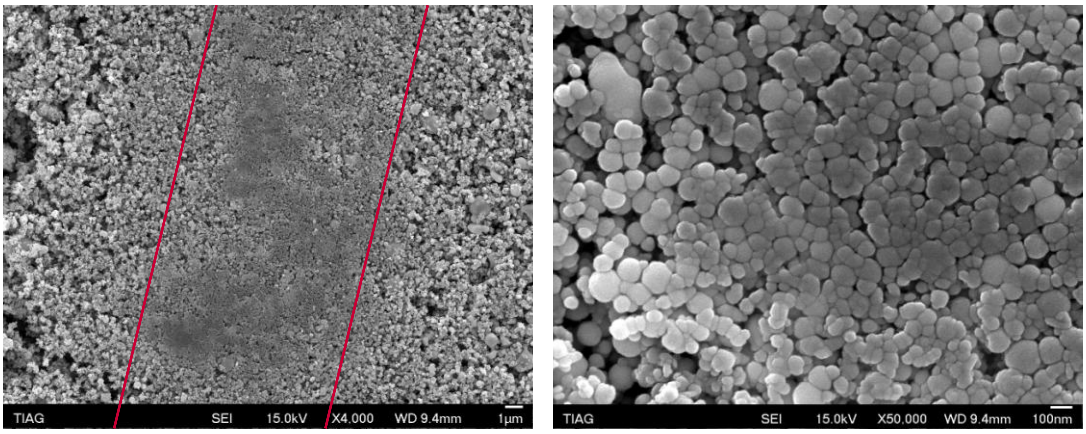

Fig. 6 Densification of the RNC layer along the laser treated paths (right: zoom on the reacted zone)

The reactivity of the nanocomposites was further characterized by an additional experimental procedure, where the complete sample was heated in a controlled manner on a heater chuck. Comparing the results to the laser exposed samples could allow an estimate of the temperatures effectively reached in the laser focus.

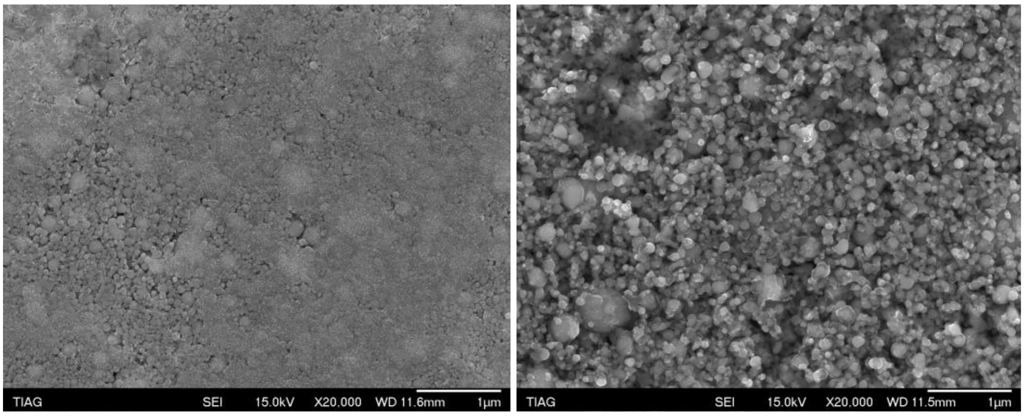

Fig. 7 SEM images of two samples after heating to 660°C. left: Al18 + Ti60, right: Al18 + Ni60

A drop of sample material was deposited on a silicon wafer and then pressed together by hand in a vise. Then the sample was heated to a temperature of 660 ° C within 10 mintes. The temperature was held for 10 minutes at 660°C and then the sample was cooled down slowly.

The results are shown in Fig. 7, which shows SEM images of two mixtures: (AL18 + Ti60 and AL18 + Ni60) after heating according to the temperature profile. For the temperature used (660°C) no explosive or self-propagating reaction was observed. While the particles of AL18 + Ti60 sample sintered together extensively, this sintering effect is not observed in the AL18 + Ni60 sample.

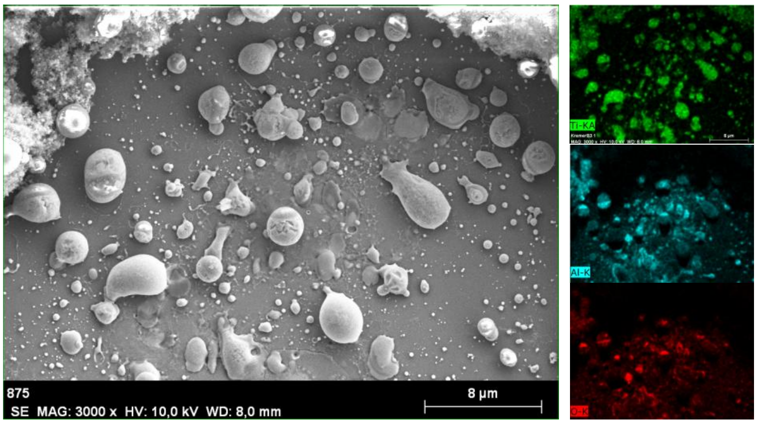

Fig. 8. Al-Ti sample after ignition with a laser. (Large image: SEM image. Small images: EDX analysis (from top to bottom): titanium concentration, aluminum concentration, and oxygen concentration).

The RNC layers after longer exposure to the laser heater were analyzed via SEM and EDX. Fig. 8 shows the results from a mixture of Al and Ti after treatment with a laser together with the corresponding EDX mapping images. Single-colored images show relative concentration of titanium, aluminum, and oxygen.

