the ascending sections of the curves corresponding to α_v above 0.6 steadily approaches the supposed limit 3 corresponding to freely oscillating rods. Hence, from a rather general point of view the location of $\nu^*_{R2}/\nu^*_{R1} = 2.83$ or 2.77 between 2 and 3 is in perfect agreement with the results of the coupled rod model as represented in Fig. 2. Moreover, the proper density ratio $\rho_a/\rho_c = 0.853$ shifts all the lines in Fig. 2 to the left which makes the agreement still better. The smaller value, 2.77 at $E_c/E_a = 25$ or even at $E_c/E_a = 17$ is indeed located on the common envelope steadily rising to the limit 3 of the free rods corresponding to $E_a = 0$.

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The role of nickel in the one-coat vitreous enamelling system

In the industrial enamelling of ferrous metals it has always been necessary to add other metals, nickel and cobalt, to the system to obtain a satisfactory enamel–metal bond, i.e., one which failed in a cohesive manner. In the two-coat system these metals are added as oxides, "adhesion oxides", to the glass frit and in one-coat enamelling a thin layer of nickel is applied to the steel prior to the application of the enamel slip. There is evidence that this nickel deposit should be discontinuous to achieve a satisfactory bond between the enamel and the metal [1]. The precise function of this nickel flash has not been satisfactorily explained, but more recent publications suggest that it acts in at least two ways. When present the flash increases the proportion of Fe_3O_4 in the oxide scale which forms on the steel surface prior to the fusion of the enamel [2, 3]. Also the crystallographic structure of the nickel–iron alloy which forms during the later stages of firing is believed to promote good adherence [2,4]. These explanations which require particular chemical or physical conditions at the interface are not satisfactory in view of the demonstration by Klomp that bonds which fail cohesively could be formed between ceramics and metals without the aid of an intermediate layer at the interface [5]. The work reported here suggests that the nickel flash promotes bonding because it prevents the accumulation of hydrogen at the enamel–metal interface rather than its influence on the oxidation of the steel or the crystallographic properties of the alloy formed with the iron.

In a systematic investigation of the one-coat enamelling system various alterations were made in the pretreatment of the metal, including omitting the nickel flash. The differences observed are clearly shown in Fig. 1. Where the nickel flash was present the normal enamelling reaction sequence occurred; during the initial stages of firing the surface of the steel is oxidized by the atmosphere, the enamel then fuses, dissolves the oxide scale and further oxidation of the steel then occurs. This latter stage is accompanied by a marked roughening of the enamel–metal interface and the iron oxide formed in this second stage also diffuses into the enamel layer. In the absence of a nickel flash only the first stage oxidation had taken place and a separation of the two layers had occurred, resulting in a 30 μm gap. This gap must have formed when the enamel dissolved the

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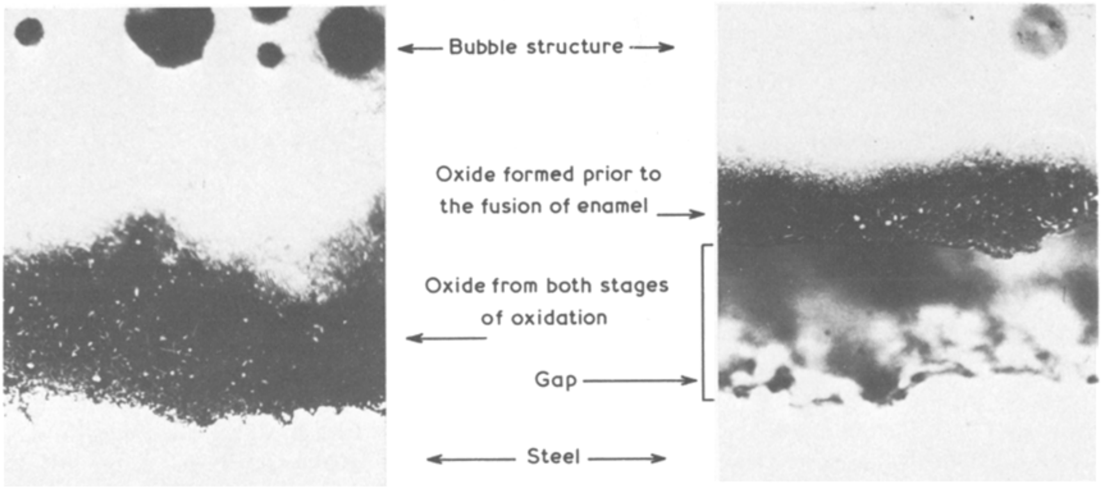

With nickel flash

No nickel flash

Figure 1 A cross-section of the interface region of enamelled specimens (× 800).

initially formed iron oxide and penetrated to the surface of the steel. Therefore the second stage oxidation process could not take place.