One can see that the layer did react, forming several micron-sized droplets rather than a continuous homogeneous intermetallic compound. Macroscopically the reaction did not expand throughout the whole layer but stayed localized to the laser spot, where the energy supplied by the laser was high enough to melt the sample and initiate the intermetallic reaction. Detailed analysis shows that the distribution of oxygen concentration is very similar to the aluminum distribution, indicating that despite the handling under argon atmosphere, some of the aluminum has oxidized. Interestingly, oxidization of titanium is much less.

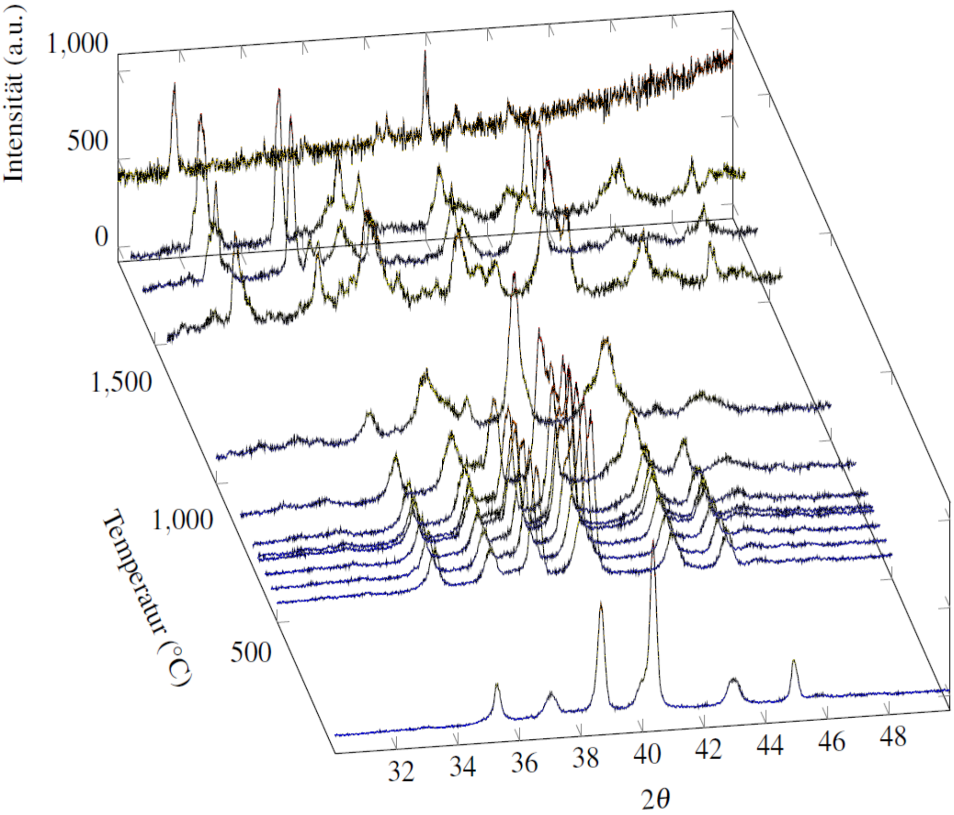

Fig. 9: High temperatrue XRD measurements.

For further analysis, the AL18 + Ti60 sample was measured by powder x-ray diffraction in the temperature range from room temperature to 1800 °C.

Fig. 9 shows the recorded spectra of this in-situ high temperature XRD measurement (HT-XRD). Initially, as expected the most prominent peaks stem from Al (38.1° , 44.4°) and Ti (40.2°, 38.4° , 35.1°) But already in initial configuration some additional peaks can be observed, which are attributed to signatures of oxidization. According to literature the expected starting reaction for the intermetallic reaction is the melting point of aluminum (660°C) [6]. However, up to temperatures of 800°C only two changes can be perceived in the spectrum: the shift of the entire spectrum in the direction of smaller angle of reflection due to the higher temperature and the growth of the Al2O3 content with simultaneous decrease of the TiO2 content. The latter indicates that the aluminum particles oxidize at the expense of titanium oxide, but do not enter the formation of the intermetallic phase. At temperatures in the range 800 to 1700°C various higher Al and Ti oxides can be observed. Finally at 1800°C almost the entire nano-composite has molten and the spectrum corresponds to an amorphous structure. The only peaks, which are still visible in the spectrum, correspond to aluminum oxide, which has an even higher melting point (2050°C).

V. Conclusion

In this paper we presented a novel joining concept based on reactive nano-composites, which would combine the versatility of reactive joining with the benefits of mask-less patterning of active layers by printing or manual deposition. In particular, the nanocomposite, when applied in the form of a dispersion, can be generated directly in the required pattern in a single process step without a complicated patterning by mask processes.

The nanocomposites prepared have been used for various first reactivity tests. The starting materials and the reaction products were analyzed with various techniques including electron microscopy and powder X-ray diffraction. First results are promising and underline the validity of the project, but they also point to certain issues, which have to be dealt with in order for this technique to be used in actual bonding processes. Thorough milling of the nano-particles will be necessary to obtain a self-sustaining reaction. Ultrasonic mixing is not sufficient under realistic conditions. Furthermore, the high temperature XRD measurement showed that initial oxygen contamination of the nano-particles can be a serious obstacle for the intended reaction. Further analysis steps are required to fully characterize the reactivity and to generate a reactive nanocomposite based on the results.

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