Similar experiments and results were reported by Nedeljkovic but he does not identify the separation between the enamel and the metal layers referring to it as a "typical microstructure" without any further explanation [2].

Previous studies have indicated that the source of oxygen for the second stage oxidation is most probably the water dissolved in the enamel [6] and it is therefore suggested that the gap shown in Fig. 1 is the result of the accumulation of hydrogen from this source at the interface. This evidence indicates that the function of nickel is to facilitate the diffusion of this initially formed hydrogen into the steel. The increased rate of diffusion could be the result of the enhanced solubility of the hydrogen in the surface layer of nickel–iron alloy formed [7] or the nickel may act as a catalyst in the atomization of the hydrogen [8] which is necessary before it can diffuse into the steel [9]. This rapid diffusion is probably less important in the later stages of this process as the hydrogen may then be formed away from the interface and enter the bubble structure of the enamel.

This concept was further tested by applying cobalt, the other "adhesion oxide", as a metallic deposit on the surface of the steel. Although a gap did not appear to be present between the enamel and the steel the bond was weak and adhesive failure occurred. This together with the small amount of iron oxide diffused into the enamel and the smooth interface indicated that the enamelling reaction had not gone to completion.

The division of ceramic–metal bonds into diffusional and non-diffusional types has been reported previously [10, 11], but the essential difference between them has not been obvious. If, as the present work suggests, the problem with the diffusional type of bond is the prevention of the accumulation of hydrogen at the interface, then the difference is more apparent than real.

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Forming rapidly cooled materials using a laser beam

The formation of metastable alloy phases by rapid cooling was demonstrated by Duwez *et al.* [1, 2] in an apparatus in which a molten globule was ejected from a melting chamber onto a rotating cylinder or a stationary copper target. Similar rapidly cooled alloys of more uniform thickness were made by Pietrokowsky [3] employing an anvil device in which the samples were melted by a gas flame. Laser usage as a source of heat has also produced rapid quenching of metallic alloys [4–7]. A complex triggered device was reported by Krepski *et al.* [8] which incorporated both the laser and a triggered hammer–anvil technique for quenching of their specimens.

This paper describes experiments in a simplified apparatus which employs a laser beam for heating and melting a specimen and copper-cooled anvils for the then rapid cooling of the molten globule (Fig. 1).

The advantages of this device are: (1) high melting point materials can be melted with a reasonable power laser, (2) the oxidation of the specimen is minimized because the entire operation is extremely rapid, (3) there is no container problem since the specimen rests on a relatively massive copper plate, (4) no complex triggering device is needed to close the anvils because the laser beam can be kept on while the copper anvil is in motion.

The sample is placed on a copper plate which serves as a broad track for the moving anvil. The specimen is melted with the prefocused laser beam and the solenoid is then activated. The moving anvil sweeps the molten specimen along the track and against the stationary cooled specimen plate forming a thin foil.

Melting of samples was accomplished using a continuous, convectively cooled, high-power CO_2 laser of 10.6 μm output wavelength. The unit used was a 12 tube laser built by United Technologies Research Center which could be operated in any one of three output modes. As an oscillator/amplifier (Gaussian output energy distribution), the unit is nominally specified as a 6 kW laser. As an unstable resonator (hollow output beam), the laser has produced 9 kW and in the "top hat" mode (uniform energy distribution) the laser has produced powers to 10 kW. Power densities by any of

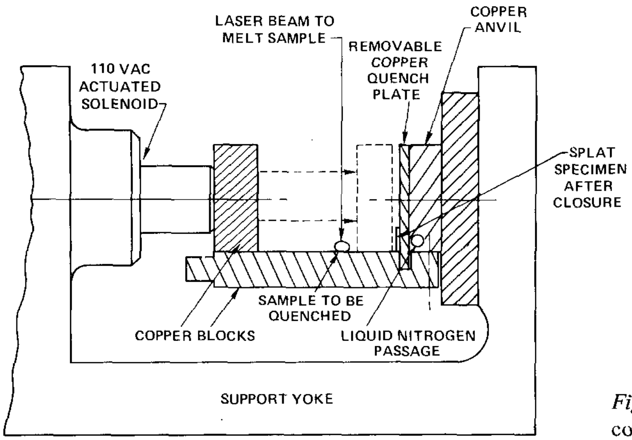

Figure 1 Simplified apparatus for forming rapidly cooled material.

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